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Preparation and characterization of VO_x/TiO_2 catalytic coatings on stainless steel plates for structured catalytic reactors

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Abstract

The parameters to be controlled to coat metallic walls by VO_x/TiO_2 catalysts which are used in the mild oxidation of hydrocarbons and NO_x abatement are studied. Stainless steel (316L) was chosen because of its large application in industrial catalytic reactors. TiO_2 films on stainless steel were obtained by dip-coating in two steps. Superficially oxidized plates were first dipped in Ti-alkoxide sol–gel to be coated by a very thin layer of TiO_2. On this anchoring layer was then deposited a porous film of titania by dipping plates in an aqueous suspension of TiO_2 particles. After calcination, VO_x species were grafted to TiO_2/SS plates and their loading was determined by means of X-ray photoelectron spectroscopy. The chemical and mechanical resistances of films were controlled by several tests. Laser Raman spectroscopy, X-ray diffraction and scanning electron microscopy were used to characterize the samples after each step of preparation. The porous texture was determined using a thermobalance. The dispersion and the nature of VO_x species and the value of theoretical monolayer of VO_x on TiO_2/stainless steel are shown to depend on the surface V/Ti ratio, in the same manner as for VO_x/TiO_2 coating anodised aluminum plates and as for VO_x/TiO_2 powders. Therefore, we have demonstrated that the shaping of TiO_2 has no influence on the characteristics of the active phase, which is of prime importance for catalytic applications in structured reactors.

Keywords: Structured reactors; Catalytic wall reactors; Stainless steel; Dip-coating; V_2O_5/TiO_2 catalyst; XPS

1. Introduction

Heat exchanger type reactors are studied till recently because of their potential applications in highly exothermic reactions [1,2] like, for example, the oxidative dehydrogenation of C_2–C_4 alkanes [3–6]. Compared to fixed bed reactors in which heterogeneous catalytic reactions are most often carried out, structured reactors could be profitably used because the heat transfer between the poorly conducting oxidic material and the metallic wall would be better controlled [7]. In such cases, the catalytic active phase must be deposited onto the metallic plates that constitute the reactor walls, or directly onto the walls, according to the reactor design. Obviously, this assembly must be mechanically and thermally stable, chemically resistant to the reactants, while the coating must retain its specific textural and catalytic properties. Once the active oxidic material is chosen, the coating procedure must be adapted case by case according to the nature of the metallic substrate (e.g., aluminum or stainless steel) and, eventually, its shape.

We have recently studied the coating of aluminum plates with VO_x/TiO_2 catalyst [8]. This catalyst is well-known to be active and selective in several types of reactions like the mild oxidation of hydrocarbons (*o*-xylene oxidation to phthalic anhydride, oxidative dehydrogenation of propane, etc.) as well as in pollution abatement (selective catalytic reduction of NO_x by ammonia). Aluminum is a good thermal conductor (237 $W\,m^{-1}\,K^{-1}$). Its surface is naturally covered by a layer of alumina which may serve as an anchoring layer for other oxides [9]. As its porosity can be increased by anodization, high surface area coatings are expected. Among other V/Ti compositions we studied, a monolayer of VO_x onto anatase, itself coating anodized Al, was deposited by dip-coating of the plates in a sol–gel of Ti-alkoxide precursor. Dipping in sol–gel medium is one of the most appropriate ways to prepare thin oxide coatings because of several advantages, among which a high homogeneity, an easy control of composition and a low processing temperature. After grafting TiO_2 onto alumina, we thought that a high amount of porous titania layers could be

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deposited on plates, in particular by using a porogenic agent. However, we have demonstrated by varying several parameters [8], that it is not possible to obtain films with well-defined porous structures because of a demixtion phenomenon occurring at the solution–plate interface. This work illustrated the difficulties encountered when transposing technologies initially developed for powders to plate-supported catalysts.

The coating of stainless steel plates with VO_x supported on titanium dioxide (anatase) is presented here. Even if its thermal conductivity (46 W m^{-1} K^{-1}) is lower than that of aluminum, stainless steel stands high temperatures and is the preferred material of most industrial reactors. Obviously this metal cannot be anodised, and consequently it is not easy to get a porous oxide layer onto which TiO_2 films could be anchored. Therefore, we have adapted the method elaborated to make $TiO_2/Al_2O_3/Al$ by using a suspension of TiO_2 powder to coat stainless steel once a thin layer of titanium dioxide has been grafted. The hypothesis is that, after deposition, the titanium dioxide film will present the same properties than the initial corresponding powder. Such suspensions of TiO_2 (generally TiO_2-P25 from DEGUSSA) have already been proposed for the coating of glass plates [10–13]. Two main applications are photocatalysis for the decomposition of organic compounds in waste water [12,14], and optical thin films because of the high refractive index and the chemical stability of TiO_2 [15,16]. Fernandez et al. [17] and Byrne et al. [18] have used the electrophoretic method for such coating on stainless steel but, up to our knowledge, there is no paper concerning the deposition of anatase on stainless steel by dip-coating in suspensions of TiO_2. The anatase form is preferred for catalytic applications because its strong interaction with vanadium oxide allows to generate a molecular dispersion of VO_x oxide layer, which exhibits the best activity and selectivity in most reactions [19].

In this paper we report on the grafting of VO_x monolayer on TiO_2-anatase coated stainless steel plates. The characterization of the deposits at the various stages of the preparation suffers from several difficulties because of the large contribution of the metallic plate, whereas most of the experimental equipments used in the field of catalysis are designed for powders. As developed in a previous paper [8], we have used X-ray photoelectron spectroscopy (XPS) which allows to control and to quantify the amount of active phase VO_x as well as of TiO_2 deposited on metallic plates. The structural properties of coated plates have been studied by scanning electron microscopy (SEM), laser Raman spectroscopy (LRS), and their texture has been analysed using the Brunauer–Emmet–Teller (BET) method. Results will be compared to those obtained in [8] for $VO_x/TiO_2/Al_2O_3/Al$ as well as with powders of VO_x/TiO_2 which have also been prepared.

2. Experimental procedure

2.1. Physicochemical analyses

The specific surface area and the porosity of the film on plates at various stages of coating were determined from the nitrogen adsorption and desorption isotherms, to which the BET method was applied. The partial pressure of nitrogen varied from 10^4 to 10^5 Pa at 77 K. All samples were first degassed at 150 °C for 4 h in vacuum. Because of the large weight and size of the metal plate as compared to that of the coating, these isotherms were obtained using a thermobalance (Sartorius GmBH, model S3D-V), the reference being a bare stainless steel plate of the same size. For the same reason, it is more appropriate to consider the developed surface area – as compared to the geometric surface area of the plate – instead of the specific surface area.

Laser Raman spectra were recorded on a LabRAM Infinity spectrometer (Jobin Yvon) equipped with a liquid nitrogen detector and a frequency-doubled Nd:YAG laser supplying the excitation line at 532 nm. The power on the sample was less than 5 mW. The spectrometer was calibrated daily using the silicon line at 521 cm^{-1}.

After grafting or coating, VO_x and TiO_2 deposits were analysed by XPS using VG Escalab 220XL spectrometer. The residual pressure in the ultra-high vacuum chamber was about 10^{-9} Pa. Al Kα X-ray source was used to study VO_x/TiO_2/stainless steel plates. The spectra were referenced to O 1s photopeak (from TiO_2) with binding energy BE = 530 eV.

Surface images were obtained by means of Hitachi 4100 S scanning electron microscope equipped with a field emission gun, with numerical image acquisition.

X-ray diffractograms (XRD) were obtained by reflection with a Siemens D5000 diffractometer (Cu $K\alpha_1$ line, λ = 154.2 ppm). The $K\alpha_2$ line contribution was eliminated by mathematic treatment with the software Eva ver. 9.0 (Brucker Advanced X-Ray Solutions).

The mechanical and chemical resistances of the films were studied according to two qualitative tests:

- *Test 1*. The adhesion of coatings was investigated by means of a piece of adhesive tape (Scotch 3 M) sticked onto the surface. The tape was firmly rubbed with finger tip and removed. Only oxide coatings with no particles left on the adhesive tape were further processed [20].
- *Test 2*. Plates were introduced in the thermobalance after a precise weighing. Temperature cycles (10 °C/min) were successively performed under different atmospheres (air, nitrogen, hydrogen). The temperature was held at 200 °C during 12 h, then decreased to room temperature and again increased up to 500 °C (12 h).

2.2. Preparation of plates before the film deposition

Stainless steel 316L is an austenitic alloy containing 18% of chromium, 13% of nickel and 2.5% of molybdenum (Table 1), the later being used to decrease the sensitivity to corrosion. Passivation oxides like $(Fe,Cr)_2O_3$ are present on the surface (Fig. 1), but their developed surface area (m^2 per geometrical m^2 of plate) is practically the same than the geometric surface area of stainless steel.

Plates (5 cm × 2 cm × 0.5 mm) of 316L were chemically treated by a sulphuric acid solution (30 wt.%) during 2 h in