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Catalytic wall reactor
Catalytic coatings of stainless steel by VO_x/TiO_2 and Co/SiO_2 catalysts

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Abstract

Catalytic wall (structured) reactors and structured supports are suitable to study the catalytic properties of nanosized materials. The coating of metallic (aluminum and stainless steel) plates by thin layers of active phase is presented in two cases, VO_x/TiO_2 and Co/SiO_2, catalysts used in the oxidative dehydrogenation (ODH) of propane and in Fischer–Tropsch synthesis (FTS) of clean fuels, respectively. The preparation of coated plates and their characterisation by various methods of physicochemical analysis are described. Both chemical and physical methods were used for coating. VO_x/TiO_2 layers were obtained by grafting of Ti (on Al or stainless-steel plates) and V (on TiO_2) alkoxides and use of sol–gel media or suspension. A silica primer was deposited (on stainless-steel plate) by plasma-assisted chemical vapour deposition (PACVD) onto which Co oxide and silica were coprecipitated from sol–gel. The catalytic experiments in the respective reactions were carried out in special plate reactors and compared with those of catalytic powders. The study shows that the coating of a metallic substrate by a catalyst is not straightforward and requires specific studies dealing with both chemistry (chemical affinity between substrate and catalytic layers) and catalytic engineering (catalytic performance in taylor-made reactors).

Keywords: Nanosized catalysts; Microstructured reactors; Catalytic wall reactors; Coating of stainless steel; Oxidative dehydrogenation of propane; Fischer–Tropsch synthesis; VO_x/TiO_2; Co/SiO_2

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1. Introduction

There is a strong, quite universal effort to prepare catalysts at the nanoscale for various applications in chemical, fuel and environmental processes. Various methods can be used to make nanoparticles of oxides, that may be chemical as sol–gel techniques [1,2], microemulsions [3,4], and the like, or more physicochemical as CVD, flame generation, plasma-assisted deposition, magnetron sputtering [5–8], etc. Whatever the method, a main concern is the stability of these nanosized particles in real chemical reactors, as most catalytic data are obtained by using few cubic centimeters in conventional flow millireactors. In several cases where the best catalyst is usually not supported (e.g., bulk catalysts of mild oxidation of hydrocarbons), it would be interesting to use nanoparticles in their nanosized state. However, neither fixed bed (owing to high pressure drop and of hot spots), nor fluidised bed reactors (because fluidisation requires particle sizes ca. 20–80 μm) are convenient. A solution, that would also meet the process intensification requirements [9,10], is to make deposits of nanoparticles directly on the metallic (structured) walls of reactors [11–14], or alternatively onto structured carriers (monoliths, foams, etc.) housed in reactors [15–17]. On the other hand, to be stabilised, nanoparticles or nanodomains of active phase are most often supported on oxides (alumina, silica, titania, magnesia), or confined in host materials like micro/mesoporous zeotypes [18,19]. To maintain their nanosize and associated properties, it is again necessary to avoid hot spots. Therefore, the use of structured carriers catalytic reactors or catalytic wall reactors (CWR) would be a good solution to maintain high activity and selectivity. The problem to solve is the same: how to make mechanically, thermally and chemically stable deposits on the structured carrier or the reactor walls while maintaining the required catalytic properties. The solutions are plural but they obviously depend on the nature of both catalyst and wall materials. We have studied the coating

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of metallic plates by VO_x/TiO_2 [20] and by Co/SiO_2 [21], catalysts used in the oxidative dehydrogenation (ODH) of propane and in Fischer–Tropsch synthesis (FTS) of clean fuels, respectively. The most important results are presented here, after some comments on the relative interest of using structured carriers and catalytic wall reactors.

2. Structured carriers reactors and catalytic wall reactors

Monoliths, plates, foams, wires, etc., to be housed in a reactor are more and more used for several applications, owing to high heat and mass transfers, low pressure drops, and possible high gas velocities [16–18]. The first straight-channel ceramic carrier was developed for automotive gasoline catalytic converters in the early 1980s [22]. In the selective catalytic reduction of NO by ammonia for stationary sources, monoliths made up of VWO_x supported on extruded TiO_2 monoliths are also in use [23]. Alpha-alumina honeycombs or foams, coated by Pt or various precious metals supported on Al_2O_3, have been tried for the oxidative dehydrogenation of alkanes to alkenes or the partial oxidation of methane to syngas at very short contact times (ms), high temperature (1000–1150 °C) and high HC/O_2 ratio [23,24]. Metallic foams are one of a number of alternatives for high temperature monolithic catalyst carrier for reforming reactions [18]. Typically the metal foam has an open, reticulated structure with a void volume greater than 85%. Their 3D structure allows radial heat and mass transfer that is not possible in conventional straight-channel monoliths. Finally, the choice between a ceramic material and a metal is dictated by their relative thermal conductivity (low vs. high), processing, porosity (high vs. low), chemical and mechanical stability, and cost. As far as possible, the choice should be done by considering the compatibility between the material and the type of catalyst. For example, the dilatation coefficient of cordierite $Mg_2Si_5Al_4O_{18}$ is close to that of γ-alumina, and the presence of Al offers enough sites to anchor alumina during the coating (chemical compatibility). Another interest of ceramics lies in their porosity which allows a 'mechanical' anchoring of the coating material.

Catalytic wall reactors were proposed as early as 1975 by Smith and Carberry [25] who carried out the oxidation of naphtalene to phthalic anhydride in a tube-wall reactor internally coated by V_2O_5. Among other advantages, the authors noticed that, since heat is generated at the wall and not in the gas phase, the large gas–solid thermal resistance is eliminated, permitting much higher heat generation rates without excessive temperature rise [26]. A comparison with packed bed reactor showed that the productivity per unit tube cross sectional area was greatly enhanced. Other configurations of CWRs are now proposed, like plates, channelled plates, etc., for various applications [12–14,27–30]. Besides high heat and mass transfers important for strongly exothermic/endothermic reactions,the modularity, e.g., the stacking of plates leading to the decrease of size with similar performance than by scale-up, is advantageous. The coating of active catalysts onto metallic walls, whatever their shape (plate, foam, tubes, etc.) and size (micro and larger) is a general problem that must be addressed. Highly developed surface areas are wanted to get active catalytic surfaces but the metallic geometric surface is intrinsiquely low. Metal like aluminum (for alumina deposits) or special steels may be chosen in order for the coating to be compatible. However, the preferred material of industrial reactors is stainless steel owing to its good thermal conductivity, easy processing, chemical inertness, relative cheapness, etc. Passivation oxides like $(Fe,Cr)_2O_3$ are present on the surface of, e.g., 316L alloy, but its developed surface area is quite the same than the geometrical surface of stainless steel. As very few hydroxyl groups are available to graft an oxidic support, a pre-treatment is necessary to increase their density. The coating by a primer that may act as a barrier to hinder the diffusion of unwanted elements of the metal during reaction is followed by wash-coating, or other method of deposition of the active phase/support. Drying and calcination/activation steps may be necessary to strengthen the holding of layers. It must also be noticed that methods used for characterisation of the thin active layers have to be adapted owing to the strong contribution of metal which decreases their sensitivity. Finally, other drawbacks like the diffusion outwards or the occurrence on surface of the metallic elements of the substrate are worthwhile to evoke.

2.1. VO_x/TiO_2 plates for the oxidative dehydrogenation of propane to propene

We have recently studied the coating of metallic plates with VO_x/TiO_2 catalyst [31,32]. This catalyst is well known to be active and selective in several types of reactions like mild oxidation of hydrocarbons (*o*-xylene oxidation to phthalic anhydride, oxidative dehydrogenation of propane, etc.) as well as in pollution abatement (NO_x SCR by ammonia). A simple sol–gel method was chosen to coat plates of aluminum or stainless steel owing to its efficiency in producing thin multicomponent oxide layers on various substrates [3]. Other advantages of the method are a high homogeneity, an easy control of composition, a low processing temperature and low equipment cost even for obtention of large area coatings [33]. The large contribution of the metal as compared to the coating films makes it difficult to determine precisely the amount of surface hydroxyls on alumina or stainless steel (for TiO_2 coating), or on TiO_2 (for VO_x coating), to be grafted. X-ray photoelectron spectroscopy (XPS) was the preferred method in order to relate the concentration of raw specie (from, e.g., a metallic alcoholate in alcoholic solution) to the final composition of the film, at the various stages of coating. A three-steps procedure was adopted after a proper modification of the metallic carrier intended to increase the roughness and then the concentration of surface OH groups for anchoring of the primer (Fig. 1).

2.1.1. Coating of plates by VO_x/TiO_2

2.1.1.1. Coating of aluminum. A three-step procedure consisting in dip-coating plates (anodised Al) in sol–gel medium (alcoholates) with control of hydrolysis and condensation

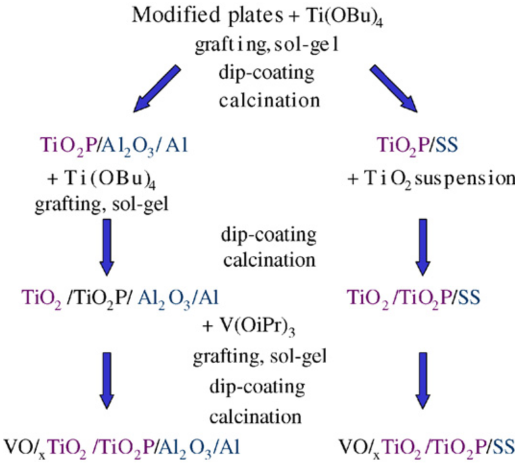

Fig. 1. Steps of coating of Al- and stainless-steel plates by VO_x/TiO_2 catalyst.

followed by drying and/or calcination was elaborated [31] (Fig. 1). In all cases the plates were withdrawn at constant rate (6 mm s^{-1}) after dipping. Successively, a monolayer of TiO_2 primer (TiO_2P) was grafted (dip-coating in titanium alcoholate alcoholic solution), porous layers of TiO_2 were grown on the resulting $TiO_2P/Al_2O_3/Al$ plates using the same method, and $TiO_2/TiO_2P/Al_2O_3/Al$ plates were dip-coated in various amounts of $VO(OPr)_3$ in dry ethanol. A final calcination was performed at 450 °C. XPS carried out on $VO_x/TiO_2/TiO_2P/Al_2O_3/Al$ showed that the surface vanadium concentration is directly related to the initial concentration of $VO(OPr)_3$ in ethanol solutions.

2.1.1.2. Coating of stainless steel. The formation of a porous oxide layer of $(Fe,Cr)_2O_3$ on stainless steel 316L (Cr/Ni/Mo = 18/13/2.5) was obtained after a surface acidic corrosion by H_2SO_4. After grafting of a thin layer of titanium dioxide (primer) as above, the TiO_2P/SS plate was dipped in a suspension of TiO_2 powder while stirring (Fig. 1). The hypothesis was that, after deposition, the properties of the initial TiO_2 powder would be maintained in the titanium dioxide film [32]. However, adhesion tests showed that it was necessary to calcine TiO_2P primer coating SS and TiO_2/TiO_2P/SS at 900 °C (2 h) in order to get mechanically stable deposits. Before loading vanadium by dipping plates in $VO(OPr)_3$ as above, titania powder was collected after scraping off the plates. XRD showed that the anatase form remained, 0.7% of rutile being present, and the specific surface area was 10 m^2/g by using BET method, value which is the same than for the raw anatase powder.

2.1.2. Catalytic properties of VO_x/TiO_2 plates in the oxidative dehydrogenation of C_3H_8

As the enhancement factor of the titania coating on alumina plates was not high enough, catalytic experiments have only been performed on $VO_x/TiO_2/TiO_2P$/SS and compared with those obtained with VO_x/TiO_2 powders. The latter were prepared by impregnation of Aldrich powder (10 m^2/g) by various amounts of NH_4VO_3 in oxalic acid [34], and calcined in the same conditions than plates. XPS data show (Table 1) that, for powders as well as for Al or SS plates, V/Ti increases up to ca. 0.2. Upon increasing V loading, a plateau is reached (between 1.25 and 1.7%) in case of plates before V/Ti increases again [31,32], while in case of powder the slope decreases slightly after 0.2. Up to the plateau at V/Ti ∼ 0.2, which is a characteristic of the VO_x/TiO_2 system, VO_x mono- and then polyvanadates are built up [35–37]. Above that value a disordered V_2O_5-type oxide is built followed by the formation of microcrystalline 'towers' of V_2O_5. Consequently we have demonstrated that the shaping (powder or plate) of TiO_2 has no influence on the characteristics of the active phase. This is of prime importance for catalytic applications in structured reactors.

A conventional fixed bed reactor (FBR) was used for powders (1 cm^3), which were studied at contact time 0.6–1.2 s (flowrate 50 cm^3 min^{-1} STP), $C_3H_8/O_2 = 2/1$ and 200–400 °C. No conversion of propane was found in the empty reactor, nor in the presence of TiO_2 powder alone. An example of catalytic performance is given for two theoretical monolayers of VO_x on TiO_2 (1.4 wt% V_2O_5). The conversion of propane $X_{C_3H_8}$ increases (0–20 mol%) and the selectivity to propene decreases (100–58 mol%) when T increases from 350 to 550 °C (temperature at which oxygen becomes fully converted) (Table 2).

A special reactor was designed to house several plates. It consisted of a stainless-steel cylinder, in which a square section was hollowed. In the bottom part seven pairs of slidings (0.8 mm wide × 1 mm thick) were receiving seven plates (Fig. 2). Gases were fed through the square male part

Table 1
Vanadium to titanium ratio (V/Ti) by X-ray photoelectron spectroscopy, related to the initial concentration of V alkoxide in ethanol solution for coating of Al or stainless-steel plates, and of V_2O_5 content during impregnation of TiO_2 particles

$VO(OPr)_3$ (wt%)	V/Ti[a] (Al)	$VO(OPr)_3$ (wt%)	V/Ti[a] (SS)	V_2O_5 (wt%)	V/Ti[a] (powder)
0.25	0.092	0.25	0.104	1	0.06
0.5	0.124	0.375	0.114	2	0.132
0.75	0.153	0.5	0.136	2.5	0.173
1	0.18	0.6	0.164	3	0.18
1.25	0.195	0.75	0.183	3.5	0.203
1.5	0.20	0.9	0.197	6.25	0.3
2	0.38	2	0.20	11.25	0.43
		2.25	0.28	20	0.6

[a] V/Ti: ratio of intensity of V $2p_{3/2}$ to Ti $2p_{3/2}$ photopeaks.

Table 2
Catalytic properties of VO_x/TiO_2 powders and of $TiO_2/TiO_2P/SS$ and $VO_x/TiO_2/TiO_2P/SS$ plates in the oxidative dehydrogenation of propane (0.2 g of active phase; two monolayers VO_x/TiO_2 Aldrich; $C_3H_8/O_2 = 2/1$)

Temperature (°C)	Propane conversion (mol%)			Selectivity to C_3H_6 (mol%)		
	Powder	T/TP/SS[a]	V/T/TP/SS[b]	Powder	$TiO_2/TiO_2P/SS$	V/T/TP/SS
350	2.5	0.2	0.2	100	100	100
400	4.8	1.5	1.5	92	98	100
450	9.8	2.6	3.1	71	62	88
550	20[c]	13.8	8.3	58	18	59

[a] $TiO_2/TiO_2P/SS$.
[b] $VO_x/TiO_2/TiO_2P/SS$ (2 ML VO_x).
[c] Conv. $O_2 > 100\%$.

(20 mm × 11.6 mm) containing also a well for the thermocouple, both being at 1 mm above the plates. The total void volume was 4.6 cm^3 and the residence time 0.54 s for a total flowrate 50 $cm^3\ min^{-1}$ STP. Each plate (3 cm × 2 cm and 0.5 mm thickness) was covered by 30 mg of VO_x/TiO_2 Aldrich (2 ML). In this way, the total amount of active phase on seven plates was quite the same (0.21 g) than for the studied powders [21].

The activity of $TiO_2/TiO_2P/SS$ was first examined. Data show that the TiO_2 support coating SS is already active and selective to propene at 400 °C (Table 2), contrarily to what was observed with TiO_2 powder. This activity is attributed to iron(III) oxide specie which are present, not only on the surface of TiO_2P as shown by XRD owing to the detection of Fe_2TiO_5, but also in the 15 μm-thick layer of $TiO_2/TiO_2P/SS$. No iron oxide or Fe-Ti-O mixed oxide could be identified by XRD or by Raman spectroscopy, but XPS analysis showed that Fe/Ti = 0.07 (BE Fe(III) = 711 eV). However, the presence of VO_x specie does modify the behaviour of TiO_2/plates. At $X_{C_3H_8} = 10\,mol\%$ the selectivity to propene increases from 23 mol% on $TiO_2/TiO_2P/SS$ to 52 mol% on $VO_x/TiO_2/TiO_2P/SS$. Compared to VO_x/TiO_2 Aldrich powders in the FBR, the plates are less active, the same conversions (C_3H_6 and O_2) being reached at ca. $T_{FBR} + 80$ °C, and $S_{C_3H_6}$ is lower at isoconversion. For example, at $X_{C_3H_8} = 14\,mol\%$ the selectivity to C_3H_6 is 60 and 43 mol%, respectively. For the same amount of active phase, and (theoretically) the same surface arrangement of VO_x specie (2 ML) on the same TiO_2 support (Aldrich, 10 m^2/g) with the same V/Ti ratio (0.2), the plates are less active and less selective than powders.

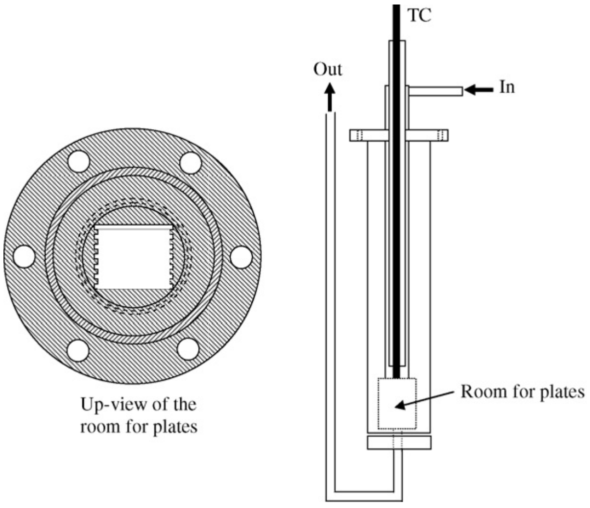

Fig. 2. Simplified schematic of the multiplate reactor used for ODH of propane (left: upview; right: lengthwise view).

There are several explanations to account for these findings (Table 3), which are related either to the operating conditions and the type of reactor, or to the catalyst itself and its shaping. First, the residence time is higher in CPR than in FBR owing to the larger void volume between plates, which may favour consecutive reactions like combustion of adsorbed propene to carbon dioxide. That seven-plates reactor was designed without any optimisation of the flow and heat/mass transfers. Second, the post mortem characterisation showed differences in the composition of the used plates vs. used powders, which may or may not be due to the higher temperature experienced by plates (600 °C vs. 500 °C). Indeed, the initial colour of plates, which was light yellow (due to vanadium oxide specie), became light pink and locally reddish-brown. The surface Fe/Ti ratio (XPS experiments) initially equal to 0.07 increased up to 0.19 and 4.6 in these zones, respectively. The high amount of Fe(III) on the surface of plates is probably the most important factor accounting for the observed decreasing selectivity. Finally, the brown tint due to the high amount of Fe(III) occurred very locally at the same height on plates (parallel to the flow), as if it was due to a kind of "plate-chromatographic" effect. Further experiments are needed to understand if this phenomenon is due to, e.g., unexpected hot spots, that would enhance the rate of diffusion of Fe(III) to the surface of plates.

Table 3
Comparison of some parameters and catalyst features during ODH of propane in fixed bed (FBR) and catalytic plate (CPR) reactors

Parameter or feature	FBR	CPR
Contact/residence time (20 °C)	0.6 s	5.4 s
Maximum temperature	500 °C	600 °C
XRD analysis	TiO_2 anatase	TiO_2P: $Fe_2O_3 + Fe_2TiO_5$ TiO_2: anatase (3% rutile)
Raman spectroscopy	TiO_2 anatase	TiO_2 anatase
XPS (before reaction)	V/Ti = 0.2 K/Ti = 0.1	V/Ti = 0.19 K/Ti = 0.1 Fe/Ti = 0.07

2.2. Coating of plates by Co/SiO_2 for Fischer–Tropsch synthesis

There is an enormous commercial interest in the Fischer–Tropsch synthesis by means of which syngas is converted to a large range of hydrocarbons (paraffins, olefins, etc.) [38–40]. These synthetic ‘‘clean’’ fuels contain very little sulphur or aromatics. Most catalysts are made up of metallic cobalt particles dispersed on alumina or silica when the targeted products are in the Diesel cut. Besides the tubular, fluidised beds or slurry reactors used in commercial processes, the development of alternative reactors is ongoing. Examples are membrane reactors [41] allowing a staged distribution of hydrogen which enhances the selectivity to Diesel cut but at lower conversion of CO [42], or monoliths which can be operated in triphasic mode or used as filtering membranes [43,44].

The coating of stainless-steel plates by cobalt supported on silica as catalyst was studied for converting syngas to Diesel cut in a home-designed single plate reactor [22,45]. Contrary to the case of TiO_2, the grafting of silica on SS plates using sol–gel methods was unsuccessful and a plasma-assisted chemical vapour deposition (PACVD) of tetramethyldisiloxane [21,46,47] was finally adopted to get a silica primer before deposition of cobalt/SiO_2.

2.2.1. Coating of stainless-steel plates by Co/SiO_2

The coating of stainless-steel plates by Co/SiO_2 was carried out using a three-steps procedure (Fig. 3). The method used to polymerise tetramethyldisiloxane to get films of polymers on various substrates like aluminum and silicon by PACVD [48] was adapted to stainless steel [46,47]. Raman spectroscopy and XPS were used to characterise the deposits at various steps, their thickness increasing at 300 nm min^{-1} rate. Tests of adhesion and of reducibility in pure H_2 up to 350 °C showed that the SiO_2 primer film (thickness 5 μm) was mechanically stable and chemically inert in regard of reactants under reaction relevant conditions. SEM showed that its surface had an irregular, more or less glazy aspect.

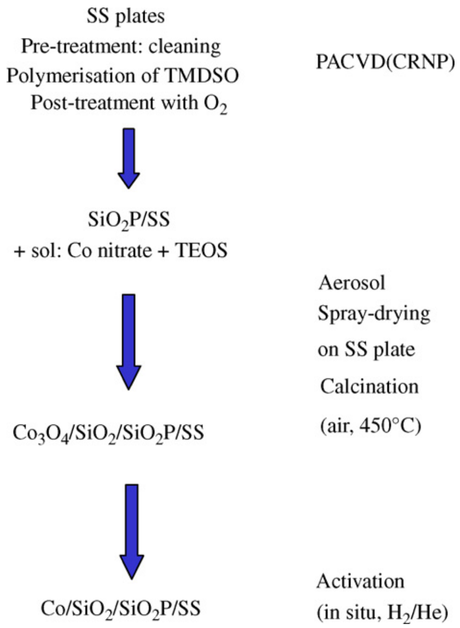

Fig. 3. Steps of coating of stainless-steel plates by Co/SiO_2 catalyst for Fischer–Tropsch synthesis.

Cobalt and silica were spray-coated onto the SiO_2P/SS plates heated at 145 °C. An aerosol of cobalt nitrate and maturated tetraethylorthosilicate in diluted ethanol (solution formulated to finally obtain 20 wt% Co/SiO_2 catalyst) was prepared (Fig. 3). That step could be repeated with intermediate calcination at 300 °C (30 min), yielding films of 5–110 μm. In the coated plates after calcination at 450 °C, Co_3O_4 was identified by XRD, silica being amorphous. The analysis of the texture by BET, BJH and Dubinin methods showed about 50% of micropores among mesopores (mean diameter <4 and 135 nm, respectively), the specific surface area being 265–275 m^2/g. SEM-EDX was carried out to examine the aspect and composition of the films. Finally, metallic cobalt was obtained by treating the plates in pure hydrogen inside the reactor up to 450 °C before carrying the catalytic reaction. Details can be found in Refs. [22,45]. An important issue is the absence of formation of Co_2SiO_4 which is known to hinder the reduction of cobalt.

2.2.2. Catalytic plate reactor and Fischer–Tropsch reaction

A reactor containing one catalytic SS plate (40 mm × 20 mm × 2 mm) stacked between two thick 316L stainless-steel plates heated by electric resistances was designed (Fig. 4). The tightness was ensured by an Al foil gasket. The void volume over the plate located in between was 200 μL. One plate contained 31.5 mg of active phase (thickness 50 μm). Operating conditions were contact time $\tau = 0.92$–1.80 s, $H_2/CO = 1.5$–3 at $T = 150$–220 °C and atmospheric pressure ($P = 1$ atm). Experiments of residence time distribution using hydrogen in N_2 at room temperature showed that a CSTR (ca. 230 μL) accounted for the behaviour of the reactor, a plug flow contribution being mostly characterising the inlet and outlet nozzles (ca. 80 μL at 1.11 L/h flowrate) [22,45].

The catalytic data show that the behaviour of Co/SiO_2 when coated on SiO_2P/SS plates is similar to that of other Co/SiO_2 powders studied in fixed bed reactors. At constant contact time ($\tau = 1$ s), the conversion X_{CO} increases from 10 to 16 mol% with $H_2/CO = 1.5$–3. The selectivity to the three cuts, LPG (C_1–C_4), gasoline (C_5–C_9) and Diesel (C_{10}–C_{19}) obeys also to usual

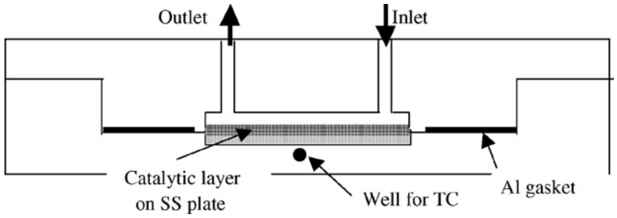

Fig. 4. Simplified schematic of the plate reactor used for FTS (arrows for in and out effluents).

Table 4
Catalytic properties of Co/SiO_2 catalysts in Fischer–Tropsch synthesis for two H_2/CO ratios

	$H_2/CO = 2$		$H_2/CO = 3$		
	Powder 31.5 mg	Plate 31.5 mg	Powder 1330 mg	Powder 31.5 mg	Plate 31.5 mg
X_{CO}	2.2	12	14	4.7	16
$S_{C_1-C_4}$	47	53	55	51	59
$S_{C_5-C_9}$	34	28	30	34	27
$S_{C_{10+}}$	20	19	16	14	14
α	0.77	0.75	0.76	0.73	0.74

Comparison of powder and plates at the same mass (31.5 mg) or at isoconversion ($X_{CO} \approx 12$ mol%) ($\tau = 1.06$ s, $T = 180$ °C, $P = 1$ atm).

trends observed with cobalt catalysts [45,49–51], even though the pressure is 1 atm. As H_2/CO increases from 1.5 to 3, gasoline remains the same ($S_{gaz} = 25–28\%$), LPG increases ($S_{LPG} = 46–60\%$) and Diesel cut decreases ($S_D = 29–14\%$), respectively. After 530 h of operation, the performance remained the same and no deactivation was detectable. The alpha coefficient (characteristic of the growing of hydrocarbon chains) calculated from the slope of the product distribution curve under Anderson-Schultz-Flory coordinates gave values close to those usually observed in literature for Co/SiO_2 catalysts at 1ow temperature and pressure. Varying the contact time or the temperature (150–220 °C) leads also to figures in accordance with literature for cobalt catalysts in fixed bed reactors. For thickness of coated films in the 30–70 μm range, the selectivities vary very little while conversion X_{CO} increases (11–15 mol% at 180 °C and $H_2/CO = 2$). This shows that intraparticle diffusion limitation can be neglected, but also that Co is actually distributed inside the silica layers and not only on the upper surface [22].

The coating layers on SS plates were scraped off and the gathered powder was diluted with SiC to examine its catalytic properties in a tubular fixed bed reactor. 31.5 mg of 20% Co/SiO_2 was collected, which is the same mass than for a coating thickness of 50 μm. The comparison with films on plates shows that selectivities remain in the same range (Table 4), but that X_{CO} is far greater on plates than in FBR. Another experiment has been performed in order to increase the conversion by using a larger amount of active phase. All other conditions being equal, the comparison at similar conversion ($X_{CO} = 12–14$ mol%) shows that the plate reactor leads to higher amounts of Diesel cuts at the expense of both LPG and gasoline cuts (Table 4). Moreover, the catalyst productivity, expressed in $kg\,CO\,h^{-1}\,kg_{cat}^{-1}$, is 24 times greater than that of the FBR. Therefore it seems that far more numerous active sites of a 50 μm thick film of Co/SiO_2 participate to the reaction as compared to those of packed grains. A similar enhancement was also observed by Babovic et al. [52] and Mazanec et al. [53]. Because cracks were present in the non-uniform coating of Co/SiO_2 obtained by sol–gel spray, some metallic atoms of SS (Cr, Fe, Ni) may participate to the reaction. Indeed, plasma-sprayed bimetallic Co-5%Fe catalysts on tube-wall reactor exhibited higher activity in FTS [43,54] than Co alone.

3. Conclusion

Whatever the support, structured metallic carrier or (structured) reactor walls to be coated, the issue is the same: making highly active catalytic but stable deposits strongly anchored on a low surface area material, that may have little compatibility with the active phase. Every system (catalytic active phase/support/carrier or walls) is a special case requiring a detailed study, particularly when the coated material is a metal. Besides the mechanical stability, a strong concern is the enhancement factor [55], from the low, geometric area of the metal to the required high surface area of the active coating. Chemical as well as physical methods of coating are worthwile to use, some being more adapted than others, as shown in a recent review [56]. In this exploratory work we have studied the coating of stainless steel by two very different systems for different reactions. The main point is the primer, which is needed in order to make a transition layer between the metal and the catalytic coating. High temperature calcinations are often required to strongly anchor the active phase which may lead to sintering and/or formation of unwanted phases. In the case of $Ti(OiPr)_3$ grafted on SS the result was not surface TiO_2 but the formation of Fe_2TiO_5 besides Fe_2O_3. The intermediate layer was also expected to act as a barrier to Fe(III) specie, but on the contrary Fe(III) diffused to the outer surface, as shown after the catalytic oxidation of propane by VO_x. A thermal plasma sprayed TiO_2 coating of SS has been recently proposed, that could also be denser [57]. In the case of the FTS catalyst, the silica primer has been deposited by grafting in partial vacuum and subsequent polymerisation of an organosilicon material using plasma-assisted CVD. As this technique allows to avoid the corrosion pre-treatment of stainless steel, it is certainly more convenient. After reduction by H_2 and after reaction, some atoms of SS were probably exposed owing to cracks in the non-uniform Co/SiO_2 coating made by sol–gel spray. In the case of FTS they could play a positive role.

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References

[1] J. Livage, M. Henry, C. Sanchez, Prog. Solid State Chem. 18 (1988) 259.
[2] C.J. Brinker, G.W. Scherer, Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing, Academic Press, San Diego, 1990.
[3] J. Agrell, K. Hasselbo, S. Järs, M. Boutonnet, Stud. Surf. Sci. Catal. 130 (2000) 1073.
[4] J.Y. Ying, T. Sun, J. Electroceram. 1 (1997) 219.
[5] J.S. Yoo, Catal. Today 41 (1998) 409.
[6] P.F. Miquel, E. Bordes, J.L. Katz, J. Solid State Chem. 124 (1996) 95.

[7] G. Vissokov, J. Univ. Chem. Technol. Metall. 39 (2004) 121.
[8] W. Zhang, Y. Li, S. Zhu, F. Wang, Catal. Today 93–95 (2004) 589.
[9] C. Ramshaw, Chem. Eng. 415 (1985) 30.
[10] R.S. Benson, J.W. Ponton, Trans. Chem. Eng. 71 A (1993) 160.
[11] A. Cybulski, J. Moulijn, Structured Catalysts and Reactors, Marcel Dekker, New York, 1997.
[12] E.V. Rebrov, M.H.J.M. de Croon, J.C. Schouten, Catal. Today 69 (2001) 183.
[13] H. Redlingshöfer, O. Kröcher, W. Böck, G. Emig, Ind. Eng. Chem. Res. 41 (2002) 1445.
[14] P. Pfeifer, K. Schubert, G. Emig, Appl. Catal. A: Gen. 286 (2005) 175.
[15] A.N. Pestryakov, V.V. Lunin, A.N. Devoschkin, L.A. Petrov, N.E. Bogdanchikova, V.P. Petranovskii, Appl. Catal. A: Gen. 227 (2002) 125.
[16] T. Kodama, A. Kiyama, K.I. Shimizu, Energy Fuels 17 (2003) 13.
[17] A. Shamsi, J.J. Spivey, Ind. Eng. Chem. Res. 44 (2005) 7298.
[18] M.E. Davis, A. Katz, W.R. Ahmad, Chem. Mater. 8 (1996) 1820.
[19] W. Li, G.D. Meitzner, R.W. Borry, E. Iglesia, J. Catal. 191 (2000) 373.
[20] T. Giornelli, Ph.D. Thesis, Université de Technologie de Compiègne, 2004.
[21] L. Guillou, Ph.D. Thesis, Université de Technologie de Compiègne, 2005.
[22] R.J. Farrauto, C.H. Bartolomew, Fundamentals of Industrial Catalytic Processes, Blackie Academic & Professional, London, 1997.
[23] L.D. Schmidt, C.T. Goralski Jr., Stud. Surf. Sci. Catal. 110 (1997) 491.
[24] R.P. O'Connor, E.J. Klein, L.D. Schmidt, Catal. Lett. 70 (2000) 99.
[25] T.G. Smith, J.J. Carberry, Chem. Eng. Sci. 30 (1975) 221.
[26] R. Chandrasekharan, P.H. Calderbank, Chem. Eng. Sci. 35 (1980) 1523.
[27] B. Amon, E. Klemm, G. Emig, Stud. Surf. Sci. Catal. 122 (1999) 247.
[28] G. Groppi, W. Ibashi, E. Tronconi, P. Forzatti, Catal. Today 69 (2001) 399.
[29] Microreaction technology, A. Renken, J.P. Baselt, M. Matlosz (Eds.), Chem. Eng. J. 101 (2004) 1;
Baerns, Manfred; Renken, Albert. Chemical reaction technology. Winnacker-Kuechler: Chemische Technik (5.uflage) (2004) 1 453-643.
[30] A.L. Tonkovich, Y. Wang, ACS Symp. Ser. 914 (2005) 47.
[31] T. Giornelli, A. Löfberg, E. Bordes-Richard, Thin Solid Films 479 (2005) 64.
[32] T. Giornelli, A. Löfberg, E. Bordes-Richard, Appl. Catal. A: Gen. 305 (2006) 197.
[33] D.J. Kim, S.H. Hahn, S.H. Oh, E.J. Kim, Mater. Lett. 57 (2002) 355.
[34] G.C. Bond, J. Perez Zurita, S. Flamerz, Appl. Catal. 27 (1986) 353.
[35] G.-C. Bond, P. Köning, J. Catal. 77 (1982) 309.
[36] J.C. Védrine, Catal. Today 20 (1994) 109.
[37] B. Grzybowska Swierkosz, Appl. Catal. A: Gen. 157 (1997) 263.
[38] www.fischer-tropsch.org.
[39] E. Iglesia, S.C. Reyes, R.J. Madon, S.L. Soled, Adv. Catal. 39 (1993) 221.
[40] M.E. Dry, Fischer–Tropsch technology, Stud. Surf. Sci. Catal. 152 (2004) 1.
[41] J. Coronas, J. Santamaria, Catal. Today 51 (1999) 377.
[42] D. Vanhove, S. Léonard, Récents Progr. Gén. Proc. 89 (2003) 297.
[43] T. Boger, S. Roy, A.K. Heibel, O. Borchers, Catal. Today 79 (2003) 441.
[44] M.C.J. Bradford, M. Te, A. Pollack, Appl. Catal. A: Gen. 283 (2005) 39.
[45] L. Guillou, D. Balloy, P. Supiot, V. Le Courtois, Appl. Catal. A: Gen. 324 (2007) 42.
[46] L. Guillou, P. Supiot, V. Le Courtois, European Patent Application EP 1,741,495 (2007).
[47] L. Guillou, P. Supiot, V. Le Courtois, Seventh World Congress on Chemical Engineering, Glasgow, UK, July 10–14, (2005), p. 85018.
[48] P. Supiot, C. Vivien, A. Granier, A. Bousquet, A. Mackova, D. Escaich, R. Clergereaux, P. Raynaud, Z. Stryhal, J. Pavlik, Plasma Proc. Polym. 3 (2006) 100.
[49] I.C. Yates, C.N. Satterfield, Energy Fuels 6 (1992) 308.
[50] T. Ngwenya, D. Glasser, D. Hildebrand, N.CP. Mukoma, Ind. Chem. Eng. Res. 44 (2005) 5987.
[51] L. Fu, J.L. Rankin, C.H. Bartholomew, C_1 Mol. Chem. 1 (1986) 369.
[52] M. Babovic, A. Gough, P.D. Leveson, C. Ramshaw, Better processes for better products, in: Fourth International Conference on Process Intensification for the Chemical Industry, Brugge, Belgium, September 10–12, (2001), p. 167.
[53] T. Mazanec, T. Dritz, F. Daly, AIChE Spring National Meeting, Atlanta, 2005.
[54] A.K. Dalai, N.N. Bakhshi, Can. J Chem. 70 (1992) 269.
[55] K. Haas-Santo, M. Fichtner, K. Schubert, Appl. Catal. A: Gen. 220 (2001) 79.
[56] V. Meille, Appl. Catal. A: Gen. 315 (2006) 1.
[57] R. Tomaszek, L. Pawlowski, L. Gengembre, J. Laureyns, Z. Znamirowski, J. Zdanowski, Surf. Coat. Technol. 201 (2006) 45.