Review of patent publications from 1990 to 2010 on catalytic coatings and different substrates, including microstructured channels : preparation, deposition techniques, applications

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Review of Patent Publications from 1990 to 2010 on Catalytic Coatings on Different Substrates, Including Microstructured Channels: Preparation, Deposition Techniques, Applications

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Abstract: A review of patent publications on preparation, deposition, characterization, and application of the catalytic coatings is given in this paper with view on their application in microstructured reactors for heterogeneous gas-phase processing. The paper consists of two main parts: in the first part the total overview of patents, the distribution by countries and patent applicants is shown. The main topics (coatings preparation, application, removal etc.) are discussed in the second part of the review, including description of some selected patent publications. The aim of the present review is to show the ‘hot’ topics of patent publications on catalytic coatings and the main interests of the big patentees; special attention is given to catalytic coatings on the channel walls in microstructured reactors.

Keywords: Catalytic coatings, deposition techniques, microstructured reactors, patents.

1. INTRODUCTION

The eminent importance of catalyst coating development and industrial use of microstructured reactors and process intensification up to the production scale is evident when reading the conclusions of the German Demis project with the two large-group companies Evonik-Degussa and Uhde, heading for the largest catalytic reactor built so far ever (about 6m long; two-storey high) – given mostly in German literature, however [1]. The counter play of catalyst and structured reactor as well as the enabling function of catalyst activity on overall process cost competitiveness is pointed out strongly.

It is well known, that structured catalysts and reactors are gaining more importance each year. The manufacture of chemicals in microstructured reactors has become recently a new branch of chemical reaction engineering focusing on process intensification and safety. Microreactor technology is one of the powerful techniques of process intensification. Over the last two decades, multiphase microstructured reactors have been used in the laboratory as well as in industries [2]. A number of comprehensive reviews, including one patent survey on microstructured reactors and two overviews dedicated towards heterogeneous gas-phase micro processing [2-5] were published in the last 5 years. The efficient use of microstructured reactors requires frequently deposition of the catalytically active component onto microchannel walls, since many chemical reactions are processed this way and particularly those with industrial motivation (>80%). However, the geometric surface area of the walls of the microchannels on its own usually is not sufficiently large for the

deposition of a catalyst. To overcome this challenge, catalytic coatings with large surface areas need to be introduced onto the walls of the reactor channels. Micro-packed beds of powder catalysts can be used sometimes, but in general, a thin layer of catalyst deposited on the reactor wall is preferred, because of mass and/or heat transfer improvement and for keeping pressure loss low [6]. Many methods can be used to deposit a catalyst layer on a surface, depending on the properties of the surface and the catalyst that has to be deposited.

An extensive article review on deposition of catalysts on a structured surface was published in 2006 [6]. The review includes pretreatment procedures prior to the coating deposition, various coating preparation methods (sol-gel, chemical vapour deposition, anodic oxidation, etc.), and deposition of zeolites. A review of patent publications on ceramic coating technologies was published in 1991 and contains the description of some patents of the years 1988-1990 [7].

The present paper consists of two main parts: in the first part the total overview of patents, the distribution by countries and patent applicants is shown. The main topics (coatings preparation, application, removal etc.) are discussed in the second part of the review, including description of some selected patent publications. The aim of the present review is to show the ‘hot’ topics of patent publications on catalytic coatings and the main interests of the big patentees; special attention is given to catalytic coatings on the channel walls in microstructured reactors.

2. METHODOLOGY

For the research of the number of patent publications the patent database Espacenet (<http://ep.espacenet.com>) was used. The search was realized using the International European Patent Classification and key words.

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3. RESULTS AND DISCUSSION

3.1. Patent Activity and National Origin – Total View

The total number of patents on catalytic coatings strongly increased from 1990 to 2010 as an overall trend see Fig. (1). Especially from 2002 to 2009, a strong increase is visible, while before also minor declines in patent activity occurred (ca. 140); since the data of 2010 are given only for 10 months (until October), it is not yet clear if a maximum and plateau have been reached or if the increasing protection activities go on.

Fig. (2) shows that the number of Japanese (JP) patents is much higher in comparison with other countries such as USA, China, or Korea (US, CN, KR etc.). A very strong increase of the JP patent publications was observed in 2008-2009 (from ca. 50 to ca. 90). The amount of CN, US and KR publications is increasing over the last 3-4 years.

Fig. (1). Total number of patent publications on catalytic coatings from 1990 till 2010 year.

Fig. (2). Number of patent publications on catalytic coatings from 1990 till 2010 year in different countries (WO: worldwide; US: United States of America; JP: Japan; CN: China; KR: Korea; other: other patent publications).

The ranking of the 15 most active patent applicants is shown in Table 1. The Top-15 constitutes mostly Japanese companies; there are also positions for European, Korean and US companies and institutes. Some large automobile companies are observed in the Top-15 patentees (Nissan motor, Honda motor Co. Ltd., Volkswagen AG etc). Their patent publications are mostly devoted to catalytic coatings

for fuel cells and catalyst layers for cleaning exhaust gases. Actually, few European chemical companies (such as Evonik-Degussa, Shell, Umicore) appear in this listing.

The distribution of European patent publications on catalytic coatings from 1990 until 2010 is presented in Fig. (3). The leading position belongs to Germany, which is represented mostly by automobile and chemical companies (Volkswagen AG, BASF, Evonik-Degussa etc).

Fig. (3). Number of patent publications on catalytic coatings from 1990 till 2010 year in different European countries (AT: Austria; DE: Germany; FR: France; GB: United Kingdom; IT: Italy; PL: Poland; CZ: Czech Republic; HU: Hungary; EP: European Patents).

3.2. Contents of the Patents – Details

3.2.1. Patent Publications on the Preparation of Catalytic Coatings

3.2.1.1. Improvement of the Physico-Chemical Properties of Catalytic Coatings

The most important coating properties, which affect the coating performance, are referred to

- Adhesion to the substrate,
- Thermal stability,
- Thickness,
- Corrosion resistance, and others.

Adhesion is the tendency of dissimilar particles and/or surfaces to stick to one another (cohesion refers to the tendency of similar or identical particles/surfaces to cling to one another). Adhesion mostly depends on the type of coating, deposition procedure and substrate pretreatment and has an effect on important properties of the coatings such as shock resistance, flexibility, corrosion stability and so on. It is well known that increasing the surface roughness and decreasing the coating thickness have positive effects on the adhesion strength. A low degree of adhesion leads to break-away of the coating during operation. Adhesion strength can be also increased by adding binders to the coating precursor sol [8-11].

Table 1. Ranking of 15 Most Active Patent Applicants in the Field of Catalytic Coatings

Ranking	Number of Patent Publications	Applicant	Country
1	93	Dainippon Printing Co. Ltd.	Japan
2	87	Toyota Motor	Japan
3	40	Matsushita Electric Ind Co. Ltd.	Japan
4	37	Nissan Motor	Japan
5	35	Velocys	US
6	27	Canon KK	Japan
7	24	Fuji	Japan
8	22	Shell	The Netherlands
9	21	Sumitomo	Japan
10	17	Asahi Co. Ltd.	Japan
11	16	Mitsubishi Corp	Japan
12	15	Honda Motor Co. Ltd., N E Chemcat Corp, Toppan Printing Co. Ltd.	Japan
13	11	Cataler Corp, Umicore, Forschungszentrum Juelich GmbH	Japan, Belgium, Germany
14	10	Evonik-Degussa, Basf, Samsung	Germany, Korea
15	9	Kaneka Corp, Volkswagen AG	Japan, Germany

SK Corporation / Korea made an invention about the improvement of the cohesion between substrate and supported-catalyst. Polymethylphenyl silicone resin and calcium aluminate were used as a binder for the catalytic coating consisting of an active component such as vanadium, nickel, molybdenum, tungsten, iron, sulfur, or silicone and a support such as alumina or titania. A binder was prepared from either 10-50wt.% of polymethylphenylsilicone resin dissolved in organic solvent or 10-50wt.% of calcium aluminate dissolved in water. Coatings were applied on the surface of a metal plate and a cordierite honeycomb monolith, then dried and calcined [12].

In patent CN1223977A of Xinjiang Institute of Physics and Chemistry CAS / China a process for forming a copper-containing ceramic coating on the wall of a catalytic reactor was reported. The procedure includes pre-treatment of the substrate, preparation the precursor from basic components: co-solvent, binder, emulsifier, oxidant and multi-element adhering oxide, glazing, drying, and calcination. The advantages of the resulting coating are a thermal shock resistance of 300K temperature difference, a high adhesion onto a metal substrate and a high thermal expandability [13].

The invention of Umicore / Belgium, EP2247385A1, presents a diesel particle filter with a zeolitic coating evenly distributed over the entire length of the particle filter and with another non-zeolitic coating applied from the inlet side of the filter up to only a certain length of the filter. It is proposed first to apply the non-zeolitic coating from the inlet side of the filter and only then to apply the zeolitic coating over the entire length of the filter from the outlet side of the filter. Through this sequence of coatings better adhesion

strength of the coatings is guaranteed than if both coatings are applied from the inlet side Fig. (4) [14].

Fig. (4). Diesel particle filter: (1) wall river filter, (2) outer surface, (3) entrance front surface, (4) withdrawal front surface, (5 and 6) flow channels for the exhaust gas, (7) channel walls, (8) gastight plug, and (9) withdrawal front surface [14].

Patent WO9941011 of BASF AG *et al.* / Germany [15] is devoted to a metallic reaction tube with a catalytic coating with a thickness of 10-1000 μm on the inner wall. The coating process covers the following steps: (1) preparation of solutions or emulsions of components in the multi-metallic oxide catalyst, (2) addition of adhesion promoters, bonding agents, viscosity- and pH-regulating agents, (3) applying the solutions or emulsions on the reaction tube or the reaction tubes by spraying or immersion, and (4) heating of the coated reaction tube, if necessary in presence of inert or reactive gases, to a temperature within the range of 200 to 400°C, (5) calcination.

Akzo Nobel / The Netherlands made the invention on coatings which possess extended potlife and a good balance of physical and mechanical properties making them especially well-suited for impregnating, sealing and bonding compositions. The coatings consist on (1) an activated unsaturated group-containing compound, (2) an activated CH group-containing compound and (3) a basic catalyst, wherein the basic catalyst is blocked with an acidic compound whereby the so-blocked catalyst becomes unblocked under the influence of UV light [16].

The invention US6139649A of Alon Inc. / USA [17] provides a method of applying the chromium, chromium-silicon, or chromium-magnesium coatings onto the inner surface of furnace tubes, used for ethylene production, via physical vapour deposition (PVD). The inside surface of the tube is first prepared by cleaning to remove all corrosion products. The initial metal barrier is deposited in a single step. This initial metal barrier is either diffusion heat treated in situ or is layered with subsequent intermediate PVD deposited layers such as silicon, aluminum, magnesium, manganese and titanium. The last layer consists of rare earth metals or metals such as yttrium or zirconium which form oxide stabilizers. Since the diffusion heat treatment step can be done after the deposition of each layer or intermediately after all layers have been deposited, the diffusion thickness varies from 10 to 250 μm . Once the layers have been treated by heat, the near surface is further converted to ceramic via heating the surface in an atmosphere consisting of a combination of argon, nitrogen, helium, and/or oxygen. The PVD transport method can utilize solid master alloys, sintered powder, powder, inserts, slurry, or ceramic cartridge. This method results in a slightly rougher surface than base material tubular Fig. (5).

Invention of BASF Corporation / USA EP2242581A1 is directed to a catalyst for treatment of pollutants in a gaseous stream. The catalyst consists of substrate coated with a metallic anchor layer to enhance the adherence of a catalytic washcoat layer [18].

A technology that can realize a thick film, which is superior in adhesion, transparency, and optical catalytic activity, was proposed in JP2005171029A by Nihon Parkerizing, Asahi Glass Co. Ltd. and Dokai Chemical Ind. Co. Ltd. / Japan [19]. The coating composition contains optical catalytic particles (titania and titanate), organic alkali (alkanolamine, tetraalkyl ammonium, oxazine, piperidine), anionic dispersant (phosphoric acid, hydroxycarboxylic acid, polyhydric carboxylic acid, polycarboxylic acid), and harde-

nable platy particles containing SiO_2 as their main component [19].

Fig. (5). Cross sectional view of a furnace tube to which the coating has been applied (2 – furnace tube, 4 – PVD target) [17].

To improve the etch resistance and durability of coatings the following coating composition including anhydride resins is proposed in CN1152321A by Du Pont / USA [20]. Sprayable coating composition contains organic solvent, binder: (1) anhydride resin, (2) polymeric resin (copolymerized monomers of alkyl-methacrylates or -acrylates), and a catalyst. The coating precursor is typically applied to a substrate by spraying, dipping or brushing.

The invention DE19500997C1 of Daimler-Benz AG / Germany [21] relates to a method of preparation of a catalytic good adhesive, thermal and mechanically stable coating on the piston head of an engine for the ignition of gaseous fuels in the combustion chamber Fig. (6). The catalytic layer of Pt or Pt alloy is applied on the basic coating (Zr oxide).

Fig. (6). Schematic cross section of the cylinder of the combustion engine (17, 18 – inlets, 12 – cylinder cap, 16 – gases, 21 – support layer, 11 – cylinder, 22 – coating, 13 – cylinder wall) [21].

3.2.1.2. Improvement of the Catalytic Properties of the Coatings

Usually the composition of a catalytic coating depends on its applications in a specified process.

Many patent publications are devoted to catalytic active coatings for the treatment of exhaust gases [22-24]. There is present need for new, improved processes for the preparation

of effective oxidation catalyst compositions. Improvements in the process which increase the versatility, effectiveness, durability, activity, and operating life of the oxidation catalyst satisfy this need. A new type of NO_x reduction catalytic coating for diesel exhaust treatment is provided by Hyundai Motor Co. Ltd. / South Korea in KR20070075194A to divide the coating layers depending on their functions to effectively remove the NO_x . The NO_x reduction catalyst contains the carrier which is formed of a cordierite, an inner coating layer (absorption material resistant to thermal damage: Ba, K, and Ca), and an outer coating layer consisting of Pt or Rh with high oxidation power [23]. A similar process of obtaining catalytic coatings for low temperature oxidation is described in US6753293B1 by Nasa / USA [25]. New catalytic films containing less noble metal and being used in automotive industry to promote the conversion of CO into CO_2 and NO_x to N_2 are described in FR2896436A1 by Peugeot Citroen Automobiles SA / France Fig. (7) [24].

Fig. (7). Scheme of the experimental setup (2 – catalytic reactor, 4 – inert oxide material, 5 – nanoparticles, 6 – core) [24].

The invention US2010126154A1 of Klingmann Raoul / Germany [26] relates to a three-way catalyst with high catalytic activity and aging stability for the cleaning of exhaust gases of internal combustion engines. Three-way catalysts are widely used for the cleaning of the exhaust gases of combustion engines operated under essentially stoichiometric conditions. They are able to convert three significant pollutants: hydrocarbons, carbon monoxide and NO_x simultaneously to harmless components. The catalyst has a catalytically active coating on an inert catalyst support such as ceramic honeycomb monolith. The catalyst consists of an active aluminum oxide coating and two cerium/zirconium mixed oxide (CeZrO_x) coatings. The first CeZrO_x layer is impregnated with rhodium and has a higher Zr oxide content than the second CeZrO_x layer, which is impregnated with palladium. The thermal stability of both coatings can be improved by stabilizing them with the oxides of iron, manganese, tin, titanium, silicon, etc.. The catalyst has very good light-off performance, possesses a high thermal stability, and has a low exhaust gas backpressure [26].

The invention CN1479650A by BASF AG / Germany [27] describes a catalyst for the hydrogenation of C4-dicarboxylic acids and/or their derivatives (for example, maleic anhydride in the gas phase). The catalyst contains 40-

90 wt.% copper oxide and 10-60 wt.% of one of the metals (or their compounds) from the group of Al, Si, Zn, Pd, La, Ce as active component which is deposited on an inert support in a form of a thin layer.

The patent publication WO2008063038A1 by Uab Norta *et al.* / Lithuania [28] relates to methods for producing catalytic coatings by thermal spraying powder material, and can be used in different branches of chemistry, power engineering and in automobile production. Powder material consists of an aluminum metal core, an intermediate aluminum hydroxide layer, and a hydrotalcite coating on a particle surface, which is applied to the intermediate layer. The coating is sprayed on a metal substrate Fig. (8). The resulting catalytic double-sided coating shows high catalytic performance in NO_x reduction and hydrocarbon oxidation reactions, possesses high mechanical stability, i.e. a high adhesion to a metal substrate, and a high resistance to contamination by sulphur dioxide gas and water vapour.

Fig. (8). Coating layer formation (1 – hydrotalcite, 2 – aluminum hydroxide, 3 – aluminum) [28].

Another issue for catalytic coatings is films for fuel cells applications [29-34]. Films, made of nitrogen containing carbon nanofibers with supported catalytic particles [30], and platinum particles on carbon paper [33, 34] are reported.

Some publications are devoted to catalytic layers on gas sensors [35-37]. One of the compositions was reported in EP0902278A2 by Heraeus Electro Nite International / Belgium [35]. The coating precursors ("print-screen" pastes) were made from Pt and SrTiO_3 powders for the first layer and from Al_2O_3 , SiO_2 , BaO, SrTiO_3 for the second layer. The precursors were applied by screen printing on a substrate, dried, calcined and cooled down slowly. Another gas-sensitive layer was prepared from SnO_2 , ZnO, Fe_2O_3 , TiO_2 or CoO impregnated with aqueous solution of chloroplatinic acid, with a subsequent thermal treatment [36].

A new composition of the slurry for coating of soot filters made of ceramic substrate materials (aluminum titanate, cordierite, silicon carbide) is reported by BASF Catalysts LLC and Li Yuejin / USA in WO2009079250A1 [38]. The recipe includes carboxylic acid instead of nitric or acetic acid which is usually used during or prior to milling of the washcoat slurry. An emission treatment system for simultaneously remediating the nitrogen oxides (NO_x) and gaseous hydrocarbons present in diesel engine exhaust streams includes a catalyzed soot filter consisting of a wall flow monolith which is washcoated with a slurry containing catalytic support

particles without applying a passivation layer to the wall flow monolith [38].

3.2.1.3. Photocatalytic Coatings

A large number of patent publications on catalytic coatings is related to the synthesis of photocatalytic coatings. Certain semiconductive materials based on metal oxides, which are able, under the effect of radiation of an appropriate wavelength, to initiate radical reactions, are generally referred to as “photocatalytic” [39]. Titanium dioxide, particularly in the anatase form, is a photocatalyst under UV-light.

Usually the synthesis mixtures for photocatalytic coatings described in the patent publications consist of titanium oxide, solvents, water, and acidic agent; the coating is deposited via the sol-gel technique [40-50]. Although there are no significant innovations in materials (principally the main component is titanium oxide), some improvements in recipes are described. In the synthesis procedure described in invention CN101486867A by Wenlei Zhang / China [40] photocatalytic paint was prepared from a mixture of titanium dioxide, titanium phosphate, silicon dioxide, defoaming agent, coupling agent, dispersant, thickener and water. The paint can purify air in a rapid, efficient and lasting manner, completely remove harmful gases such as formaldehyde, ammonia and so on, and inhibit microorganism growth; furthermore, the preparation equipment and technology are simple, and the product is safe and environmentally friendly [40]. The patent EP1914283A1 of Global Engineering and Trade S.P.A. / Italy [42] describes the synthesis procedure and composition of a photo-catalytic coating which consists of epoxy-siloxane resin (film-forming substance), butyl acetate (solvent), calcium carbonate (inert material), rutile (pigment) and photo-catalytic particles (anatase) Fig. (9).

Fig. (9). Flow diagram indicating the components of the photocatalytic coating (1 – photo-catalytic coating, 2 – film-forming substance: liquid resin which consists of one basic component 3 and one catalyst or hardener 4, 5 – butyl acetate, 6 – charges, which should include: inert materials 7, pigments 8 and the photo-catalytic particles 9 [42].

Inventions [51, 52] are related to coatings consisting of oxides and metal salts, preferably titanium dioxide doped with metals (Ag, Fe) or oxides of transient metals, such as Fe, Co, Ni, Mn, Cr, V, Ta, Nb, W, lanthanoids, or Li and Sb salts. Coatings are applied by dipping [51], spraying, or with a brush or roller. The photocatalytic coating proposed in WO2007106357A2 by Roberson Mary *et al.* / USA [53] is a combination of a silica gel (a hydrophilic agent, which acts as a carrier for catalytic metal particles), titanium dioxide, copper, nickel, and rhodium, having size in the range of 50-100 nm. The nanoparticles increase the surface area of the catalyst, improving the reaction rate. The coating can be applied by dipping to any appropriate substrate (metal, plastic), which can be disposed at 360°C with an UV lamp [53].

The Tongji University / China, CN1844001A, invented the synthesis procedure of a TiO₂/organic hybrid film with photocatalytic and self-cleaning functions. An organic monomer is added to the film precursor mixture; the film is obtained via sol-gel method. The preparation is based on the effect of formation of a nanometer crystal phase TiO₂/organic hybrid film after heat treatment. The thickness of the hybrid film is not less than 300 nm, which is higher than the anatase film obtained from common pure titanium sol. The photocatalytic and self-cleaning properties of the hybrid film are better than those of common titanium oxide film; meanwhile, the hybrid film has a good chemical stability [54].

Although the sol-gel technique is often used to produce photocatalytic (particularly titania) coatings, other methods can be also applied. For example, a process for preparing a photocatalytic TiO₂ film by wet and thermal oxidizing was invented by Fudan University / China [55]. The procedure includes magnetically controlled sputtering of a Ti film on a glass substrate, and heating it in air or O₂ containing water vapour for oxidizing it until it becomes transparent. Another process for preparing a photocatalytic TiO₂ film with a nanocrystal structure includes an electrochemical oxidizing step in a dielectric solution, where one Ti plate or foil is used as an electrode and another Ti plate as its counter-electrode, and thermal crystallization. Its advantages are low cost, no size limitation, high uniformity and catalytic activity [56]. Electrophoretic deposition is reported to be a simple, efficient and environmentally friendly method for preparing high-catalytic activity TiO₂ film on the surface of a plastic substrate [57].

3.2.1.4. Zeolitic Coatings

Zeolite interfaces are excellent candidates for microreactor applications because of their remarkable and versatile possibilities in adsorption and catalysis. Zeolitic coatings are defined as composite materials, comprising a substrate onto which zeolites are physically or chemically bonded. They are especially of interest for use as catalysts, adsorbents, membranes, and sensors [58-60]. Zeolitic coatings can be deposited on a substrate by means of slurry coating, washcoating, or hydrothermal synthesis. In the slurry coating method, zeolitic coatings are obtained after contacting of the substrate with a dispersion of zeolite crystals, followed by evaporation of the liquid. The main disadvantage of this technique is the relatively weak Van der Waals bonding of the zeolite crystals with the substrate. In wash-coating, the zeolite crystals are “glued” to the substrate with a binding agent, which

causes a low accessibility of the crystallites. Moreover, both these methods result in rather non-homogeneous coatings, in which the crystals are randomly oriented. In case of hydrothermal synthesis, also called *in-situ* synthesis, the zeolite crystals can be directly grown on a substrate from a synthesis precursor gel.

Many patent publications are related to formation of zeolite coatings on the surfaces [58, 59, 61-66]. Zeolite can be deposited on the substrate in mixture with other slurries, such as alumina, ceria, zirconia, titania etc. [62]. Often zeolite is formed on the substrate by an *in-situ* crystallization process [58, 59, 61, 66]. For example, the invention KR20070084291A by SORTECH AG / Germany relates to a method for production of a zeolite layer on a metal containing substrate, comprising the following method steps: production of an aqueous suspension, comprising several components (at least one cross-linking element from the third, fourth or fifth main group of the periodic table), introduction of the substrate containing metal to the aqueous suspension, heating the aqueous suspension and the substrate for the *in-situ* crystallisation of a zeolite layer on the substrate containing metal, whereby the cross-linking elements in the substrate containing metal are extracted and included in the zeolite layer, a cross-linking element present in the suspension for formation of the zeolite layer is present at a concentration so low that a crystallisation in the suspension is largely or completely avoided and said element is principally provided by the substrate [61].

The invention CN101147853A by University Tianjin / China discloses a preparation method of zeolite molecular sieve membrane reactor coated with noble metal. Preparation of zeolite coating includes the following steps: stainless steel tube treatment, preparing binding agent, preparing coating solution, utilizing gas auxiliary coating technique to obtain the stainless steel tube coated with zeolite molecular sieve membrane. Then after several steps: formation of sensitizing agent, activating agent, sensitizing and activating the stainless steel tube, mixing the solution containing noble metal ions and complexing agent, injecting the solution into the interior of stainless steel tube, calcinations, gas treatment, the invented zeolite molecular sieve membrane reactor coated with noble metal is obtained [63].

A device comprising a zeolite coating is described in the invention WO2006005286A1 by FRAUNHOFER GES FORSCHUNG / Germany. The zeolite coating contains zeolite powder and a silicate matrix in which zeolite powder grains are embedded Fig. (10). A mixture is produced from zeolite powder, water, and water glass such that the metrological advantages of zeolite coatings can be utilized also in rough measuring conditions due to the great sensitivity and the great mechanical stability [64].

The invention US2001048971A1 / USA relates to a method for manufacturing zeolite which is useful as catalyst carrier for exhaust gas clean up by decomposition, reduction or oxidation catalyst carrier for synthesis and/or decomposition of organic or inorganic chemicals, and membrane for selective separation of organic substances, gases and inorganic cations. This new method is one in which a crystalline silica or amorphous glass contained in a fired ceramic substrate is used as a silica source for forming a natural or syn-

thetic zeolite film on the ceramic substrate, while at the same time making the ceramic substrate porous. The invention provides a method for manufacturing a high silica-content zeolite film on the surface of a ceramic substrate using a natural zeolite or synthetic zeolite (such as silicalite, ZSM-5, aluminosilicates, aluminosilico phosphates, aluminophosphates, metal aluminophosphates, gallophosphates, or iron-phosphates molecular sieve). Raw materials are chosen for making the ceramic substrate that contain natural silicate minerals to use as a silica source for the zeolite film. A combination of silica and alumina powders along with or without other chemical additives is molded in various shapes to form the ceramic substrate. The molded shape is then sintered at 1000 to 1700°C to create the ceramic substrate. The resulting substrate is then subjected to a hydrothermal treatment at 100 to 250°C together with an inorganic or organic base such as sodium, potassium, calcium or ammonium hydroxide, or mixtures thereof, water; and tetrapropyl-ammonium-bromide. The hydrothermal treatment is usually performed under pressure. Utilizing the reaction of the dissolution and re-crystallization of quartz, cristobalite, tridymite, or amorphous glass in the above described aqueous alkali solution, a porous ceramic having a zeolite film on its surface is obtained. The zeolite film formed by this method possesses no cracks Fig. (11). The adhering strength between the surface of porous ceramic and zeolite film is improved because the zeolite film has penetrated and bonded to the structure of the ceramic substrate. This provides a porous material with excellent bending strength and compressive strength. There is a wide range of zeolites available for use as catalyst carriers that can be synthesized using this method. These synthesized zeolites include not only the high silica-content silicalite, but also a zeolite which contains alumina partially eluted from the fired silicate mineral and an added alkaline earth oxide and/or an alkali oxide (such as aluminosilicate with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2 to 300). These zeolites can be formed on the substrate by varying the hydrothermal treatment conditions such as organic template, chemical composition, temperature, time, and concentration of alkali hydroxide for the hydrothermal reaction. The thickness and morphology of zeolite film on the porous materials can be controlled by the addition of colloidal silica or silica glass powder during the hydrothermal treatment [65].

Fig. (10). Schematic view of a support (which can be ceramic or of silicon, for example). 1 - support, 2, 3 and 4 – electrodes, 5 - zeolite coating, 6 – silica matrix, 7 - zeolite powder grain [64].

Fig. (11). Porous ceramic with a zeolite coating [65].

The invention US5871650A by Exxon Research Engineering CO / USA is directed toward a new zeolite membrane grown by hydrothermal synthesis. The membrane exhibits a columnar cross-sectional morphology and preferred crystallographic orientation comprising a porous substrate having coated thereon a mesoporous growth enhancing layer Fig. (12). The latter layer with thickness of 2-200 nm comprises nanocrystalline and/or colloidal sized zeolites or/and metal oxide. Zeolite layer is a polycrystalline layer wherein 99.9% of zeolite crystals have at least one point between adjacent crystals that is ≤ 2 nm [67].

Fig. (12). Scanning electron micrograph of the morphology of a MFI zeolite layer, a Growth Enhancing Layer, and a porous substrate. The layer labeled (A) is the porous substrate formed of α -alumina with 80 nm pores. The layer labeled (B) is the mesoporous layer. The layer labeled (C) contains MFI zeolite crystals, free of voids and defects [67].

The synthesis and deposition procedure of acid-modified zeolitic coatings for the adsorption of hydrocarbons is described in US6004896A by Corning Inc / USA. A method for improving the adsorption properties of a hydrocarbon adsorber which involves contacting a molecular sieve adsorber at ambient temperature with an agent for modifying the acid sites of the molecular sieve is reported. The average pore diameter of the molecular sieve is about 3 to 20 Å. The

modified molecular sieve has an ability to retain adsorbed hydrocarbons at higher temperatures than the unmodified one. The acid-modified adsorber is prepared as follows: the adsorber is mixed with the acidity-modifying agent in the form of a slurry; the material is then calcined at ca. 550°C and mixed with a suitable binder such as boehmite, in a slurry. The solids content is about 85 wt. % zeolite with about 15 wt. % binder. The water-to-solid ratio for the washcoat slurry is about 1:1 to 1.5:1. The pH of the slurry is adjusted to about 4 with nitric acid. The adsorber-agent-binder slurry can then be washcoated onto a substrate directly. For example, honeycombs are washcoated by dipping them into a slurry, removing them, clearing them of excess slurry, drying, and calcination. The advantage of preparing a separate precipitate with the acidity-modifying agent before forming a washcoating slurry is to ensure that all the acidity-modifying agent has been impregnated into the adsorber and not on the binder. The acid-modified molecular sieve described above can be used to remove hydrocarbons from a hydrocarbon-containing stream. The stream is passed through the modified adsorber at atmospheric pressure at a temperature ranging from room temperature to about 150°C to cause adsorption and retention of the hydrocarbons. The adsorbed hydrocarbons can then be desorbed at a higher temperature than would otherwise occur with an unmodified adsorber [100].

3.2.2. Patent Publications on the Methods of the Deposition of Catalytic Coatings on the Substrates

Catalytic coatings can be applied to substrates by several methods, including painting a slurry carried in organic or inorganic media, slurry spraying onto a hot or cold substrate, spray pyrolysis onto a hot substrate, flame spraying, solution spraying, dipping the substrate into the sol and heating, screen printing, electrolytic deposition, electrophoretic deposition, physical or chemical evaporation, sputtering, electrostatic spraying, plasma spraying, laser techniques, etc. [68].

Usually, the catalytic layer is formed on the substrate by slurry impregnation in the following manner. A support powder such as, for example, Al_2O_3 , ZrO_2 , CeO_2 , TiO_2 and SiO_2 is mixed with a binder component such as an aluminum salt, acid and water to make a slurry. The resulting slurry is deposited on the substrate. Thereafter, the substrate with deposited slurry is calcined. Then, an active component is impregnated into the coating [69].

Some variations of applying the slurry onto the support are described in the following patent publications. Invention US2008145531 of BASF Catalysts LLC / USA [70] is devoted to the catalyst slurry which is applied to an interior of a hollow substrate. The slurry is coated on the substrate by immersing the substrate into a vessel containing a bath of coating slurry. A vacuum is then applied to the partially immersed substrate. The intensity of the vacuum and its application time should be sufficient to draw the coating slurry upwardly from the bath into each of a plurality of channels located in the interior of the hollow substrate. After removing the substrate from the bath, it is rotated 180°. A blast of pressurized air is applied at intensity and for a time sufficient to distribute the coating slurry within the channels of the substrate to form a uniform coating profile therein Fig. (13).

Fig. (13). Procedure of coating the substrate by immersing the substrate into a vessel containing a bath of coating slurry [70].

Invention US5866210A of Engelhard Corporation / USA [71] reports a method for applying a coating on a substrate having many channels Fig. (14). The substrate is partially immersed into a vessel containing a coating sol. A vacuum is applied to the partially immersed substrate at an intensity and time sufficient to draw the coating sol upwardly from the bath into each of the channels to form a uniform coating. After the vacuum is imposed, the substrate is inverted and coated from the opposite end producing two coatings having uniform coating profiles. Each of the channels of the substrate is coated with the same thickness of coating and is characterized by a uniform coating profile. Moreover, substrates coated in accordance with the present invention exhibit lower wet gain.

Fig. (14). Method for applying a coating on a substrate having many channels [71].

Umicore / Belgium, WO2008113801A1, invented a method for coating ceramic honeycomb bodies with a catalyst suspension. Parallel flow ducts extend through the honeycomb bodies. The walls of the flow ducts have an open pore structure. In order to coat the duct walls, and particularly also the inner surfaces of the pores with the catalyst suspension, the inlet and outlet faces of the perpendicularly oriented honeycomb bodies are brought in contact with a shadow mask. The masks are disposed in such way that the open regions of the mask on the one face are located opposite the closed regions of the mask on the other face, and vice versa. Then, the catalyst suspension is pumped or suctioned from beneath into the honeycomb bodies until it is at the upper face. Thereafter, excess suspension is removed by blowing or vacuuming, the contact with the shadow masks is eliminated, and the honeycomb body is calcined [72].

The process proposed by Honda Motor Co. Ltd. / Japan, EP1775021A1 [69] can be divided into three stages. In the first stage, aerosol droplets containing catalyst precursor materials are generated. Next, the aerosol droplets are thermally treated ($100\text{--}500^{\circ}\text{C}$) to decompose the catalyst precursor salts and to produce metal oxide catalytic particles. In a third stage, the catalyst nanoparticles are deposited on the support. This technique for catalyst nanoparticle synthesis and in-situ deposition on porous supports is called Aerosol Spray Pyrolysis. In addition, catalyst nanoparticle deposition depends on various process parameters, such as reactor temperature and precursor type. The coating was observed to be adhesive [69]. Fig. (15) shows an example of a hot wall aerosol reactor used to carry out the process of the invention.

Fig. (15). Hot wall aerosol reactor (1 – hot wall aerosol reactor, 2 – container with catalyst precursor, 3 – carrier gas, 4 – small droplets, 5 – first heating zone, 6 – second heating zone, 7 – filter support) [69].

It is difficult to see too much innovation given in the above mentioned publications, however the refinements of the coating deposition procedures are clearly observed.

The invention of He Ting and Honda Motor Co. Ltd. / Japan, US2002081243A1 relates to a method of coating a substrate with ceria CeO_2 and a noble metal catalyst (such as palladium) by thermal spraying a mixture of large size metal component precursor particles, such as cerium carbonate $\text{Ce}_2(\text{CO}_3)_3$, mixed with large size noble metal precursor particles, such as palladium hydroxide $\text{Pd}(\text{OH})_x$. A mixture of large size ($>10\mu\text{m}$) ceria and Pd particles is injected into a thermal sprayer, the Pd/ CeO_2 coating is obtained directly onto a substrate surface. The coating has a nominal particle size diameter of $<1\mu\text{m}$. Fine particle coating with good mechanical adhesion to a substrate, high porosity, stability and surface area, useful for catalytic reactor applications was obtained [73].

The patent of Alon Inc. / USA, US6165286A [74], describes a single or multiple deposition of thermally sprayed coatings of selected metals onto iron-, nickel-, cobalt-, and

titanium-base materials to provide a corrosion resistant surface. First of all, the optimal surface preparation via abrasive blasting was developed. The surface of the metal substrate is then cleaned to remove all diffusion barriers such as dirt or hydrocarbons. Then the coating is sprayed onto the base material. The heat treatment cycle consisting of four steps is unique for each iron-, nickel-, cobalt-, or titanium-base material, requiring (1) special heat up rate, (2) intermediate hold temperature based on thermal spray coating composition, (3) final heat up rate and (4) final hold temperature and time [74].

The publication of Sander Karel and ACS Industries Inc. / USA, US2002100994A1, describes a method of coating monolithic catalyst structures with seal material by a high speed extrusion coating operation in which a number of monoliths are passed through an extrusion chamber. In the chamber the monoliths are coated with the seal mixture in a continuous operation. This continuous process methodology shortens the time needed to apply the seal coating to each of the monoliths, thereby resulting in faster production and a cost savings [75].

The invention EP0705914A1 by Allrgheny Ludlum Corporation / USA [76] relates to a method for providing a coating of alumina to metallic structures which operates at high temperatures to conduct waste exhaust gases Fig. (16). The coating with the gaseous mixture also may remove the necessity of adding an alumina washcoat prior to depositing the catalytic metal coating. This benefit may be particularly important in lowering overall production costs of exhaust components and improving catalytic efficiencies. Metal substrate is coated with a gaseous mixture (trimethyl or triethyl aluminum as a precursor, argon, nitrogen, or helium as a carrier gas and hydrogen to lower the dew point of the mixture) to form an aluminum coating and the coating is either oxidized to form alumina or heat treating to form a diffusion layer of aluminum within the metal substrate, or both.

Fig. (16). Scheme of the method of the invention [76] as applied to a batch type process (40 – furnace, 42 – timer, 44 – flow valve, 46 – line, 48 – vessel which forms gaseous mixture, 50 – bath with Al precursor, 52 – conduit line (argon), 53 – dry hydrogen, 54 – supply line, 56 – valve).

Nowak *et al.* invented an inexpensive process for producing a coated, structured heat exchanger plate for a reactor in a fuel cell system. The coating of the structured plates is

carried out by pad printing. Pad printing is an indirect printing process, i.e. a plate, which is known as an engraving, serves as the original, on which the image to be printed is present in the form of a recess. The thickness of the layer applied by pad printing is in the range of approximately 5 to 50 μm . The printing step is followed by a drying step in a temperature range of 100–200°C in order to improve adhesion of the coating. Further printing operations may follow the drying step. This method has few advantages if compared to, for example, spraying, dip-coating or wash-coating. Spray-coating causes a loss of coating material of up to 50% as a result of overspray, also during this process complex masking of the respective zones would be necessary. Zoned coating cannot be achieved by means of wash-coating or dip-coating, so at best it is possible to apply a gradient in coating height using these methods [77].

The coatings preparation and deposition methods are summarized in Table 2 according to general classification of coatings in terms of pore size (microporous, mesoporous and macroporous).

3.2.3. Patent Publications on Apparatus for Deposition of Catalytic Coatings on the Substrates

Some inventions are related to the equipment for the coating deposition [78–80]. The devices described in these patent publications are mainly concerned to be applied to coat certain supports (tube or membrane etc.) which are used in different industrial areas.

In EP1325781A1 by Cataler Corporation / Japan [79] an apparatus for applying a catalytic coating solution containing noble metal on a catalyst support (alumina) is described. The coating apparatus Fig. (17a) was arranged as to coat a catalytic coating solution inside a bent tubular catalyst support. As illustrated in Fig. (17) the catalyst support was formed of a pipe which was bent like an arc [79].

A method and an apparatus for coating a ceramic monolithic support with catalytic slurry, wherein a deviation in deposition of the upper and lower sides of a coating can be minimized, are provided in JP2000202307A by Nissan Motor / Japan [78]. In the case where a monolithic support is placed and pressurized or sucked, conditions for pressure and time are previously set so that pressure is stepwise or continuously changed and so that the total pressurization or suction time is made T hours, an x_1 pressure is applied for the initial t_1 hours, an x_2 pressure is generated for the next t_2 hours, and an x_3 pressure is generated for the succeeding t_3 hours, wherein, $T = t_1 + t_2 + t_3 + \dots + t_n$ ($n \geq 2$).

The designs of two different chemical vapour deposition (CVD) apparatuses are presented in [81, 82]. A thin film formation method and apparatus which can efficiently form a film by catalytic chemical vapour deposition, even if the film is formed from a mixture of two or more gaseous compounds was described in JP2006278459A by Ulvac Corporation / Japan [82]. The film is deposited via the following procedure: a potential is applied to a catalyst (5 on Fig. (18)) to generate an electric field near the surface of the catalyst, a material gas is decomposed by the action between the electric field and electrons emitted from the heated catalyst to generate the deposition species, and then a thin film is formed.

Table 2. Coatings Preparation and Deposition Methods

Pore Size	Type of Catalytic Support	Preparation and Deposition Techniques
Microporous (<2 nm)	Zeolites, metal oxides	Hydrothermal synthesis, washcoating
Mesoporous (2-50 nm)	Metal oxides, mesoporous carbon	Sol-gel: dip-coating, spin-coating, washcoating; anodic oxidation
Macroporous (>50 nm)	Metal oxides, carbon	Washcoating, CVD, anodic oxidation

Fig. (17). **a** – Apparatus for applying catalytic coating solution according to the invention [79]; **b** – conventional apparatus for or applying catalytic coating solution, prior art [79]; 11, 12 – tank with catalytic coating solution; 2, 25 – catalyst-support holding unit; 61, 62 – catalyst support; 7 – catalytic-coating-solution circulation passage; 71 – control valve; 72 – pump; 3 – catalytic-coating-solution distributor pipe (internal diameter 25 mm); 51 – sensor; 4 – driving unit; 52 – arithmetic unit; 41 – motor).

Fig. (18). Catalytic film deposition equipment [82].

The invention WO2006005493A1 of Sartorius GMBH *et al.* / Germany [83] relates to a method and a device for applying a catalytic layer to a membrane in order to produce a membrane/electrode unit for a fuel cell Fig. (19). A catalytic coating material is provided in the form of an electrostatically active toner powder, whereupon the catalytic layer is xerographically transferred to the membrane and fixed. Two xerographic printer units are arranged opposite one another and enable the membrane to be coated on both sides in one pass.

3.2.4. Patent Publications on Catalytic Coatings in Micro-channels

In this section attention will be given to catalytic coatings for microstructured reactors. It is well-known that the efficient use of microstructured reactors requires deposition of the catalytically active component onto microchannel walls.

Micro-packed beds of powder catalysts can be used sometimes, but, in general, a thin layer of catalyst deposited on the reactor wall is preferred, because of mass and/or heat transfer improvement and keeping pressure loss low.

Fig. (19). Device for applying a catalytic layer to a membrane (2 – membrane, 6, 6' – xerographic printer units, membrane, 7, 7' – drums, 8, 8' – developer unit, 9, 9' – corona unit) [83].

The invention of Commissariat Energie Atomique *et al.* / France, WO2010049655A1, relates to methods of catalyst deposition on microstructured substrates. In order to improve the adhesion, the stability as well as the uniformity of the catalytic coatings for microstructured reactors it was proposed to adapt methods of a catalyst deposition on a solid support. Suspension or chemical vapour deposition is proposed to use to deposit the catalytic coating. The active component can be chosen from the following group: nickel, rhodium, platinum and palladium. Preferably, the support of catalyst is selected from aluminium oxide, zirconium oxide, lanthanum oxide or cerium oxide. The catalyst can also include one or more promoters (such as La, Ca, Cs, K etc.) As an example, preparation of Ni/Al₂O₃ catalytic coating is described as follow. First, a layer of alumina is deposited on the previously thermally treated microstructured plate (5,5-6 wt.% Al, 19-21 wt.% Cr, the rest is Fe). The plate is pre-treated in a distilled acetone bath then in a bath with a mixture of H₂O:H₂O₂:H₃PO₄:CH₃CO₂H (5:1:1:1). Then the plate is calcined at 1200°C under nitrogen for one hour. After this procedure, formation of a thin (20-30 μm) layer of α-alumina is observed. The γ-alumina is then deposited from slurry, prepared from suspension of γ-alumina, boehmite and binders (acetic or acrylic acid). The size of the suspended parti-

cles, measured by granulometry laser, should be lower than 5 μm . The metal plate with deposited alumina slurry is then dried and calcined at 800 $^{\circ}\text{C}$ for 4 hours. The resulting layer of alumina possesses a surface area of 149 $\text{m}^2 \text{g}^{-1}$, a pore volume of 0.48 $\text{cm}^3 \text{g}^{-1}$ and an average pore radius of 6.4 nm. The stability of the alumina coating is tested via the treatment of the plate in petroleum under ultrasound. After one hour treatment, the weight loss of alumina is found to be ca.7%, which indicates a good adhesion and stability of the alumina layer. It is also observed that the catalytic coating has a constant thickness along the walls and along the base of the channels. In the second step, alumina layer is impregnated with nickel nitrate solution. Then the plates are dried in vacuo for 20 min before calcination at 800 $^{\circ}\text{C}$ for 4 hours. The resulting microstructured reactor is tested in iso-octane reforming. It is found that more than 80wt.% of iso-octane were converted during the reaction at 725 $^{\circ}\text{C}$ -750 $^{\circ}\text{C}$ and ca. 60% at 700 $^{\circ}\text{C}$. The method presented in the invention is found to be reproducible and easy to implement [84].

One example of micro-packed beds of catalyst is shown in CN101060176A by Samsung Electro-Mechanics / South Korea [85]. Catalyst is filled in the microchannels using water; unidirectional pressure is applied to the catalyst in the microchannel to fill the microchannel with high density. The proposed method provides uniform filling the catalyst particles in the micro channel of the reformer with high density, increasing the reactive surface area of the catalyst particles with the fuel, thereby providing high efficiency Fig. (20).

Fig. (20). Filling of the catalyst into the microchannels [85].

The patent publication of Shida Geng / China, CN101837292A, relates to a preparation of a catalytic coating for a micro-channel reactor for hydrogen synthesis from methanol and steam. The micro-channeled reactor is uniformly coated with the catalytic coating which is prepared by

mixing one or more of CuO , ZnO , La_2O_3 and Ce_2O_3 and scale Al_2O_3 . The catalytic layer is deposited on the inner wall of the reactor by spraying, washing, drying and calcination. The micro-channel reactor prepared shows the improvement in the conversion rate of the methanol and the selectivity towards carbon dioxide [86].

Patent of Japan Science & Technology Agency / Japan, JP2009214056A, describes a method for immobilizing a catalyst to a microcapillary, the construction of a micro-reactor and the performance of solid-liquid-gas phase reaction in the micro-reactor. The micro-reactor is a capillary Fig. (21); the reaction solution supplying part is used to supply a solution, in which a substrate is dissolved. The gas supplying part serves to supply a gas to the capillary and a recovery part is used to recover the reaction product. A polymer film is coated onto the inner wall of the tube and serves to keep metal catalyst encapsulated in the polymer film. One end of the capillary is connected with the reaction solution supplying part and the gas supplying part. The other part is connected with the recovery part [87].

Fig. (21). (1) Micro-reactor, (2) capillary, (3) tube body, (4) high polymer molecule film, (5) catalyst, (6) substrate, (7) solution, (10) reaction solution supplying part, (20) gas supplying part, (22) gas, (30) recovery part [87].

Invention of Atotech Deutschland GMBH and Sued Chemie AG / Germany, DE102007063040A1 [88], is devoted to production of micro-reactors consisting of micro-channeled plates. A catalytic support (aluminum or silicon oxides) suspension is deposited in the channels; active metal (platinum, palladium, rhodium, ruthenium, nickel, cobalt, silver or copper) is impregnated from a solution or suspension; the plates are stacked with the joining layer on each other and heated to a temperature at which the joining layer bonds with the plates and the catalyst support layer is calcined Fig. (22).

A micro channel reactor which can improve the adhesive force of the reforming catalyst is proposed in KR100746344B1 by Korea's Advanced Institute of Science and Technology / South Korea [89]. Reforming catalyst is deposited in the microchannels already coated with an oxide layer Fig. (23).

Fig. (22). Scheme of coating formation and assembly of microchanneled plates [88].

Fig. (23). Typical microchanneled plate [89].

3.2.5. Patent Publications on Catalytic Coatings in Microchanneled Reactors on Pilot Scale

The development of a commercial microreactor for chemical production is an endeavour that has been undertaken by a number of companies and research centres. Some key reactor systems that have been used industrially are from Corning, DSM, Forschungszentrum Karlsruhe, IMM and others. The various reactors are made out of different materials, have various channel geometries, diverse mixing and heat exchange structures, have distinctive scale-up strategies [90].

Although benefits of flow chemistry using microreactors are now well established, the aspect of scalability still remains a relatively unexplored field. Only a small number of examples on a production scale have so far been reported. In 2001, Degussa AG and Uhde GmbH together with partners from academia started the DEMiS project. The main goal of the project is the investigation of heterogeneously catalyzed reactions (for example, epoxidation of propylene on the titanium silicate catalyst) in microstructured reactors at pilot-plant scale. In pilot scale microchanneled plate with dimensions of 0.6 x 1 m and grooves with a depth of up to 1 mm and a width of 2 cm was coated. As coating technology, a spray technology was used, and a slurry of TS-1 and a colloidal silica binder was sprayed in multiple cycles on the bottom of the grooves [91, 92].

The invention US2005165121A1 / USA relates to a process for converting a reactant composition comprising H_2 and CO to a product comprising at least one aliphatic hydrocarbon having at least about 5 carbon atoms. The process consist of flowing the reactant composition through a microchannel reactor in contact with a Fischer-Tropsch catalyst to convert the reactant composition to the product, the microreactor consisting of microchannels containing the catalyst,

transferring heat from the process microchannels to a heat exchanger, and removing the product from the microchannel reactor. The production is at least about 0.5g of aliphatic hydrocarbon having at least about 5 carbon atoms per gram of catalyst per hour, the selectivity to methane in the product is less than 25%. The invention also relates to a supported catalyst comprising Co, and a microchannel reactor. An example of a microchannel that may be used with the inventive process as a process microchannel and/or a heat exchange microchannel is illustrated in Fig. (24a). The height (h) or width (w) of the microchannel may be in the range of about 0.05 to about 10 mm. The length (l) of the microchannel may be of any dimension, for example, up to about 10 meters. Although the microchannel illustrated in Fig. (24a) has a cross section that is rectangular, however the microchannel may have a cross section having any shape, for example, a square, circle, semi-circle, trapezoid [93].

Fig. (24). (a) Schematic illustration of a microchannel, (b) schematic illustration of a layer of process microchannels and a layer of heat exchange microchannels that may be used in the microchannel reactor core of the microchannel reactor [93].

3.2.6. Patent Publications on Methods of the Removal of Catalytic Coatings

Valuable catalytic materials often remain behind when the coated substrate (reactor) is removed from service [94]. Moreover the removal of the coatings allows not only to collect spent catalytic materials but also to renew the substrates for its further utilization.

A simple and effective method for destroying the bonding between the coating and the metal support structure was reported in WO2005100622A1 by Holgersen James / USA [94]. The process is based on the effect on contact between the catalytic coating and the metal support by nitric acid, which leads to destroying the bonding between the film and the metal substrate. Once the bonding is destroyed, the catalytic coating is removed by ultrasonic agitation or detergent solution rinse.

The usual deterative agents such as H_2SO_4 , HCl , HNO_3 , HF , alkaline oxidizing salts etc. are effective for certain applications; however, they have certain drawbacks. For example the caustics for deterative action are harsh, and skin and eye contact must be avoided. The toxicity and disposal problems of mineral acids are also well known. Electrolytic aqueous baths also require energy to operate and also usually are toxic, and have somewhat narrow ranges of use [95].

General Electric / USA, CN1702196A, invented a method of removing a metal oxide coating from an alloy substrate via the following procedure: contacting the substrate having an oxide coating on the surface with an aqueous coating removal solution for 1-2 hours at a temperature from 77°C to 99°C . The coating removal solution consists on alkali (Na, K, Li) hydroxide, alkanolamine, and gluconate salt. The above described method can be applied to a wide variety of alloy substrates. If any trace of the metal oxide coating remains, the procedure can be repeated, until none of the metal oxide coating is observed on the substrate. Then the substrate is removed from the solution and rinsed with water at room temperature. If any loose metal oxide coating residue is observed on the surface of the substrate, the rinsing can be accomplished additionally in deionized water at 70°C . Loose residue on the surface can also be removed by brushing the surface of the article with a nonmetallic, soft-bristle brush. It is assumed that the coating-removal solution attacks the binder system in the metal oxide coating, causing the layers of the coating to release from the surface of the alloy substrate. Once released from the substrate, the oxide coating can be gently removed with water and/or nylon brushing [96].

Another relatively mild, non-toxic solution for coating (metal oxide containing Fe, Ni, Cu, Be, Cr, Au, Zn, Pb and Sn) removal from a variety of metal alloys was invented by Wood *et al.*, US4264418A [96]. The composition includes gluconic, tartaric and citric acids or its alkali metal salts, sodium gluconate, non-ionic surfactant, and water ($\text{pH} \leq 4$). The tests performed on stainless steel with the above solution showed a good removal of a thin oxide film, leaving a bright substrate. Also, when a material, such as stainless steel or copper alloys has heavy oxides coatings, the solution of this invention can be used with electric current. The current should be as high as the conductivity of the solution allows, and periodic reversal of polarity every few seconds is desirable. The mechanism of the action of the solution is not completely understood. It is theorized that citric acid is effective in attacking and dissolving the oxides that are on the surface of the metals, especially the Cu, Fe, Cr and Ni. Tartaric acid is a somewhat stronger acid than citric acid, and will attack metal oxides vigorously without attack of the metal. Also, it will chelate both ferrous and ferric oxides as well as Fe_3O_4 ; also tartrate chelates Zn, Be, Cr, Ni and Cu. Sodium gluconate is especially effective in chelating both ferrous and ferric ions in acid. With respect to time of treatment, it has been found that the optimal time is about 10 minutes in a 10% solution of the proposed composition at 65°C .

The methods of the coatings removal described above can be used with a quite wide variety of coatings and substrates. However, there are some patent publications related

to the removal of a particular coating from certain substrates [97, 98]. For example, chromium oxide coating can be removed from a surface of nickel-base alloy at $80\text{--}90^\circ\text{C}$. A method of removing a chromium oxide coating from a surface of a compressor blade Fig. (25) consists of few steps: providing an article with chromium oxide coating, cleaning the article in an alkaline degreasing/rust removal solution at about $80\text{--}90^\circ\text{C}$, contacting the article with an alkaline permanganate solution and contacting the article to a water solution consisting of hydrochloric acid. After each of these steps the substrate should be washed in water, and gently brushed to remove loose material from the surface [97].

Fig. (25). An elevational view of a compressor blade (18 – article, 22 and 32 – compressor blade, 20 – gas turbine component, 24 – airfoil, 30 – openings, 28 – platform, 25 – root) [97].

A method for removal of coatings containing noble metal from monoliths is described in IT1249659B by Fiat Ricerche / Italy [99]. The method includes the following cycles: in the first step monolith is impregnated with water, the second step is cooling of the monolith, and in the third step the monolith is heated in a water bath exposed to ultrasound. A sudden variation of temperature causes a series of cracks in the coating, whereas the ultrasound vibrations cause the particles of the coating to be detached from the monolith.

The innovations in improvement of the removal and renewal methods are mainly related to usage of mild, non-toxic reagent which causes less safety precautions.

4. CONCLUSIONS

The analysis of the patent publication in different countries in years 1990-2010 showed that Japanese and German companies have leading position as patentees. These countries were found to be also active in providing patents on different catalytic systems, reactors, and particularly micro-structured reactors. The latest patent publications are mostly devoted to the catalytic coatings for exhaust gases treatment and fuel cells. The increasing amount of patent publications on catalytic coating in microstructured reactors during the

last few years corresponds to the commercialization of microstructured reactor technology as was mentioned in [3]. Mostly and unlike the other patents mentioned using conventional reactors, the patents on catalytic coatings in microstructured reactors contain not only the coating preparation method, but also construction of the microstructured reactor and its test in a certain reaction – showing the relationship between structured reactors and structured supports, which in an extreme can merge to one body. It can be anticipated that further development of microstructured reactors will require more advanced catalytic coatings (i.e. with higher stability, improved catalytic properties etc.), so the further increase of number of patent publications can be expected. Future topics for microstructured reactor catalysts are how to enhance catalyst stability, to recover activity, or to exchange non-active catalyst modules.

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ABBREVIATIONS

UV light	=	Ultraviolet light
PVD	=	Physical Vapour Deposition
CVD	=	Chemical Vapour Deposition

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