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Sol–gel synthesis and catalytic properties of vanadium phosphates

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Vanadium phosphates with variable specific surface areas were synthesized from vanadium alkoxides and phosphoric acid by precipitation in various solvents. The catalytic properties were studied in the reaction of methanol oxidation. Although the specific activities increase with the specific surface areas (BET), the intrinsic activities seem to depend on the particle morphology. The selectivities do not vary within a large range. The same method of precipitation was applied to prepare vanadium phosphates on a silica support. It is shown that the supported phase is highly dispersed, and that these supported catalysts are more stable than silica-supported vanadium oxide for methanol oxidation.

Keywords: vanadium phosphate, sol–gel, catalysis, methanol oxidation

1. Introduction

Vanadium phosphates such as $VOPO_4$ and $(VO)_2P_2O_7$ are known as catalysts for the mild oxidation of hydrocarbons and alcohols [1]. They exhibit a high activity and selectivity and do not significantly sinter [2–4]. Vanadyl phosphate dihydrate $VOPO_4{\cdot}2H_2O$ is a common precursor for the synthesis of $VOPO_4$ catalysts. It is readily obtained by refluxing vanadium oxide in phosphoric acid for several days [5].

Previous works have shown that other precursors such as alkoxides can be used to synthesize $VOPO_4{\cdot}2H_2O$, and its morphology depends on the nature of the precursor and the presence of water during precipitation [6,7]. Vanadium alkoxides can react with anhydrous phosphoric acid in various organic solvents and form $VOPO_4$:

$$VO(OR)_3 + H_3PO_4 \rightarrow VOPO_4 + 3ROH \qquad (1)$$

This overall reaction can be analyzed through the reaction mechanism of phosphatation, i.e., the formation of a V–O–P bond and the elimination of alcohol:

$$=V\text{–}OR + H\text{–}O\text{–}P= \rightarrow =V\text{–}O\text{–}P + R\text{–}OH \qquad (2)$$

The kinetics of precipitation depends on the solvent used and on the starting alkoxide. Precipitation is fast in aprotic solvents, such as tetrahydrofuran (THF) or diethyl ether [7]. In contrast, it is slow and reversible when vanadium alkoxides react with phosphoric acid in their parent alcohol. In primary and secondary alcohols (R = propyl), water ($0 < H_2O/V < 10$) acts as an inhibitor of the reaction. It causes the hydrolysis of the vanadium alkoxides and the condensation of oxovanadate species, such as decavanadic acid. Hence, there is an equilibrium between condensed oxo species (V–O–V) and phosphates (–V–O–P–O–V) [6]. As a result, the morphology of the crystallites depends on the reaction mechanism (with or without hydrolysis) as well as on the reaction kinetics [7,8]. Such precipitation methods can also be applied to prepare supported catalysts.

The oxidation of methanol is an appropriate catalytic reaction for the study of the acid–base properties of the active sites (figure 1). In addition, it is a structure-sensitive reaction with vanadium and molybdenum oxides ([9] and references therein).

In the following, we study the catalytic properties for methanol oxidation of $VOPO_4{\cdot}xH_2O$ prepared by various methods, unsupported and supported on silica. They will be compared to those of V_2O_5.

2. Experimental

2.1. Sample preparation

2.1.1. Bulk vanadium phosphate

Isopropanol (2-propanol), diethyl ether and tetrahydrofuran (THF) were distilled over sodium before use. Vanadium isopropoxide ($VO(OR)_3$, R = 2-propoxy) was prepared by reaction of ammonium vanadate with 2-propanol and elimination of ammonia and water, according to a procedure already described [10]. Two solutions were prepared:

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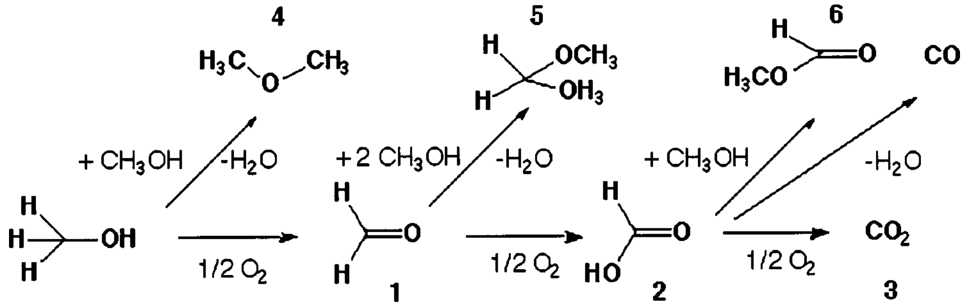

Figure 1. Methanol oxidation steps (derived from [9]).

(i) vanadium alkoxide, 1 M, in 2-propanol; (ii) H_3PO_4 (anhydrous solid, Fluka), 1 M, in 2-propanol with water added in the atomic ratio $h = H_2O/P$ with $h = 0$, 3 and 10. The solutions of vanadium alkoxide and of phosphoric acid were mixed in the ratio $V/P = 1$. Complete precipitation occurred within 1 h, as already described [6]. Powders were obtained after filtration of the precipitates and drying in air at 80 °C.

The same method was used in THF and diethyl ether by the rapid mixing of phosphoric acid ($h = 0$) and vanadium alkoxide solutions (1 M for THF, 0.2 M for diethyl ether). In these cases, the precipitations were instantaneous.

$VOPO_4{\cdot}2H_2O$ was also synthesized upon reflux of V_2O_5 in phosphoric acid, according to the Ladwig method [5].

The V_2O_5 powder was prepared from an aqueous solution of vanadyl oxalate obtained from the reaction of ammonium metavanadate NH_4VO_3 (32 $g\,l^{-1}$) with oxalic acid $C_2H_2O_4$ (60 $g\,l^{-1}$), and evaporated at 80 °C for 60 min. The residue was ground and calcined under oxygen flow at 450 °C for 15 h (heating rate of 10 $°C\,min^{-1}$ under an O_2 flow rate of 145 $ml\,min^{-1}$).

2.1.2. Silica-supported samples

Silica spherosil XOA 400 supplied by Rhône Poulenc (France) was used as the support (400 $m^2\,g^{-1}$, pore volume = 1.25 $cm^3\,g^{-1}$, average pore diameter ~80 Å, 4 ppm of Ca and 60 ppm of Na).

Vanadium phosphate supported on silica (VP/SiO_2) was prepared in alcohol because, as mentioned above, the precipitation is slower than in THF or ether, and should lead to a more homogeneous impregnation of the silica support. The induction time of precipitation is about 15 min. Hence, silica was added to a freshly prepared solution (30 $ml\,g^{-1}$ of silica) containing the vanadium alkoxide and the phosphoric acid solutions with $h = 0$, 3 and 10. The impregnated powder was rapidly filtered before the onset of precipitation of bulk $VOPO_4{\cdot}xH_2O$. In all of the cases, the samples were dried at 80 °C overnight and equilibrated at room temperature in air to recover the exact water stoichiometry $VOPO_4{\cdot}2H_2O$. Chemical analysis of the vanadium content was performed by colorimetry. The vanadium content was 2.1, 1.4 and 1.6 wt% for the samples with $h = 0$, 3 and 10, respectively.

For comparison, vanadium oxide supported on silica (hereafter called V/SiO_2) was prepared as follows: an aqueous solution of vanadyl oxalate, obtained by dissolution of ammonium metavanadate (NH_4VO_3, Merck, 99% purity) in an aqueous solution of oxalic acid (60 $g\,l^{-1}$, Prolabo, 99.8% purity), was used to impregnate silica (7.5 $ml\,g^{-1}$ of silica). The V concentration was adjusted so as to get a sample with 1 wt% V ($1V/SiO_2$) and one with 10 wt% V ($10V/SiO_2$). The samples were dried at 60–70 °C for 1 h under continuous stirring, then at 80 °C for 5 h in air. In order to decompose and oxidise the vanadyl oxalate into vanadium oxide, a calcination treatment was performed at 450 °C (heating rate: 10 $°C\,min^{-1}$) for 2 h under pure oxygen flow (25 $ml\,min^{-1}$).

2.2. Techniques

Specific surface areas were measured using the BET method with a Quantasorb apparatus. Scanning electron microscopy was performed on a Jeol JSM35 microscope and X-ray diffraction on a Philips X-Pert diffractometer.

The methanol oxidation reaction was performed at 260 °C in a continuous-flow isothermal fixed-bed reactor operating at atmospheric pressure. The composition of the $CH_3OH/O_2/He$ reactant feed was 7.7/16.3/76 molar ratio, which corresponds to a methanol partial pressure of 58 Torr. The reactant mixture was obtained by flowing an O_2/He gas mixture through a methanol saturator maintained at 11.3 °C. The overall flow rate (17 $ml\,min^{-1}$) and the catalyst weight (100 mg for $VOPO_4{\cdot}2H_2O$ prepared by the Ladwig method and 20 mg for all the other samples) were chosen so as to get a methanol conversion lower than 10%. The catalytic measurements were performed at steady state, usually reached after 15 min of reaction. On-line computerised gas chromatography was used to determine the composition of the outlet gas during the reaction. The reaction rates or activities were expressed as the number of moles of methanol consumed per hour and gram of catalyst (specific activity) or per surface unit of active phase (intrinsic activity). The selectivity to a given product was calculated as the ratio of the number of moles of methanol consumed for the formation of this product to the total number of moles of methanol consumed.

Before reaction, the samples, whether they were supported or unsupported, were calcined in the catalytic reactor under oxygen flow at 450 °C for 2 h.

3. Results and discussion

3.1. Sample characterisation

3.1.1. Structural analysis

After synthesis and equilibration in air in order to restore the water stoichiometry, all the vanadium phosphate powders exhibit a diffraction pattern characteristic of the $VOPO_4\cdot 2H_2O$ phase [5]. The materials synthesised by rapid precipitation in THF exhibit broader diffraction peaks (figure 2(a)) than those obtained by slow precipitation (Ladwig method or in alcohol with hydrolysis) (figure 2(b)). This is consistent with the fact that a slow precipitation usually favours a better crystallisation and the formation of smaller particles. The colour, initially yellow, turned light green within a few hours. This change is a well-known effect of reduction of V(V) into V(IV). A second vanadium phosphate phase was observed as traces (marked with $*$ in figure 2(b)). Upon ageing for longer times, the powders turned dark green, and the proportion of the new phase increased, so as to be the main one after one year (figure 2(c)). Hence, $VOPO_4\cdot 2H_2O$ gradually transforms with time into another compound. The diffraction peaks at 7.14, 6.92, 5.19, 4.53, 4.24, 3.56, 3.53, 3.39 and 3.04 Å may be attributed to $H_4V_3P_3O_{16.5}\cdot xH_2O$ [11], in which the V(V) and V(IV) ions coexist. It is known that the reduction of vanadyl phosphate occurs upon reaction with alcohol and leads to vanadium(IV) hydrogen phosphates [12]. The slow reduction of nanoparticles of vanadium phosphate by the moisture in air was reported by Miquel et al. [13,14]. These phosphates were prepared from $VOCl_3$ and $POCl_3$ by a flame pyrolysis method. These authors concluded that the phase transformation was favoured by the small size of the particles. Hence, the partial reduction of V(V) into V(IV) occurs when organics (alcohol) are adsorbed onto vanadium phosphate crystallites or in the air moisture when the particles are small. Indeed, the reduction is not observed with the powders obtained by the Ladwig method, which contain large particles (see below) and no organics.

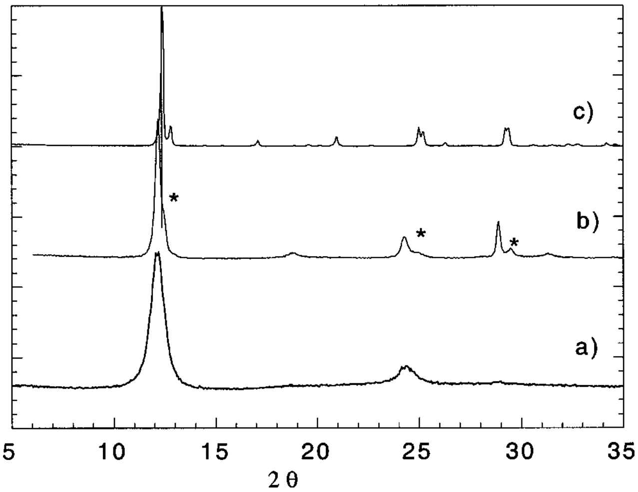

Figure 2. X-ray diffraction patterns of vanadium phosphates precipitated in (a) THF; (b) alcohol ($h = 3$); (c) alcohol ($h = 3$) then aged for one year.

The specific surface area of the vanadium phosphate powders and the morphology of the particles strongly depend on the synthesis method. For the synthesis in THF and diethyl ether, the fast precipitation yields powders with a high specific surface area (table 1). The powders are composed of tiny microcrystallites with particles smaller than 50 nm, as shown in figure 3(a) in the case of THF. In contrast, with the methods leading to slow precipitation (Ladwig method and in alcohol with $h = 0, 3, 10$), extended platelets are obtained, and the specific surface areas are much smaller (table 1). The particle size ranges from 10 μm for the precipitation in alcohol (figure 3(b)) to 50 μm for the platelets obtained by precipitation by the Ladwig method [5]. With the alcohol method, the vanadium phosphate solution can be deposited onto a glass substrate before precipitation. After precipitation, the diffraction pattern of the resulting coating is largely textured and only the (00l) and (002) diffraction lines are observed [6]. This indicates that the larger faces of $VOPO_4\cdot 2H_2O$ observed by SEM can be attributed to the (001) crystallographic planes.

The silica-supported samples do not provide any XRD pattern. Similarly to the bulk phosphates, the fresh powders are yellow and slowly turn green upon ageing. This is an indication of the formation of a phosphate.

The V/SiO_2 samples have an orange colour characteristic of dispersed vanadium oxide. A characterisation study by Raman and STEM [15,16] showed that the $10V/SiO_2$ sample contains V_2O_5 microcrystallites, supported on sil-

Table 1
Specific surface area and catalytic properties of $VOPO_4$ and V_2O_5 samples.

Sample	Specific surface area ($m^2\,g^{-1}$)	Particle size (μm)	Activity: Specific ($mmol\,h^{-1}\,g^{-1}$)	Activity: Intrinsic ($mmol\,h^{-1}\,m^{-2}$)	Selectivity (%): CH_2O	Selectivity (%): $(CH_3O)_2CH_2$
Ladwig	2	50	0.3	0.15	71	17
Alcohol, $h = 0$	9	∼10	2.7	0.3	60	25
Alcohol, $h = 3$	8	∼10	2.8	0.35	60	25
Alcohol, $h = 10$	7	∼10	2.2	0.32	55	32
Ether, $h = 0$	13	–	3.3	0.25	58	25
THF, $h = 0$	40	0.05	5.0	0.12	55	30
V_2O_5 from [15,16]	2.5		6.9	2.8	67	27

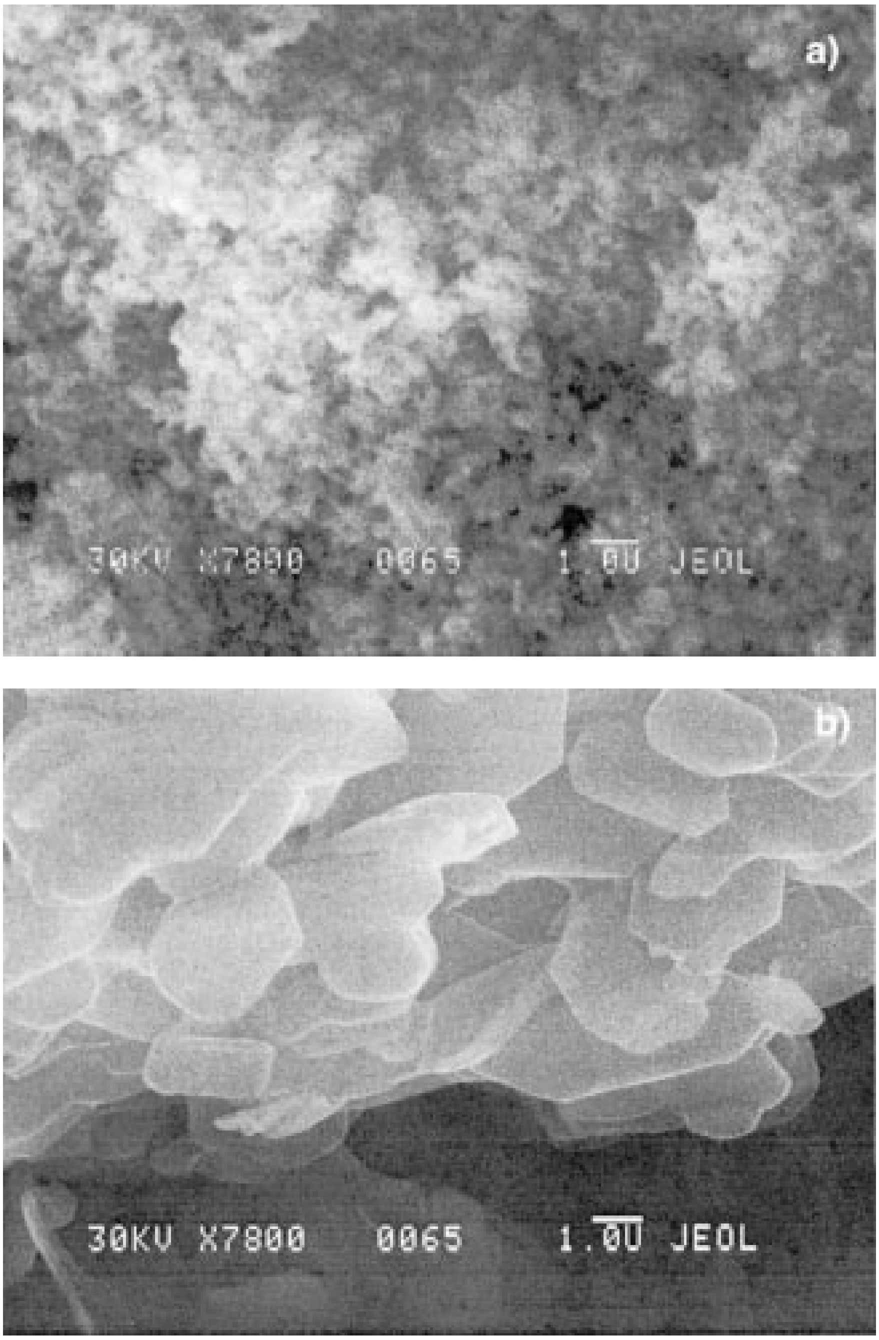

Figure 3. Scanning electron microscopy of $VOPO_4$ precipitated in (a) THF and (b) alcohol.

ica and unsupported, as well as isolated tetrahedral vanadyl species. In $1V/SiO_2$, the vanadium loading is too low to detect V species by Raman.

3.1.2. Thermal treatments

Vanadium phosphates obtained by precipitation in alcohol behave in the same way as those obtained by the Ladwig method, during thermal treatment up to 700 °C [6]. They undergo an endothermic dehydration between 100 and 200 °C corresponding to 18% weight loss, i.e., to the loss of two water molecules during the phase transformation into $\alpha_I VOPO_4$. This transformation is reversible even after heating at 700 °C for 2 h since the phase rehydrates into $VOPO_4 \cdot 2H_2O$ upon equilibration in air at room temperature [17]. The thermal decomposition of the phosphates obtained by precipitation in THF is different. They also exhibit an endothermic weight loss of 12% between 100 and 200 °C, corresponding to only 1.3 H_2O/V. This loss is followed by an additional broad exothermic weight loss up to 350 °C (10%) that corresponds to the gradual decomposition of the residual organics trapped onto or inside the vanadium phosphate because of incomplete condensation [17]. After heating at 700 °C, X-ray diffraction shows that the compound is a mixture of $\alpha_{II} VOPO_4$ and

$\beta VOPO_4$. These two phases do not easily transform back to $VOPO_4 \cdot 2H_2O$ in air at room temperature. They usually form by oxidation of reduced vanadium phosphates such as $VOHPO_4 \cdot 0.5H_2O$ or by heating $VOPO_4 \cdot 2H_2O$ containing reduced V(IV) species [18]. This may be the case here because of the presence of V(IV) produced by ageing in air or during the calcination of the residual organics.

The morphology of the powders, observed by electron microscopy is not affected either by thermal treatment at 450 °C in oxygen or by the catalytic tests.

3.2. Catalytic reaction

3.2.1. Bulk vanadium phosphates

The activity of all the $VOPO_4$ powders is constant during the catalytic reaction (up to 16 h). The specific activity increases with the surface area (table 1) whereas the intrinsic activity (activity per m^2 of catalyst) decreases (table 1 and figure 4). One should not take into account the intrinsic activity of the sample obtained by the Ladwig method because its specific area is determined with a too large error (2 ± 1 m^2/g). Hence, the highest intrinsic activities are obtained for the precipitates prepared in alcohol ($h = 0$–10). As indicated above, the most developed face in the platelets of these precipitates ($\sim$10 μm) is the (001) one. In the THF or ether-synthesised catalysts, whose intrinsic activities are lower, the particles are more tiny and spherical (50 nm). Their (001) faces are probably less developed than in the samples prepared in alcohol. This would indicate that the (001) face has the largest catalytic activity.

It is interesting to compare the structure and the catalytic properties of V_2O_5 and $VOPO_4$. $VOPO_4 \cdot 2H_2O$ is known to be modified during catalytic reactions: it transforms into $\beta VOPO_4$ during oxidation of butene and into $(VO)_2P_2O_7$ during oxidation of butane or pentane [4]. We have no information about the phases present during the methanol oxidation but the X-ray diffraction patterns of the $VOPO_4$ catalysts collected after catalytic reaction and after exposure to air indicate that the main phase is still $VOPO_4 \cdot 2H_2O$ with traces of $H_xVOPO_4 \cdot nH_2O$. Therefore, the phase present during the methanol oxidation reversibly transforms into $VOPO_4 \cdot 2H_2O$ and probably derives from it by a topotactic reaction of dehydration or a partial reduction of V(V). It is proposed that the orientation of the surface vanadyl groups during methanol oxidation is the same as in $VOPO_4 \cdot nH_2O$, i.e., perpendicular to the (001) plane [17,19]. Hence, for V_2O_5 and the phosphate catalysts, the vanadyl groups are protruding outward from the (001) plane but their environment is different. In V_2O_5, they are bonded through V–O–V bridges whereas in $VOPO_4$, they are bonded to phosphates through V–O–P bridges.

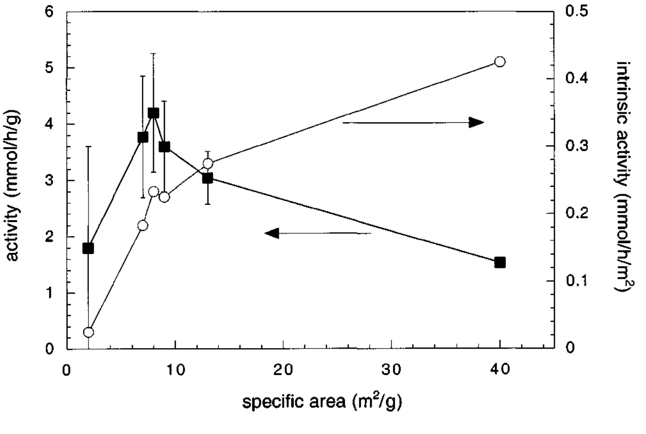

Figure 4. Specific activity and intrinsic activity of vanadium phosphate catalysts as a function of their specific surface area.

This could explain that their catalytic properties are different:

(i) The phosphates have a much smaller intrinsic activity than V_2O_5 (table 1). It has been shown that methanol oxidation on V_2O_5 is a structure-sensitive reaction. The (100) and (010) side faces do not exhibit any peculiar selectivity to a given compound, but they are more active than the (001) face by about one order of magnitude [20]. As discussed above, this is the reverse in the case of the vanadium phosphates in which the (001) face appears to be the most active.

(ii) The same reaction products are formed with the $VOPO_4$ samples and V_2O_5, i.e., formaldehyde, dimethyl ether and methylal (table 1). Although the Ladwig sample shows a slightly higher selectivity to formaldehyde (>70%), all the phosphates exhibit almost the same selectivities (table 1). The selectivity to dimethyl ether is three times larger on the $VOPO_4$ samples than on V_2O_5. It is known that the dehydration of methanol into dimethyl ether is characteristic of the presence of strong Brønsted acid sites [9] (figure 1). Hence, the comparison of the selectivities indicates a stronger acidity for the phosphates than for V_2O_5. This is consistent with the fact that the ionic character of the P–O bond is lower than that of V–O, so the oxygen atom in V–O–P is expected to be more acidic than that in V–O–V.

3.2.2. Silica-supported vanadium catalysts

No catalytic activity is observed with $1V/SiO_2$. The activity of the $10V/SiO_2$ sample passes through a maximum, drastically decreases after 100 min on stream, and vanishes after 5 h (figure 5(a)). In contrast, the VP/SiO_2 samples ($h = 0$ and 3) exhibit a constant activity within the 17 h of reaction (figure 5(b)), and the activity of VP/SiO_2 ($h = 10$) increases with the reaction time (figure 5(c), table 2). The selectivities of all these samples remain constant during the reaction time. Hence, the VP/SiO_2 catalysts are more stable than the V/SiO_2 ones.

The activities per gram of VP/SiO_2 samples are in the same range as those of the bulk $VOPO_4 \cdot 2H_2O$ (tables 1 and 2) although the amount of vanadium per gram of catalyst is about 50 times lower. This is consistent with the dispersion of the active phase onto the silica support. Using the vanadium content determined by chemical titration, one may calculate the specific activity per gram of active

Table 2
Catalytic properties of VP/SiO_2 samples.

Sample	V loading (wt%)	Specific activity[a] ($mmol\,h^{-1}\,g^{-1}$)		$VOPO_4$ activity[b] after 400 min	Surface area of supported $VOPO_4$[c]	Dispersion of supported $VOPO_4$
		After 10 min	After 400 min	($mmol\,h^{-1}\,g^{-1}$)	(m^2/g)	(%)
VP/SiO_2 $h = 0$	2.1	6.9	5.4	66	220	25
VP/SiO_2 $h = 3$	1.4	7.7	6.8	126	420	48
VP/SiO_2 $h = 10$	1.6	7.6	10.8	175	583	66

[a] Per gram of catalyst.

[b] Per gram of $VOPO_4{\cdot}2H_2O$.

[c] Assuming that the intrinsic activity of supported $VOPO_4$ is the same as that of the bulk phosphates: ~0.

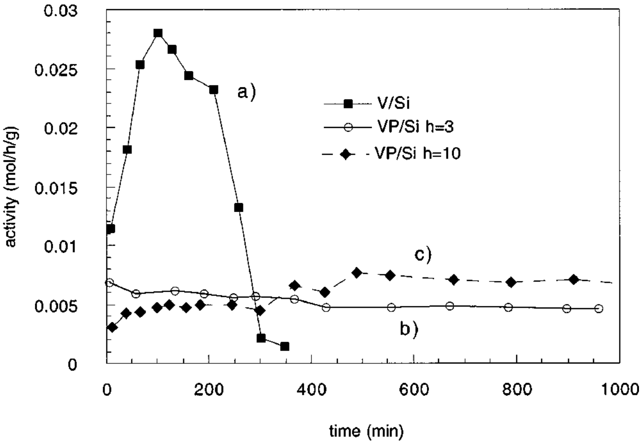

Figure 5. Activity as a function of the reaction time for (a) $10V/SiO_2$, (b) VP/SiO_2 obtained with $h = 0$, (c) VP/SiO_2 obtained with $h = 10$.

phase (table 2). The highest specific activity is obtained for the sample prepared in alcohol with $h = 10$, indicating that the dispersion of $VOPO_4{\cdot}2H_2O$ is probably higher in this sample.

Assuming that the intrinsic activity of the supported $VOPO_4$ phase is the same as that of the bulk phosphates obtained in alcohol, i.e., ~0.3 $mmol\,h^{-1}\,m^{-2}$, the surface area of the supported $VOPO_4$ phases can be estimated. It varies from 220 to 580 m^2/g (table 2). From the cell dimension of $VOPO_4{\cdot}2H_2O$ (tetragonal symmetry: $a = 6.2$ Å, $c = 7.4$ Å, density: 2.29 [5]), the specific surface area of a monolayer of $VOPO_4{\cdot}2H_2O$ oriented perpendicular to the (001) direction can be estimated to be 880 m^2/g. The dispersion of $VOPO_4$ on silica can be deduced (table 2). The highest, 66%, is obtained for the sample prepared in alcohol with $h = 10$. However, it may be noted that silica is far from covered by $VOPO_4{\cdot}2H_2O$ since the full coverage of the silica support (400 m^2/g) by a monolayer of vanadium phosphate would be reached with a vanadium loading of 7 wt%.

A difference from bulk $VOPO_4$ materials is the formation of methyl formate, CO and CO_2. This may be an effect of the silica support. Indeed, in a former work on Mo/SiO_2 [21], it has been shown that the reaction of methanol oxidation is sensitive to the dispersion of molybdenum supported on silica. In addition, previous results have shown that the nature of the crystalline $VOPO_4$ phases formed upon thermal treatment [22] as well as their reducibility [23] depend on the extent of interaction of $VOPO_4$ with silica. This interaction may induce a change in the selectivity for the methanol oxidation.

4. Conclusion

The synthesis of vanadium phosphates by reaction of vanadium alkoxides with phosphoric acid in organic solvents provides powders with specific surface area up to ~40 $m^2\,g^{-1}$. The largest specific surface areas are obtained in anhydrous and aprotic solvents such as diethyl ether and THF. This is related to the high rate of precipitation in these solvents. The highest specific activities in the reaction of oxidation of methanol are obtained with these catalysts but not the highest intrinsic activities, which are obtained with the $VOPO_4$ samples synthesized in 2-propanol. All these vanadium phosphates are less active than V_2O_5, and exhibit slightly different selectivities, indicating that they possess stronger acid surface sites.

Vanadium phosphates can be dispersed onto a silica support by reaction of phosphoric acid with alkoxides in 2-propanol. They are more active than the corresponding bulk powders because of their dispersion on silica. Their catalytic properties are very stable compared to those of supported V_2O_5 catalysts. Estimation of the surface area of the supported vanadium phosphate phase indicates a high dispersion state.

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