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Chemisorptive and catalytic properties of V_2O_5 supported on phosphate modified γ -alumina^a

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Abstract

γ -Alumina modified with phosphoric acid is used as a carrier to disperse and stabilise the active vanadia phase. Compared to conventional vanadia/ γ -alumina catalysts, these catalysts showed high V_2O_5 dispersion even at a loading as high as 20 wt.-% V_2O_5 revealed by low-temperature oxygen chemisorption (LTOC) and X-ray diffraction (XRD) data. Ammonia chemisorption at 150°C was used to determine the acidity of vanadia catalysts supported on phosphate modified alumina. Electron spin resonance spectra of the reduced catalysts further confirmed the findings of LTOC and XRD. Ammonia uptake is correlated with the activity for the partial oxidation of methanol and the oxygen chemisorption data with selectivity for formaldehyde. Phosphorus addition in the form of phosphate acts as a promoter causing a beneficial effect in substantially improving the selectivity to formaldehyde.

Keywords: ammonia adsorption; γ -alumina; catalyst characterization (ESR, LTOC, XRD); dispersion; phosphate modified γ -alumina; vanadia.

INTRODUCTION

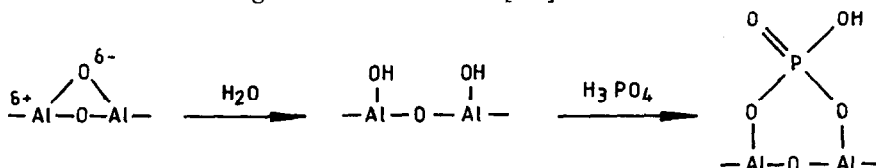
Vanadium oxide catalysts in combination with various supports and promoters are well known for selective oxidation and ammoxidation of hydrocarbons [1,2]. The commonly employed supports are Al_2O_3 , TiO_2 , SiO_2 and ZrO_2 [3-10]. Supports are often found to modify the physicochemical properties of vanadia catalysts. Phosphorus, present as phosphate in the oxidic catalysts, is frequently applied as a secondary promoter. In molybdenum based hydrotreating catalysts, phosphate anion was considered as one of the effective additives [11-18]. Phosphoric acid impregnation is reported to modify the alumina sup-

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port and to have a beneficial effect on its strength and thermal stability. The promotional effect of phosphate anion on the catalytic activity is sometimes explained in terms of improved dispersion of precursor metal salts on the support [19,20]. Phosphate ion is irreversibly adsorbed on alumina and thereby modifies its surface reactivity. It strongly interacts with alumina through a mechanism involving surface basic sites [17].



Although phosphate-modified γ -alumina has been extensively studied as a support for molybdena-based catalysts, such a study on vanadia has not been reported so far. It is, therefore, interesting to study the structure and activity of vanadia on phosphate-modified alumina support. In the present investigation we report the results on the dispersion of vanadia at different loadings on phosphate modified γ -alumina (pma) studied by X-ray diffraction and low-temperature oxygen chemisorption and the acidity of the catalysts by ammonia chemisorption. The activity of the catalysts for the partial oxidation of methanol was studied as a model reaction.

EXPERIMENTAL

A 5 wt.-% phosphate-modified γ -alumina support was prepared by impregnating γ -alumina (Harshaw S.A. 196 m²/g) with requisite amount of 2 wt.-% phosphoric acid (BDH Chemicals, AR grade) in water. The excess solvent (water) was evaporated until the solid was almost dry and the resulting material was dried at 110°C overnight and then calcined at 500°C for 5 h. Catalysts with vanadia loadings ranging from 3 to 20 wt.-% were prepared by impregnating the phosphate-modified support with aqueous solution containing requisite amount of ammonium *meta*-vanadate and then allowed to soak for 14 h followed by evaporation to near dryness on a water bath. The catalysts were further dried and then calcined in air at 500°C for 6 h. The vanadium contents of the samples were determined by inductively coupled plasma analysis (Labtam Instruments, Australia). The calcined catalysts were characterized by X-ray diffraction (XRD), electron spin resonance (ESR), low-temperature oxygen chemisorption (LTOC) and ammonia chemisorption. XRD patterns of the catalysts were recorded on a Philips PW 1051 diffractometer by using Ni filtered Fe K α radiation. ESR spectra were obtained at room temperature on a Bruker ER 200D-SRC X-band spectrometer with 100 kHz modulation. Low-temperature oxygen chemisorption measurements were made on a conventional volumetric high vacuum system, with the facility for reducing

the samples in situ by flowing hydrogen. Details of the set up and chemisorption procedure have been described elsewhere [6]. In a typical experiment about 300 mg of the catalyst was reduced at 500°C in flowing hydrogen (35 cm³ min⁻¹) for 5 h, evacuated for 1 h at the same temperature and then cooled to -78°C under vacuum (10⁻⁶ Torr, 1.33·10⁻⁴ Pa). The first adsorption isotherm representing both irreversibly and reversibly adsorbed oxygen was measured at -78°C. After evacuating the catalyst at 10⁻⁶ Torr for 1 h at -78°C a second isotherm representing only reversibly adsorbed oxygen was generated in an identical manner. The quantity of chemisorbed oxygen was determined as the difference between the two adsorption isotherms. A stoichiometry of one 'O' atom for one "V₂O₄" unit is assumed for LTOC. Recently it has been reported [21] that upon reduction in hydrogen at 500°C, the V₂O₅/γ-Al₂O₃ catalysts showed stable V⁴⁺ state as inferred by gravimetric measurements. After the oxygen chemisorption experiment the BET surface areas of the catalysts were determined by nitrogen adsorption at liquid nitrogen temperature by taking 0.162 nm² as the cross sectional area of N₂. The total acidities of the catalysts were determined from ammonia adsorption at 150°C according to procedure described by Kanta Rao et al. [22]. From preliminary experiments, ammonia chemisorption at 150°C was chosen for adsorption measurements as it was found that at this temperature maximum ammonia uptake was observed. The irreversibly chemisorbed ammonia was calculated from the difference between the first and second adsorption isotherms generated in an identical manner as for LTOC. A microreactor interfaced with a gas chromatograph by a six-way gas sampling valve was used to study the vapour phase oxidation of methanol at 175°C under differential conditions. The feed gas consisted of 72, 24 and 4% by volume of nitrogen, oxygen and methanol vapour, respectively. For each run about 0.25 g of the catalyst was used and the products were analysed with 10% Carbowax 20M column. The major products were formaldehyde and dimethyl ether with some traces of methyl formate, carbon monoxide and carbon dioxide, respectively.

RESULTS AND DISCUSSION

Oxygen chemisorption capacities, active site density and surface coverage values derived from oxygen chemisorption data along with BET surface areas of the reduced catalysts are presented in Table 1. The conversion of methanol and selectivities to formaldehyde and dimethyl ether of various catalysts are also presented in Table 1. The data show that oxygen uptake on the reduced catalysts increases with increase in vanadia loading at all the vanadia loadings (3-20 wt.-%) studied. This is an indication that reducible vanadia species (active sites) are increasing with V₂O₅ loading. Active sites are the vacancies created by removal of labile oxygen atoms (by reduction) that take part in the redox processes upon which the dissociative chemisorption of oxygen takes

TABLE 1

Composition, oxygen uptake, surface coverage, active site density, BET surface area, ammonia chemisorption, methanol conversion and product selectivities of various catalysts

| Catalysts | O ₂ uptake (μ mol/g) | Surface coverage ^a (%) | Active site density ^b (nm ⁻²) | BET S.A. (m ² /g) | NH ₃ uptake (μ mol/g) | Con- version (%) | Selectivity | |
|---|---|---|---|------------------------------------|---|------------------------|-------------|----------------------------------|
| | | | | | | | HCHO | CH ₃ OCH ₃ |
| γ -Alumina | - | - | - | 196 | 27 | 10 | - | 100 |
| Phosphate-modified γ -alumina (pma) | - | - | - | 161 | 41 | 13 | - | 100 |
| 3% V ₂ O ₅ /pma | 44.7 | 8.78 | 0.36 | 151 | 81 | 19.9 | 44 | 54 |
| 9% V ₂ O ₅ /pma | 58.8 | 10.76 | 0.44 | 152 | 107 | 23.9 | 59 | 38 |
| 15% V ₂ O ₅ /pma | 76.9 | 15.13 | 0.62 | 150 | 129 | 27.3 | 73.7 | 24.3 |
| 20% V ₂ O ₅ /pma | 84.7 | 17.93 | 0.73 | 140 | 147 | 30.5 | 83.5 | 14.5 |

^aDefined as $100 \times$ active metal area/BET S.A. of reduced catalyst.

^bEqual to no. of oxygen atoms chemisorbed per unit area of catalyst.

place. The support (unmodified or modified with phosphate) has shown negligible oxygen uptake. However, according to Nag et al. [6] when V₂O₅ was supported on unmodified γ -alumina (BET surface area = 180 m²/g) the oxygen uptake increased with V₂O₅ loading upto 11.9 wt.-% and then decreased with further loading indicating the completion of monolayer coverage of the support surface by vanadium oxide phase. This is a significant effect of the modification of γ -alumina support by phosphate (BET surface area = 161 m²/g) which altered the support surface, enabling vanadia to disperse better even beyond the monolayer loading possible on unmodified alumina. The amount of V₂O₅ necessary to form a monolayer mainly depends on the specific surface area and nature of the support and hence the oxygen uptake capacity [5,6,8,23].

The X-ray diffractograms of γ -alumina, phosphate modified γ -alumina (pma) and V₂O₅/pma catalysts are shown in Fig. 1. The absence of characteristic V₂O₅ peaks at all the vanadia loadings can be taken as the indication of high dispersion of V₂O₅ on pma or otherwise are amorphous in nature. This observation agrees well with earlier published works [6]. An important point to mention here is that no compound formation could be seen between phosphate and vanadia or phosphate and alumina. However, the possibility of formation of AlPO₄ or VOPO₄ or the presence of crystalline V₂O₅ with crystallite sizes smaller than 40 Å, which is beyond the detection capacity of X-ray diffraction method, cannot be ruled out. The XRD data further confirms the results of LTOC of V₂O₅/pma catalysts. It is generally believed that oxygen chemisorbs selectively at low temperature (-78°C) on coordinatively unsaturated sites (CUS) generated upon reduction and having a particular coordination environment. The surface coverage and adsorption site density of the catalysts (Table 1) also show trends similar to oxygen chemisorption with regard to

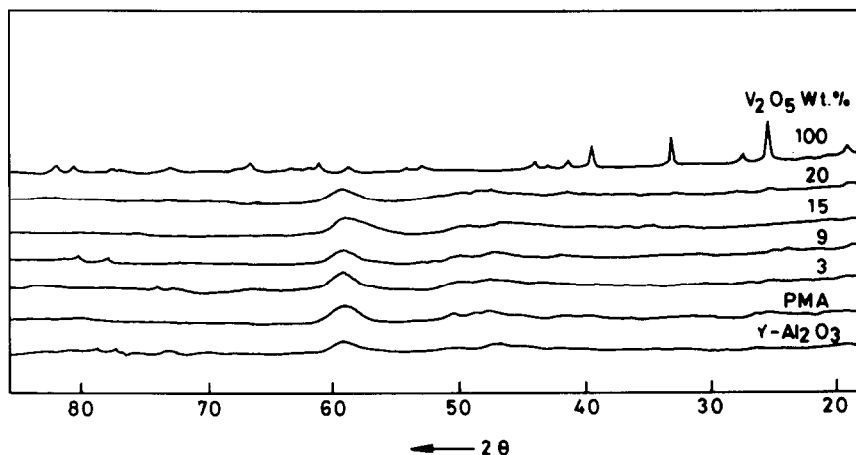


Fig. 1. X-ray diffraction patterns of γ - Al_2O_3 , phosphate modified γ - Al_2O_3 (pma) and V_2O_5 /pma catalysis.

vanadia loadings. This result is expected as the data are derived from oxygen chemisorption capacities.

The ESR spectra of reduced and unreduced V_2O_5 /pma catalysts obtained at room temperature are reported in Fig. 2. Well resolved spectra with hyperfine splitting (hfs) due to ^{51}V ($I=7/2$) could be seen. Unmodified γ -alumina supported V_2O_5 catalysts were reported to show ESR with well resolved hfs at -164°C only [6]. The absence of hfs at room temperature was explained as due to shorter relaxation times arising due to very closely spaced ground and excited states. ESR data of both oxidized and reduced samples obtained at room temperature are given in Table 2. Phosphate modified γ -alumina support did not show any ESR signal. Unmodified vanadia/ γ -alumina catalysts [6] showed well resolved spectra with hyperfine splitting due to ^{51}V ($I=7/2$) only at the lower temperature of -164°C due to shorter relaxation times arising from the closely spaced ground and excited states of paramagnetic ions in axially symmetric octahedral or tetrahedral surroundings. Distortion of these symmetries may lead to longer relaxation times showing the hfs at temperatures as high as room temperature. Thus we can say that V^{4+} in unmodified vanadia alumina catalyst is in undistorted surroundings whereas modification of γ -alumina support with phosphoric acid causes the distortion in C_{4v} symmetry of V^{4+} . This can be seen from hfs of the spectrum even at room temperature. According to Yoshida et al. [24] vanadium oxide is stabilized by interaction with γ -alumina as square pyramids. Van Reijen and Cossee [25] observed that on γ -alumina support V^{4+} remained in vanadyl configuration. Ueda [26] reported the ESR spectra of reduced vanadia catalysts on various supports. According to Ueda the g values and hfs constants of $\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts are as follows: $g_{\parallel}=1.949$, $g_{\perp}=1.998$, $A_{\parallel}=158$ G, $A_{\perp}=63$ G. We obtained the

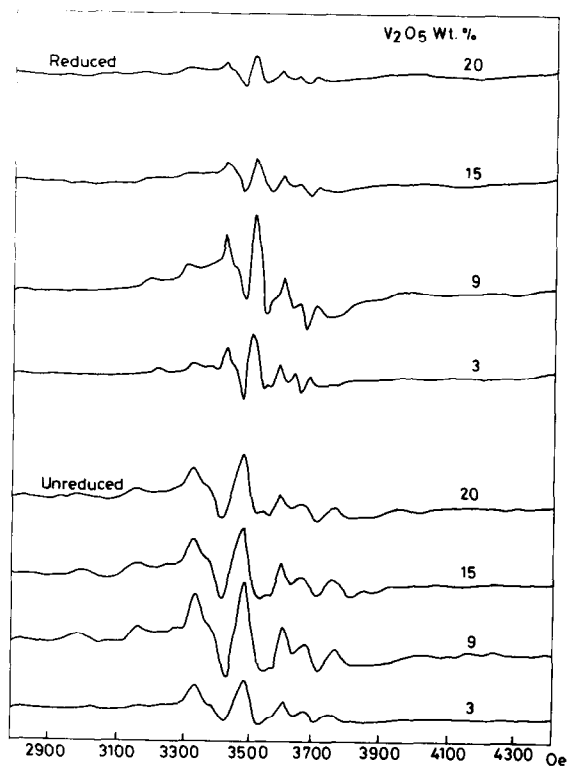


Fig. 2. ESR spectra of reduced and unreduced V₂O₅/pma catalysts recorded at ambient temperature (25°C).

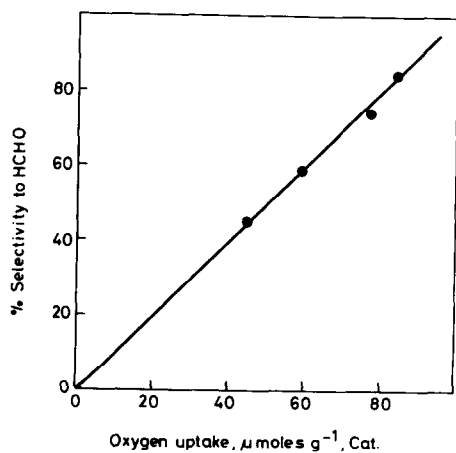


Fig. 3. Selectivity for formaldehyde as a function of oxygen uptake by various V₂O₅/pma catalysts.

following parameters for g and hyperfine coupling constants from ESR spectra (Table 2): $g_{\parallel} = 1.9227$, $g_{\perp} = 2.0029$, $A_{\parallel} = 177.5$, $A_{\perp} = 62.5$. While g_{\parallel} values obtained in the present investigation are smaller than Ueda's, A_{\parallel} values shows an opposite trend. This suggests that V^{4+} centres in V_2O_5/pma catalysts are $(V\text{-----}O)^{2+}$ rather than VO^{2+} [24]. As can be seen from Fig. 2 at lower loadings the spectra are well resolved, indicating greater dispersion of V^{4+} on pma support but at higher loadings they tend to broaden due to possible agglomeration of V^{4+} ions leading to dipolar broadening.

It is seen from Table 1 that ammonia uptake is increasing with increase in vanadia loading. Ammonia adsorption of supported oxides is comparatively higher than the corresponding pure oxides. In other words, with the addition of vanadia the total acidity of mixed oxides increases. This is in agreement with the observation that addition of vanadia increases the acidity of pure oxides [27]. Ammonia gas has been widely employed as a basic adsorbate to count the number and strength of acid sites on various solid surfaces [28,29]. The nature and strength of these acid sites may relate the activity and selectivity character of the catalysts. Ammonia has been selectively used because all acid sites on the catalyst surface are easily accessible for its small molecules (kinetic diam. 0.26 nm) and these molecules also selectively adsorb in the presence of sites of different strengths [30].

A close look at the conversion of methanol and ammonia uptake data shows that ammonia uptake is directly proportional to methanol conversion, indicating that ammonia uptake is a measure of the number of active sites upon which the reaction takes place. This finding supports the observation of Ai [31] that the oxidation of hydrocarbon on heteropoly compounds is derived from a cooperative action of two strong functions: an oxidising function and

TABLE 2

Spin Hamiltonian parameters of V^{4+} in V_2O_5/pma catalysts

| Catalyst composition (wt.-% of V_2O_5 on pma) | g_{\parallel} | g_{\perp} | $ g $ | A_{\parallel} (G) | A_{\perp} (G) | $ A $ (G) |
|--|-----------------|-------------|--------|---------------------|-----------------|-----------|
| <i>A. Reduced</i> | | | | | | |
| 3 | 1.9182 | 2.0041 | 1.9755 | 177.5 | 62.5 | 100.8 |
| 9 | 1.9274 | 2.0015 | 1.9768 | 174.63 | 61.89 | 99.87 |
| 15 | 1.9221 | 2.0026 | 1.9758 | 174.38 | 62.5 | 99.79 |
| 20 | 1.9232 | 2.0035 | 1.9767 | 174.89 | 62.13 | 99.71 |
| <i>B. Unreduced</i> | | | | | | |
| 3 | 1.8763 | 1.9912 | 1.9534 | 183.125 | 59.375 | 100.625 |
| 9 | 1.8763 | 1.9883 | 1.9509 | 183.125 | 59.625 | 100.792 |
| 15 | 1.8725 | 1.9873 | 1.9493 | 181.25 | 59.375 | 100.000 |
| 20 | 1.875 | 1.9886 | 1.9507 | 182.5 | 59.375 | 100.000 |

an acidic function. A direct correlation has also been proposed earlier between acid-base properties of V_2O_5/TiO_2 catalysts and their activity and selectivity to *o*-xylene oxidation to phthalic anhydride [32].

It can be seen from Table 1 that both phosphate modified and unmodified $\gamma-Al_2O_3$ supports show total selectivity to dimethyl ether. Impregnation of vanadia has significantly reduced the dehydration product dimethyl ether, with selectivity to the dehydrogenation product formaldehyde increasing with vanadia loading. While dehydration takes place on Brønsted acid sites of the catalyst surface [33], dehydrogenation is likely to involve the VO_x species acting as an electron acceptor, with the consequent formation of an adsorbed methoxy radical followed by abstraction of a methyl hydrogen by a $V=O$ group and desorption of formaldehyde [34-36].

A linear correlation between selectivity for formaldehyde and oxygen uptake by various V_2O_5/pma catalysts (Fig. 3) further demonstrates that $V=O$ sites which are measured by oxygen chemisorption at $-78^\circ C$ on pre-reduced catalysts are responsible for the selective formation of formaldehyde in the partial oxidation of methanol. Similar observations were made recently on supported vanadia catalysts [37]. It is well established that highly dispersed vanadia phase on various supports is known to show oxidation-reduction cycles according to a Mars and Van Krevelen mechanism [38] of sequential reduction and reoxidation of the catalyst surface under steady-state conditions in oxidation reactions. So, although the catalysts were not pre-reduced before the oxidation reaction commenced, essentially the catalysts are partially reduced during the reaction by reactant. The selectivity to formaldehyde increased from 44% at a V_2O_5 loading of 3 wt.-% to 83.5% at a vanadia loading of 20 wt.-%. This is an indication that dispersed vanadia phase is responsible for the selective conversion to formaldehyde. It is very significant to note that phosphate modification of $\gamma-Al_2O_3$ has increased the formaldehyde selectivity by 3-4 fold upon impregnation with V_2O_5 compared to unmodified $\gamma-Al_2O_3$ supported vanadia catalysts [39].

CONCLUSIONS

γ -Alumina is showing ultra dispersion of V_2O_5 even at fairly high vanadia loadings, when its surface is modified by phosphoric acid impregnation. Compared to γ -alumina supported vanadia catalysts, phosphate modified $\gamma-Al_2O_3$ supported vanadia is showing higher selectivity (ca. 84%) to the dehydrogenation product formaldehyde.

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