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Vanadium oxides supported on amorphous aluminum phosphate: Structural and chemical characterization and catalytic performance in the 2-propanol reaction

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ABSTRACT

The synthesis of vanadium oxide systems with V_2O_5 loadings below, above or corresponding to the theoretical monolayer (1–34 wt.% of V_2O_5) obtained by impregnation with vanadyl oxalate or vanadyl acetylacetonate of a mesoporous amorphous aluminum phosphate, $AlPO_4$, calcined at different temperatures (from 350 °C to 650 °C), has been carried out. Materials were characterized by XRD, Raman, DR UV–vis, ^{51}V, ^{27}Al and ^{31}P MAS NMR and nitrogen adsorption. Their acidity and reducibility were evaluated through pyridine TPD and hydrogen TPR, respectively, and their catalytic behavior in the 2-propanol reaction. The vanadium salt promoted the crystallization and loss of porosity of $AlPO_4$, to a greater degree when acetylacetonate of vanadyl was the vanadium source and the vanadium loading increased. Similarly, the highest vanadia dispersion was obtained on $AlPO_4$ calcined at 350 °C and impregnated with vanadyl oxalate. The vanadium systems were more active than their respective supports in the 2-propanol reaction. Furthermore, the weak-medium acid sites that predominate in $AlPO_4$ and vanadia species are the active sites for the propene formation. The formation of propanone required redox sites, the most active being those of the vanadia species in close contact with $AlPO_4$, which were also more easily reducible. Both parallel reactions would proceed though concerted mechanisms.

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1. Introduction

One of most studied vanadia supported systems is vanadia/titania due to their high commercial potential as oxidation catalysts in several industrial processes, including the phthalic anhydride production from *o*-xylene. However, other conventional supports such as Al_2O_3 and SiO_2 have also been intensively investigated mainly in order to obtain efficient catalysts for the olefin production from alkane oxidative dehydrogenation reactions. It is well known that the type of vanadium species in the supported vanadia systems depends on the nature and surface area of the support, as well as the vanadium content [1–7]. Amorphous aluminum phosphate ($AlPO_4$) is iso-structural with silica and exhibits parallel polymorphic transformation [8]. The textural and acid-base properties of $AlPO_4$ are dependent on a number of variables, such as aluminum salt, the precipitation agent or calcination temperature [9]. $AlPO_4$ has been studied not only as a catalyst but also as a metal support in a great variety of liquid or gas-phase reactions including the oxidative dehydrogenation of ethylbenzene [10]. It has also been demonstrated to provide good support for vanadium [11] and vanadium-phosphorus [12] oxides in the oxidative dehydrogenation of propane and the selective oxidation of n-butane, respectively. Furthermore, we have previously reported that the presence of aluminum in the precipitation medium of the vanadium-phosphorous system had a decisive role in its morphology and porosity as well as in its chemical properties (acid properties and reducibility) and consequently in its catalytic performance in the selective oxidation of aromatic hydrocarbons; benzene, toluene and o-xylene [13–15]. The surface acidity and the strength of the acid sites, and the reducibility of the ternary systems increased when the aluminum content increased [13,14]. These results seem to indicate that a chemical interaction between the aluminum and vanadium phases exists, which could affect the vanadium active sites. On this basis, we have studied $AlPO_4$ supported vanadium oxides, in order to know more about this possible chemical interaction. Specifically,

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Table 1
Textural properties; acidity and strength of acid sites obtained from Py-TPD; total H_2 consumption and temperature (T_i) and percentage of each peak after deconvolution from TPR, of all the solids studied.

Catalyst	Textural properties				Py-TPD				TPR	
	S_{BET} (m^2/g)	V_p (mL/g)	d_p (Å)	Mesop (%)	Acidity[a]	Strength (%)			H_2[a]	T_i (°C)
						W	M	S		
$AlPO_4$350	248	1.13	182	91	0.48	87	13	–	–	–
1V/$AlPO_4$350	102	0.76	301	73	0.93	71	19	10	–	–
16V/$AlPO_4$350	109	0.59	215	85	1.11	64	18	18	10	372(15)[b];462(79)
27V/$AlPO_4$350	23	0.09	148	61	1.18	76	15	9	73	450(14);526(77)
34V/$AlPO_4$350	5	–	–	–	–	–	–	–	515	442(13);512(31);560(22);614(13);713(14)
$AlPO_4$450	199	0.82	165	86	0.72	72	20	8	–	–
8V/$AlPO_4$450	78	0.46	236	60	0.83	69	23	8	6	424(16);505(77)
8V(Ac)/$AlPO_4$450	45	0.26	236	54	0.90	69	13	18	13	434(9);495(42);561(49)
$AlPO_4$650	159	1.09	275	94	0.82	72	17	11	–	–
10V/$AlPO_4$650	86	0.68	314	52	1.15	68	20	12	10	457(10);509(50);555(10);631(27)
$V_2O_5$450 + $AlPO_4$450	53	0.43	170	59	0.95	85	15	–	81	596(19);655(41);756(40)

[a] μmol/m^2; W(weak) = 80–200 °C; M(medium) = 200–300 °C; S(strong) = > 300 °C.
[b] Percentage.

the present work is aimed at the preparation and the textural, structural and surface chemical characterization of vanadium systems with different V_2O_5 loadings supported on $AlPO_4$ calcined at several temperatures (from 350 °C to 650 °C). Their catalytic behavior has been evaluated in the 2-propanol reaction. The solids were prepared by wet impregnation and their characterization was carried out by X-ray diffraction (XRD); Raman and Diffuse Reflectance Ultraviolet–visible (DR-UV–vis) spectroscopy; ^{51}V, ^{27}Al and ^{31}P Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectroscopy and nitrogen adsorption techniques. The surface acidity was evaluated through pyridine (Py) chemisorption by Temperature Programmed Desorption (TPD) and the capacity of the reducibility of the solids was studied by H_2 Temperature Programmed Reduction (TPR). The 2-propanol decomposition is a test reaction widely used for the characterization of acid and basic and/or redox metal oxide sites. The alcohol decomposes through two parallel reactions: dehydration to propene mainly on acid sites, and dehydrogenation to 2-propanone on basic, or concerted acid-base pair sites, or on active sites with redox or basic properties. In some conditions the formation of diisopropyl ether by dehydration involving two molecules of 2-propanol, also takes place on acidic sites. However, the role of acidic and basic sites in the formation of propene and 2-propanone has not yet been well established. Thus, recently it has been reported that the mechanism of the propene formation will be E_1 (acid sites) o E_2 (acid-base pair sites) depending on the strength of Bronsted sites [16], and that this test reaction can be used not only to determine the type of sites implicated, but also the strength of such sites [17]. In the present paper, the comparison of the results obtained in this test reaction with those from Py adsorption and H_2-TPR, allow us to know more about superficial chemical properties and of 2-propanol reaction mechanism.

2. Experimental

2.1. Catalyst preparation

The $AlPO_4$ was prepared from $AlCl_3.6H_2O$ and H_3PO_4 (85 wt.%) by precipitation with aqueous ammonia as previously reported [18]. The pH value at the "endpoint" precipitation was 7.2. The solid was calcined in air at 350 °C, 450 °C and 650 °C during 4 h. Vanadium oxide systems were prepared by wet impregnation with desired volumes of vanadyl oxalate in methanol solution in order to obtain loadings below, above or corresponding to theoretical monolayer, calculated as 0.15 wt.% V_2O_5 per m^2 of support [19] and calcined at 450 °C for 4 h. These systems will be denoted xV/$AlPO_4$-T where x indicates the theoretical percentage of V_2O_5 in relation to weight of solid (x = 1, 8, 10, 16, 27 and 34 wt.%) and T the temperature of calcination of support. Thus, according to this nomenclature the weight percentage of V_2O_5 corresponding to theoretical monolayer is 27, 22 and 18 wt.% depending on the calcination temperature of $AlPO_4$, 350 °C, 450 °C and 650 °C, respectively. Another [8V(Ac)/$AlPO_4$450] system was prepared by using a methanol solution of vanadyl acetylacetonate. As a reference, a mechanical mixture of 50 wt.% V_2O_5 (commercial from Merck) and 50 wt.% $AlPO_4$ both calcined at 450 °C with a P/V + Al molar ratio = 0.43 was also prepared. The solids were mixed and stirred in n-hexane to form a suspension. After 1 h of stirring at room temperature, the solvent was removed under reduced pressure and the mixture was dried in the same way as the vanadium systems.

2.2. Catalyst characterization

Information about the surface area and pore size was obtained from the adsorption–desorption isotherms of nitrogen at its liquid temperature, using a Micromeritis ASAP 2000 apparatus. Prior to measurements, all the samples were degassed to 0.1 Pa. BET surface areas were calculated assuming a cross-sectional area of 0.162 nm^2 for the nitrogen molecule.

XRD patterns were obtained using Ni-filtered Cu Kα radiation (λ = 1.5418 Å). Finely ground samples were scanned at a speed of 2°/min (2θ = 2–80°) using a Siemens D-500 diffractometer (40 kV, 30 mA).

FT-Raman spectra were recorded at room temperature on a RenishawinVia Raman microscope with Nd:YAG laser of 532 nm and a grating of 1200 lines/mm. The laser powder was adjusted at 1% with an exposure time of 10 s after 10 accumulations.

Diffuse reflectance spectra in the UV–vis region (200–800 nm) were collected at room temperature with a Variant Cary 1E UV–vis spectrophotometer equipped with reflectance attachment using $BaCl_2$ as reference.

^{51}V, ^{27}Al and ^{31}P MAS NMR experiments were performed at a resonance frequency of 105.25, 104.26 and 161.98 MHz, respectively, corresponding to a field of 9.4 T on a BRUKER AVANCE 400WB spectrometer using a 2.5 mm BRUKER double resonance MAS probe. All experiments were performed nominally at room temperature. The ^{51}V spectra were recorded at different spinning speeds (from 13 to 30 kHz) to specifically determine the unshifted spinning sidebands (SSB) and, accordingly, the isotropic chemical shift (δ_{iso}) values. $VOCl_3$ solid, $Al(H_2O)_6^{3+}$ and H_3PO_4 solutions were used as external standard references for V, Al and P chemical shifts,

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