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Bimetallic Cu-Ag and Au-Ag catalyst for ethylene epoxidation reaction

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Summary

Bimetallic Cu-Ag and Au-Ag catalysts were synthesized on α-Al₂O₃ with 10% Ag and varying Cu or Au loadings, each ranging from 250 ppm to 1500 ppm. The catalyst samples were synthesized with incipient wetness co-impregnation as well as sequential impregnation method for Cu-Ag and by co-impregnation method for Au-Ag catalyst. The average particle size of these catalysts was in the range of 120-140 nm as determined from the analysis of many TEM images. The bulk composition of these bimetallic catalyst samples was confirmed by the ICP-AES technique and the surface composition was examined using XPS technique. We also calculated the Auger parameter for Ag and found that the shift in Auger parameter due to the presence of Cu or Au was in the same range as reported for other dilute Ag alloys and it showed that these bimetallic alloys decreased the silver oxidation state to be partially negative. By doing O₂-TPD experiments, we were able to observe various peaks corresponding to different types of oxygen adsorbed on the catalyst. The general observation was that Cu-Ag catalyst adsorbed more oxygen than Au-Ag catalyst. We observed lower selectivity for bimetallic Cu-Ag or Au-Ag catalyst compared to 10% Ag only catalyst for ethylene epoxidation reactions performed at 1 bar as well as 20 bar. Our approach to the catalyst testing was to keep the reaction temperature constant and study the selectivity and activity. While literature reports a higher selectivity at constant conversion achieved by lowering the temperature, we are doubtful of this approach since ethylene epoxidation is a kinetically preferred reaction while combustion reaction is thermodynamically preferred. Thus changing the reaction temperature to obtain a constant conversion also changes the energy of the system and thus the selectivity comparison will not be very reliable. Also the literature reported catalysts had a higher metal coverage on alumina compared to our catalyst which can also result in lower performance of our catalyst. The catalyst restructuring due to the epoxidation reaction was studied and it was found that there were pores formed in the active metal. We also observed an increase in the average particle size after the reaction which proves that ethylene epoxidation reaction agglomerates the active metal particles.

Keywords: ethylene epoxidation, bimetallic catalyst, Cu-Ag, Au-Ag
Chapter 1: Introduction

1.1 Introduction to catalysis

A catalyst can be described simply as a substance that increases the reaction rate without being consumed. A more precise definition of a catalyst and catalysis is given by IUPAC as ‘A substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis’ [1]. In most cases, just a tiny amount of a catalyst is enough to make a significant difference in the reaction.

A catalyst simply accelerates a chemical reaction by forming bonds with the reactant molecules and allowing them to react to form a product. Later the product molecule detaches from the catalyst and leaves it unaltered such that it is available for the next reaction. Thus we can describe the catalytic reaction as a cyclic event in which the catalyst participates and is recovered in its original form at the end of the cycle. This can be easily explained by Figure 1 (left) which shows a catalytic reaction cycle where two molecules A and B are reacting to form products P. The cycle starts with the bonding of molecules A and B to the catalyst. A and B then react within this complex to give a product P, which is also bound to the catalyst. In the final step, P separates from the catalyst, thus leaving the reaction cycle in its original state. Thus it can be concluded that every catalytic reaction is a sequence of elementary steps, in which reactant molecules bind to the catalyst, where they react, after which the product detaches from the catalyst, liberating the latter for the next cycle.

![Figure 1: A typical catalytic reaction cycle (left) and the potential energy diagram (right) of a heterogeneous catalytic reaction [5]](image)

Catalysts work by providing an (alternative) mechanism involving a different transition state resulting in a lower activation energy. Consequently, more molecular collisions have the energy needed to reach the transition state. Hence, catalysts can enable reactions that would otherwise be blocked or slowed by a kinetic barrier. The catalyst may increase reaction rate or selectivity, or enable the reaction at lower temperatures. This effect can be illustrated with an energy profile diagram as seen in Figure 1 (right). Consider the same reaction system as before. Here A and B react exothermically to form P. The reaction releases energy and so the product P is at lower energy level compared to reactants A and B. In absence of a catalyst,
the activation energy required for the reaction would be quite high. The presence of the catalyst opens a different reaction pathway with a lower activation energy. However, the final result and the overall thermodynamics are still the same. Moreover, catalysts do not change the extent of a reaction and they have no effect on the chemical equilibrium of a reaction because the rate of both the forward and the reverse reaction are equally affected.

Catalysis is often classified into groups such as biocatalysis, homogeneous catalysis, and heterogeneous catalysis.

Biocatalysis is nature’s catalysis where enzymes act as catalysts. Generally, enzymes are large proteins but other non-protein based classes of biomolecules also exhibit catalytic properties including ribozymes, and synthetic deoxyribozymes [2]. Biocatalysis plays an important part in the metabolism of a living organism and the sustenance of life. Humans have been using biocatalysis and enzymes since ancient times for other purposes such as the production of alcohol, vinegar, cheese, yogurt etc. Most of the times, the reaction conditions for biocatalysis have to be mild, such as room temperature, atmospheric pressure or neutral pH because of the delicate structure of the enzymes. Very often the biocatalysts or enzymes are stereo-selective and are very specific in substrate bonding. [3]

In homogeneous catalysis, both the catalyst and the reactants are in the same phase. Typically homogeneous catalysts are dissolved in a solvent with the substrates. One example of homogeneous catalysis involves the influence of acids on the esterification reactions [4]. Another industrial process requiring a homogeneous catalyst is hydroformylation reaction to produce an alkyl aldehyde. Since the reactants, products and the catalysts are in the same phase in the homogenous catalysis, often an additional separation step is required to recover the catalyst from the reaction system.

Heterogeneous catalysis refers to the branch of catalysis where the reacting and the catalytic species are in different phases. Most common, as well as the one implemented in this project, is the case of solid metal catalyst and gas phase reactants. The solid catalytic particles can be either supported or unsupported. Heterogeneous catalysis is the most abundant type of catalysis for industrial applications. Some of the largest industrial processes based on heterogeneous catalysis are: cracking and hydrotreating of crude oil, gasoline production from naphtha, reforming, alkylation, polymerizations, production of vinyl chloride and acrylonitrile, epoxidation of ethylene, methane steam reforming, water-gas shift reaction, methanation, production of ammonia and urea, production of sulfuric acid, etc. [5]

1.2 The importance of catalysis

The chemical industry could not have developed to its present status on the basis of non-catalytic, stoichiometric reactions alone. In general, reactions can be controlled on the basis of temperature, concentration, pressure or contact time. For example, higher temperature and pressure can enable some stoichiometric reactions to proceed at a reasonable rate of production. However, the reactors in which such conditions can be safely maintained become progressively more expensive and difficult to design and operate. Furthermore, there are thermodynamic limitations to the conditions under which products can be formed.
Without catalysts, many reactions that are common in the chemical industry today would not be possible, and many other processes would not be economical. Catalysts accelerate reactions by orders of magnitude, enabling them to be carried out under the most favorable thermodynamic regime, and at much lower temperatures and pressures. In this way, efficient catalysts, in combination with the optimized reactor and total plant design, are the key factor in reducing both the investment and operation costs of chemical processes.

The influence of catalysis on today’s society is also enormous. Catalysis plays an important role in products ranging from fuels and fertilizers to plastics and pharmaceuticals. Most chemical products are produced using catalysis and it is estimated that approximately 90% of today’s chemical processes rely on catalysis [6]. Thus it is obvious that the impact of catalysis is also seen economically in our society. It is estimated that more than 35% of the global gross domestic product (GDP) originates from catalytic processes [7]. Thus catalysis plays a very important part of chemical engineering as well as chemistry studies. A lot of industrial and academic research is currently taking place for the generation of scientific and technological knowledge in the field of catalyst systems relevant to the development of clean and sustainable processes for the production of fuels and chemicals.

### 1.3 Ethylene oxide

The focus of this project is the partial oxidation of ethylene to produce ethylene oxide (EO), also called as oxirane by IUPAC. This reaction is known as ethylene epoxidation reaction. Ethylene oxide was first reported in 1859 by the French chemist Charles-Adolphe Wurtz [8]. Ethylene Oxide is a small molecule containing one oxygen and two carbon atoms, all bonded to each other via single bonds, in a relatively high strain three-member ring configuration as seen in Figure 2 (right).

![Charles-Adolphe Wurtz and Ethylene Oxide Molecule](image)

*Figure 2: Charles-Adolphe Wurtz, 26/11/1817 – 10/5/1884 (left) and ethylene oxide molecule structure (right)*
Ethylene oxide is a colorless and flammable gas with a faintly sweet odor. At room temperature, it is a flammable, carcinogenic, mutagenic, irritating, and anesthetic gas [9]. OSHA cautions that acute exposures to EO gas may result in respiratory irritation and lung injury, headache, nausea, vomiting, diarrhea, shortness of breath, and cyanosis. Chronic exposure has been associated with the occurrence of cancer, reproductive effects, mutagenic changes, neurotoxicity, and sensitization [10]. On account of these nasty physical properties, handling of ethylene oxide requires care and caution.

Because of its strained ring, ethylene oxide easily participates in a number of addition reactions that result in ring-opening. The reactivity that is responsible for many of ethylene oxide’s hazards also makes it a very useful compound. Although too dangerous for direct household use and generally unfamiliar to consumers, ethylene oxide (EO) is typically used as an intermediate for many organic syntheses. Derivatives of EO (especially ethylene glycol) are commonly used in the plastics industry for manufacturing bottles and to produce polyester fibers for clothing and furniture, automotive coolants, industrial coolants, heat transfer fluids, detergents, and surfactants. EO is also an intermediate used in the manufacture of flexible and rigid polyurethane foams, brake fluids and water-soluble solvents [11]. As a toxic gas that leaves no residue on items it contacts, ethylene oxide is a surface disinfectant that is widely used in hospitals and the medical equipment industry to replace steam in the sterilization of heat-sensitive tools and equipment, such as disposable plastic syringes [12].

Figure 3 shows some of the products derived from EO which are commercially available and can be easily recognized by consumers.
1.4 Ethylene epoxidation

Ethylene epoxidation reaction refers to the partial oxidation reaction of ethylene to produce ethylene oxide (EO). Catalysis can make a process more efficient by using raw materials efficiently in such a way that the use of toxic and hazardous reagents or solvents can be avoided while the formation of waste or undesirable by-products is minimized. The historical developments in ethylene epoxidation is a textbook example [5] of a case where catalysis helped to commercially produce a chemical in more efficient and environmentally friendly way.

EO was first prepared by Charles-Adolphe Wurtz in 1859 by treating 2-chloroethanol with potassium hydroxide [8].

\[
CH_2Cl - CH_2OH + KOH \rightarrow C_2H_4O + KCl + H_2O
\]

Wurtz’s 1859 synthesis long remained the only method of preparing ethylene oxide, despite numerous attempts, including by Wurtz himself, to produce ethylene oxide directly from ethylene [14]. Decades later, ethylene oxide production was first commercialized by BASF in 1914. It was a non-catalytic route (called the chlorohydrin process or the epichlorohydrin process) which had a three-step synthesis [15].

\[
Cl_2 + NaOH \rightarrow HOCl + NaCl
\]

\[
C_2H_4 + HOCl \rightarrow CH_2Cl - CH_2OH \text{ (epichlorohydrin)}
\]

\[
CH_2Cl - CH_2OH + \frac{1}{2} Ca(OH)_2 \rightarrow C_2H_4O + \frac{1}{2} CaCl_2 + H_2O
\]

Overall the reaction can be written as:

\[
Cl_2 + NaOH + \frac{1}{2} Ca(OH)_2 + C_2H_4 \rightarrow C_2H_4O + \frac{1}{2} CaCl_2 + NaCl + H_2O
\]

The chlorohydrin process was unattractive for several reasons, including low efficiency and loss of valuable chlorine into calcium chloride. Also for every molecule of ethylene oxide, one molecule of sodium salt and 0.5 of the calcium salt was formed. This created a waste problem that was traditionally solved by simply dumping the salts in a river or some other water bodies. Though this was a common practice in old times, it would be totally unacceptable in modern environmental aware society.

Soon after the commercialization of chlorohydrin process, French chemist Theodore Lefort developed a method of direct oxidation of ethylene by air in the presence of a silver catalyst in 1931 [16]. The catalytic route patented by Lefort for ethylene epoxidation was simple and clean compared to chlorohydrin process; although it did produce a small amount of CO₂. This new catalytic technology was revolutionary and Union Carbide opened its first ethylene oxide plant using this new technology in 1937. In 1952, another major breakthrough in ethylene epoxidation was the discovery that adding a trace amount of chlorinated hydrocarbons to the reactant feed improved selectivity towards ethylene oxide [17]. During this era, many other companies including Shell Oil Co., Dow Chemical, and others contributed to the initial research and development in the ethylene epoxidation catalyst.
Today ethylene epoxidation is a major industrial process as it serves as a very useful chemical intermediate from which further products such as plastics, polyester, and glycols can be derived. Companies including Dow Chemical, Eastern Petrochemical Company (SHARQ), SABIC, Formosa Plastics, Yansab, Shell, Al-Jubail Petrochemical Company, Sinopec, Reliance, BASF, Indorama Ventures, Ineos, Huntsman, PTT Global Chemical, LyondellBasell, Indian Oil, Oriental Union Chemical, CNPC and many others are active in the research or operations of ethylene oxide units [18]. Furthermore, it is reported that in 2016, the global EO capacity was 34.5 million tons/annum which is projected to further grow at the annual average growth rate of around 2.0% during 2017-2021 [19], thus emphasizing the importance of ethylene epoxidation reaction.

1.5 The mechanism of ethylene epoxidation

Today in industry, silver particles dispersed on low surface area alumina (\(\alpha\)-\(\text{Al}_2\text{O}_3\)) is used as a catalyst for ethylene epoxidation reaction. It is found that the EO selectivity of un-promoted metallic silver lays around 50% [20]. However, various promoters are added during catalyst preparation as well as during the process to enhance the catalyst performance. The incremental research in this field has led to the industrial processes that yield ~90% selectivity for ethylene oxide [20]. However, these improvements have come about by trial and error methods and most of the reaction mechanism lack a clear fundamental understanding [21].

Following its discovery, ethylene epoxidation was found to follow two parallel paths, both of which are catalyzed by silver. It is well-known fact that the ethylene oxide is formed directly from \(\text{C}_2\text{H}_4\) and \(\text{O}_2\) by partial oxidation. This process involves two competing parallel reactions \((k_1\) and \(k_2\)) to form either ethylene oxide or acetaldehyde. Ethylene oxide can also further isomerize \((k_3)\) to acetaldehyde. Formation of acetaldehyde acts as an intermediate for total combustion \((k_4)\) which produces \(\text{CO}_2\) and water. This reaction scheme can be explained as shown in Figure 4. Although thermodynamically preferred reaction path is the complete combustion leading to \(\text{CO}_2\) and \(\text{H}_2\text{O}\) \((\Delta H_{\text{rxn}} = -1327 \text{ kJ/mol})\), it is found that the kinetics dictates that EO \((\Delta H_{\text{rxn}} = -105 \text{ kJ/mol})\) is the major product [22] in the silver catalyzed ethylene epoxidation reaction.

![Figure 4: Ethylene epoxidation mechanism][20]
Silver catalyzed ethylene epoxidation has long been an interesting topic for the heterogeneous catalysis. Although it is the simplest kinetically controlled reaction [23], mechanism of this reaction is still under debate. A major advancement in the understanding of ethylene epoxidation reaction has been the discovery of the oxometallacycle (OMC) surface intermediate which was identified on the silver surface by experimental studies [24]. OMC is found to be the common precursor for both the parallel reaction channels that produce EO and acetaldehyde on the un-promoted metallic catalyst.

Formation of EO through an Eley-Rideal (E-R) type direct mechanism by reaction of gas phase ethylene and surface oxygen is also proposed [25]. It is proposed that ethylene is converted to ethylene oxide by an E-R mechanism, where gas-phase ethylene reacts with adsorbed oxygen on the silver surface. Depending on the state of oxygen adsorbed, selective oxidation or total oxidation of ethylene is observed [22]. Recent computational studies have identified such a direct route for EO formation, which is enabled by the electrophilic oxygen on the model Ag$_2$O (001) surface. Bridging O$_s$ on the oxide surface causes a totally different epoxidation path compared to the two-step OMC mechanism [26]. It is believed that O$_s$ interacts directly with the C=C double bond, resulting in the non-activated formation of EO. However, this direct reaction path does not include an intermediate such as OMC.

The activation energies of the rate controlling steps in both reaction paths (i.e. OMC vs. direct) are similar and agree with experimentally reported values that are around 70 kJ/mol [22]. However, the corresponding reaction steps that go through a barrier are different (i.e. OMC activation versus EO desorption). Also on the oxygen covered oxide surface, ethylene cannot directly interact with the silver surface ions, thus no OMC intermediate forms. This prevents C–H bond activation, therefore acetaldehyde formation. On the oxide surface, an additional prerequisite for high selectivity is the absence of O-vacancies, where the non-selective reaction takes places through OMC intermediate. It is believed that initial selective production of EO is followed by acetaldehyde production as the surface oxygens are consumed. The initial and highly selective production of EO proceeds in an E-R manner and removes the surface oxygens, which causes O-vacancy formation on the surface and enables the OMC path. Ethylene adsorption on the oxygen vacant surface sites opens the non-selective reaction path. Obviously to maintain high EO selectivity rapid silver re-oxidation should occur, while the O-vacancies are being blocked or suppressed. Furthermore, there are different reports on the reaction order of the epoxidation reaction [22] [27]. Thus, the debate on the exact mechanism of the EO formation still continues with both mechanisms in question.

### 1.6 Ag catalyst for ethylene epoxidation

Silver is the only catalyst with a feasible selectivity for the partial oxidation of ethylene to EO [20]. Other common oxidation catalysts such as palladium (Pd), platinum (Pt) or nickel (Ni) cause complete combustion reactions [28]. The Sabatier principle states that the interactions between the catalyst and the reactants/products should neither be too strong nor too weak. If the interaction is too weak, the reactants will fail to bind to the catalyst and no reaction will take place. On the other hand, if the interaction is too strong, the product fails to dissociate [29]. Thus the optimum selectivity for ethylene epoxidation can be obtained for the catalysts that have metal–oxygen interaction strong enough to dissociate O$_2$ molecule and supply the
stable atomic oxygen species required for the epoxidation. In contrast, it should not be too strong to prevent desorption of the product EO or to cause C–H activation and cause other side reactions. From this perspective, the interaction of atomic oxygen and the silver surface lies at an optimum point compared to other metals [20] and so silver is the only feasible catalyst for ethylene epoxidation.

The industrial catalyst for ethylene epoxidation consists of silver particles supported on low surface alumina (α-Al₂O₃). The complete oxidation of ethylene and EO to CO₂ and H₂O occurs primarily on the support surface. This is the reason why low-area supports are used for this reaction. Since more of the α-Al₂O₃ surface is covered by Ag, the complete oxidation reaction is suppressed resulting in improved selectivity [30]. A small ppm amounts of chlorine is added to the feed in the form of chlorinated hydrocarbons to enhance the EO selectivity [25]. In addition to this chlorine moderator, metals such as Cs [25] and Re [31] are also added as promoter metals during catalyst synthesis in the industry. Patent literature [32] [33] also cites the addition of other elements like K, Li, Cs, Re, S, etc.; either some or all of them, in varying concentrations during the catalyst synthesis process.

Since ethylene needs to be only partially oxidized for forming ethylene epoxidation, it is obvious that oxygen will play an important role in the reaction. The intermediate value of Ag₂O’s stability and its oxygen bond strength placed between Au₂O and Cu₂O relate the uniqueness of the silver catalyst for ethylene epoxidation. It is believed that Au₂O is not a stable structure and Cu₂O does not favor the EO formation [34]. The interaction of Ag surface with molecular oxygen is strong enough to re-oxidize the Ag surface to the oxide; on the other hand, weak enough to prevent the ring opening of EO as well as to prevent the activation of the CH bonds.

It is found that catalytically active silver surface contains two types of oxygen species; namely nucleophilic and electrophilic oxygen [35]. Nucleophilic oxygen has an oxidic nature and is formed as result of silver surface reconstruction in the course of oxygen adsorption, whereas electrophilic oxygen is adsorbed on the silver surface without reconstruction [36] [37]. The nucleophilic oxygen is active in the nucleophilic attack of the C–H bond as the first step in C₂H₄ combustion because of its oxidic nature and thus it leads to total oxidation of ethylene to CO₂ and H₂O. On the other hand, electrophilic oxygen participates in the electrophilic interaction with the C=C double bond of ethylene to predominantly form EO.

In addition to the various types of surface oxygen, subsurface or ‘dissolved’ oxygen is also believed to be a key factor regarding the catalyst performance in these reactions [38]. The presence of different types of oxygen species leads to the restructuring of active nanoparticles on the catalyst surface and affects the reaction yield [39]. Therefore, the introduction of metals with a different affinity for oxygen could help to investigate the role of oxygen in nanoparticle restructuring and ethylene epoxidation reaction. Cu [25] and Au [30] are of particular research interest as a possible catalyst promoter because of their similar crystal structure as silver in oxide form.
1.7 Bimetallic Cu-Ag and Au-Ag catalyst for ethylene epoxidation

Using transition metals like copper or gold instead of silver as a catalyst for ethylene epoxidation is not feasible because Au as a catalyst fails to dissociate oxygen and provide stable oxide surface layer for reaction whereas using only Cu as a catalyst will strongly bind oxygen to give a very high activation barrier and high desorption energy [20]. However, bimetallic catalysts such as Ag-Cu and Ag-Au has been the focus of extensive research in the field of heterogeneous catalysis because the catalytic activity, as well as the selectivity of a metal, can be modified substantially by alloying it with another metal [40]. For example, geometrical and electronic effects obtained by varying the alloy composition may play an important role in determining the properties of the catalyst and how it behaves in a reaction [41]. One interesting aspect of bimetallic catalysts is the possibility of rationally designing the catalytic properties of the material by changing the type of metal and its composition.

The mechanism of ethylene epoxidation and the use of the silver catalyst has been studied in great detail using a combination of experimental and theoretical techniques [24] [42]. It has been proposed that both the selective (producing ethylene oxide) and unselective (producing the acetaldehyde intermediate and finally leading to total oxidation) reaction pathways have a common intermediate, a surface oxometallacycle. This intermediate can react to form either ethylene oxide or acetaldehyde with similar activation barriers. The same authors also reported, on the basis of both first-principles calculations [27] and experiments [25] that if a Cu-Ag alloy, rather than pure Ag, is used as a catalyst, the selectivity toward ethylene oxide can be improved. On the other hand, it is also reported [43] that OMC intermediate is not present on the phase diagrams of any facets of Cu-Ag catalyst under any condition of temperature and partial pressures due to its lower stability.

Alternatively, other research results [44] also suggest that there is not a unique surface structure that is solely responsible for the catalytic activity of the Cu-Ag alloy. Depending on the facet and the conditions of temperature and oxygen partial pressure, several surface structures can form. It is claimed that the reaction mechanism of ethylene epoxidation is influenced by the underlying surface structures and that the reactions always proceed through the formation of an oxometallacycle intermediate. In summary, the Ag–Cu alloy material, in an oxygen atmosphere, forms thin copper oxide layers on top of the silver. These structures are stable against reduction by ethylene under reaction conditions, as predicted theoretically and confirmed experimentally by the authors [45]. It is also noted that the geometry of the transition states is not very sensitive to the surface structure and that activation barriers and enthalpies of reaction are approximately related by the linear Brønsted–Evans–Polanyi relation. The DFT estimates of the activation barriers for the competing processes suggest that these thin Cu–O layers can enhance the selectivity toward the formation of EO. However, these calculations suggest that the improvement in the selectivity is very small.

Another research work [46] also suggests the enhanced catalytic activity for ethylene epoxidation near the phase transition from Cu2O to CuO due to the presence of metastable adsorbed oxygen species on Cu2O that are precursors for CuO formation and form close to the Cu2O–CuO phase transition. The DFT calculations and the experimental results show that the reaction involves an adsorbed oxygen species that forms on the Cu2O surface at the onset of oxidation to CuO. By modeling this surface as a Cu2O(110) surface with interstitial O ions (a precursor to the CuO structure), DFT- based minimum energy pathway calculations reveal...
that such an oxygen species would give rise to an increased epoxidation activity due to its high energy.

Some research [30] also claims that the bimetallic Au-Ag catalyst is also a good candidate for the ethylene epoxidation because of the existence of the bimetallic Au and Ag structures which creates new single silver sites favoring molecular oxygen adsorption leading to the enhancement of the ethylene oxide selectivity. It is found that the catalytic activity of the gold catalysts depends not only on the support material but also on the catalyst preparation method which governs the Au particle size and the interaction between the Au particles and the support. On the other hand, it is also found that the presence of Au decreases the activity and selectivity of the catalyst [47]. It was found that instead of forming a bimetallic, Au particles were formed on the Ag and causing a blockage of active sites.

The only agreeable conclusion from all of the above described research is that for bimetallic Cu-Ag and Au-Ag catalyst for ethylene epoxidation, the selectivity is very sensitive to the presence of a second phase of the added metal and this behavior identifies catalyst composition as a key parameter for optimization of selectivity and activity. Thus, the chemical and structural changes due to Cu and Au promotion and its effect on epoxidation selectivity would be an interesting research topic. This could also aid in understanding the underlying mechanism of this reaction and it may be finally linked to the performance of the catalyst.

1.8 Scope of this project

In this project, we will investigate the role of Cu-Ag and Au-Ag bimetallic catalyst in the ethylene epoxidation reaction. The project includes finely controlled synthesis of Cu-Ag and Au-Ag bimetallic catalysts on α-Al₂O₃ by using synthesis method derived and adjusted from patent literature [48]. The amount of promotion will vary between 250 ppm to 1500 ppm of Cu or Au based on total catalyst mass [25], [30] and [49]. The synthesis will be carried out by incipient wetness co-impregnation method as well as sequential impregnation method.

The physical and chemical properties of the catalyst will be studied by using different characterization techniques such as TGA (Thermal Gravimetric Analysis), XPS (X-ray Photoelectron Spectroscopy), HR-TEM (High-Resolution Transmission Electron Microscopy), XRD (X-Ray Diffraction), TPD (Temperature Programmed Desorption) and ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy).

The Cu-Ag and Au-Ag bimetallic catalysts will be tested under industrial reaction conditions (225°C and 20 bar) as well as at lower atmospheric pressure. By doing this project, we aim to get a deeper insight in the epoxidation reaction over the bimetallic catalyst and to verify the claims for higher selectivity and activity for the bimetallic catalysts. We would also like to obtain crucial information on the role of oxygen in the reaction mechanism and get insight on how to optimize the catalyst performance for industrial use. Catalyst characterization after the reaction can also provide some knowledge for the better design of an industrial catalyst. The insights gained from this project can give some direction for the future research in this topic.
Chapter 2: Experimental

2.1 Pre-treatment of $\alpha$-Al$_2$O$_3$

The $\alpha$-Al$_2$O$_3$ used for catalyst preparation was sourced from Saint-Gobain NorPro. The sample code was SA 5102, which refers to 3 mm pellets of low surface alumina [50]. These pellets were crushed using mortar and pestle and then they were sieved to get particles in the range of 125-250 $\mu$m. We followed a pre-treatment procedure that involved washing the $\alpha$-Al$_2$O$_3$ support with distilled water. Conceptually our washing procedure was similar to the one cited in the literature [25] where they used alumina monolith and washed it in boiling distilled water.

For our procedure, the crushed support was filled in a cellulose thimble and placed inside the Soxhlet equipment. A temperature controlled oil bath was used to boil the distilled water in the Soxhlet equipment and a cooling water was used to condense the vapors formed in the equipment. The alumina support was washed continuously with distilled water which was dripping due to the condensation of vapors from the top of the equipment. The catalyst sample chamber was completely filled with water in approximately 20 minutes and then it was emptied automatically by siphon effect. This entire procedure was allowed to continue for approximately 2 days (48 hours). Thus the cycle of washing the alumina support and emptying the water was repeated for approximately 150 times during the complete washing procedure.

After the washing procedure, the support material was dried at room temperature under vacuum for several hours and then at 110°C for 1 hour to remove any residual moisture and then it was stored for later catalyst synthesis procedure. Before proceeding for the synthesis of the bimetallic catalyst, the alumina support was heated and held overnight at 550°C to remove any organic impurities from the catalyst surface.

2.2 Synthesis of precursor solutions

Silver oxalate ($\text{Ag}_2\text{C}_2\text{O}_4$) was used as the silver precursor in all subsequent synthesis procedures. It was prepared by mixing silver nitrate ($\text{AgNO}_3$) (Alfa Aesar, 11414 Silver nitrate, ACS, 99.9+% (metals basis)) with excess of oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) (Sigma Aldrich, 241172 ALDRICH, Oxalic acid, ReagentPlus®, ≥99%) dissolved in distilled water and filtering out the precipitates. The precipitates were washed with water to remove excess acid and later dried in vacuum to remove moisture.

Copper nitrate ($\text{Cu(NO}_3)_2$) (Sigma Aldrich, 229636 ALDRICH, Copper(II) nitrate hydrate, 99.999% trace metals basis) was used as a precursor for copper. It was prepared by dissolving $\text{Cu(NO}_3)_2$ powder in distilled water to form a 0.1 g/ml solution which was used for all subsequent synthesis procedures.

Chloroauric acid ($\text{HAuCl}_4$) (Strem Chemicals, 79-2200 Hydrogen tetrachloroaurate(III) hydrate (99.9985%-Au) (49% Au) PURATREM) was used as a precursor for gold. It was prepared by dissolving the $\text{HAuCl}_4$ powder in distilled water to form a 0.1 g/ml solution which was used for all subsequent synthesis procedures.
2.3 Synthesis of bimetallic Cu-Ag/α-Al₂O₃ catalyst

Bimetallic Cu-Ag catalyst was synthesized using incipient wetness co-impregnation method. A calculated quantity of silver oxalate powder was dissolved in approximately three molar equivalent of ethylenediamine (C₂H₄N₂) (Sigma Aldrich, E26266 SIGMA-ALDRICH, Ethylenediamine, ReagentPlus®, ≥99%) in a measuring cylinder. Since the dissolution was exothermic, the measuring cylinder was kept in an ice bath during the entire time. A calculated amount of Cu(NO₃)₂ solution was added and then distilled water was added to increase its volume up to the pore volume (approximately 0.75 ml/g) of the alumina support. The bimetallic Cu-Ag precursor solution was added to the alumina support and was allowed to dry at room temperature under vacuum for approximately one hour. The catalyst was then calcined at 275°C for 4 hours under 10% oxygen environment. The amount of alumina support, Cu and Ag precursors and the total Cu and Ag deposited on each of the catalyst samples is shown in Table 1.

<table>
<thead>
<tr>
<th>Code</th>
<th>ppm Cu</th>
<th>Al₂O₃ (g)</th>
<th>Ag (g)</th>
<th>Cu (g)</th>
<th>Ag₂C₂O₄ (g)</th>
<th>Cu(II)(NO₃)₂ solution (µL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA 02</td>
<td>250</td>
<td>2.0000</td>
<td>0.2223</td>
<td>0.0006</td>
<td>0.3130</td>
<td>16.40</td>
</tr>
<tr>
<td>SA 03</td>
<td>500</td>
<td>2.0000</td>
<td>0.2223</td>
<td>0.0011</td>
<td>0.3131</td>
<td>32.81</td>
</tr>
<tr>
<td>SA 04</td>
<td>750</td>
<td>2.0000</td>
<td>0.2224</td>
<td>0.0017</td>
<td>0.3131</td>
<td>49.23</td>
</tr>
<tr>
<td>SA 01</td>
<td>1000</td>
<td>2.0000</td>
<td>0.2225</td>
<td>0.0022</td>
<td>0.3132</td>
<td>65.74</td>
</tr>
<tr>
<td>SA 05</td>
<td>1500</td>
<td>2.0000</td>
<td>0.2226</td>
<td>0.0033</td>
<td>0.3134</td>
<td>98.55</td>
</tr>
</tbody>
</table>

Two Cu/Ag bimetallic catalyst samples were also synthesized with sequential impregnation method. For it, first, a 10% Ag on α-Al₂O₃ was prepared by depositing a silver precursor (silver oxalate dissolved in ethylenediamine solution) on the alumina support and then drying and calcining as described previously. In next step, a calculated amount of Cu(NO₃)₂ solution was dissolved and then distilled water was added to increase its volume up to the pore volume (approximately 0.75 ml/g) of the 10% Ag catalyst on the alumina support. The Cu precursor solution was then added to the 10% Ag catalyst and was allowed to dry at room temperature under vacuum for approximately one hour and then calcined at 275°C for 4 hours in 10% oxygen atmosphere. The amount of alumina support, Cu and Ag precursors and the total Cu and Ag deposited on the catalyst sample is shown in Table 2.

<table>
<thead>
<tr>
<th>Code</th>
<th>ppm Cu</th>
<th>Al₂O₃ (g)</th>
<th>Ag (g)</th>
<th>Cu (g)</th>
<th>Ag₂C₂O₄ (g)</th>
<th>Cu(II)(NO₃)₂ solution (µL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA02 - 2 step</td>
<td>250</td>
<td>1.3500</td>
<td>0.1500</td>
<td>0.0004</td>
<td>0.2112</td>
<td>11.06</td>
</tr>
<tr>
<td>SA05 - 2 step</td>
<td>1500</td>
<td>1.3500</td>
<td>0.1500</td>
<td>0.0023</td>
<td>0.2112</td>
<td>66.50</td>
</tr>
</tbody>
</table>
2.4 Synthesis of bimetallic Au-Ag/α-Al2O3 catalyst

Bimetallic Au-Ag catalyst was synthesized using incipient wetness co-impregnation method. A calculated quantity of silver oxalate powder was dissolved in approximately three molar equivalent of ethylenediamine (C2H8N2) in a measuring cylinder. Since the dissolution was exothermic, the measuring cylinder was kept in an ice bath during the entire time. A calculated amount of HAuCl4 solution was added and then distilled water was added to increase its volume up to the pore volume (approximately 0.75 ml/g) of the alumina support. The bimetallic Au-Ag precursor solution was added to the alumina support and was allowed to dry under vacuum at room temperature for approximately one hour. The catalyst was then calcined at 275°C for 4 hours under 10% oxygen environment. The amount of alumina support, Au and Ag precursors and the total Au and Ag deposited on the catalyst sample is shown in Table 3.

<table>
<thead>
<tr>
<th>Code</th>
<th>ppm Au</th>
<th>Al2O3 (g)</th>
<th>Ag (g)</th>
<th>Au (g)</th>
<th>Ag2C2O4 (g)</th>
<th>HauCl4 solution (µL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA 11</td>
<td>250</td>
<td>2.0000</td>
<td>0.2223</td>
<td>0.0006</td>
<td>0.3130</td>
<td>11.11</td>
</tr>
<tr>
<td>SA 12</td>
<td>500</td>
<td>2.0000</td>
<td>0.2223</td>
<td>0.0011</td>
<td>0.3131</td>
<td>22.23</td>
</tr>
<tr>
<td>SA 13</td>
<td>750</td>
<td>2.0000</td>
<td>0.2224</td>
<td>0.0017</td>
<td>0.3131</td>
<td>33.35</td>
</tr>
<tr>
<td>SA 14</td>
<td>1000</td>
<td>2.0000</td>
<td>0.2225</td>
<td>0.0022</td>
<td>0.3132</td>
<td>44.48</td>
</tr>
<tr>
<td>SA 15</td>
<td>1500</td>
<td>2.0000</td>
<td>0.2226</td>
<td>0.0033</td>
<td>0.3134</td>
<td>66.75</td>
</tr>
</tbody>
</table>

For removal of chlorine from the gold precursor, the Au-Ag bimetallic catalysts were heated up to a temperature of 350°C under 10% H2 flow (5 ml/min H2 + 45 ml/min He) in TPD experimental setup (described later). The system was held at this temperature for around 90 minutes before cooling it to room temperature. The current intensity for different species including He, H2, Cl2, and HCl was measured by mass spectrometry (MS).

2.5 Thermal Gravimetric Analysis (TGA)

The thermal characterization of the catalyst synthesis procedure was carried out in a thermogravimetric analyzer (Mettler Toledo TGA/DCS1, STAR® System).

The three catalyst samples used for analysis contained 10% Ag and 1000 ppm of Cu, Au, and Cs respectively on α-Al2O3 support. The catalyst samples were prepared as per the procedure described above. However, before using the samples for TGA, they were only dried in vacuum at room temperature for one hour and they were not calcined (or heat treated) at higher temperatures.

The TGA experiment was carried out in 10% oxygen environment (6 ml/min of O2 and 54 ml/min of He). The catalyst samples were heated up to 750°C with the heating rate of 5°C/min. Each sample used for testing weighed around 25–35 mg. The change in mass of the samples with respect to temperature and time was measured. The first derivative of the change in mass
with respect to temperature (or time) is also calculated for each sample for better visualization of the results.

2.6 Transmission Electron Microscopy (TEM)

For each catalyst sample, the particle size distribution of the active metal on the catalyst support was calculated using TEM images. TEM images were acquired on a FEI Titan 80-300 aberration corrected electron microscope operated at 300 kV. The images were acquired by a Fischione model 3000 HAADF STEM detector and energy dispersive X-ray spectra (EDX) was acquired by an EDAX SUTW EDX detector. The particle size was determined by measuring the diameter of the bright particles using ImageJ® program. Typically the catalyst samples were finely crushed using mortar and pestle and then they were suspended in ethanol, sonicated and dispersed over a Cu grid with a holey carbon film. The average particle size and particle size distribution were determined by analysis of a substantial number of electron micrographs.

2.7 X-ray Photoelectron Spectroscopy (XPS)

For each catalyst sample, the surface composition of the active metal, as well as the other impurities on the catalyst, was measured using XPS. XPS measurements were carried out with a Thermo Scientific K-Alpha, equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminum anode (Al Kα = 1486.6 eV) operating at 72W and a spot size of 400 µm. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. Typically, the catalyst samples were finely crushed using mortar and pestle and deposited on the double-sided carbon tape which was attached to the sample strip to be used for measurements. XPS spectra were fitted with CasaXPS® software. A Shirley background subtraction was applied and Gauss-Lorentz curves were fitted.

2.8 X-ray Diffraction (XRD)

The catalyst samples were characterized by XRD technique using Bruker D2 Phaser powder diffraction system using Cu Kα radiation (1.5406 Å). The readings were taken for 2θ values ranging from 5° to 90°. The scan time was 0.5 seconds and step size was 0.01°. For each scan results, K-α2 was stripped, the background was subtracted and the offset was adjusted based on the maximum intensity of alumina peak.

2.9 Temperature Programmed Desorption (TPD) of Oxygen

The O₂-TPD experiments were carried out in a plug flow system in a glass reactor setup. The reactor was heated in a controlled manner by an oven. The setup was equipped with gas lines
for He, O₂ and H₂. Gas analysis was performed by the mass spectrometer (quadrupole mass spectrometer, Balzers TPG 251). The monitored gases were H₂ (m/e 2), He (m/e 4), CH₄ (m/e 16), H₂O (m/e 18), N₂ (m/e 28), O₂ (m/e 32), CO₂ (m/e 44). The current intensity was measured against time and the measured intensities were divided by the corresponding He signal intensity.

The catalyst samples used for each experiment weighed around 250 mg. All experiments were carried out at atmospheric pressure. The sample was first heated to 250°C under 10 ml/min flow of O₂. The heating rate was 20°C/min. The sample was held for 3 hours under these conditions and then it was allowed to cool to 50°C under same O₂ flow. Upon reaching 50°C, the O₂ flow was stopped and it was switched to He flow for flushing out the excess O₂ from the reactor or the tubing. He was flushed at a flowrate of 50 ml/min for 30 minutes. After this, the temperature was ramped up at the rate of 10°C/min up to 550°C for O₂-TPD experiment. The He flow was maintained at 50ml/min during the entire TPD experiment.

2.10 Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES)

Catalyst metal loading was determined by ICP-AES analysis done with a SpectroBlue CCD ICP optical emission spectrometer with axial plasma viewing. Five standard solutions for Ag were prepared with different concentrations ranging from 0 mg Ag/l to 10.0 mg Ag/l. Six standard solutions each for Cu and Au were prepared with different concentrations ranging from 0 mg metal/l to 2.5 mg metal/l.

For measuring silver content, around 25 mg of sample was crushed and mixed with 20 ml 3 molar HNO₃ in a beaker. The solution was stirred and heated to 80°C for 1 hour to leach out all Ag from the catalyst. The solution was then cooled to room temperature and diluted to 50 ml in a volumetric flask. The alumina residue was allowed to settle down and then 5 ml of this solution was taken in another volumetric flask and diluted to 50 ml. Around 25 ml of this diluted solution was used for measurements.

For measuring copper content, around 25 mg of sample was crushed and mixed with 20 ml 3 molar HNO₃ in a beaker. The solution was stirred and heated to 80°C for 1 hour to leach out all Cu from the catalyst. The solution was then cooled to room temperature and diluted to 50 ml in a volumetric flask. The alumina residue was allowed to settle down and then around 25 ml of this solution was used for measurements.

For measuring gold content, around 50 mg of sample was crushed and mixed with 3 ml conc. HCl (37%) and 1 ml conc. HNO₃ (65%) in a beaker. The solution was stirred and heated to 80°C for 1 hour to leach out all Au from the catalyst. The solution was then cooled to room temperature and diluted to 50 ml in a volumetric flask. The alumina residue was allowed to settle down and then around 25 ml of this solution was used for measurements.
2.11 Catalyst activity and selectivity tests

Catalyst testing was carried out in a stainless steel fixed bed reactor operated in a plug-flow manner. Approximately 20 mg of the catalyst sample was loaded into the reactor tube and kept in between two layers of quartz wool. The reactor was heated by an oven and temperature was controlled by the computer. The gas lines were heat traced at 100°C. There were back pressure regulators to maintain a desired pressure in the reactor. The catalysts were tested with a total reactant flowrate of 20 ml/min. The partial pressure of the reactants was 5% ethylene, 10% oxygen, and remaining helium.

Before starting the reaction, the pre-treatment gases with 10% O$_2$ and 90% He flowed for 3 hours at the desired reaction pressure (either 1 bar or 20 bar) and temperature (225°C). The reaction was allowed to run for the desired duration before switching the gases to He flow and subsequent cooldown of the reactor. During the 3 hours of the pre-treatment and during the reaction duration, the products were continuously analyzed by an online GC (Interscience CompactGC$^4.0$ using Agilent’s EZChrom Elite data system) which monitored the presence of CO, O$_2$, C$_2$H$_4$, EO, and acetaldehyde.
3.1 Removal of impurities from \( \alpha{-}\text{Al}_2\text{O}_3 \)

The \( \alpha{-}\text{Al}_2\text{O}_3 \) used for catalyst preparation had a minimum bulk purity of 99\%, with a maximum 0.2\% \( \text{CaO-MgO} \) and 0.4\% \( \text{Na}_2\text{O-K}_2\text{O} \) impurities; as claimed by the product supplier. Furthermore, the XPS scan of this alumina support also confirmed the presence of impurities like sodium (Na), calcium (Ca) and silicon (Si). It is possible that these unwanted metal impurities may interfere with the catalyst performance during the epoxidation reaction. To avoid any unexpected effects, the alumina support was washed in a pre-treatment step as described earlier before proceeding for the catalyst synthesis.

It can be seen from Figure 5 that the XPS scans of the alumina support clearly showed the presence of Na, Ca and Si. However, other impurities like K, Li, and Mg were not detected in the XPS. The XPS scans shown here are for Na1s, Ca2p, and Si2p. It also compares XPS scans for unwashed alumina support, washed alumina support which was crushed before XPS and the washed alumina support which was not crushed before XPS.

Figure 5: XPS spectra of Na, Ca & Si for unwashed as well as washed (crushed & not crushed) alumina
The amount of Na, Ca, and Si impurities present on the alumina support was quantified based on the peak fitting in CasaXPS® software. The results are shown in Table 4.

**Table 4: Surface concentration of impurities in Al₂O₃**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Unwashed</th>
<th>Washed and crushed before XPS</th>
<th>Washed, but not crushed before XPS</th>
<th>% Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1.43%</td>
<td>0.29%</td>
<td>0.05%</td>
<td>96.5%</td>
</tr>
<tr>
<td>Ca</td>
<td>1.30%</td>
<td>0.49%</td>
<td>0.16%</td>
<td>87.7%</td>
</tr>
<tr>
<td>Si</td>
<td>3.04%</td>
<td>2.24%</td>
<td>0.81%</td>
<td>63.8%</td>
</tr>
<tr>
<td>K, Mg, Li</td>
<td>Not found</td>
<td></td>
<td></td>
<td>---</td>
</tr>
</tbody>
</table>

It can be seen above that the unwashed alumina support shows a sharp XPS peak for Na, Ca, and Si which means that they are present on the surface of the alumina support that was obtained from Saint Gobain. The surface concentration of each impurity was over 1%. Washing the alumina support in Soxhlet equipment as described in the Experimental section removes most of these impurities from the surface. This can be concluded from the absence of sharp peaks in the XPS scan for the washed support that was not crushed.

However, these peaks reappear (though not as sharp as before) when the washed sample is crushed before using it for the XPS. Thus it can be concluded that the impurities which were present in the alumina bulk came on the surface upon crushing the sample before XPS. This proves that the washing procedure does not completely remove the impurities from the bulk of the alumina support and it removes most of these impurities from the surface. Upon comparing the results for the impurities removed during the washing procedure, we can see that almost all of the Na is removed from the alumina support while most of the Ca and Si are also removed from the surface.

### 3.2 Composition of bimetallic Cu-Ag/α-Al₂O₃ catalyst samples

It is found in the literature [25] that Cu(II)(NO₃)₂ is used as copper precursor together with AgNO₃ for Cu-Ag bimetallic catalyst. We also used the same precursors for the synthesis procedure. However, the main difference between the literature reported synthesis and our procedure was that we used 125-250 µm particles of α-Al₂O₃ while they have used α-Al₂O₃ monolith measuring 18 mm diameter X 10 mm length with 45 ppi. Also, the Ag loading was 10% for our catalysts while it varied between 11-13% in literature. As mentioned earlier, we made Cu-Ag catalysts with different Cu loadings ranging from 250 ppm to 1500 ppm. While we have synthesized the Cu-Ag catalysts by incipient wetness co-impregnation method, we have also synthesized two samples (with 250 ppm and 1500 ppm Cu loadings) by sequential impregnation method. Depending on the amount of each precursor used during the synthesis, the concentrations of these bimetallic catalyst samples can be described in different forms as shown in Table 5.
Table 5: Catalyst composition in different units for Cu-Ag catalysts

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>ppm Cu (based on total catalyst weight)</th>
<th>Cu wt.% (based on total catalyst weight)</th>
<th>gram Cu / gram Ag</th>
<th>mole Cu / mole Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA 02</td>
<td>250</td>
<td>0.025%</td>
<td>0.25%</td>
<td>0.42%</td>
</tr>
<tr>
<td>SA 03</td>
<td>500</td>
<td>0.050%</td>
<td>0.5%</td>
<td>0.84%</td>
</tr>
<tr>
<td>SA 04</td>
<td>750</td>
<td>0.075%</td>
<td>0.75%</td>
<td>1.26%</td>
</tr>
<tr>
<td>SA 01</td>
<td>1000</td>
<td>0.1%</td>
<td>1%</td>
<td>1.67%</td>
</tr>
<tr>
<td>SA 05</td>
<td>1500</td>
<td>0.15%</td>
<td>1.5%</td>
<td>2.48%</td>
</tr>
<tr>
<td>SA 02 – 2 Step</td>
<td>250</td>
<td>0.025%</td>
<td>0.25%</td>
<td>0.42%</td>
</tr>
<tr>
<td>SA 05 – 2 Step</td>
<td>1500</td>
<td>0.15%</td>
<td>1.5%</td>
<td>2.48%</td>
</tr>
</tbody>
</table>

The composition of some of the Cu-Ag samples was determined using ICP-AES technique. It was found that the ICP results were identical to the expected concentration of Ag and Cu as seen in Table 6.

Table 6: Cu-Ag catalyst composition based on ICP-AES results

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Based on synthesis</th>
<th>Based on ICP-AES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt.% Ag</td>
<td>Wt.% Cu</td>
</tr>
<tr>
<td>SA 00a</td>
<td>10</td>
<td>---</td>
</tr>
<tr>
<td>SA 02</td>
<td>10</td>
<td>0.025</td>
</tr>
<tr>
<td>SA 05</td>
<td>10</td>
<td>0.15</td>
</tr>
<tr>
<td>SA 02 – 2 Step</td>
<td>10</td>
<td>0.025</td>
</tr>
<tr>
<td>SA 05 – 2 Step</td>
<td>10</td>
<td>0.15</td>
</tr>
</tbody>
</table>

XPS is a surface-sensitive technique that determines the concentration of various elements in the top few layers of the catalyst. Since catalytic reactions occur on the surface, the XPS results are very helpful in determining the surface composition of the active metal for a given catalyst sample. The summary of the XPS scan of the Cu-Ag catalyst as seen in Table 7 suggests that that the concentration of Cu in the top few layers is much greater than the overall bulk concentration of Cu. This is in line with the XPS results that are reported in the literature [27], for e.g. a catalyst with 0.1 wt.% Cu was reported to have ~9 Cu surface atoms per 100 Ag atoms.
The enrichment of the catalyst surface with Cu is not surprising considering the fact that the synthesis was done in an oxygen atmosphere. Oxygen is more oxyphilic and it binds to Cu more strongly than to Ag. Thus it tends to come on the surface during the synthesis process which is clearly seen in the XPS scans of these catalysts. It is experimentally shown [51] that, in the absence of oxygen, copper impurities in silver prefer to stay directly below the silver surface, rather than in the bulk or on the surface. However, the presence of oxygen has the effect to induce copper to segregate to the surface due to the strength of the O-Cu bond relative to the O-Ag one. The XPS results of the two-step sequential impregnation synthesis method of the Cu-Ag catalyst shows that the surface is more concentrated with Cu atoms compared to the co-impregnation method. This is expected as the sequential impregnation will deposit Cu atoms on top of the Ag particles.

### 3.3 Composition of bimetallic Au-Ag/α-Al₂O₃ catalyst samples

In the literature, both gold cyanide (Au(CN)) [52] or chloroauric acid (HAuCl₄) [30] are reported as a possible gold precursor for the synthesis of the bimetallic Au-Ag catalyst and we have used HAuCl₄ as a gold precursor. AgNO₃ is reported as the silver precursor and we have used the same as well. While 13.18% Ag loading was used in the literature, we have kept the Ag loadings at 10% for all samples. Depending on the amount of each precursor used during the synthesis, the concentrations of these bimetallic catalyst samples can be described in different forms as shown in Table 8.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>ppm Au (based on total catalyst weight)</th>
<th>Au wt.% (based on total catalyst weight)</th>
<th>gram Au / gram Ag</th>
<th>mole Au / mole Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA 11</td>
<td>250</td>
<td>0.025%</td>
<td>0.25%</td>
<td>0.14%</td>
</tr>
<tr>
<td>SA 12</td>
<td>500</td>
<td>0.050%</td>
<td>0.5%</td>
<td>0.27%</td>
</tr>
<tr>
<td>SA 13</td>
<td>750</td>
<td>0.075%</td>
<td>0.75%</td>
<td>0.41%</td>
</tr>
<tr>
<td>SA 14</td>
<td>1000</td>
<td>0.1%</td>
<td>1%</td>
<td>0.55%</td>
</tr>
<tr>
<td>SA 15</td>
<td>1500</td>
<td>0.15%</td>
<td>1.5%</td>
<td>0.82%</td>
</tr>
</tbody>
</table>
The composition of the Au-Ag sample with lowest and the highest loading was determined using ICP-AES technique. It was found that the ICP results were identical to the expected concentration of Ag and Au as seen in Table 9.

Table 9: Au-Ag catalyst composition based on ICP-AES results

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Based on synthesis</th>
<th>Based on ICP-AES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt.% Ag</td>
<td>Wt.% Au</td>
</tr>
<tr>
<td>SA 11</td>
<td>10</td>
<td>0.025</td>
</tr>
<tr>
<td>SA15</td>
<td>10</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The summary of the XPS scan (Table 10) of the Au-Ag catalyst suggests that the concentration of Au in the top few layers of the catalyst is somewhat lower than the overall bulk concentration of Au in the catalyst. Though we could not find the XPS results for Au-Ag bimetallic catalysts for comparison, our results look reasonable considering the fact that Ag is more oxyphilic compared to Au. Thus when we synthesize the catalyst in an oxygen environment, we should expect more Ag on the surface because of the stronger interaction of Ag with O$_2$ compared to Au.

Table 10: Surface composition (from XPS results) for Au-Ag catalysts synthesized by co-impregnation method

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Au loading, ppm</th>
<th>mole Au / mole Ag in bulk (based on calculations)</th>
<th>mole Au / mole Ag on surface (based on XPS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA 11</td>
<td>250</td>
<td>0.14%</td>
<td>0.08%</td>
</tr>
<tr>
<td>SA 12</td>
<td>500</td>
<td>0.27%</td>
<td>0.23%</td>
</tr>
<tr>
<td>SA 13</td>
<td>750</td>
<td>0.41%</td>
<td>0.26%</td>
</tr>
<tr>
<td>SA 14</td>
<td>1000</td>
<td>0.55%</td>
<td>0.36%</td>
</tr>
<tr>
<td>SA 15</td>
<td>1500</td>
<td>0.82%</td>
<td>0.75%</td>
</tr>
</tbody>
</table>

### 3.4 Thermal Gravimetric Analysis (TGA)

The TGA technique was employed to analyze bimetallic catalyst samples that had 10% Ag and 1000 ppm each of Cu, Cs, and Au respectively. We have used TGA to analyze our catalyst synthesis procedure and to confirm that the temperatures used during the heat treatment were sufficiently high to remove all of the precursors used during the synthesis. The change in weight of the samples with respect to temperature and the first derivative of the change in weight was measured for each catalyst sample.

The typical catalyst synthesis had a heat treatment step that was carried out at 275°C and it can be seen from Figure 6 that all precursors were removed by thermal decomposition at this temperature.
Upon further zooming in on the first derivative of the change in weight, it is found that there are two temperature ranges in which we see a drop in weight. First, it is seen in the temperature range of 100-120°C, this could be the mass lost from the sample due to moisture and the oxalate decomposition. Since this drop is consistent in all three samples, it could be either water or oxalate since these two are the only common species in all of them.

The second drop in mass is seen at a higher temperature. It is at approximately 200°C for Au-Ag catalyst sample, 215°C for Cs-Ag catalysts sample and around 240°C for Cu-Ag catalyst sample. These can be attributed to the other precursor used in the bimetallic catalyst synthesis, namely HAuCl₄ CsNO₃ and Cu(NO₃)₂ respectively for Au, Cs, and Cu. These peaks are clearly shown while zooming in at around these temperatures as seen in Figure 7.
3.5 The chloride problem in Au-Ag/α-Al₂O₃ catalysts

It is found in the literature that either gold cyanide (Au(CN)) [52] or chloroauric acid (HAuCl₄) [30] can be used as a gold precursor for the synthesis of the bimetallic Au-Ag catalyst. The advantage of using Au(CN) is that it avoids contamination of the catalyst by chlorine which is a well-known promoter of ethylene epoxidation reaction [53]. However, its biggest drawback is the acute toxicity and extreme care required in its handling. Thus we chose to use the chloroauric acid as a gold precursor in our synthesis.

Since HAuCl₄ was used as a precursor in the catalyst synthesis, it was possible that some form of chlorine could be present in the catalyst sample. The XPS scan of these catalyst samples also confirmed the presence of chlorine. Though initially we were not sure that in which form we will see the chlorides, it was found that the chlorine was present in the form of AgCl crystals as identified by the XRD peaks.

The XRD scan of the Au-Ag catalyst with maximum Au content is shown in Figure 8. The analysis of the XRD scan clearly shows the presence of AgCl peaks (PDF database PDF 01-071-5209) at their maximum intensities of ~32.3° and ~27.8° respectively for 2Θ values.

![Figure 8: XRD scan of Au-Ag catalyst (left) and the clear presence of AgCl peaks seen (right)](image)

The presence of AgCl crystals was also very clearly seen in the TEM images. The AgCl was present in the form of small particles together with larger Au-Ag bimetallic particles. Upon zooming in on these smaller particles, it was found that they were sensitive to the electrons and showed characteristic shape of crystals as seen in Figure 9.
As discussed in the Experimental section, we used a heat treatment procedure where the catalyst sample was heated up to a temperature of 350°C under 10% H\textsubscript{2} environment to remove these chlorides species. A distinct peak for HCl was observed in mass spectrometry (MS) for this heating procedure. Figure 10 which plots the current intensity of HCl normalized with the helium signal shows that when we ramp up the temperature, the HCl peak develops at around 350°C (~10 minutes). The sample was held at this temperature for around 90 minutes until the chloride signal tapers off as the chlorides are removed from the catalyst. At the end of 90 minute period, all of the chlorine has been removed and it was found that HCl peak tapered off to the initial intensity.

Figure 9: Presence of small AgCl crystals seen in the TEM image (left) and zooming in on those crystals (right)

Figure 10: HCl peak in mass spectrometry during H\textsubscript{2} treatment
We checked the presence of chlorine in the Au-Ag bimetallic catalyst by using XPS technique. The Cl2p XPS scans of the catalyst sample before and after H₂ treatment is shown in Figure 11. It is seen clearly that there is no more Cl found on the catalyst after the treatment.

![XPS scan for Cl on the catalyst sample before (left) and after (right) H₂ treatment](image1)

*Figure 11: XPS scan for Cl on the catalyst sample before (left) and after (right) H₂ treatment*

Based on the above discussion, it can be concluded that the H₂ treatment proved successful in the removal of the chlorine species from the catalyst samples. However, it was found that after the heat treatment procedure, the AgCl particles were broken down into Ag particles which were much smaller in size compared to other bimetallic particles. The smaller sized Ag particles were very clearly seen in the TEM images, for example, see Figure 12.

![TEM image showing AgCl crystals (before treatment) converted into smaller Ag particles (after treatment)](image2)

*Figure 12: AgCl crystals (before treatment) converted into smaller Ag particles (after treatment)*
Since smaller sized particles have a higher surface area compared to larger sized particles, it is important to calculate the number of such smaller particles and compare their surface area with respect to the total surface area of the active bimetallic particles in the catalyst. If the surface area of the smaller particles is significant compared to the total active metal surface area then we need to take that into account while evaluating the catalyst performance. However, if it is less (~1-2%) then we could neglect their effect. This is further elaborated in the next section where the surface area of the smaller particles is calculated and it is shown that smaller particles contribute to only 1-2% of the total surface area of active metal.

### 3.6 Particle size distribution of bimetallic catalysts

The particle size distribution of the active metal on the catalyst support was calculated using many TEM images. It is observed that the particle size distribution resembles a normal distribution. Since heterogeneous catalysis is a surface phenomenon, the equivalent surface diameter for the given particle size distribution is defined as:

$$D_{eq} = \left( \frac{\sum n_i \cdot A_i}{\sum n_i} \cdot \frac{1}{n} \right)^{0.5}$$

where $n_i$ is the number of particles of diameter $d_i$ as seen in TEM images

and area of each small metal particle is $A_i = \pi d_i^2$

Mean diameter ($\mu$) defined as the simple average of the particle diameters and the standard deviation ($\sigma$) of the particle size distribution are also calculated and reported. The standard error mean defined as $\sigma / \sqrt{n}$ is also calculated for each sample.

It is reported in literature that the alumina monolith used for bimetallic Cu-Ag catalyst was almost completely covered with Ag as seen by their SEM images [25]. Similarly the Au-Ag catalyst as reported in the literature [30] also showed very high dispersion for Ag. For both of these cases, it was reported that the Cu or Au was present on the silver surface as determined by TEM/EDS technique. For our bimetallic Cu-Ag and Au-Ag catalysts, we do not observe the entire alumina surface covered by Ag in our TEM images. Thus it may be possible that instead of being present on the Ag surface, some of the Cu or Au is present directly on the alumina. However, we have not analyzed the exact location of Cu or Au on the catalyst and since their loading is very less compared to Ag loading on the alumina, we have ignored their presence as individual metal clusters and the particle size distribution is reported for combined Cu-Ag and Au-Ag bimetallic catalyst itself.

**Cu-Ag/\(\alpha\)-Al\(_2\)O\(_3\) bimetallic catalyst**

For Cu-Ag catalyst synthesized using the co-impregnation method, the summary of the catalyst particle size distribution can be seen in Table 11 and the histogram of the particle size distribution of these samples can be seen in Figure 13. The equivalent surface diameter for all of the Cu-Ag catalysts was found to be in the range of 130-140 nm.
Table 11: Particle size distribution for Cu-Ag bimetallic catalyst synthesized by co-impregnation method

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>ppm Cu</th>
<th>Particles counted</th>
<th>Equivalent surface diameter, nm</th>
<th>Mean diameter, nm</th>
<th>Standard deviation, nm</th>
<th>Standard Error Mean, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA 02</td>
<td>250</td>
<td>361</td>
<td>129.1</td>
<td>122.4</td>
<td>41.1</td>
<td>2.2</td>
</tr>
<tr>
<td>SA 03</td>
<td>500</td>
<td>242</td>
<td>132.1</td>
<td>125.5</td>
<td>41.2</td>
<td>2.6</td>
</tr>
<tr>
<td>SA 04</td>
<td>750</td>
<td>193</td>
<td>126.6</td>
<td>122.5</td>
<td>32.0</td>
<td>2.3</td>
</tr>
<tr>
<td>SA 01</td>
<td>1000</td>
<td>196</td>
<td>137.7</td>
<td>128.6</td>
<td>49.4</td>
<td>3.5</td>
</tr>
<tr>
<td>SA 05</td>
<td>1500</td>
<td>259</td>
<td>132.3</td>
<td>127.5</td>
<td>35.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Figure 13: Particle size distribution histogram for Cu-Ag catalyst synthesized by co-impregnation method

For Cu/Ag catalyst synthesized by sequential impregnation, initially the 10% Ag on α-Al₂O₃ was made and then Cu was deposited in the second step of the synthesis. The summary of the catalyst particle size distribution can be seen in Table 12 and the histogram of the particle size distribution of these samples can be seen in Figure 14.
Table 12: Particle size distribution for Cu-Ag bimetallic catalyst synthesized by sequential impregnation method

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>ppm Cu</th>
<th>Particles counted</th>
<th>Equivalent surface diameter, nm</th>
<th>Mean diameter, nm</th>
<th>Standard deviation, nm</th>
<th>Standard Error Mean, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA 00-a</td>
<td>---</td>
<td>349</td>
<td>135.3</td>
<td>126.8</td>
<td>47.3</td>
<td>2.5</td>
</tr>
<tr>
<td>SA 02 – 2 Step</td>
<td>250</td>
<td>397</td>
<td>131.2</td>
<td>123.3</td>
<td>44.8</td>
<td>2.3</td>
</tr>
<tr>
<td>SA 05 – 2 Step</td>
<td>1500</td>
<td>355</td>
<td>148.7</td>
<td>139.0</td>
<td>52.9</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Comparing the particle size distribution for all of the Cu-Ag catalysts, we find that the equivalent surface diameter for all samples is roughly in the same range. Thus we can conclude that the Cu loadings used in these samples have no influence on the particle size and these catalysts can be compared directly for their activity.

**Au-Ag/α-Al₂O₃ bimetallic catalyst**

For Au-Ag catalyst synthesized using a co-impregnation method, the summary of the catalyst particle size distribution before the H₂ treatment was carried out to remove chlorines can be seen in Table 13 and the histogram of the particle size distribution of these samples can be seen in Figure 15. We have not considered the AgCl particles in this particle size distribution calculations as they are treated in the next step. While all of the samples show the nearly identical histogram for particle size distribution, the SA15 (1500 ppm Au) sample shows a more broad particle size distribution. Though we are not sure of the reason for this, this could have occurred due to some mistake in our synthesis of this sample or it could be due to the effect of Au in Ag catalyst.
Table 13: Particle size distribution for Au-Ag bimetallic catalyst before H\textsubscript{2} heat treatment

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>ppm Au</th>
<th>Particles counted</th>
<th>Equivalent surface diameter, nm</th>
<th>Mean diameter, nm</th>
<th>Standard deviation, nm</th>
<th>Standard Error Mean, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA 11</td>
<td>250</td>
<td>123</td>
<td>138.5</td>
<td>131.1</td>
<td>44.7</td>
<td>4.0</td>
</tr>
<tr>
<td>SA 12</td>
<td>500</td>
<td>208</td>
<td>142.2</td>
<td>134.0</td>
<td>47.6</td>
<td>3.3</td>
</tr>
<tr>
<td>SA 13</td>
<td>750</td>
<td>353</td>
<td>146.1</td>
<td>138.9</td>
<td>45.3</td>
<td>2.4</td>
</tr>
<tr>
<td>SA 14</td>
<td>1000</td>
<td>217</td>
<td>142.0</td>
<td>133.6</td>
<td>48.2</td>
<td>3.3</td>
</tr>
<tr>
<td>SA 15</td>
<td>1500</td>
<td>367</td>
<td>156.2</td>
<td>146.5</td>
<td>54.2</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Figure 15: Particle size distribution histogram for Au-Ag catalyst before H\textsubscript{2} treatment

Earlier we discussed that the H\textsubscript{2} treatment of the Au-Ag catalyst samples created smaller Ag particles on the catalyst which were the result of the decomposition of the AgCl particles. The size of these smaller particles was measured and compared with the particles of other sizes to see how much was their impact on the total surface area. Here we have defined a smaller particle as the one with less than 50 nm diameter. This is chosen because for all the TEM images that we have analyzed for other bimetallic catalysts, we hardly saw any particles smaller than 50 nm in size and this can be seen from the particle size distribution histogram.
of those samples. The summary of the catalyst particle size distribution after the H\textsubscript{2} treatment was carried out to remove chlorines can be seen in Table 14 and the histogram of the particle size distribution of these samples can be seen in Figure 16.

Table 14: Particle size distribution for Au-Ag bimetallic catalyst after H\textsubscript{2} treatment

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>ppm Au</th>
<th>Particles counted</th>
<th>Equivalent surface diameter, nm</th>
<th>Mean diameter, nm</th>
<th>% surface area of smaller particles</th>
<th>Standard deviation, nm</th>
<th>Standard Error Mean, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA 11 – 350C</td>
<td>250</td>
<td>391</td>
<td>119.0</td>
<td>105.2</td>
<td>1.6%</td>
<td>55.7</td>
<td>2.8</td>
</tr>
<tr>
<td>SA 12 – 350C</td>
<td>500</td>
<td>189</td>
<td>111.0</td>
<td>97.3</td>
<td>1.9%</td>
<td>53.5</td>
<td>3.9</td>
</tr>
<tr>
<td>SA 13 – 350C</td>
<td>750</td>
<td>247</td>
<td>125.8</td>
<td>112.3</td>
<td>1.0%</td>
<td>56.8</td>
<td>3.6</td>
</tr>
<tr>
<td>SA 14 – 350C</td>
<td>1000</td>
<td>348</td>
<td>123.7</td>
<td>104.1</td>
<td>1.9%</td>
<td>66.8</td>
<td>3.6</td>
</tr>
<tr>
<td>SA 15 – 350C</td>
<td>1500</td>
<td>411</td>
<td>135.1</td>
<td>118.2</td>
<td>1.1%</td>
<td>65.5</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Figure 16: Particle size distribution histogram for Au-Ag bimetallic catalyst after H\textsubscript{2} treatment
It can be seen from the particle size distribution histogram that there are as many particles of smaller size (less than 50 nm) as there are particles in the range around the mean of the distribution (between 100 nm to 150 nm). However, due to the small size of the particles, their contribution to the total metal surface area is 1-2% only. Since the contribution of the smaller particles is very small, we still consider these catalysts with the same equivalent diameter based on the external surface area. Consequently, all the Au-Ag catalysts described in this report from now onwards are the ones that are treated in H₂ environment to remove chlorides; unless otherwise stated explicitly.

3.7 X-ray Photoelectron Spectroscopy (XPS)

Photoelectron lines and X-ray excited Auger lines often exhibit differences in chemical shifts which are a function of the chemical environment of the atom. The Auger parameter, involving measurements of both Auger and photoelectron line energies, provides abundant chemical state information without the necessity or concern for charge correction and work function measurements. Since the change in Auger parameter is equal to twice the change in extra-atomic relaxation energy, it is also a direct measure of the electronic interaction with the surrounding atoms [54]. The Auger parameter concept is based on the following ideas:

- There is a fixed difference between two line energies (Auger and photoelectron) of the same element in the same sample.
- Charge corrections to the individual peak measurements are unnecessary because they simply cancel during the estimation of the Auger parameter.
- Work function corrections are also unnecessary, and vacuum level data can be compared to Fermi level data directly.

Auger parameter is defined as the sum of the binding energy of the ground level and kinetic energy of the Auger line for that element.

\[ \alpha + hv = E_b(PE) + E_k(Auger) \]

For silver, the formula involves the Ag 3d_{5/2} ground level and Auger line Ag M4N4, 5N4, 5 [55].

\[ \alpha + hv = E_b\left(\text{Ag } 3d_{5/2}\right) + E_k(\text{Ag } M4N4, 5N4, 5) \]

The shifts in Auger parameter exhibits the difference in the chemical environment of the atoms [54]. Though an empirical concept, it is a direct measure of the electronic interaction of the metal with the surrounding atoms. Thus we should be able to see a shift in Auger parameter due to the presence of Cu or Au in the catalyst. This was indeed confirmed as shown in Figure 17 which plots Auger parameter for different catalyst samples.
Though Auger parameter shift for Cu-Ag and Au-Ag alloy is not reported in the literature, we can compare it to the other compounds of silver for which these values are reported (see Figure 18). The Auger parameter for the Ag is reported to be ~726.1 eV [54], which is same as what we have obtained (726.0685 eV) from our 10% silver only catalyst sample SA00a.

While the silver oxides have Auger parameter shift of approximately -2.0 eV for AgO (Ag oxidation state of +2) and -1.6 eV for Ag₂O (Ag oxidation state of +1), for dilute alloys of silver
with aluminum and magnesium are shown to have Auger parameter values higher by ~0.4 eV and ~0.8 eV respectively than elemental silver. This means that these alloys make silver oxidation state to be partially negative. Our calculated values for the average Auger parameter were higher by 0.2943 eV for Au-Ag catalyst while it was higher by 0.3704 eV for Cu-Ag catalyst; which are in the same range as the other reported alloys. Also, this shows that the bimetallic Cu-Ag and Au-Ag catalyst makes the oxidation state of silver atoms partially negative. Since the Auger parameter for Cu-Ag is higher than the Au-Ag catalysts, this also shows that the presence of Cu affects the electronic behavior of silver surface more than the presence of Au.

Table 15: Auger parameter calculations

<table>
<thead>
<tr>
<th>Catalyst Code</th>
<th>Composition</th>
<th>Binding Energy of Ag 3d$_{5/2}$ (eV)</th>
<th>Kinetic energy of Auger line Ag M4N4, 5N4, 5 (eV)</th>
<th>Auger parameter, (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA00a</td>
<td>10% Ag</td>
<td>368.3</td>
<td>357.8</td>
<td>726.1</td>
</tr>
<tr>
<td>SA 02</td>
<td>250 Cu</td>
<td>368.2</td>
<td>358.1</td>
<td>726.3</td>
</tr>
<tr>
<td>SA 03</td>
<td>500 Cu</td>
<td>368.1</td>
<td>358.4</td>
<td>726.6</td>
</tr>
<tr>
<td>SA 04</td>
<td>750 Cu</td>
<td>368.1</td>
<td>358.5</td>
<td>726.6</td>
</tr>
<tr>
<td>SA 01</td>
<td>1000 Cu</td>
<td>368.2</td>
<td>358.2</td>
<td>726.4</td>
</tr>
<tr>
<td>SA 05</td>
<td>1500 Cu</td>
<td>368.2</td>
<td>358.3</td>
<td>726.5</td>
</tr>
<tr>
<td>SA02_2-step</td>
<td>250 Cu</td>
<td>368.2</td>
<td>358.2</td>
<td>726.4</td>
</tr>
<tr>
<td>SA05_2-step</td>
<td>500 Cu</td>
<td>368.3</td>
<td>358.1</td>
<td>726.4</td>
</tr>
<tr>
<td>SA 11</td>
<td>250 Au</td>
<td>367.9</td>
<td>358.5</td>
<td>726.4</td>
</tr>
<tr>
<td>SA 12</td>
<td>500 Au</td>
<td>367.8</td>
<td>358.5</td>
<td>726.3</td>
</tr>
<tr>
<td>SA 13</td>
<td>750 Au</td>
<td>367.7</td>
<td>358.7</td>
<td>726.5</td>
</tr>
<tr>
<td>SA 14</td>
<td>1000 Au</td>
<td>368.0</td>
<td>358.4</td>
<td>726.3</td>
</tr>
<tr>
<td>SA 15</td>
<td>1500 Au</td>
<td>367.6</td>
<td>358.7</td>
<td>726.3</td>
</tr>
</tbody>
</table>

3.8 X-ray Diffraction (XRD)

XRD is an analytical technique primarily used for phase identification of a crystalline material. We have used this technique to identify the metallic phase on our bimetallic catalyst and to see if we obtained an alloy or the metals segregated into individual metals during the synthesis. However, it is very difficult to identify XRD peaks for Cu or Au differently from Ag peaks because of two reasons. Firstly, the maximum intensity peaks for Ag, Cu & Au are very close to each other and thus it is very difficult to see them apart. Secondly, the concentration of Cu and Au in the catalyst samples is very small (maximum 1500 ppm or 0.15 wt.%) and XRD is not sensitive enough technique to record a peak for such low concentrations of metals. However, it is still possible to study the changes in the Ag peaks (location as well as shape) due to the presence of Cu or Au on the catalyst.

As discussed earlier, our Au-Ag catalyst samples were heat treated in H$_2$ to remove chlorine. The only difference that was particularly visible in the XRD scan of the samples before and
after the heat treatment was the absence of AgCl related peaks in the treated samples. Otherwise, the position and the shape of the peaks for these samples were almost identical.

Figure 19 shows the XRD scans of Cu-Ag and Au-Ag (treated) catalysts. Two XRD peaks can be seen in each of them; the smaller peak near $2\Theta = 37.8^\circ$ corresponds to $\alpha$-Al$_2$O$_3$ (Corundum syn, PDF database 00-010-0173) and larger peak at $2\Theta = 38.1^\circ$ corresponds to Ag (Silver-3C, syn, crystal system: cubic, space group: Fm3m, space group number: 225, PDF database 00-004-0783). The maximum intensity of Ag peak is expected at $2\Theta = 38.117^\circ$ and we find that the presence of Cu or Au in the catalyst has no significant effect on the position of the maximum intensity Ag peak.

![Figure 19: Silver XRD peaks for bimetallic Cu-Ag (left) and Au-Ag (right) catalysts](image)

Table 16 compares the FWHM (full width at half maximum) values for these bimetallic catalyst samples. It is found that the bimetallic Cu-Ag catalyst has higher FWHM compared to 10% Ag only catalyst which in turn has higher FWHM compared to Au-Ag catalyst. Generally, FWHM is indicative of crystal size and strain and it is inversely related. Thus, smaller the crystal size, greater is the value of FWHM; and the same holds true for the strain. For our case, it is difficult to draw many conclusions from the XRD analysis. Though the FWHM pattern follows the average particle size that we had calculated, it shows nothing about the effect of Cu or Au present in addition to the Ag particles.

![Table 16: FWHM comparison for 38.1° Ag peak for different catalysts](table)
3.9 Temperature Programmed Desorption (TPD) of Oxygen

For Ag catalyst supported on $\alpha$-Al$_2$O$_3$, several insights can be drawn from the interpretation of the O$_2$-TPD curve. It is a well-known fact that various oxygen species are present on the silver surface during the ethylene epoxidation reaction, for instance, the molecular oxygen, subsurface oxygen and various forms of surface atomic oxygen (nucleophilic and electrophilic) [39] [56]. It is also reported [57] that these distinct oxygen species can co-exist on Ag surface at temperatures and pressure of industrial interest in ethylene epoxidation.

10% Ag catalyst

For Ag supported on $\alpha$-Al$_2$O$_3$, it is found in the literature [58] that the oxygen peak at around 280°C is associated with the associative desorption of oxygen from the catalytically active silver. It is believed that this surface-bound atomic oxygen occurs on multi-atom sites and preferentially leads to the formation of complete oxidation products [56]. The peak at a higher temperature of 380°C is associated with the subsurface oxygen that is present due to the pre-treatment of the catalyst at a higher temperature before the TPD experiment [56]. The formation of subsurface oxygen is considered necessary for the activation of the silver catalysts for ethylene epoxidation reaction.

Figure 20 shows the O$_2$-TPD curve for 10% Ag on $\alpha$-Al$_2$O$_3$ catalyst. Since several oxygen species can co-exist on the catalyst surface, we need to perform deconvolution of these oxygen peaks to identify the quantity of each of the oxygen species. For all the subsequent O$_2$-TPD curves, the deconvolution was done using Gauss function in Origin® 2015 software and the adjusted R-squared value for the fit was ~0.98-0.99 for all the curves.

![Figure 20: O₂-TPD curve for 10% Ag catalyst and the deconvolution fitting for different oxygen peaks](image-url)
A pulse experiment was also conducted on this 10% Ag/α-Al₂O₃ catalyst for determining the amount of oxygen that was adsorbed. A known loop volume (100 µl) of the oxygen pulse was related to the current intensity and the integrated area to determine a correlation between the adsorbed oxygen (in µmol) to the area under the curve for all of the O₂-TPD experiments.

Cu-Ag/α-Al₂O₃ bimetallic catalyst

The result for O₂-TPD experiments for Cu-Ag bimetallic catalyst that was synthesized by co-impregnation method is shown in Figure 21. It shows the various peaks for desorbed oxygen at different temperatures. At first glance, two distinct peaks at 240°C and 300°C, as well as a shoulder or a long tail at around 380°C can be observed.

![Figure 21: O₂-TPD curves for bimetallic Cu-Ag catalyst synthesized by co-impregnation method](image)

Compared to 10% Ag only catalyst, it can be seen in Figure 21 that there is an additional peak at around 240°C in the O₂-TPD. This peak is only seen in the catalysts that had Cu in bulk and it is not seen in the catalyst that was prepared by sequential impregnation and thus had Cu only on the surface. Thus this peak can be attributed to the presence of Cu atoms in the bulk of the silver catalysts.

It is also found that the peak associated with surface oxygen has shifted to a slightly higher temperature from 280°C in the silver only catalyst to about 300°C in Cu-Ag catalyst. This observation can be explained by the fact that Cu binds oxygen stronger than the silver. So the presence of some Cu on Ag surface will bind the oxygen stronger resulting in shifting of the peak towards a higher temperature.
It is also observed that the shoulder associated with subsurface oxygen remains at around 380°C for all catalysts that had Cu in it. Additionally, these shoulders have a broader tail and thus they had more subsurface oxygen compared to the silver only catalyst. It is also found that for higher Cu loadings, a distinct peak can be seen instead of a broad shoulder.

The summary for the amount of oxygen adsorbed on the catalyst corresponding to each O₂-TPD peak is shown in Table 17. It also compares the amount of oxygen adsorbed on the bimetallic Cu-Ag catalyst with respect to 10% Ag only catalyst. Figure 22 plots the oxygen adsorbed for different loadings of Cu.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Cu loading, ppm</th>
<th>Oxygen adsorbed (nmol/g_{cat})</th>
<th>% of adsorbed on Cu-Ag catalyst w.r.t. 10% Ag catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Peak 1 (~240°C)</td>
<td>Peak 2 (~300°C)</td>
</tr>
<tr>
<td>SA00a</td>
<td>0 (10% Ag)</td>
<td>0</td>
<td>1271</td>
</tr>
<tr>
<td>SA 02</td>
<td>250</td>
<td>361</td>
<td>1121</td>
</tr>
<tr>
<td>SA 03</td>
<td>500</td>
<td>331</td>
<td>1461</td>
</tr>
<tr>
<td>SA 04</td>
<td>750</td>
<td>155</td>
<td>1290</td>
</tr>
<tr>
<td>SA 01</td>
<td>1000</td>
<td>311</td>
<td>957</td>
</tr>
<tr>
<td>SA 05</td>
<td>1500</td>
<td>280</td>
<td>418</td>
</tr>
</tbody>
</table>

Figure 22: Oxygen adsorbed on bimetallic Cu-Ag catalyst in O₂-TPD experiments
It can be seen here that the total oxygen adsorbed on the bimetallic Cu-Ag catalyst is higher thanAg only catalyst but it shows a decreasing trend with increasing Cu loadings. If we break down the total oxygen adsorbed on the catalyst into different peaks then it is observed that oxygen adsorbed due to the presence of bulk Cu (Peak 1 (~240°C)) remains nearly constant for different loadings of Cu. The amount of surface oxygen (Peak 2 (~300°C)) also shows a decreasing trend with the increasing Cu loading. However, it remains nearly the same up to 750 ppm Cu loadings and then it shows a sharp decline for higher loadings. This could possibly happen due to the silver surface being killed for oxygen adsorption by the excess Cu on the surface. It is also observed that the presence of Cu increases the subsurface oxygen (Peak 3 (~380°C)) as compared to the silver only catalyst.

The combined effect of Cu in the O₂-TPD of the bimetallic Cu-Ag catalyst synthesized by the co-impregnation method is that maximum oxygen is adsorbed for 250 ppm Cu loading and it shows decreasing trend in such a way that at 1500 ppm Cu, the total adsorbed oxygen is only slightly more than Ag only catalyst.

The result for O₂-TPD experiments for Cu-Ag bimetallic catalyst that was synthesized by sequential impregnation method is shown in Figure 23 and summarized in Table 18. The most striking difference between the O₂-TPD curves for two different synthesis method is that we do not see a peak at ~240°C in sequential impregnation catalyst. This validates our previous assumption that this peak corresponds to the presence of bulk Cu in the catalyst. Another observation is that there is a definite peak instead of a shoulder (at ~380°C) for subsurface oxygen in sequential impregnation catalyst even at lower Cu loadings, but it is only seen for highest Cu loading in co-impregnation catalyst.

Figure 23: Comparison of O₂-TPD curves for bimetallic Cu-Ag catalyst synthesized by co-impregnation and sequential impregnation
Comparing the total oxygen adsorbed on the sequential impregnated Cu-Ag catalyst, we find that the oxygen adsorbed is lower than any of the co-impregnated Cu-Ag catalyst. This seems counter-intuitive considering the fact that Cu is more oxyphilic so it must hold more oxygen than silver. However, it may be possible that excess of Cu kills the adsorption capacity of Ag surface to hold oxygen or the oxygen adsorbed on Ag/Cu is too strong to desorb at TPD temperatures. Since we have the average particle size of Ag particles from TEM analysis and we know the amount of Cu that was deposited during sequential impregnation, we can calculate theoretically how much surface area of Ag can be covered by Cu atoms. We find that for 250 ppm sample, the coverage is ~44.1% while it is ~265% for 1500 ppm sample. This validates our argument that the sequential impregnated catalyst has a very high Cu content on the surface.

Table 18: Comparison of O$_2$-TPD curves for bimetallic Cu-Ag catalyst synthesized by co-impregnation and sequential impregnation method

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Cu loading, ppm</th>
<th>Oxygen adsorbed (nmol/g$_\text{cat}$)</th>
<th>% of adsorbed on Cu-Ag catalyst w.r.t. 10% Ag catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Peak 1 (~240°C)</td>
<td>Peak 2 (~300°C)</td>
</tr>
<tr>
<td>SA00a</td>
<td>0 (10% Ag)</td>
<td>0</td>
<td>1271</td>
</tr>
<tr>
<td>SA 02</td>
<td>250</td>
<td>361</td>
<td>1121</td>
</tr>
<tr>
<td>SA 05</td>
<td>1500</td>
<td>280</td>
<td>418</td>
</tr>
<tr>
<td>SA02_2-step</td>
<td>250</td>
<td>0</td>
<td>680</td>
</tr>
<tr>
<td>SA05_2-step</td>
<td>1500</td>
<td>0</td>
<td>932</td>
</tr>
</tbody>
</table>

**Au-Ag/α-Al$_2$O$_3$ bimetallic catalyst**

The result for O$_2$-TPD experiments for Au-Ag bimetallic catalyst that was synthesized by co-impregnation method (and the samples were heat treated to remove H$_2$) is shown in Figure 24. It shows the various peaks for desorbed oxygen at different temperatures. For Au-Ag catalyst, the O$_2$-TPD gave some very interesting results. At first glance, it is clearly seen that the current intensity in the O$_2$-TPD curve for all Au-Ag catalysts is quite low compared to 10% Ag only catalyst. Thus we can conclude that the amount of oxygen adsorbed on these catalysts is lower than the silver only catalyst.
It can be seen that the addition of Au shifts the peak corresponding to surface oxygen species from 290°C for Ag only catalyst to around 250°C for the bimetallic catalyst. This observation can be explained by the fact that Au binds oxygen much weaker than the silver. So the presence of some Au on Ag surface will reduce the strength of oxygen bound to the surface resulting in shifting of the peak towards a lower temperature. Another observation is that the TPD peak for subsurface oxygen species does not change its position and it remains at 380°C.

The summary for the amount of oxygen adsorbed for Au-Ag catalyst corresponding to each O$_2$-TPD peak is shown in Table 19. It also compares the amount of oxygen adsorbed on the bimetallic Au-Ag catalyst with respect to 10% Ag only catalyst. Figure 25 plots the oxygen adsorbed for different loadings of Au.

**Table 19: Summary of the O$_2$-TPD curves for bimetallic Au-Ag catalyst**

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Au loading, ppm</th>
<th>Oxygen adsorbed (nmol/g-cat)</th>
<th>% of adsorbed on Au-Ag catalyst w.r.t. 10% Ag catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Peak 1 (~250°C)</td>
<td>Peak 2 (~380°C)</td>
</tr>
<tr>
<td>SA00a</td>
<td>0 (10% Ag)</td>
<td>1256</td>
<td>248</td>
</tr>
<tr>
<td>SA11</td>
<td>250</td>
<td>261</td>
<td>204</td>
</tr>
<tr>
<td>SA12</td>
<td>500</td>
<td>380</td>
<td>211</td>
</tr>
<tr>
<td>SA13</td>
<td>750</td>
<td>319</td>
<td>195</td>
</tr>
<tr>
<td>SA14</td>
<td>1000</td>
<td>361</td>
<td>168</td>
</tr>
<tr>
<td>SA15</td>
<td>1500</td>
<td>323</td>
<td>109</td>
</tr>
</tbody>
</table>

*Figure 24: O$_2$-TPD curves for bimetallic Au-Ag catalyst*
It can be seen that the adsorption of surface oxygen shows a sharp decline with the mere presence of Au and the total oxygen amount remains almost the same for different loading of Au. It is reported [49] that the Au atoms function as diluting agents on Ag surface and does not favor atomic oxygen adsorption which explains why we see a sharp decline in surface oxygen adsorption. Compared to the surface oxygen, the amount of sub-surface oxygen shows a steady decline with the increasing Au loading. However, since the total oxygen adsorbed is largely influenced by the surface atomic oxygen species and the subsurface oxygen has lesser influence, we see a large drop in the total adsorbed oxygen which then remains nearly constant for different loadings of Au. Quantitatively speaking, the amount of total oxygen adsorbed on the gold catalyst is lower, only around 30-40% of oxygen adsorbed on the silver only catalyst.

3.10 Catalyst selectivity and activity tests

The catalyst was tested in the reactor at 225°C with a 1:2 ratio of ethylene-to-oxygen, i.e. 5% ethylene and 10% oxygen. Industrial ethylene epoxidation processes are carried out both with ethylene-rich conditions (oxygen-based process) and equimolar to slightly oxygen-rich conditions (air-based process). For the oxygen-based process, typical ethylene-to-oxygen ratios of 3:1 to 4:1 are used, whereas the air-based process is typically run at an ethylene-to-oxygen ratio of 1:2 [25]. Generally the industrial EO reactors are run at higher pressure, for e.g. 20 bar [59]. We have tested the catalyst at 1 bar as well as at 20 bar conditions.
**Catalyst testing at 1 bar**

For the reactions done at 1 bar, the results for the selectivity of bimetallic Cu-Ag and Au-Ag catalyst compared to Ag only catalyst are shown in Figure 26. Figure 27 shows the rate of EO formation and rate of combustion in mol/(h*g\textsubscript{cat}) at 1 bar reaction pressure.

![Selectivity for catalyst reactions done at 1 bar](image1)

*Figure 26: Selectivity for catalyst reactions done at 1 bar*

![Rate of EO formation (left) and rate of combustion (right) for reactions done at 1 bar](image2)

*Figure 27: Rate of EO formation (left) and rate of combustion (right) for reactions done at 1 bar*

Here, we observe that the selectivity for bimetallic Cu-Ag or Au-Ag catalyst is lower compared to 10% Ag only catalyst. This is in contradiction with the results that are reported in the literature and the same is explained below.
While the literature reports [25] increase in the EO selectivity for Cu-Ag bimetallic catalyst, the experiments are always carried out at constant conversion (~2%) by changing the reaction temperature. For example, the temperature used for Ag only catalyst for 2% conversion was 217°C and the temperature was reduced to 202°C, 208°C, 197°C, 186°C for increasing Cu loading on the silver catalyst to achieve the same conversion. The reported increase in selectivity is from 36% (for Ag only catalyst at 217°C) to 52% (for 1% Cu/Ag at 186°C). Thus, our results which indicate ~3% conversion at 225°C (instead of 2% at 217°C) for Ag only catalyst with ~33% selectivity (instead of 36%) seems logical considering the fact that combustion reaction which is thermodynamically more favorable will occur at higher temperatures.

Since Cu is more oxyphilic than Ag, it is reported [60] that under epoxidation conditions oxygen covers the metal surface much faster than it can be removed by epoxidation of ethylene. It is also observed that the presence of Cu increases combustion reactions much more than the epoxidation reaction. This is expected since Cu acts as a combustion catalyst which burns ethylene in presence of oxygen at reaction temperatures. Thus, the increase in overall conversion can be attributed to the higher combustion and not to increased EO formation.

Though Au-Ag catalyst activity and selectivity is not reported for 1 bar reaction conditions, the general trend reported [30] for higher pressure is that the presence of Au increases the conversion at higher temperatures but reduces the selectivity. The authors have changed the temperatures to match the conversion and then report higher selectivity.

It can also be observed that for catalysts that showed higher oxygen adsorption in our O$_2$-TPD experiments also show higher activity. Albeit, the higher oxygen adsorption does not clearly co-relate to higher epoxidation reaction but it shows higher combustion reaction.

**Catalyst testing at 20 bar**

For the reactions done at 20 bar, the results for the selectivity of bimetallic Cu-Ag and Au-Ag catalyst compared to Ag only catalyst are shown in Figure 28. Figure 29 shows the rate of EO formation and rate of combustion in mol/(h*g$_{cat}$) at 20 bar reaction pressure.

The results for catalyst activity and selectivity for reactions done at 20 bar are similar to the results that we obtained at lower pressure. One clear observation was that all catalysts showed a higher selectivity at 20 bar as compared to 1 bar pressure. Also, the rate of EO formation, as well as rate of combustion, were higher at 20 bar as compared to 1 bar pressure.
While a higher selectivity can be seen for Au-Ag catalyst, it is only temporary and the selectivity drops sharply after some time to a lower value. This could happen for quite some reasons. First, it must be noted that our Au-Ag catalyst was synthesized using HAuCl₄ and thus there was a presence of Cl on the catalyst which was removed by H₂ heat treatment. Though XPS results proved that Cl was not present anymore on the surface, it is still possible that some very small trace amount of it remains on the catalyst which caused the higher selectivity. Only ppm amounts of Cl is required for promotion and it is shown that Cl suppresses both epoxidation and combustion reactions and increases EO selectivity with a loss in overall activity [23]. In our experiments, we see that for Au-Ag catalysts, the highest selectivity is
accompanied by the lower activity of both EO and combustion reaction. Thus it is more likely that instead of seeing the effects of Au promotion, we are seeing the effects of Cl in the reaction. After few hours of reaction when all of the Cl has been used up, we see a sharp rise in the activity together with a sharp drop in selectivity.

However, the above explanation raises a very important question that if the Cl was present on the catalyst then why it showed its effect only at 20 bar experiments and had no effect on 1 bar experiment. It is reported [61] that the general mechanism of chlorine promotion is that it forms an intermediate that is common to both ethylene epoxide and CO₂ production but the rapid branching of this intermediate by ensemble effect influences the selectivity. It is therefore possible that the presence of this intermediate is only seen at higher pressure and at lower pressure, it is either not formed or too unstable to affect the reaction.

Other reason for seeing temporarily such higher selectivity could be the result of particle agglomeration in the Au-Ag catalyst. It was discussed earlier that the Au-Ag catalyst showed a presence of smaller Ag particles that were leftovers from AgCl decomposition. The TEM analysis of the spent Au-Ag catalyst showed that all of the smaller Ag particles have agglomerated into larger Ag particles and the smaller particles were either absent or very few left on the catalyst. It is reported in the literature [62] that selectivity depends on particle size (at constant conversion). However, there is no report on the dependency of the selectivity on particle size at a constant temperature. It is also reported [63] that smaller Ag nanoparticles have higher concentration of Ag(100) facets than Ag(111) and DFT calculations show that EO formation is more favorable on Ag(100) surface than Ag(111). Though there have been some attempt to determine the relationship between morphological changes in the catalyst and its activity in epoxidation reaction, nothing conclusive has been reported yet [64].

Though Cu-Ag catalyst activity and selectivity is not reported for 20 bar reaction conditions, the general trend reported [25] for atmospheric pressure is that the presence of Cu increases the conversion at higher temperatures but reduces the selectivity. The authors have changed the temperatures to match the conversion and then report higher selectivity.

While the higher selectivity for bimetallic Cu-Ag and Au-Ag catalyst are commonly reported at constant conversion as discussed above, this approach introduces a major drawback. It is well-known fact that the ethylene epoxidation on Ag catalyst is a kinetically preferred reaction while combustion reaction is thermodynamically preferred [22]. Thus changing the reaction temperature to obtain a constant conversion also changes the energy of the system. Thus to compare the performance of bimetallic Cu-Ag and Au-Ag catalyst, it is advisable to compare their performance at a constant temperature as it is done in this project and not at constant conversion.

It is also noteworthy that while our catalysts showed low coverage of Ag on α-Al₂O₃ support, the alumina monoliths reported in the above-mentioned literature had either fully covered surface or had a very high surface coverage with Ag. It is reported [65] that the lower Ag dispersion gives lower yields and selectivity and that is the reason why commercial catalysts use low surface area alumina with very high silver loadings. Also, the literature reported catalysts had Cu or Au on the Ag surface and it was not present as an individual cluster of metal on the support material as determined by them through TEM/EDS mapping. Since we do not see the entire alumina surface covered by Ag in our TEM images, it may be possible
that instead of being present on the Ag surface, some of the Cu or Au is present directly on
the alumina. The presence of individual clusters of Cu will act as combustion catalyst while Au
cluster will fail to dissociate oxygen for EO formation, thus giving either lower selectivity or
lower activity. This combined with the fact that we saw very less Ag dispersion could have
resulted in the poorer performance of our bimetallic catalyst as compared to the literature.

3.11 Catalyst restructuring during epoxidation reaction

The particle size distribution of the active metal on the catalyst support after the reaction was
studied using STEM images. The summary of the particle size distribution for fresh catalyst
and for the spent catalyst (for both 1 bar and 20 bar reaction pressure) is shown in Table 20
and the differences are plotted as shown in Figure 30. Reaction time for spent catalyst was 60
h for SA00a (10% Ag), 40 h for SA05 (1500 ppm Cu) and SA15 (1500 ppm Au) for both
pressures, while it was different for SA05_2-step (1500 ppm Cu) and SA11 (250 ppm Au) for
1 bar and 20 bar pressures.

Table 20: Particle size comparison for fresh catalyst and spent catalyst (P1 = 1 bar, P20 = 20 bar)

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Loading (ppm)</th>
<th>Fresh catalyst</th>
<th>Spent catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Particles counted</td>
<td>Eq. diameter (nm)</td>
<td>Std. deviation (nm)</td>
</tr>
<tr>
<td>SA00a 10% Ag</td>
<td>349</td>
<td>135.3</td>
<td>47.3</td>
</tr>
<tr>
<td>SA05 1500 Cu</td>
<td>259</td>
<td>132.3</td>
<td>35.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA05_2-step</td>
<td>1500 Cu (2-step)</td>
<td>355</td>
<td>148.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA11 250 Au</td>
<td>391</td>
<td>119</td>
<td>55.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA15 1500 Au</td>
<td>594</td>
<td>135.1</td>
<td>65.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Comparing the average particle size for fresh catalyst and the spent catalyst, we find that the average size is higher for all spent catalysts. Also, the catalyst that was tested at higher pressure showed more increase in the average particle size compared to the catalyst that was tested at 1 bar. Our calculation shows that on average particle size increased by ~9 nm for 1 bar while it increased by ~19 nm for 20 bar reaction conditions. The reason for an increase in particle size during the reaction could be due to the agglomeration of silver particles during the epoxidation reaction. This kind of accumulation of the silver particle is also reported in the literature [22] for ethylene epoxidation reaction. Since we saw higher activity at 20 bar pressure, it is natural that agglomeration will also be more at this pressure. Intuitively we can say that the reaction time should also affect the particle size and longer reaction time should give more agglomeration. However, due to lack of enough data points we cannot definitely comment on this.

Since we saw agglomeration of active metal particles in the spent catalyst, it is also interesting to note that we saw this phenomenon in the smaller Ag particles (~20-30 nm) of the Au-Ag catalyst as well. It was discussed earlier that these smaller Ag particles were the leftovers after the H₂ treatment to remove chlorides. These smaller particles were either totally absent or only a few of them were seen in the TEM images of the spent catalyst (Figure 31). Thus it can be safely concluded that these smaller silver particles agglomerated to form larger particles.
Figure 31: Fewer smaller particles (~20-30 nm) or absence of smaller particles on bimetallic Au-Ag catalyst after the reaction

The particle size distribution for fresh Au-Ag catalyst and the spent Au-Ag catalyst (at 20 bar) is shown in Figure 32. It can be seen from the histogram that the frequency of particles less than 50 nm has significantly dropped and a spike in particle size frequency in the range of 50-60 nm is seen. Thus proving our point that smaller particles accumulated to form bigger particles.

Figure 32: Particle size distribution histogram for Au-Ag catalyst before (left) and after (right) the reaction at 20 bar
Another interesting observation was the pore formation in the active metal particles during the reaction (see Figure 33). The pore formation was consistent and seen in all the cases of Ag only, Cu-Ag as well as the Au-Ag bimetallic catalysts after the reaction. Though we have not quantified the number of pores or the size of the pores, a quick glance at the TEM images of the spent catalyst gave us an impression that the pores of bigger size were seen in catalysts that were tested at 20 bar as compared to the ones tested at 1 bar. However, this needs to be looked into more details by quantifying the number and size of pores.

Figure 33: Pores formed in the active metal for bimetallic Cu-Ag (left) as well as Au-Ag (right) catalyst
Chapter 4: Conclusions & Recommendations

4.1 Conclusions

We were able to synthesize bimetallic Cu-Ag and Au-Ag catalyst on α-Al₂O₃ via a procedure adapted and adjusted from patent literature. All of the bimetallic catalysts had a particle size distribution with surface averaged particle size of nearly 120-140 nm determined by TEM. The TGA experiments concluded that the temperatures used during synthesis were sufficient to remove all precursor solutions from the catalyst. Still, for the Au-Ag catalyst, a small amount of AgCl particles were left on the support as identified and confirmed by XPS and XRD. Catalyst heat treatment in the H₂ environment at 350°C was sufficient to remove the AgCl remains. Although, this heat treatment procedure inevitably formed smaller silver particles (less than 50 nm) together with larger bimetallic particles, the surface area of these smaller particles was less than 2% of the total surface area of the active metal particles.

The surface composition of bimetallic catalysts was determined by using the XPS. For the Cu-Ag catalysts, it was found that the catalyst surface was enriched with Cu more than the bulk concentration. As expected, the Cu-Ag catalyst synthesized by sequential impregnation showed higher Cu surface concentration than the ones that were synthesized using co-impregnation. However, exactly opposite was observed for Au-Ag bimetallic catalyst which showed that the concentration of Au in top few layers of catalyst was less than the overall bulk concentration. This observation validates the fact that Cu is more oxyphilic than Ag, which in turn is more oxyphilic than Au. Thus, the oxygen environment during synthesis calcination will enrich the surface with Cu for Cu-Ag catalyst and with Ag for Au-Ag catalyst.

Another interesting conclusion from XPS results was the shift in Auger parameter for bimetallic Cu-Ag and Au-Ag catalyst. The shift in the Auger parameter also shows that these bimetallic alloys decrease the silver oxidation state to be partially negative. Since the Auger parameter for Cu-Ag is higher than the Au-Ag catalysts, this qualitatively proves that the presence of Cu affects silver surface more than the presence of Au on the catalyst.

Using O₂-TPD, we were able to identify peaks corresponding to the various oxygen species that are present on the silver surface as reported in the literature. For Ag supported on α-Al₂O₃, we found the oxygen peak corresponding to the associative desorption of oxygen at around 280°C. Another peak at 380°C was also found which was associated with the subsurface oxygen. For the bimetallic Cu-Ag catalyst, we conclude that total oxygen adsorbed is higher than Ag only catalyst but it shows a decreasing trend with increasing Cu loadings. Since Cu is more oxyphilic than Ag, we also saw the surface oxygen peak shifting to a higher temperature. We also saw a distinct new peak due to bulk Cu at ~240°C that was absent in sequential impregnated Cu-Ag catalyst. The position of the sub-surface oxygen peaks did not show much change due to the presence of Cu. For sequential impregnated Cu-Ag catalysts, the total oxygen adsorbed was less than the Ag only catalyst which we believe is due to the excess Cu on the surface. For Au-Ag catalyst, we found a sharp decline in surface oxygen with the mere presence of Au particles. Since Au atoms functions as a diluting agent on Ag surface, it does not favor atomic oxygen adsorption which explains why we had this observation. We also found the sub-surface oxygen to show a steady decline with the increasing Au loading.
We observed lower selectivity but higher activity for bimetallic Cu-Ag or Au-Ag catalyst compared to 10% Ag catalyst for tests performed at 1 bar as well as 20 bar. We also saw some catalyst restructuring when testing it during the ethylene epoxidation reaction. The first observation while looking at the TEM images of the spent catalyst was that there were pores formed in the active metal after the reaction. We also observed an increase in the average particle size after the reaction. The absence of smaller Ag particles of less than 50 nm in Au-Ag catalyst very clearly concludes that ethylene epoxidation reaction agglomerates the active metal particles.

Based on the experimental results, we can say that the bimetallic Cu-Ag or Au-Ag catalyst gives lower selectivity for ethylene oxide as compared to 10% Ag only catalyst. This is the case for the reactions performed at 1 bar as well as 20 bar. Our approach to the catalyst testing was to keep the reaction temperature constant and study the selectivity and activity for these catalysts. While the literature reports increase in the EO selectivity for bimetallic catalysts, their experiments are always carried out at constant conversion achieved by changing the reaction temperature. We are doubtful of this approach since ethylene epoxidation is a kinetically preferred reaction while combustion reaction is thermodynamically preferred. Thus changing the reaction temperature to obtain a constant conversion also changes the energy of the system and thus the selectivity comparison cannot be very reliable. Furthermore, our catalyst samples had low coverage of Ag on alumina support while the literature reported catalyst monoliths had either fully covered surface or had a very high surface coverage with Ag. Because of this, their catalyst had Cu or Au predominantly on the Ag particles and not as individual clusters. The low Ag coverage combined with the possibility of individual clusters of Cu or Au metal present on the alumina could also be the reason for lower selectivity and activity for our catalysts.

**4.2 Recommendations**

Based on the results of this report and the various data published in the literature, the following recommendations have been made:

- The spent catalyst samples can be characterized by XPS technique to study the surface composition after the reaction. The changes in the surface composition of the bimetallic Cu-Ag and Au-Ag catalyst can give some information about the restructuring of the active metal during the epoxidation. Since we observed pore formation in the active metal for all of the spent catalysts whether they were tested at 1 bar or at 20 bar, the number of pores formed and the size of the pores can be studied for different cases and may be linked to the catalyst performance.

- Since we suspect that our bimetallic Au-Ag catalyst is contaminated with chlorine, it is recommended to synthesize it with another precursor (e.g. AgCN as reported in the literature) that does not contaminate the catalyst with chlorine. This will help us to better understand the promotion effects of Au in the epoxidation reaction without being affected by the chlorine. Also it will be interesting to perform TEM/EDS analysis for the bimetallic catalysts that will help to get elemental mapping of the presence of Cu or Au on the catalyst surface.
- Although all of the literature reports selectivity at constant conversion and varying temperature, it is recommended that the reactions can be performed with different catalyst weight or the reactant space velocity to get a nearly constant conversion at the uniform reaction temperature. This experiment can give an idea if bimetallic catalyst indeed has higher selectivity or was the result of other research due to reduced temperature.

- Another recommendation is to test the bimetallic catalyst samples for chlorine promotion. Since we already saw a temporary increase in the selectivity for Au-Ag bimetallic catalyst that we suspect is due to chlorine promotion, this recommendation will clear the doubt for this behavior.

- We have seen different peaks in O$_2$-TPD experiments for the bimetallic catalyst as compared to the silver only catalyst. Thus an experiment is recommended with adsorption of labeled $^{18}$O, followed by a few pulses of ethylene reaction and then desorption. Since we already know which catalyst gives more oxygen adsorption for each type of oxygen species, this experiment can help us to get more information about the oxygen species which are most active in ethylene epoxidation and the ones that give combustion products. Thus we can design the catalyst with higher selectivity with this information.
Acknowledgements

I am delighted with the successful completion of my master project at the Inorganic Materials Chemistry research group in the Department of Chemical Engineering and Chemistry at the Eindhoven University of Technology. This project would not have been possible without the kind support and help of many individuals throughout the project and I would like to extend my sincere gratitude to each one of them.

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