The effect of chlorine in the hydrogenation of carbon monoxide to oxygenated products at elevated pressure on Rh and Ir on SiO₂ and Al₂O₃

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THE EFFECT OF CHLORINE IN THE HYDROGENATION OF CARBON MONOXIDE TO OXYGENATED PRODUCTS AT ELEVATED PRESSURE ON Rh AND Ir ON SiO_2 AND Al_2O_3

B.J. Kip, F.W.A. Dirne, J. van Grondelle and R. Prins

Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

ABSTRACT

The catalytic behaviour of silica- and alumina-supported rhodium and iridium catalysts in synthesis gas reaction at elevated pressures was investigated. Temperature programmed reduction and hydrogen chemisorption measurements were used to characterize the catalysts. Rhodium was more active than iridium and had a better selectivity to higher hydrocarbons and C_2 -oxygenates. For rhodium on silica high oxo-selectivities were obtained (40%), while on chlorine containing alumina this selectivity was rather low. When a chlorine-free metal precursor was used or when special pretreatments were applied to a $\text{RhCl}_3/\text{Al}_2\text{O}_3$ catalyst, oxo-selectivities of rhodium on alumina were also rather high (30%).

INTRODUCTION

The reaction of CO and H_2 over group VIII metals yields a wide range of products, such as alkanes, olefins and oxygenated hydrocarbons, the latter being the most interesting from an economical point of view. In recent investigations on supported rhodium catalysts a large percentage of oxygenated hydrocarbons has been reported (methanol, ethanol, acetaldehyde and acetic acid) [1-7]. The activity and selectivity depended markedly on the support and promoters. Ichikawa [2-4], used various oxides to support metal carbonyl clusters, and found better selectivities towards oxygenates on basic oxides than on acidic oxides at atmospheric pressures or below. Rh/ZnO and Rh/MgO mainly produced methanol, while on Rh/ La_2O_3 the main product was ethanol and Rh/ SiO_2 only produced hydrocarbons. Bhasin and O'Connor observed that Rh/ SiO_2 can also produce C_2 -oxygenates (ethanol, acetaldehyde and acetic acid) with selectivities up to 80% [8] at higher pressures (7 MPa, high pressure assists in shifting equilibria to the oxygenated products side). Since rhodium can produce C_2 -oxygenates and platinum was reported to produce large amounts of methanol [9], it might be of interest to also investigate iridium in synthesis gas reaction at elevated pressures.

The mechanism for the formation of oxygenated products has not been elucidated so far. Recently Takeuchi and Katzer [10] and Tamaru et al. [11] demonstrated that the formation of methanol takes place by hydrogenation of nondissociatively adsorbed

carbon monoxide. According to Watson and Somorjai [5-6] and Driessen et al. [12], the active sites for this reaction are metal ions. For C_2 -oxygenates different mechanisms have been proposed. Takeuchi and Katzer [13] suggested a complicated mechanism involving CO insertion into adsorbed carbene species resulting in an adsorbed ketene or oxirene intermediate, thus indicating a common C_2 -intermediate for C_2 -hydrocarbons and C_2 -oxygenates. The Schulz-Flory distribution of hydrocarbons and oxygenates supports this conclusion [14]. On the other hand Van den Berg et al. [1] and Tamaru et al. [7] proposed a mechanism in which carbon monoxide insertion in CH_X-Rh^{n+} intermediates takes place, leading to C_2 -oxygenates. In this mechanism C_1 -hydrocarbons and C_2 -oxygenates have a common intermediate.

In this work, the catalytic behaviour in synthesis gas reaction at elevated pressure (4 MPa) of Al_2O_3 - and SiO_2 -supported rhodium and iridium catalysts has been studied. Special attention has been paid to the effect of chlorine remaining on the support after reduction of catalysts prepared with metal chloride precursors. This chlorine might influence the acidity of the catalyst and the amount of metal ions present in the reduced catalyst and therefore the catalytic behaviour.

EXPERIMENTAL

Catalyst preparation

Catalysts were prepared by the incipient wetness technique using $RhCl_3 \cdot xH_2O$, $Rh(NO_3)_3 \cdot xH_2O$, $H_2IrCl_6 \cdot xH_2O$, $IrCl_3 \cdot xH_2O$ and $Ir(NO_3)_3 \cdot xH_2O$ in aqueous solution. SiO_2 from Grace (Type S.D. 2-324.382, surface area $290 \text{ m}^2 \text{ g}^{-1}$, pore volume 1.2 ml g^{-1}) and $\gamma-Al_2O_3$ from Ketjen (Type 000-1.5E, surface area $200 \text{ m}^2 \text{ g}^{-1}$, pore volume 0.6 ml g^{-1}) were used as support material. Impregnated catalysts were dried in air at 395 K for 16 h (heating rate 2 K min^{-1}). Some catalysts were calcined in air at 723 K for 2 h. In-situ reduction of the catalysts was carried out in a high pressure reactor in pure hydrogen at 0.1 MPa, using a temperature ramp of 5 K min^{-1} between 298 K and 623 K, and holding that final temperature for 0.5 h.

Characterization techniques

Reducibility of the catalysts was studied by temperature-programmed reduction (TPR) using the apparatus described extensively in ref. [15-16]. Reduction was done in a flow of 4% H_2 in Ar at a heating rate of 5 K min^{-1} . Volumetric hydrogen chemisorption measurements were performed in a conventional glass system at 298 K. After reduction in flowing purified hydrogen for 1 h at 673 K (heating rate 8 K min^{-1}), evacuation at 673 K for 0.5 h, hydrogen admission at 473 K and cooling to room temperature, desorption isotherms were measured at room temperature. Following the method of Benson and Boudart [17] the total amount of chemisorbed H atoms was obtained by extrapolating the linear higher pressure region ($0.02 < P < 0.1 \text{ MPa}$) of the isotherm to zero pressure.

The CO-H₂ reaction

Hydrogenation of carbon monoxide was carried out in a continuous flow stainless-steel high pressure fixed-bed reactor. After in-situ reduction of the catalysts (see catalyst preparation), the reactor was cooled down to the reaction temperature and pressurized with H₂ to the desired level. After stabilisation an additional CO flow was started. All catalysts were measured under the same reaction conditions (GHSV = 4000 l l⁻¹ h⁻¹, H₂/CO = 3, P = 4 MPa). The reaction temperature was adjusted so that conversion of CO was around 2.0 %. The reactor effluent was analyzed using a column with Chromosorb 102 (3 m) and Porapak T (0.6 m) in series operated at 423 K. Peak area integration was carried out with a Nelson Analytical Interface- IBM PC configuration.

RESULTS AND DISCUSSION

Characterization

Hydrogen chemisorption measurements show that the silica-supported systems were well dispersed (H/Ir=0.7 for 2.5 wt% Ir and H/Rh=0.6 for 1.5 wt% Rh), and that the alumina-supported systems were even highly dispersed (H/Ir=1.7 for 2.5 wt% Ir and H/Rh=1.6 for 1.5 wt% Rh) as shown in Tables 1 and 2. Since most of the H/M ratios exceed unity, it is impossible to calculate particle sizes and dispersions from chemisorption data and use these for calculating turnover frequencies. Therefore the H/M values were only used to compare dispersions.

The TPR profiles of several catalysts are presented in Figure 1. The reduction of the silica-supported catalysts occurred at significant higher temperatures than the reduction of the alumina-supported catalysts. Figure 1-c shows that when a

FIGURE 1 TPR profiles of impregnated catalysts dried at 393 K for 16 h.
 (a) RhCl₃/Al₂O₃. (b) IrCl₃/Al₂O₃. (c) Rh(NO₃)₃/Al₂O₃. (d) RhCl₃/SiO₂.
 (e) IrCl₃/SiO₂. (f) RhCl₃/Al₂O₃, calcined at 723 K, 2 h.

metal-nitrate precursor is used, the nitrate also reduces during the TPR-run, causing a huge hydrogen consumption. From these experiments it can be concluded that reduction at 623 K for 0.5 h in pure hydrogen will be sufficient to completely reduce the Rh and Ir catalysts, except may be for the calcined $\text{RhCl}_3/\text{Al}_2\text{O}_3$ sample, for which reduction during TPR was complete only at 773 K.

The CO-H₂ reaction

The catalytic properties of the various rhodium and iridium catalysts in the synthesis gas reaction at standard conditions after 11 h time on stream are shown in Tables 1 and 2. To keep the conversion below 5% (differential conditions) and above 0.5% (necessary for accurate product analysis), catalysts were tested at different temperatures between 506 and 633 K.

$\text{RhCl}_3/\text{Al}_2\text{O}_3$ (1.5 wt% Rh), dried at 383 K for 16 h before in-situ reduction (Table 1-1) mainly produced methane, but also some methanol, dimethylether, ethanol, ethylmethylether, acetaldehyde and higher hydrocarbons. The total oxo-selectivity was 11%. The ethers are believed to be formed by dehydration of alcohols on acidic sites of the support. During the first hours of reaction a marked deactivation was observed, while after several hours all catalysts showed a small and constant relative deactivation ($0\text{--}2\% \text{ h}^{-1}$). Total oxo-selectivity increased during the first hours and became constant after about 4 h.

The $\text{H}_2\text{IrCl}_6/\text{Al}_2\text{O}_3$ catalyst (2.5 wt% Ir, dried at 383 K before in-situ reduction, cf. Table 2-1) differed significantly from the rhodium catalyst. To obtain an activity similar to that of the rhodium catalyst the reaction temperature had to be increased to 593 K. Using a value of 100 kJ mol^{-1} for the total activation energy [1, 7, 18], it can be calculated that $\text{Rh}/\text{Al}_2\text{O}_3$ is 15 times more active than $\text{Ir}/\text{Al}_2\text{O}_3$. This difference in activity was also reported by Vannice [18], although he measured at atmospheric pressure. $\text{Ir}/\text{Al}_2\text{O}_3$ also showed a completely different selectivity. It only produced methane, methanol, dimethylether and higher hydrocarbons, while C_2 -oxygenates were absent. The total oxo-selectivity was 11%. The chain-growth probability was found to be higher for the rhodium than for the iridium catalysts. The observed differences might be explained on the basis of the CO dissociation activity of transition metals [19]. Metals that easily dissociate CO catalyze hydrocarbon synthesis (i.e. Ru and Fe), metals that adsorb CO non-dissociatively at room temperature catalyze synthesis of methanol (i.e. Cu, Pd and Pt) [20]. Rh lies between Ru and Pd and catalyzes the formation of both alcohols and hydrocarbons from CO and H₂. Since it is capable of synthesizing both types of compounds, small effects can markedly alter its selectivity. There is no consensus in literature about iridium. Poutsma et al. [20] reported non-dissociative adsorption of carbon monoxide on Ir, while van den Berg [21] reported dissociative adsorption. The results of the present study suggest that both Rh and Ir partly adsorb CO nondissociatively under reaction conditions and that Rh dissociates CO more easily than Ir. Vannice [18] suggested that the difference in activity between Rh and Ir is caused by a difference in heat

TABLE 1

CO + H₂ reaction over various 1.5 wt% rhodium catalysts supported on Al₂O₃ and SiO₂.^a

no. catalyst system ^b	H/Rh	Acti- vity ^c	Selectivity (%) ^d				
			CH ₄	C ₂ ^{+e}	tot. ^f C ₁ -OH	tot. ^g C ₂ -OH	tot. ^h oxo
1 RhCl ₃ /Al ₂ O ₃ ⁱ , 1.8 mol % Cl	1.6	2.3	72.0	16.3	3.5	3.7	11.1
2 RhCl ₃ /SiO ₂ ^j , 0.1 mol % Cl	0.6	0.6	48.0	11.3	26.7	14.0	40.7
3 Rh(NO ₃) ₃ /Al ₂ O ₃	1.3	0.6	45.4	14.4	27.5	11.1	38.6
4 Rh(NO ₃) ₃ /Al ₂ O ₃ , calcined at 723 K	1.6	1.8	50.8	11.9	19.5	14.1	35.3
5 Rh(NO ₃) ₃ /Al ₂ O ₃ , calcined at 723 K HCl treated, 1.4 mol % Cl	1.4	0.9	61.3	24.9	9.3	0.0	11.7
6 Rh(NO ₃) ₃ /SiO ₂ ^k	0.4	1.1	44.2	7.1	35.6	13.1	48.6
7 RhCl ₃ /Al ₂ O ₃ , 4% H ₂ O	1.6	2.6	63.9	4.1	14.7	14.8	29.5
8 RhCl ₃ /Al ₂ O ₃ , 1% H ₂ O ^l , 1.8 mol % Cl	1.6	1.5	72.8	15.3	4.9	4.9	11.9
9 RhCl ₃ /Al ₂ O ₃ , 1% H ₂ O, heating rate during reduction 30 K min ⁻¹ , 1.5 mol 5 Cl	1.6	2.2	60.1	7.3	16.0	12.6	30.8
10 RhCl ₃ /Al ₂ O ₃ , H ₂ O injection during reduction, 0.9 mol % Cl	1.3	4.0	57.0	5.8	9.5	17.0	29.6
11 RhCl ₃ /Al ₂ O ₃ , calcined	1.6	3.1	65.7	4.7	13.1	12.1	26.4
12 RhCl ₃ /Al ₂ O ₃ , calcined, reduction at 723 K	1.6	1.9	60.1	14.7	8.5	11.9	22.0

(a) T_{react} = 523 K, unless stated otherwise. (b) standard reduction (see experimental). (c) Activity in mmole CO (mole Rh)⁻¹s⁻¹. (d) calculated by carbon efficiency.

(e) C₂⁺ = C₂ + C₃ + C₄ hydrocarbons. (f) tot.C₁-OH = C₁-OH + C₁-O-C₁ + 1/3 C₂-O-C₁.

(g) tot.C₂-OH = C₂-OH + 2/3 C₂-O-C₁. (h) tot.oxo = tot.C₁-OH + tot.C₂-OH + C₂=O.

(i) dried in-situ at 383 K, 16 h before reduction. (j) T_{react} = 623 K. (k) T_{react} = 628 K. (l) T_{react} = 506 K.

of adsorption of CO (for Ir around 210 kJ mol⁻¹, for Rh around 185 kJ mol⁻¹).

The silica-supported Rh catalyst (RhCl₃/SiO₂, 1.5 wt% Rh, dried at 383 K for 16 h before in-situ reduction, Table 1-2) was less active than the 1.5 wt% Rh/Al₂O₃ catalyst, since the reaction temperature had to be increased up to 623 K to obtain a comparable conversion. In spite of this high temperature, its oxo-selectivity was much better, even though thermodynamically high temperature disfavours formation of oxygenates. Considerable amounts of methanol, dimethylether, ethanol and ethylmethylether were formed and total oxo-selectivity was 41%.

The observed difference in oxo-selectivity between the alumina- and silica-supported Rh catalyst might be due to the difference in chlorine content of the reduced catalysts. XPS showed that after reduction of the dried RhCl₃/Al₂O₃ and RhCl₃/SiO₂ (heating rate 5 K min⁻¹, 0.5 h at 623 K) there was a large difference in chlorine content. The surface of the reduced Rh/Al₂O₃ contained 1.8 mol% Cl, whereas the

TABLE 2

CO + H₂ reaction over various iridium catalysts supported on Al₂O₃ and SiO₂.

no. catalyst system ^a	wt% Ir	H/Ir	Temp. (K)	Acti- vity ^b	Selectivity (%) ^c		
					CH ₄	C ₂ ⁺	tot.oxo ^d
1 H ₂ IrCl ₆ /Al ₂ O ₃ ^e	2.5	1.7	593	2.5	73.2	15.6	11.2
2 H ₂ IrCl ₆ /Al ₂ O ₃ , 4% H ₂ O, heating rate reduction 30 K min ⁻¹	2.5	--	591	1.8	69.1	18.4	12.5
3 IrCl ₃ /Al ₂ O ₃ , 4% H ₂ O, heating rate reduction 30 K min ⁻¹	2.6	--	563	3.6	58.8	22.6	18.6
4 Ir(NO ₃) ₃ /Al ₂ O ₃	1.3	1.2	598	0.8	64.5	17.7	17.8
5 IrCl ₃ /SiO ₂	2.5	0.7	633	1.0	72.6	16.3	11.1
6 Ir(NO ₃) ₃ /SiO ₂	1.0	0.6	633	0.9	70.4	19.8	9.8

(a) Reduced in pure H₂, heating rate 5 K min⁻¹, 0.5 h at 623 K (b) Activity in mole converted CO (mole Ir)⁻¹s⁻¹. (c) Calculated by carbon efficiency. (d) tot.oxo = C₁-OH + C₁-O-C₁. (e) dried in-situ at 383 K, 16 h before reduction.

surface of the reduced Rh/SiO₂ contained only 0.1 mol% Cl. To further investigate this chlorine effect, Al₂O₃ was impregnated with Rh(NO₃)₃ (Table 1-3). This catalyst showed a dispersion (H/Rh = 1.3) comparable to that of RhCl₃, a relatively low activity and a high oxo-selectivity (39%). Calcination of the dried Rh(NO₃)₃/Al₂O₃ catalyst before reduction (Table 1-4) resulted in an increased activity without much loss of oxo-selectivity (35%), while the selectivity to C₂-oxygenates was increased. Thus, when a chlorine-free precursor is used, the oxo-selectivity can amount to about 40% on Rh/Al₂O₃, significantly higher than the 10% obtained with dried RhCl₃/Al₂O₃. Treating the calcined Rh(NO₃)₃/Al₂O₃ with gaseous HCl at 423 K in N₂ atmosphere before reduction (Table 1-5) caused a dramatic decrease in the oxo-selectivity. Only small amounts of methanol, dimethylether and acetaldehyde were formed, ethanol and ethylmethylether were not formed at all and the total oxo-selectivity was only 12%. Impregnation of SiO₂ with Rh(NO₃)₃ (Table 1-6) also resulted in a catalyst with a high oxo-selectivity (49%). Further investigations showed that the pretreatment procedure before synthesis gas reaction has an important influence on the oxo-selectivity (Table 1-7,8,9,10,11,12). Normal reduction (heating rate 5 K min⁻¹, final temperature 623 K) of a rather wet RhCl₃/Al₂O₃ (stored for half a year and containing 4 wt% H₂O) resulted in a high oxo-selectivity (30%). RhCl₃/Al₂O₃ only stored for one week (1% H₂O) and reduced at 5 K min⁻¹ showed a low oxo-selectivity (12%), while reduction of this catalyst at 30 K min⁻¹ improved the oxo-selectivity to 31%. Reduction of a dried RhCl₃/Al₂O₃ in the presence of water vapour (water injection in the reactor during reduction) also increased the oxo-selectivity (30%, Table 1-10). These results indicate that the water vapour pressure during the reduction of RhCl₃/Al₂O₃ is an important factor. The observed differences can not be explained by differences in metal dispersions as can be seen in Table 1. RhCl₃/Al₂O₃,

calcined at 723 K for 2 h followed by reduction at 623 K (Table 1-11) had a relatively high oxo-selectivity (26%), reduction of this catalyst at 723 K showed a somewhat lower oxo-selectivity caused by a decreased C_1 -OH selectivity (Table 1-12).

For the alumina-supported iridium catalysts the differences in oxo-selectivity were smaller. Reduction of dried H_2IrCl_6/Al_2O_3 at 5 K min^{-1} , final temperature 623 K (Table 2-1) resulted in 11% oxo-selectivity. $Ir(NO_3)_3/Al_2O_3$ (Table 2-4) showed an oxo-selectivity of 18%. Thus, also for iridium the chlorine-free precursor gives a higher oxo-selectivity. Reduction of the chlorine containing iridium catalysts in the presence of water vapour resulted in oxo-selectivities of 13% and 19% (Table 2-2,3). However, on SiO_2 the oxo-selectivities of iridium catalysts were low (10%).

We think that the observed chlorine effect can be understood in the following way. During the reduction of the $RhCl_3/Al_2O_3$ catalyst, the following reactions take place:

When the reduction of $RhCl_3$ (1) and the dehydroxylation of alumina surface OH-groups (2) take place at the same time, the chloride can be trapped by the alumina next to the reduced rhodium particles (3). During the reduction of the metal chloride a high water vapour pressure shifts the second equilibrium to the left and thus prevents the trapping of the chlorine. On SiO_2 almost no chlorine was trapped during the reduction of the metal chlorides as shown by the XPS measurements. Therefore oxo-selectivities were high. Calcination of the catalyst before reduction probably removed the chlorine and therefore increased the oxo-selectivity.

Several explanations might be given for the observed influence of chlorine on the oxo-selectivity:

- Secondary reactions might play an important role. Once oxygenates are formed, they might decompose to hydrocarbons on acidic sites of the alumina (thermodynamically hydrocarbons are favoured over oxygenates). Chlorine increases this acidity and thus favours the decomposition of oxygenates.

- The different pretreatment procedures and the presence of chlorine might cause different amounts of metal ions in the reduced catalyst and thus cause different selectivities to methanol (which is supposed to be formed on metal ions [5-6,12]).

- C_2 -oxygenates might be formed by intermediates that have a structure like acetate ions ($CH_3C(=O)O-M$) with one oxygen atom of the support [7]. The chlorine remain-

ing on the support next to the rhodium particles after reduction of the $RhCl_3$ may inhibit the formation of these intermediates.

In summary, Rh/Al_2O_3 was more active and had a higher chain-growth probability than Ir/Al_2O_3 . Rh catalysts produced methanol, dimethylether, ethanol, ethylmethylether, acetaldehyde and hydrocarbons, while Ir catalysts produced only methanol,

dimethylether and hydrocarbons. Chlorine, trapped by vacancies on the alumina surface, formed by dehydroxylation of OH-groups, disfavoured the formation of oxygenates in the hydrogenation of CO. On SiO_2 this effect was not observed. High water vapour pressure during the reduction of the metal chloride on alumina prevented the trapping of chlorine and high oxo-selectivities were measured in that case. Calcination of the $\text{RhCl}_3/\text{Al}_2\text{O}_3$ system caused removal of the chlorine, resulting in high oxo-selectivities.

The negative influence of chlorine on the activity is not completely understood. Possibly chlorine enhances the formation of coke, or alternatively it covers part of the active metal area.

Although the influences of several supports [2-6,9] and promoters [3] have been described in literature, the here observed effect has not been mentioned yet. Our study demonstrates that, in comparing the catalytic activity and selectivity of metal catalysts for CO hydrogenation the influence of the metal salt precursor and the pretreatments should be taken into account.

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