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ORIGINAL ARTICLE

Synthesis and FT–IR study of the acido–basic properties of the V_2O_5 catalysts supported on zirconia

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Abstract In this paper we describe the synthesis and characterization of the acido–basic properties of catalysts containing varied amounts of vanadium supported on ZrO_2. The preparation of the zirconia was carried out using a hydrolysis method and the vanadium was introduced by impregnation with a porous volume in several stages, followed by calcinations under air at a temperature of 723 K. The obtained samples are characterized by adsorption–desorption of nitrogen and infrared spectral analysis of different species formed by acidic and basic probes. This adsorption on the surface of these compounds has been studied in order, in the hand to investigate information on their surface acidity and in the other hand to know particularly the nature and strength of acidic and basic sites. Among the molecular probes, we used carbon monoxide, carbon dioxide, pyridine and 2,6-dimethylpyridine. The adsorption of CO has shown that contrary to pure zirconia and oxidized V_2O_5/ ZrO_2, the reduced V_2O_5/ ZrO_2 samples favour the formation of CO co-ordinated on Lewis acidic sites of reduced V_2O_5 species (CO on V^{4+} or V^{3+}). We also observe the creation of Brønsted acidic sites by means of the incorporation of vanadium.

1. Introduction

The catalysts containing vanadium supported on metallic oxides have famous industrial applications. In fact, the choice of the nature of the support depends on the reaction because the catalytic activity depends not only on the number of active sites but on their distribution on the surface and the content of the catalyst in V_2O_5. Many different synthesis methods have been used in the preparation of supported vanadium catalysts: vapour phase grafting with $VOCl_3$ (Haber et al., 1986; Koranne et al., 1994; Bond and Bruckman, 1981), vanadium

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acetate (van Hengstrum et al., 1983), non-aqueous impregnation with vanadium alkoxides (Deo and Wachs, 1994a,b), aqueous impregnation of vanadium oxalate (Wachs et al., 1985; Aderdour et al., 2005), as well as dry impregnation with crystalline V_2O_5 (Knozinger and Taglauer, 1993; Hausinger and Schmelz, 1988; Haber et al., 1995, 1985; Nousir et al., 2005).

In this work a set of zirconium oxide supports modified by the addition of V_2O_5 in different content, have been synthesized by impregnation to porous volume, and have been characterized by adsorption–desorption of nitrogen. Infrared spectroscopy is used to provide direct information about the interaction of vanadium species with the surface hydroxyls of supported oxides (Dunn et al., 1999).

2. Experimental

The preparation of zirconia was carried out from commercial zirconium (IV) propoxide in 70% 2-propanol (Fluka). The solution was hydrolysed by an excess of distilled water without stopping the vigorous agitation after the end of hydrolysis. The precipitate was filtered, then given in ebullient suspension and was agitated with 1 l of distilled water. Washing was carried out several times. The product was dried for one night at 393 K, then calcined in air at 723 K. Vanadium was introduced by impregnation with porous volume in several stages followed by calcinations under air at 723 K.

The textural properties (i.e. specific area, pore volume) were determined by nitrogen adsorption at 77 K on a Micromeritics ASAP 2000 system. For IR studies, samples (20 mg) were pressed to form self-supporting disks and the IR spectra were scanned at room temperature, using a Nicolet MX-1 FT–IR spectrometer.

3. Results and discussion

Results pertaining to the physical adsorption of nitrogen are summarised in Table 1. As the table shows, the samples exhibit analogous textural properties.

3.1. Characterisation by FT–IR

3.1.1. Oxidised V_2O_5/ZrO_2

The study of the ν(OH) vibration of surface hydroxyl groups for zirconia modified by the addition of V_2O_5, shows that ZrO_2 activated at 723 K mainly presents two bands ν(OH) at 3775 and 3670 cm^{-1} characterizing two types of OH groups (type I and type II, respectively) (Bensitel et al., 1987). From Fig. 1, it appears that the relative intensity of the band observed at 3775 cm^{-1} decrease slightly with increasing the vanadium content.

The infrared spectra obtained at room temperature after activation under O_2 of the different samples V_2O_5/ZrO_2 (Fig. 2) shows the presence of one band at 1027 cm^{-1} for sample 5% V_2O_5/ZrO_2 and 7% V_2O_5/ZrO_2 at 1036 cm^{-1} assigned to the vibration ν(V=O) of superficial groups which is accompanied by the disappearance of the hydroxyl bands located at 3775 and 3670 cm^{-1}. We also note the appearance of a weak band at 990 cm^{-1} probably due to V_2O_5 of the bulk.

Table 1 Results of physical adsorption.

Catalysts	ZrO_2	4% V_2O_5	5% V_2O_5	6% V_2O_5	7% V_2O_5
S_{BET} (m^2/g)	90	106	105	104	100
Vp (cm^2/g)	0.24	0.23	0.23	0.22	0.22
Rp (nm)	11.4	8.6	8.7	8.6	8.7

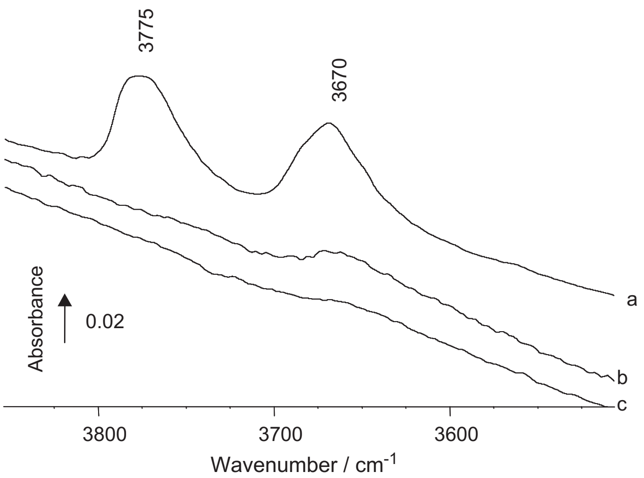

Figure 1 FT–IR spectra in the ν(OH) range, after O_2 oxidation at 723 K of the samples: (a) ZrO_2, (b) (5%) V_2O_5/ZrO_2 and (c) (7%) V_2O_5/ZrO_2.

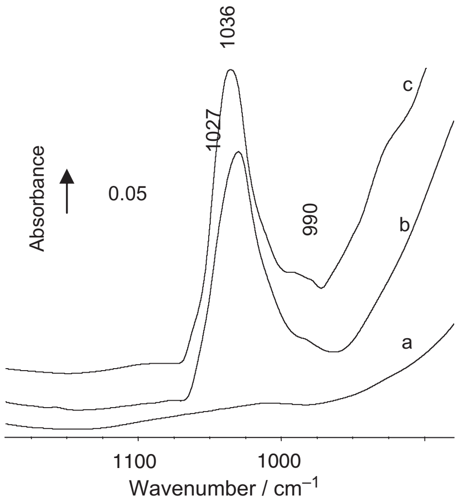

Figure 2 FT–IR spectra after activation under O_2 at 723 K of samples: (a) pure ZrO_2, (b) (5%) V_2O_5/ZrO_2 and (c) (7%) V_2O_5/ZrO_2.

3.1.2. Reduced V_2O_5/ZrO_2 by H_2

The spectra due to the hydrogen chemisorptions on different V_2O_5/ZrO_2 compounds and pure ZrO_2 at 723 K are represented in Fig. 3. It shows the presence of a doublet at 1038 and 1027 cm^{-1}. The first one located at 1038 cm^{-1} is attributed to ν(V=O) vibration of V_2O_5 superficial group, while the presence of the band at 1027 cm^{-1}, which disappears with treatment under O_2, is assigned to ν(V=O) vibration of V_2O_5 reduced species. In conclusion, the H_2 reduction of zirconia modified by the introduction of vanadium leads to

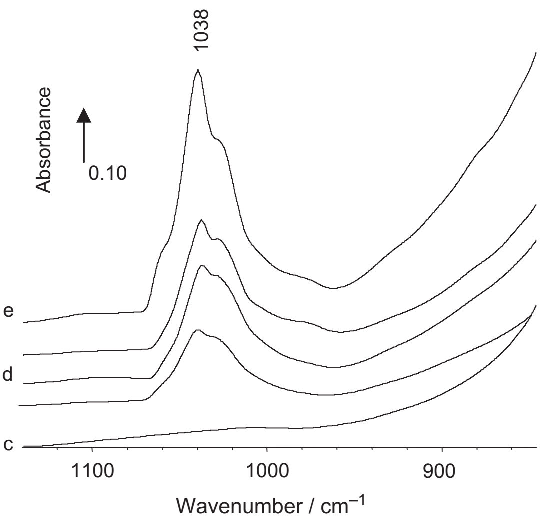

Figure 3 FT–IR spectra obtained: (a) Pure ZrO_2 activated under H_2 at 723 K, (b) (5%) V_2O_5/ZrO_2 reduced by H_2 at 723 K, (c) (5%) V_2O_5/ZrO_2 reduced by H_2 at 873 K, (d) (7%) V_2O_5/ZrO_2 reduced by H_2 at 723 K and (e) (7%) V_2O_5/ZrO_2 reduced by H_2 at 873 K.

transformation of V_2O_5 to VO_2 or V_2O_3. Increasing the reduction temperature (873 K) is accompanied by the increase in the intensity of the two bands (Fig. 3).

3.1.3. Study of the acido–basic properties of V_2O_5/ZrO_2

3.1.3.1. Adsorption of carbon monoxide. CO adsorption can be used to detect both acidic and basic sites of metal oxides. It was widely studied by Lavalley et al Lavalley (1996).

In our work, two modes of activation are used to study the acid–basic properties of (7%) V_2O_5/ZrO_2: activation under oxygen and activation under hydrogen. The infrared spectra obtained characterize the linear species in the (2300–2100 cm^{-1}) range and carbonate species in the range (1700–1100 cm^{-1}).

3.1.3.1.1. Activation under oxygen of CO adsorbed on (7%) V_2O_5/ZrO_2. The infrared spectra of species adsorbed with introduction of successive doses of CO on (7%) V_2O_5/ZrO_2 oxidized at 723 K by O_2 is shown in Fig. 4A and B. The results obtained in our laboratory confirmed that the adsorption of CO on pure zirconia activated at 723 K indicates the presence of a band at 2196 cm^{-1} which shifts to 2193 cm^{-1} with increasing adsorbed CO content; this band is attributed to CO co-ordinated with Lewis acidic sites Zr^{4+}. In the case of the sample (7%) V_2O_5/ZrO_2 (Fig. 4A), we also observed the presence of the co-ordinated CO band at 2208 cm^{-1} (26 μmol/g) and it shifts to 2201 cm^{-1} (1034 μmol/g). Taking the 2196 cm^{-1} value for ν(CO) on pure zirconia as origin, the shift ($\Delta\nu$ = 12 cm^{-1}) lower than the value of ν(CO) for (7%) V_2O_5/ZrO_2 shows that the Lewis acidity increases with introducing vanadium into zirconia. This can be attributed to the band observed at 2208 cm^{-1} assigned to ν(CO) vibration on Zr^{4+} near to V_2O_5 species.

In the 1700–1100 cm^{-1} frequency range (Fig. 4B), no bands are detected when adsorbing CO on pure zirconia, but with the introduction of 7% of V_2O_5 on zirconia, several bands at 1600, 1494, 1421, 1368, 1325 and 1217 cm^{-1} are detected which characterize the formation of carbonate species. This result indicates clearly that the addition of V_2O_5 favours the oxidation of CO to carbonate species.

3.1.3.1.2. Activation under hydrogen of CO adsorbed on (7%)V_2O_5/ZrO_2. In the 2300–2100 cm^{-1} range, the spectra due to the adsorption of CO on (7%) V_2O_5/ZrO_2 reduced by hydrogen at 723 K (Fig. 5A) are different from those obtained

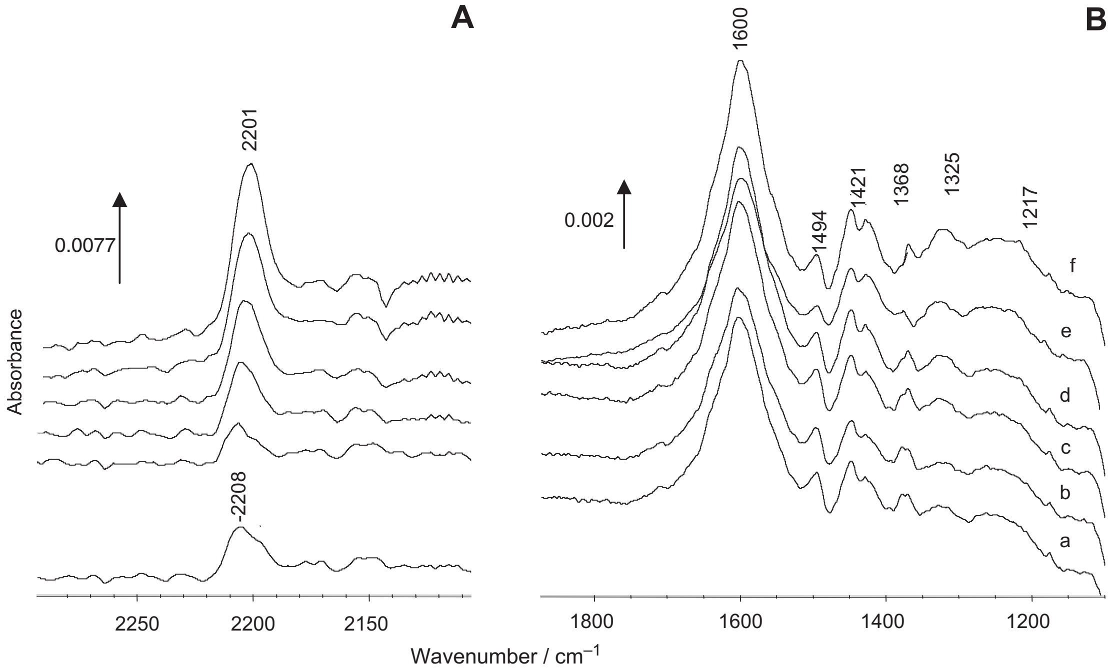

Figure 4 FT–IR spectra obtained after adsorption of successive doses of CO on (7%) V_2O_5/ZrO_2 activated under O_2 at 723 K: (a) 26, (b) 72, (c) 167, (d) 349, (e) 577 and (f) 1034 μmol/g. (A) 2300–2100 cm^{-1} range, (B) 1700–1100 cm^{-1} range.

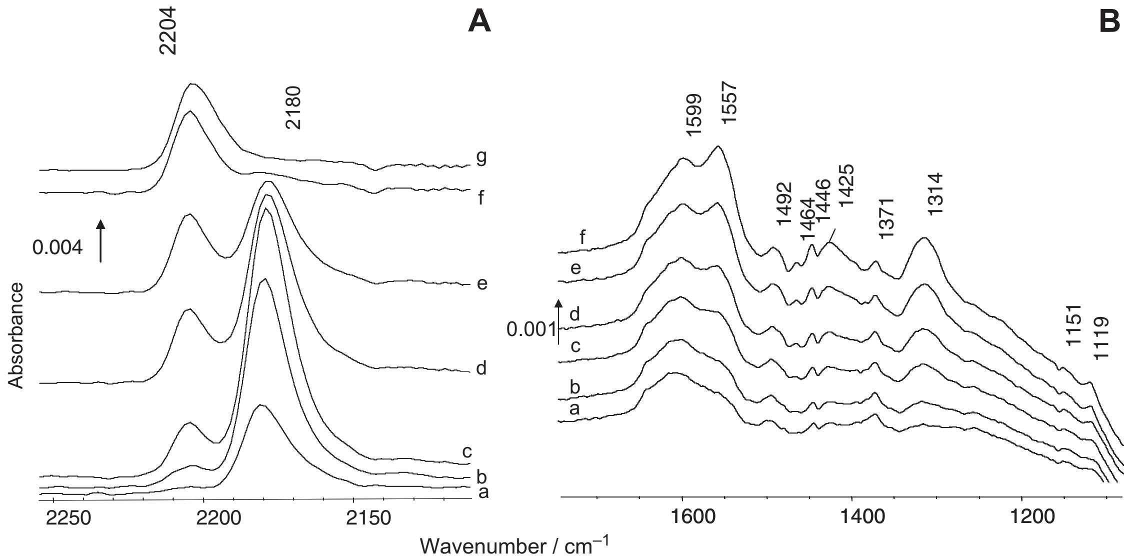

Figure 5 FT–IR spectra obtained after adsorption of successive doses of CO on (7%) V_2O_5/ZrO_2 reduced by H_2 at 723 K: (a) 24, (b) 74, (c) 168, (d) 358, (e) 503, (f) 793 and (g) 1268 μmol/g. (A) 2300–2100 cm^{-1} range, (B) 1700–1100 cm^{-1} range.

with re-oxidation treatment (Fig. 4A). When adsorbing a smaller quantity of CO (⩽24 μmol/g), one band is observed at 2180 cm^{-1}. As CO is adsorbed, a new band appears at 2204 cm^{-1} and the intensity of the two bands increases until 168 μmol/g of CO. At this value of adsorbed CO, we note a slight decline in the intensity of 2180 cm^{-1} band which disappears at 793 μmol/g (spectrum f), while the intensity of the band assigned at 2204 cm^{-1} begins to increase.

In view of the above results, the addition of CO on (7%) V_2O_5/ZrO_2 reduced by H_2 at 723 K leads to the formation of two bands at 2204 and 2180 cm^{-1} indicating the presence of two different Lewis sites. The first one can be compared to the one obtained in the case of (7%) V_2O_5/ZrO_2 oxidized and the other one (2180 cm^{-1}) which is less acidic; is absent on pure zirconia and oxidised V_2O_5/ZrO_2. Consequently, this latter band is attributed to CO co-ordinated on Lewis acidic sites of reduced V_2O_5 species (CO on V^{4+} or V^{3+}).

Variations in the 2180 and 2204 cm^{-1} bands respective areas (au cm^{-1}) with CO added (μmol/g) are reported in Fig. 6. The addition of ⩽200 μmol/g of CO gives rise to a significant increase of the 2180 cm^{-1} band integrated area, indicating the preferential adsorption of CO on reduced vanadium. This quantity is necessary in order to saturate all the sites. Exceeding 200 μmol/g, we observe a strong decrease in the area of the same band, which could be explained by the transformation of linear species into carbonate species.

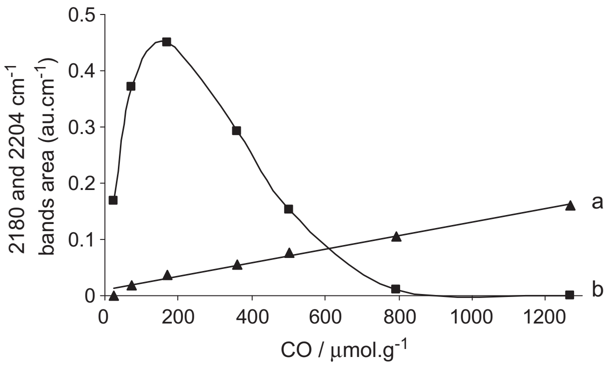

Figure 6 Evolution of the 2180 and 2204 cm^{-1} bands cm^{-1} bands area (au cm^{-1}) with CO content introduced in 7% V_2O_5/ZrO_2. (a) 2180 cm^{-1} band and (b) 2204 cm^{-1} band.

3.1.3.2. Carbon dioxide adsorption and desorption. Among probe molecules used to determine the surface basicity of metal oxides, carbon dioxide appears to be the most appropriate (Lavalley et al., 1991; Lahousse et al., 1993; M. Grigor'ev et al., 1972). We also find that the adsorption of varying concentrations of carbon dioxide on (4% and 7%) V_2O_5/ZrO_2 leads to the formation of various species.

In the 2400–2200 cm^{-1} frequency region (Fig. 7A), the spectra relative to the adsorption of CO_2 indicates the appearance of one band at 2360 cm^{-1} attributed to vibration ν_a(O=C=O) of linear species coordinated to Lewis acidic sites Zr^{4+} (Knözinger, 1976). Its intensity increases with increasing the amount of CO_2 adsorbed while its number decreases and shifts to 2353 cm^{-1}. This band completely desorbs after evacuation at r.t.

In the 1800–800 cm^{-1} range (Fig. 7B), different bands are detected. The bands assigned at ~1566, 1077 and 1059 cm^{-1}are essentially due to mono- and bidentate carbonate species, the other ones located at 1472 and 1393 cm^{-1} characterize polydentate or bulk carbonate species (Binet et al., 1992), while the negative bands at 1036 cm^{-1} characterize the ν(V=O) vibration of vanadium.

The variation of the 2350 and 1036 cm^{-1} integrate area during the addition of increasing CO_2 quantities has been illustrated in Fig. 8. It shows that the introduction of CO_2 gives rise to an increase in the 2350 cm^{-1} band area explaining an increase of the Lewis acid sites number while the addition of a weak quantity leads to a slight decrease in the ν(V=O) band area, which is stabilized after 137 μmol g^{-1}, this can be due to ν(V=O) perturbation by CO_2.

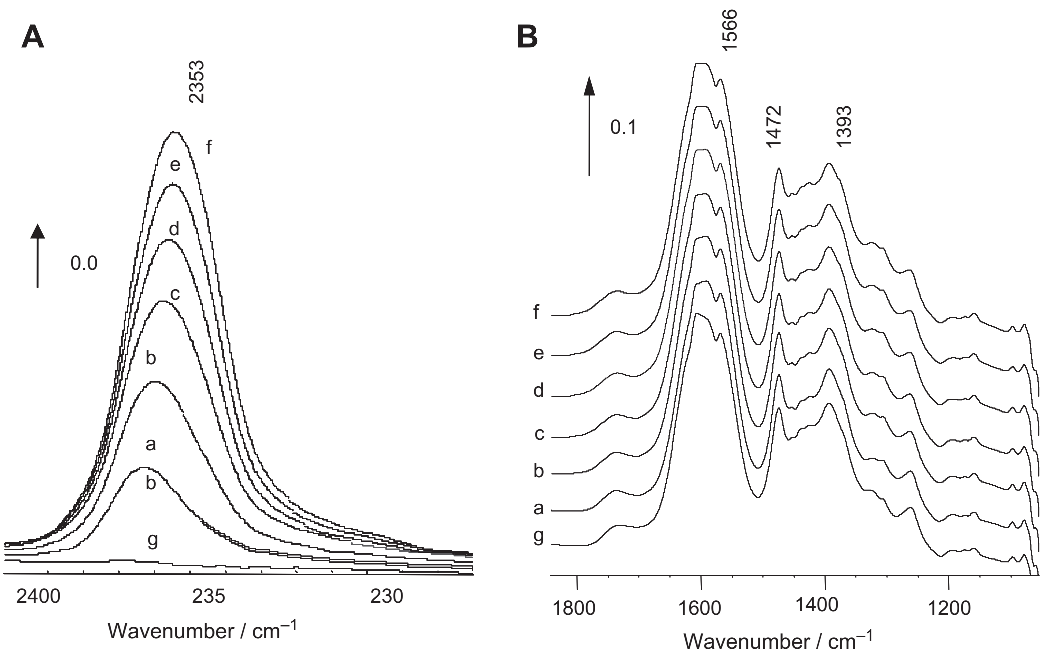

Figure 7 IR spectra taken at room temperature following CO_2 adsorption on (7%) V_2O_5/ZrO_2 activated at 450 °C as a function of the CO_2 pressure: (a) 60, (b) 183, (c) 414, (d) 776, (e) 882, (f) 910 µmol g^{-1}and (g) evacuation of CO_2 at r.t. (A) 2400–2100 cm^{-1} range, (B) 1800–800 cm^{-1} range.

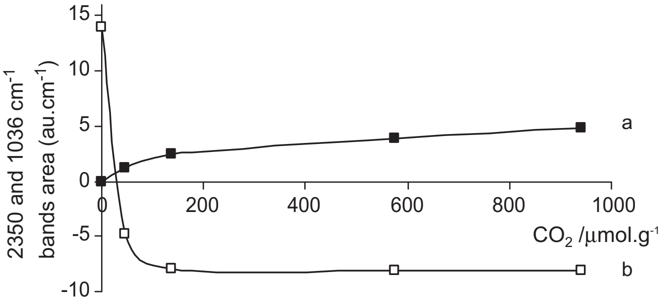

Figure 8 Evolution of the 2350 and 1036 cm^{-1} bands area (au cm^{-1}) with CO_2 content introduced in 7% V_2O_5/ZrO_2, (a) 2350 cm^{-1} band and (b) 1036 cm^{-1} band.

3.1.3.3. FTIR pyridine adsorption. Adsorption of pyridine as a base on the surface of solid acids is one of the most frequently applied methods for the characterization of surface acidity. The use of IR spectroscopy to detect adsorbed pyridine allows one to distinguish among different acid sites.

In our study, we adsorbed pyridine as a probe molecule at room temperature followed by an evacuation at increasing temperature on different V_2O_5/ZrO_2 samples activated at 723 K (with 4, 5, 6 and 7 percent of vanadium). The IR spectra of pyridine adsorbed by 5% V_2O_5/ZrO_2, (which had been chosen as an example in order to study the different species formed (Fig. 9) were obtained following outgassings at 373, 423, 473, 523, 573 and 623 K. The bands at 1608, 1574, 1489 and 1444 cm^{-1} are typical of coordinated and physisorptions species on the Lewis acid sites. The weak band detected at 1641 cm^{-1} characterizes the presence of Brönsted acid sites. Upon outgassing at increasing temperatures, the intensity of

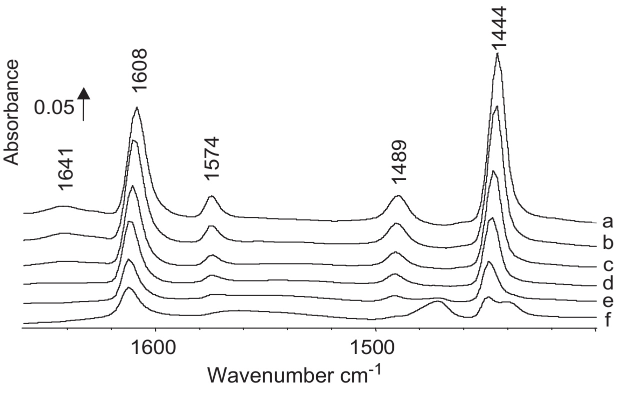

Figure 9 FTIR pyridine adsorption spectra on (5%) V/ZrO_2 followed of an evacuation at: (a) 373 K (b) 423 K, (c) 473 K, (d) 523 K, (e) 573 K and (f) 623 K.

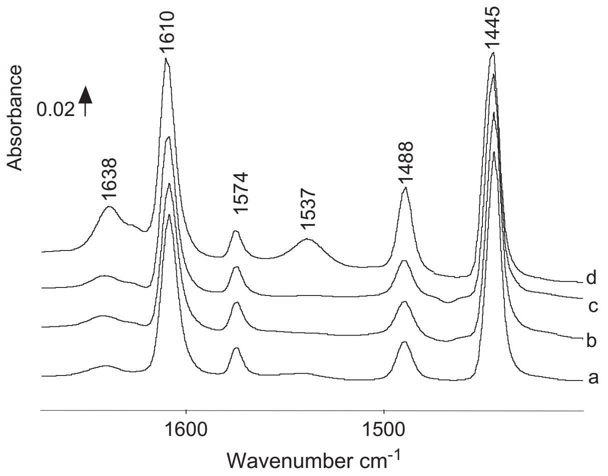

Figure 10 FTIR pyridine adsorption spectra followed of an evacuation at 373K on: (a) (4%) V/ZrO_2, (b) (5%) V/ZrO_2, (c) (6%) V/ZrO_2, (d) (7%) V/ZrO_2.

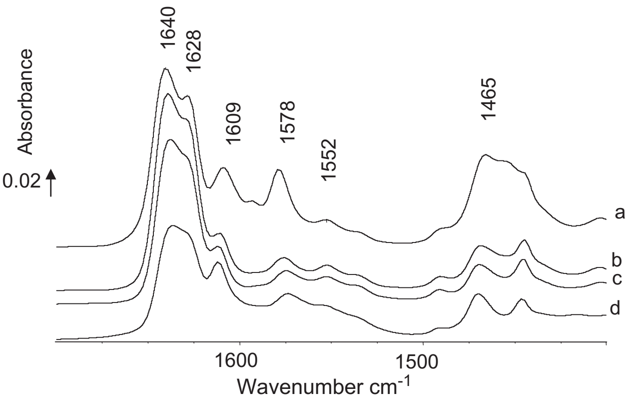

Figure 11 The adsorption of 2,6-DMP followed of an evacuation at (a) r.t, (b) 373 K, (c) 423 K and (d) 473 K on (7%) V_2O_5/ZrO_2 activated at 723 K.

all the bands decreases; which was more pronounced after 523 K.

All the bands reported above are observed in the spectra with variation in vanadium content evacuated at 373 K, which showed that the four samples were rather similar, except in the case of (7%) V_2O_5/ZrO_2 sample, in which a new band appears at 1537 cm^{-1} assigned to Brönsted acid sites (Fig. 10).

In order to confirm the presence of such sites, the adsorption of lutidine, which is more sensitive to weak Brönsted acidity, has been performed.

3.1.3.4. FTIR 2,6-dimethylpyridine adsorption. The 2,6-dimethylpyridine is classically used for the determination of the catalyst acidity. The Lewis acid sites are revealed by the formation of the coordinated species and the acid sites of Brönsted by formation of the lutidinum ions species. It is more specific than pyridine for the Brönsted acid sites.

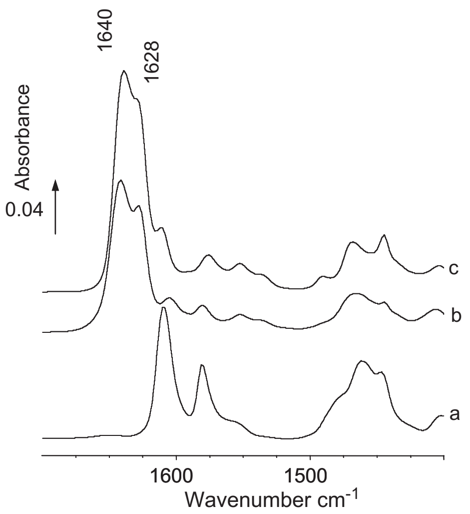

Figure 12 The adsorption of 2,6-DMP followed of an evacuation at 373 K on ZrO_2, (7%) V_2O_5/ZrO_2 and (4%) V_2O_5/ZrO_2 activated under vacuum at 423 K: (a) ZrO_2, (b) (4%) V_2O_5/ZrO_2, (c) (7%) V_2O_5/ZrO_2.

In the range 1700–1400 cm^{-1} (Fig. 11), the spectrum obtained after adsorption of lutidine at room temperature on (7%) V_2O_5/ZrO_2 sample followed by desorption at various temperatures, shows the presence of the bands assigned at 1609, 1578 and 1465 cm^{-1} characterizing Lewis acidity (DMPL) while the bands at 1640, 1552 and 1628 cm^{-1} are characteristic of Brönsted acidity (DMPH+). Upon heating at increasing temperatures, we noted the progressive decrease in the intensity of the bands (DMPH+) and (DMPL). The Lutidine is quasi-desorbed at 473 K.

In Fig. 12, the two bands positioned at 1628 and 1640 cm^{-1} are linked to the lutidine species, and increase along with the an increase in vanadium content. From this result, we can conclude that the addition of vanadium into zirconia gives rise to Brönsted acidity.

The adsorption of 2-6 DMP followed by an evacuation at 423 K on (a) ZrO_2; (b) V_2O_5/ZrO_2 reduced by H_2; and (c)

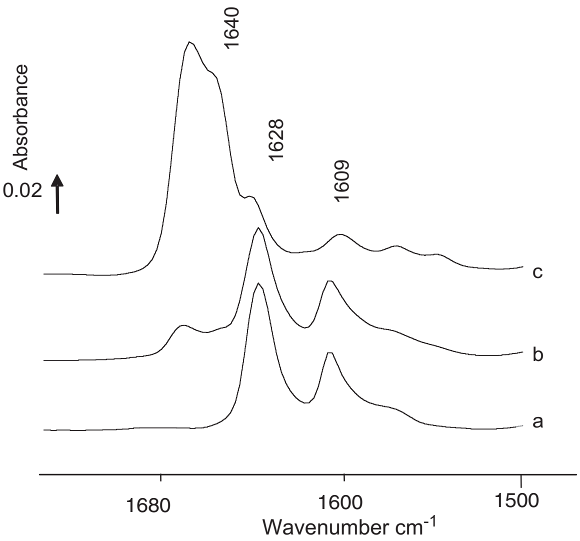

Figure 13 2,6-DMP of adsorption on ZrO_2 and (7%) V_2O_5/ZrO_2 followed an evacuation at 423 K: (a) ZrO_2, (b) V_2O_5/ZrO_2 activated under H_2, (c) V_2O_5/ZrO_2 activated under O_2.

oxidized V_2O_5/ZrO_2 are shown in Fig. 13. It was observed that in the case of pure zirconia and (7%)V_2O_5/ZrO_2 activated under H_2 the presence of a strong band at 1609 cm^{-1}, characterizing Lewis acidity is very weak in the case of oxidized (7%)V_2O_5/ZrO_2. One also notes that for (7%) V_2O_5/ZrO_2 oxidized sample, two strong bands at 1640 and 1628 cm^{-1} attributed to Brönsted acid sites appear which are very weak in the case of the zirconia and activated V_2O_5/ZrO_2 under H_2.

In conclusion, we find that the oxidization of the (7%) V_2O_5/ZrO_2 sample leads to the formation of Brønsted acidic sites, whereas the reduction of the same favours the formation of Lewis acidic sites.

4. Conclusion

FTIR spectroscopy has proven to be a useful tool for the surface characterization of catalyst oxides. Consequently, we find that the reduction by H_2 of V_2O_5 supported on zirconia exhibits two bands. The 1038 cm^{-1} band is attributed to ν(V=O) vibration of V_2O_5 superficial group which is accompanied by the disappearance of the hydroxyl bands located at 3775 and 3670 cm^{-1}, while the 1027 cm^{-1} band, absent in the case of the O_2 treatment, is attributed to the ν(V=O) vibration of reduced V_2O_5 species, (VO_2 or V_2O_3). The adsorption of CO on reduced V_2O_5/ZrO_2 indicates the presence of two different Lewis acidic sites, with the preferential one being detected on reduced vanadium. However the formation of carbonate species explains the strong decline of the linear co-ordinated CO species beyond 200 μmol g^{-1}. On the other hand, on adsorption of CO on oxidized V_2O_5/ZrO_2, we obtain only one band indicating one of the Lewis acid sites co-ordinated to Zr^{4+}. These species (linear and carbonate species) are also obtained on adding CO_2. The results of pyridine probe are confirmed by using lutidine probe, which indicates the presence of Brönsted and Lewis acid sites on different samples V_2O_5/ZrO_2 activated at 723 K.

As compared to pure zirconia, reduced V_2O_5/ZrO_2 favours the Lewis acidity and the desorption of 2,6-DMP at 423 K on samples oxidized by O_2 indicates the existence of a relatively high Brönsted acidity.

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