



Materials chemistry for catalysis: Coating of catalytic oxides on metallic foams

A. Essakhi^{a,b}, A. Löfberg^{a,b}, S. Paul^{b,c}, B. Mutel^{a,d}, P. Supiot^{a,d}, V. Le Courtois^{b,c}, P. Rodriguez^e, V. Meille^e, E. Bordes-Richard^{a,b,*}

^a Université Lille Nord de France, F-59000, Lille, France

^b UMR CNRS 8181, Unité de Catalyse et Chimie du Solide, Université Lille 1, F-59655 Villeneuve d'Ascq, France

^c Ecole Centrale Lille, F-59655 Villeneuve d'Ascq, France

^d Institut d'Electronique, de Micro électronique et de Nano technologie - UMR CNRS 8520, Université Lille 1, F-59652 Villeneuve d'Ascq, France

^e Université de Lyon, Institut de Chimie de Lyon, Laboratoire de Génie des Procédés Catalytiques, UMR CNRS 2214, CPE-Lyon, F-69616 Villeurbanne, France

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ABSTRACT

Catalytic structured reactors are designed to improve both heat and mass transfers during reactions in the presence of catalytic layers. The know-how acquired in the coating of stainless steel walls by catalytic layers of VO_x/TiO₂, active in the abatement of volatile organic compounds and in the production of chemical intermediates, was extended to metallic foams. The preferred and original way was to first make a deposit of a silica-like primer by cold plasma assisted polymerization of tetramethyldisiloxane in the presence of oxygen. After mineralisation, this layer was supposed to act as a barrier against poisoning by elements of the metallic substrate, as well as a stabilizer of the catalyst layers. The cells of the foam were homogeneously covered by a 5 μm-thick polysiloxane film ending in ca. 1 μm thick silica after calcination. After studying the textural properties and zeta potential of aqueous suspensions of TiO₂ particles, the silica-coated foams were dipped in a 37 wt.% aqueous suspension of TiO₂-anatase. The final VO_x/TiO₂/SiO₂/foams were obtained by grafting polyvanadate specie in sol-gel medium. At every step of coating, the multilayer materials were studied mainly by X-ray Photoelectron Spectroscopy and Electron Probe Micro-Analysis. Moreover the mechanical and chemical stability of the successive coatings was checked.

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1. Introduction

There are two main ways to increase the yield of products obtained by catalytic reaction, improving the properties of the catalytic material or optimizing the catalytic process. In the first case it is necessary to improve both activity and selectivity of catalysts. Oxidic materials are used either as supports (alumina, silica, zeolites, ...) or as active phases (mostly transition metal mixed oxides) in the very numerous reactions for synthesis of chemical commodities from, e.g., hydrocarbons, including alkanes, environmental issues (deNO_x, VOC abatement, ...), energetics (anodes for fuel cell) and the like. As in the case of anchored metal organic complexes, oxide particles can be inserted or oxidic species can be grafted in zeotypes. More recently several methods of preparation to obtain nanosized particles of oxides, and even special techniques to manufacture nanostructured catalysts were developed [1]. The second way is to optimize the process itself, beginning by the improve-

ment of the contact efficiency between the catalyst and the molecules to be transformed.

Since more than a decade the concept of process intensification has boosted research on structured (micro)reactors, the microscale (1–100 μm) being related to safer, cleaner, and above all more efficient heat and mass transfers [2]. One way of implementing reaction technology is in the form of a catalytic wall reactor, the walls being engraved by channels in the sub-millimetre range inside which is attached a solid catalyst. Another way is to coat the catalyst onto structured inserts like monoliths, ending in monolithic reactors. This is not so new since that technology was chosen in the 1970's to solve environmental problems due to mobile or stationary installations. For example three-way catalysts for automotive engine exhausts are made of noble metals on alumina deposited in channels of monoliths, while NO_x effluents are treated on monoliths made with vanadium–tungsten–titanium mixed oxides. In the case of exhaust pipes, metallic honeycombs were considered for a while because of their high thermal conductivity but finally they were abandoned at the profit of cordierite monoliths which could better stand the very high temperatures due to combustion reactions. The problem to solve is not so different when seeking for chemical products like acrolein, maleic anhydride, phthalic anhydride, etc., manufactured by mild oxidation

* Corresponding author at: UMR CNRS 8181, Unité de Catalyse et Chimie du Solide, Université Lille 1, F-59655 Villeneuve d'Ascq, France. Tel.: +33 320434526; fax: +33 320436561.

E-mail address: elisabeth.bordes@univ-lille1.fr (E. Bordes-Richard).

of hydrocarbons. Most reactions are consecutive and to be obtained the targeted product must be “kinetically” quenched at the expense of carbon oxides. For example, propylene obtained by oxidative dehydrogenation (ODH) of propane ($\Delta_{\text{R}}H_{298} = -118 \text{ kJ mol}^{-1}$) is very easily converted to carbon dioxide ($\Delta_{\text{R}}H_{298} = -1926 \text{ kJ mol}^{-1}$) because it is more reactive than the reactant. Several catalytic formulas have been tried with little success, as up to now yields of propylene hardly overcome 40%. To get rid of hot spots which are unavoidable in packed bed reactors and which are (partly) responsible for the formation of carbon oxides, a solution would be to structure metallic wall reactors or to use metallic substrates like honeycombs, foams, wires, and the like, as inserts. Indeed modifying the contact between the gas phase and the catalyst, and particularly increasing the heat transfer between them, should lead to an increase of yields of propene. This has just been demonstrated by Schwarz et al. [3] who deposited a $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst on micro-channels carved in stainless steel walls. They found that isothermal reaction conditions over a wide range of concentrations and temperatures could lead to substantial increase of the propylene productivity.

Some years ago we have undertaken studies about the coating of metallic (anodized aluminum, stainless steel) plates by VO_x/TiO_2 anatase layers. The properties of VO_x/TiO_2 catalyst are well documented for several reactions, including the ODH of propane [4–6]. The sol–gel method was used to graft TiO_2 and the active vanadia phase in successive layers onto plates, because it presents several advantages among which the easy control of composition, the low processing temperature, as well as the possibility of large area coatings at low equipment cost [7]. Another method for TiO_2 deposits, more simple as the textural properties of the powder (surface area, porous volume, etc.) are retained after drying, consisted of dip-coating the plates in an aqueous suspension of titania [8,9].

Foams have several interesting features thanks to their large geometric areas, high void fractions, high mechanical stability and low pressure drop, and the formation of hot spots should be avoided if the material is metallic due to its high thermal conductivity [10–12]. The amount and dispersion of the active phase can be controlled by changing the thickness of the coating, which is important because the performance of the catalyst is determined by the synthesis procedure, morphology and stability of the film [13].

The know-how that we acquired on the coating of stainless steel plates by VO_x/TiO_2 [7–9] was extended to the coating of metallic foams that we propose for the first time in the literature. The stainless steel foams were covered by three successive layers. First a primer constituted by silica was deposited by remote plasma enhanced chemical vapor deposition. The SiO_2/foam was dipped in titania aqueous suspension, and after calcination polyvanadates were grafted on $\text{TiO}_2/\text{SiO}_2/\text{foam}$ by sol–gel method. The textural properties were studied and most analyses were performed mainly by electron probe micro analysis and X-ray photoelectron spectroscopy. Attention was paid to the mechanical and chemical stability of the successive layers.

2. Experimental

2.1. Preparation of samples

Plates and foams were coated in a three-step procedure (method A), consisting of (i), deposition of a silica film by polymerization of tetramethyldisiloxane (TMDSO) by remote plasma enhanced chemical vapor deposition (RPECVD, vide infra) [14], (ii), dip-coating of $\text{SiO}_2/\text{substrate}$ in an aqueous suspension of TiO_2 while stirring (5 min) followed by calcination, (iii), grafting of vanadium oxide species on calcined $\text{TiO}_2/\text{SiO}_2/\text{substrate}$. The amount of TiO_2 particles in water was adapted to coat plates or foams (vide infra). After calcination vanadium oxide specie were grafted as in (iii). In

(ii) and (iii) steps plates or foams were withdrawn at constant rate (6 mm s^{-1}) after dipping. Solutions containing different amounts ($C = 1.0, 1.8, 3.5, 7.5 \text{ wt.}\%$ in dry ethanol) of $\text{VO}(\text{OPr})_3$ were prepared. A final calcination was carried out at $450 \text{ }^\circ\text{C}$ (2 h). ASI 316L stainless steel was chosen for the metallic substrates plates ($50 \times 20 \times 0.5 \text{ mm}$) and foams (Porvair[®], 40 ppi, density 5.4%, porosity $\varepsilon = 81\%$). Foams were cut as cylinders ($\varnothing 1.6 \times 0.7 \text{ cm}$ height) or parallelepipeds ($1.0 \times 1.0 \times 0.7 \text{ cm}$). The mean weight was 410 mg/cm^3 . Before use, the substrates were sonicated, first with ethanol (30 min) to eliminate organic traces, and then twice in deionized water (30 min) before drying at $100 \text{ }^\circ\text{C}$ for 3 h.

To compare with materials without silica primer, an alternative procedure (method B) consisted first of superficial corrosion of the metal in 30 wt.% H_2SO_4 aqueous solution at room temperature during 3 h, and followed by washing with water in ultrasonic bath (30 min) to eliminate impurities present in H_2SO_4 (e.g. K^+). The (ii) step was the same as above, the corroded substrate being dipped 5 min in aqueous suspension of TiO_2 powder while stirring. After calcination vanadium oxide specie were grafted as in (iii).

2.2. Remote plasma enhanced chemical vapor deposition (RPECVD)

The principle of the remote nitrogen plasma assisted polymerization [15] and details about the plasma reactor can be found in [16–18]. The nitrogen (1.8 L min^{-1} STP) flowing in the reactor was excited by a microwave discharge (2450 MHz–200 W) in a fused silica tube. By continuous pumping, the reactive atomic N species flowed from the discharge zone to the deposition zone located far (at 1 m) from the discharge (called CRNP, cold remote nitrogen plasma). In this way, the resulting flow was free of charged particles, so the etching effect was very low and deposition rates reaching 100 times that obtained with discharge plasma could be obtained. Tetramethyldisiloxane (TMDSO) monomer and oxygen (25 and $5 \text{ cm}^3 \text{ min}^{-1}$ STP respectively) were flowed at 550 Pa by means of MKS mass-flow controllers in the CRNP through a coaxial injector. The deposition rate of the polymer (here called ppTMDSO) on plates was *in situ* measured by interferometry using He–Ne laser and a photodetector. The ppTMDSO film was further mineralized by thermal treatment at $650 \text{ }^\circ\text{C}$ for 1 h ($5 \text{ }^\circ\text{C/min}$ heating rate) in air under forced convection in a furnace. As traces of carbon remained, a $\text{N}_2/1.5\% \text{ O}_2$ remote plasma treatment could be finally applied during 5 min.

2.3. Characterization methods

Several methods of analysis as well as tests of stability were conducted after each step of preparation of the coated plates, and on foams for some of them.

X-ray diffraction patterns were obtained on powders or on scrapped layer from the substrate when possible using Huber D5000 diffractometer ($\text{CuK}\alpha$ radiation). X-ray photoelectron spectroscopy (XPS) was carried out using Escalab 220 XL spectrometer (Vacuum Generators). A monochromatic Al $\text{K}\alpha$ X-ray source was used and electron energies were measured in the constant analyzer energy mode. The pass energy was 100 eV for the survey spectra and 40 eV for the single element spectra. All XPS binding energies were referred to $\text{C}1s$ core level at 285 eV. The angle between the incident X-rays and the analyzer was 58° , photoelectrons being collected perpendicularly to the sample surface.

To be examined by Electron Probe Micro-Analysis (EPMA), samples were embedded into epoxy resin, and successively polished with abrasive discs (2400 to $3 \mu\text{m}$ granulometry) when the core of material had to be investigated. A Bal-Tec SCD005 sputter coated allowed depositing a thin carbon film. The elemental analysis was made by wavelength dispersive X-ray spectrometry (WDS) using Cameca SX-100 microprobe analyser working at 15 kV and 15 nA

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