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Dispersion and activity of vanadia supported on phosphate modified silica*

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Abstract

Silica was modified by phosphoric acid impregnation and was used as a support in the preparation of supported vanadium oxide catalysts. The prepared catalysts were characterised by low-temperature oxygen chemisorption, X-ray diffraction and electron spin resonance techniques. Activities of the catalysts for the partial oxidation of methanol were also studied. These results suggest a higher dispersion of the active vanadia phase even at highly loaded vanadium oxide on phosphate modified silica compared to conventional V_2O_5 catalysts supported on unmodified silica. Phosphate modified silica supported V_2O_5 catalysts showed a high selectivity towards formaldehyde at a reaction temperature of 175°C. The high HCHO selectivity is in conformity with ESR spectral analysis of these catalysts which showed a stronger V=O bond strength when compared to unmodified SiO_2 supported vanadia catalysts.

Key words: catalyst characterization (ESR, LTOC, XRD); methanol oxidation; phosphate modified silica; vanadia

INTRODUCTION

Phosphorus is a common additive in some of the heterogeneous industrial catalysts for dehydration, dehydrogenation, partial oxidation, etc. Phosphorus present as phosphate is believed to stabilise the impregnating solution resulting in a better dispersion of the active phase and it may even act against sintering [1–3]. In addition to these beneficial effects, an enhanced mechanical strength of the catalyst is also attributed to the addition of phosphate ion. The promotional effect of phosphorus on the catalytic activity is sometimes explained in terms of an improved dispersion of precursor metal salts on the support. Though the influence of phosphorus on the activity of molybdena based catalysts in hydrodesulphurisation and related processes was studied

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extensively [4–7], the same has not been reported so far in the case of vanadia based catalysts.

It is well known that the efficiency of any oxide catalyst depends on the extent of dispersion of the active component on the support surface. Various spectroscopic techniques like electron spin resonance (ESR) [8–12], X-ray photoelectron spectroscopy [13–15], Laser raman spectroscopy [16–18], extended X-ray absorption fine structure [19] have been exploited for characterization of supported vanadia catalysts. Recently low-temperature oxygen chemisorption has been identified as a simple and effective tool in determining the dispersion of vanadia on various supports [20–23]. The acidic functionalities of oxide catalysts have been determined by ammonia chemisorption [24,25] and Fourier transform IR (FT-IR) and Raman spectroscopies of adsorbed ammonia [26].

The present study deals with the dispersion and activity of vanadia catalysts when supported on silica modified by phosphoric acid addition. Silica is first modified with phosphoric acid (phosphorus modified silica, pms) and then a series of V_2O_5 /pms catalysts with various vanadia loadings were prepared. These catalysts were systematically investigated using low-temperature oxygen chemisorption, ammonia chemisorption, X-ray diffraction (XRD) and ESR techniques to obtain some useful information on the surface structure of the catalysts. The activities of the catalysts were also tested in the partial oxidation of methanol to formaldehyde and correlated with their surface characteristics wherever possible.

EXPERIMENTAL

A 10% phosphate modified silica (pms) was prepared by impregnation of silica (Ketjenfine SI-6-5 P; S.A. $597\text{ m}^2/\text{g}$, pore volume $1.22\text{ cm}^3/\text{g}$) with requisite amount of 2 wt.-% phosphoric acid (BDH chemicals AR grade) in water and evaporating the excess water on a water bath. The resulting material was dried in an oven at 110°C overnight and then calcined at 500°C for 5 h. The loaded amount of PO_4^{3-} in the calcined, phosphate modified SiO_2 was determined by gravimetric analysis according to the procedure described by Vogel [27]. The sample was digested in 1:1 hydrochloric acid, the solid part was filtered off and washed with distilled water. The filtrate was neutralized with 1:1 aqueous ammonia to a pH of 8 and then aqueous ammonium heptamolybdate was added to precipitate quantitatively the $(\text{NH}_4)_2[\text{PMo}_{12}\text{O}_{40}]$ complex and allowed to stand for 2 h. After washing with 2% ammonium nitrate solution, the precipitate was dried at 280°C and weighed. The pms calcined at 500°C contained 9.9% of PO_4^{3-} . Thus the PO_4 content in the pms did not change upon calcination at 500°C . Catalysts with different vanadia loadings ranging from 5 to 20 wt.-% were prepared by impregnating the support material with an aqueous solution containing a calculated amount of ammonium

metavanadate. The catalysts were dried at 110°C for 12 h and then calcined in air at 500°C for 6 h. The V_2O_5 contents in the catalysts were estimated by inductively coupled plasma analysis (Labtam Instruments, Australia).

Low-temperature oxygen chemisorption measurements were done on a conventional glass high vacuum unit with the facility to reduce the samples *in-situ* by flowing hydrogen. Chemisorption of oxygen was determined as the difference between two oxygen adsorption isotherms generated at -78°C [20]. Prior to the first isotherm, the catalyst sample was reduced for 5 h at 500°C in flowing purified hydrogen ($35\text{ cm}^3/\text{min}$), degassed for 1 h at 500°C and cooled to -78°C under vacuum (10^{-6} Torr, 1 Torr = 133.3 Pa). Between the first and second isotherms the sample was evacuated for 1 h at -78°C . After the chemisorption experiment the BET surface areas of the catalysts were determined by nitrogen adsorption at -196°C by taking 0.162 cm^2 as the area of cross section of nitrogen.

The total acidities of the catalysts were determined from ammonia adsorption at 150°C as it was found from preliminary experiments that at this temperature a maximum ammonia chemisorption was observed. The same system, having a stationary background vacuum of 10^{-6} Torr and used for oxygen chemisorption, was employed to carry out ammonia chemisorption measurements. In a typical experiment about 0.3 g of the catalyst sample was placed in a glass adsorption cell and evacuated at 150°C (10^{-6} Torr) for 2 h. Prior to ammonia adsorption measurements, the first adsorption isotherm representing both reversible and irreversible ammonia adsorption was generated allowing 20 min equilibrium time at each pressure. Then the catalyst was evacuated at 150°C for 1 h to remove reversibly adsorbed ammonia. After this, a fresh second isotherm representing only the reversibly adsorbed ammonia was generated in an identical manner. From the difference between the first and second adsorption isotherms, the irreversibly chemisorbed ammonia was calculated [28].

X-ray diffraction patterns of the samples were recorded on a Philips PW 1051 diffractometer using Ni filtered $\text{Cu K}\alpha$ radiation. ESR spectra were recorded on a Bruker ER 200 D-SRC X-band spectrometer with 100 kHz modulation at room temperature. The catalyst sample to be studied in reduced condition were placed in a U tube attached with a graded seal which was then connected to a high vacuum system and reduced by a flow of purified hydrogen at 500°C for 5 h, followed by evacuation for 1 h at the same temperature. The sample was cooled slowly to room temperature under vacuum and then detached from the high-vacuum apparatus. The reduced catalyst was then transferred to the graded seal and sealed off under vacuum before recording the ESR signals.

Activity measurements were carried out on a microreactor interfaced by a six way gas sampling valve, with a gas chromatograph, to study the vapour phase partial oxidation of methanol under differential conditions at a reaction

temperature of 175°C. The feed gas consisted of 72, 24 and 4% by volume of N₂, O₂ and CH₃OH vapour, respectively. For each run about 0.25 g of catalyst was used and the products were analysed with a 10% Carbowax 20M column (2 m long) using a flame ionisation detector. The major products observed were formaldehyde and dimethyl ether with some traces of methyl formate, carbon monoxide and carbon dioxide.

RESULTS AND DISCUSSION

Oxygen uptake, surface coverage, active site density (calculated from oxygen uptake), ammonia chemisorption, BET surface areas of the reduced catalysts and activity for partial oxidation of methanol of various catalysts are shown in Table 1. It can be seen from the table that impregnation with phosphoric acid results in a drastic decrease in the surface area of silica, which may be attributed to pore blocking of the support by the phosphate. A similar decrease in surface area was reported when γ -Al₂O₃ was modified by phosphate anion addition [29]. Vanadia loading on the phosphate modified silica further shows a decline in the surface area. Oxygen chemisorption capacities of various catalysts are plotted as a function of vanadia loading in Fig. 1. It shows that oxygen uptake on the reduced catalysts increases as a function of vanadia loading at all the loadings (5–20 wt.-%) studied. However, according to our earlier report [21], when V₂O₅ was supported on unmodified SiO₂ the oxygen uptake increased upto 12 wt.-% V₂O₅ and then decreased with further increase in vanadia loading, indicating the completion of monolayer coverage of the support surface by the vanadium oxide phase at 12 wt.-% loading. Modification of the silica support by phosphate has, thus, significantly altered the support surface enabling vanadia to disperse better, even beyond the monolayer loading that was possible on unmodified silica. Both active site density and surface coverage

TABLE 1

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

Catalysts (wt.-%)	O ₂ uptake (μ mol/g)	% Surface coverage ^a (%)	Active site density ^b (nm ⁻²)	BET S.A. (m ² /g)	Ammonia uptake (μ mol/g)	Methanol conversion (%)	Selectivity (%)	
							HCHO	CH ₃ OCH ₃
SiO ₂	—	—	—	597	—	—	—	—
pms	—	—	—	257	223	0.4	—	100
5% V ₂ O ₅ /pms	43.8	4.99	0.20	260	106	4.9	68.6	30.4
10% V ₂ O ₅ /pms	75.3	9.62	0.39	232	149	10.9	82.2	17.2
15% V ₂ O ₅ /pms	83.8	15.17	0.61	164	189	14.3	90.2	9.0
20% V ₂ O ₅ /pms	97.2	26.53	1.08	108	199	15.1	96.4	3.5

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

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

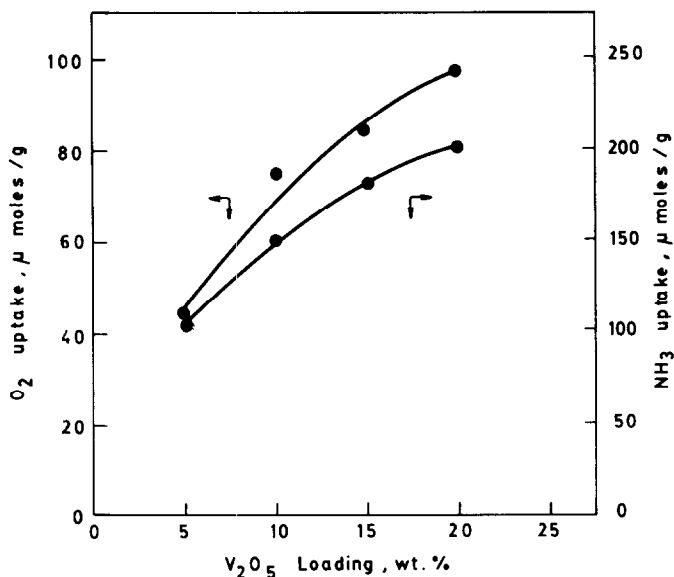


Fig. 1. Oxygen uptake as a function of V_2O_5 loading on phosphate modified silica.

are increasing continuously with vanadia loading. This observation is expected due to the fact that oxygen uptake is increasing with vanadia loading even upto 20 wt.-% (Fig. 1) and that these values are calculated from oxygen chemisorption capacities only. Apparently the monolayer coverage is not complete even at 20 wt.-% V_2O_5 loading on phosphate modified silica. Thus compared to unmodified silica, phosphate modified silica shows higher dispersion of vanadia. Unmodified silica shows monolayer coverage at 12 wt.-% vanadia loading only. The explanation given by us [21] for such a low coverage was the possible failure of the bulky polyvanadate ions in the liquid-phase preparation step to penetrate into the micropores of the support to give a more dispersed phase. Upon phosphoric acid impregnation on silica, the dispersion might have increased due to the possible formation of macroporous amorphous silicon phosphate. However, the possibility of modification of vanadates by the phosphate modified silica surface, resulting in a better dispersion cannot be ruled out.

The X-ray diffractograms of the V_2O_5 supported on phosphate modified silica are shown in Fig. 2. Pure SiO_2 and pms patterns are also shown in the figure for comparison. In the X-ray diffractograms of V_2O_5 /pms catalysts a broad band can be seen at approximately $2\theta = 22$ which is due to the amorphous carrier itself. An important point to mention here is that no compound formation could be seen between phosphate and vanadia. Except on 20 wt.-% V_2O_5 /pms no characteristic XRD peak of V_2O_5 can be seen either which indicates high dispersion of vanadium oxide on the modified support surface. Otherwise, even

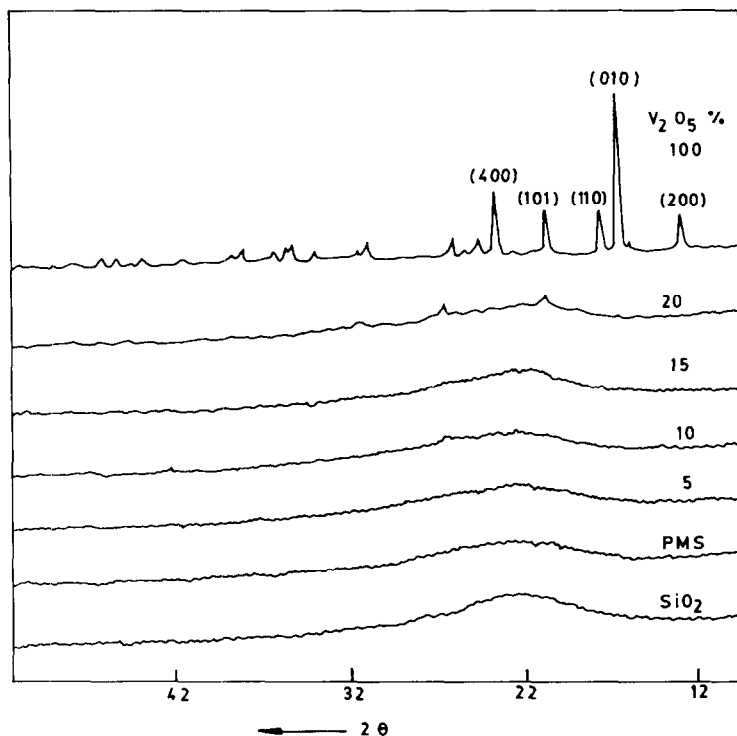


Fig. 2. X-ray diffraction patterns of SiO_2 , phosphate modified SiO_2 (pms) and $\text{V}_2\text{O}_5/\text{pms}$ catalysts.

if the crystallites are formed they are less than 4 nm which are beyond the detection limit of the technique. Even in the catalyst with 20 wt.-% V_2O_5 only small crystalline peaks corresponding to V_2O_5 were observed. These results further confirm the findings of LTOC [10,11,20–23].

The ESR spectra of unreduced and reduced $\text{V}_2\text{O}_5/\text{pms}$ catalysts recorded at ambient temperature are shown in Fig. 3. Unlike the unmodified silica supported vanadia catalysts [10] $\text{V}_2\text{O}_5/\text{pms}$ have shown clear hyperfine splitting due to $^{51}\text{V}^{4+}$ ($I=7/2$, $S=1/2$) even at ambient temperature which may be due to tetragonal distortion in symmetry resulting in larger spin lattice relaxation times. As can be seen from the figure, the spectra of unreduced samples are slightly more intense than those of reduced samples indicating more distortion of symmetry in the former.

The parameters obtained from the spectra of both reduced and unreduced samples are listed in Table 2. The g values and hyperfine coupling constants calculated from spectra are used to estimate the influence of the pms support on the vanadyl bond strength and the electron density around V^{4+} , which is represented by B_2^{*2} , was estimated from a linear combination of parallel and perpendicular components of g and A tensors. Upon reduction, the electron

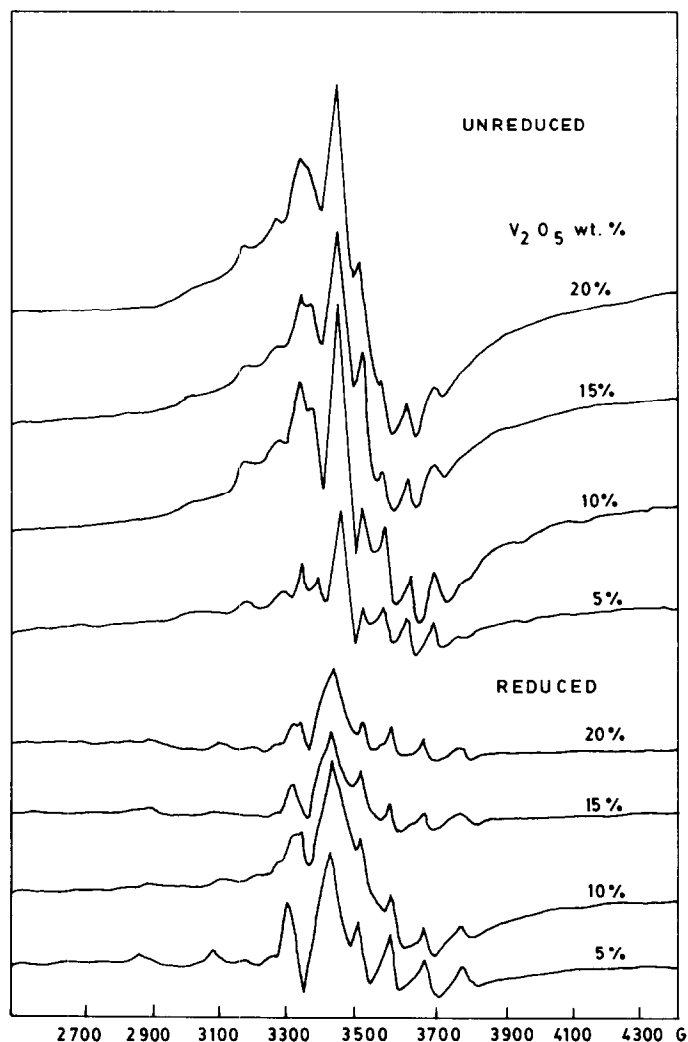


Fig. 3. ESR spectra of unreduced and reduced V_2O_5 /pms catalysts recorded at room temperature (25°C).

density around vanadium is decreased as shown in Table 2, which may be due to delocalisation of electrons on V^{4+} into the ligand orbitals. The parameter B ($\Delta g_{\parallel}/\Delta g_{\perp}$) reflects the extent of tetragonal distortion and on reduction its value increases, indicating the shortening of the $V=O$ bond, or an increase in the distance of the ligands in the basal plane, which in turn results in increasing coulomb attraction of the vanadyl oxygen. The values are high compared to unmodified SiO_2 supported vanadia system [30], which may be due to the effect of phosphate ion addition to silica.

TABLE 2

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

Catalyst composition (wt.-%)	g_{\parallel}	g_{\perp}	$\Delta g_{\parallel}/\Delta g_{\perp}$	A_{\parallel}	A_{\perp}	$B_2^{\star 2}$
<i>A. Unreduced</i>						
5% V_2O_5 /pms	1.916	1.969	2.7	186	64	0.69
10% V_2O_5 /pms	1.908	1.970	2.9	182	62	0.66
15% V_2O_5 /pms	1.908	1.967	2.8	183	62	0.68
20% V_2O_5 /pms	1.913	1.967	2.6	183	62	0.68
<i>B. Reduced</i>						
5% V_2O_5 /pms	1.924	1.979	3.4	176	62	0.64
10% V_2O_5 /pms	1.926	1.980	3.4	173	66	0.61
15% V_2O_5 /pms	1.928	1.980	3.4	174	66	0.62
20% V_2O_5 /pms	1.924	1.981	3.6	174	66	0.62

Ammonia uptake is plotted as a function of vanadia loading in Fig. 1. The surface acidity can be estimated from ammonia chemisorption because the small dimensions of ammonia allow its access to sites which are sterically inaccessible to larger bases like pyridine. Furthermore, ammonia, which is a strong base, can easily adsorb even on weak acidic sites. Dines et al. [26] have shown that ammonia adsorbs on both Brønsted and Lewis acid sites. As can be seen from Fig. 1, ammonia uptake increases with vanadia loading which may be due to an increase in acid sites arising from an increased contribution by supported vanadia species.

The methanol conversion rate is plotted as a function of ammonia uptake in Fig. 4. It can be seen from the figure that the methanol conversion rate directly correlates with ammonia uptake. This indicates that ammonia uptake is a measure of active sites upon which partial oxidation of methanol takes place. This finding supports the observation of Ai [24] that the oxidation of hydrocarbons on heteropoly compounds is derived from a cooperative action of two strong functions, an oxidising function and an acid function. Ammonia chemisorption at 150°C can thus be used to characterise supported vanadia catalysts for initially assessing their relative activity.

It can be seen from Table 1 that activities and selectivity towards formaldehyde increased with oxygen uptake and with V_2O_5 content in the catalysts. In Fig. 5 the selectivity of formaldehyde is plotted as a function of oxygen uptake by various V_2O_5 /pms catalysts. It can be noted from the figure that the selectivity towards formaldehyde is increasing linearly with oxygen uptake which is a function of surface V=O groups. It is well established that a highly dispersed vanadia phase on various supports shows oxidation–reduction cycles according to the Mars and Van Krevelen mechanism [31] of sequential reduc-

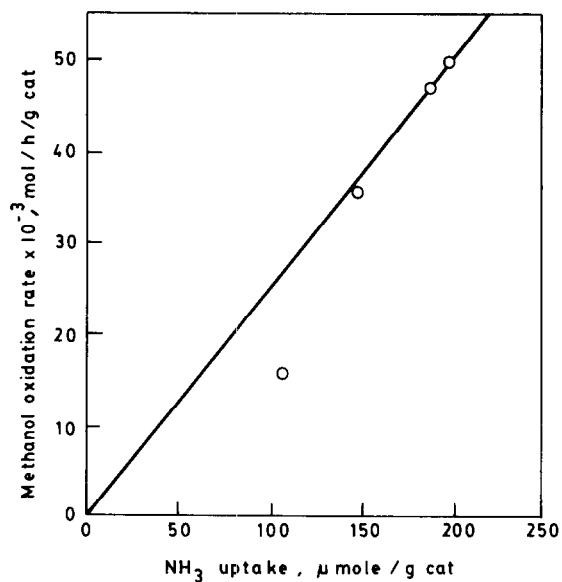


Fig. 4. Rate on methanol partial oxidation as a function of ammonia uptake of V_2O_5 /pms catalysts.

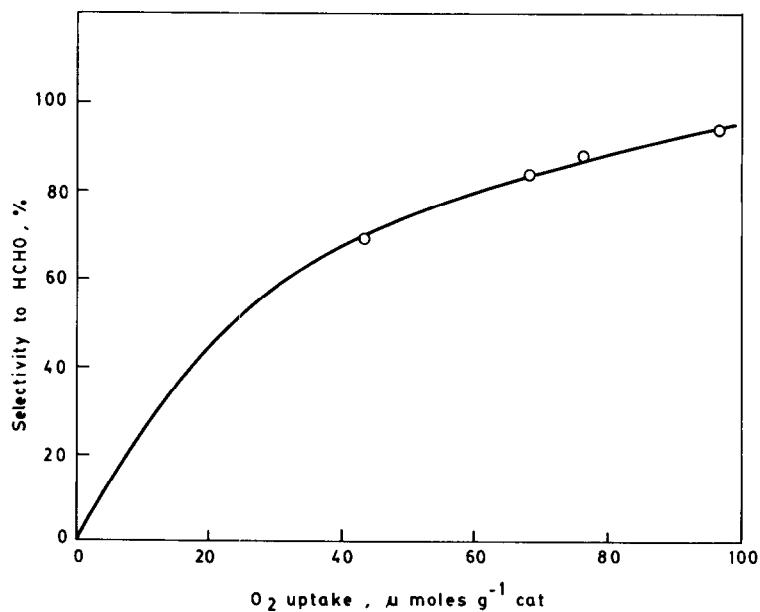


Fig. 5. Selectivity for formaldehyde as a function of oxygen uptake by various V_2O_5 /pms catalysts.

tion and reoxidation of the catalyst's surface under steady-state conditions in oxidation reactions. So although the catalysts were not prerduced before the oxidation reaction commenced, the catalysts are, essentially, partially reduced during the reaction. The selectivity to formaldehyde increased from 68% at a V_2O_5 loading of 5 wt.-% to 96% 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 SiO_2 has increased the formaldehyde selectivity even at a high loading of 20 wt.-% of vanadia in comparison to V_2O_5 catalysts supported on unmodified SiO_2 which showed highest selectivity of 66% at a loading of 6 wt.-% [21]. Supported vanadia catalysts with stronger V=O bond strength have been reported to show higher selectivity towards HCHO in the partial oxidation of methanol [32]. In the present catalysts phosphate modification of silica resulted in increased vanadyl bond strength giving higher formaldehyde selectivity.

CONCLUSIONS

Silica displays a higher dispersion of V_2O_5 even at a fairly high vanadia loading, when its surface is modified by phosphate ion addition, compared to unmodified silica supported vanadia catalysts. Phosphate modified SiO_2 supported vanadia shows higher selectivity (96%) to the dehydrogenation product formaldehyde at a reaction temperature of 175°C in comparison with V_2O_5/SiO_2 catalysts which showed a maximum of 66% selectivity towards formaldehyde at a reaction temperature of 225°C [21]. The methanol conversion rate directly correlates with ammonia uptake at 150°C and formaldehyde selectivity to oxygen uptake at –78°C. Ammonia chemisorption at 150°C titrates the active sites responsible for methanol oxidation on V_2O_5/pms catalysts.

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