

Influence of Metal Oxide Modification of Alumina on the Dispersion and Activity of Vanadia Catalysts

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Alumina was modified with 10 wt % MO_x ($\text{MO}_x = \text{TiO}_2, \text{ZrO}_2, \text{La}_2\text{O}_3, \text{ or } \text{MgO}$) prior to its impregnation with 12 wt % vanadia. The catalysts VTiAl, VZrAl, VLaAl, and VMgAl were characterized by X-ray diffraction (XRD), electron spin resonance (ESR), FT-Raman spectroscopy, ^{51}V solid state nuclear magnetic resonance (^{51}V NMR), and oxygen chemisorption. The activities of the catalysts were determined by methanol partial oxidation and their acid–base properties were evaluated for the decomposition of 2-propanol. XRD and FT-Raman spectroscopy indicated the formation of bulk TiO_2 and ZrO_2 on the titania and zirconia modified alumina. ^{51}V solid state NMR results suggest the presence of both octahedrally and tetrahedrally coordinated vanadia species in the catalysts VTiAl, VZrAl, and VAl and the presence of tetrahedrally coordinated vanadia species in the catalysts VLaAl and VMgAl. ESR spectra recorded at ambient temperature showed the presence of V^{4+} ions having axial symmetry. Oxygen chemisorption results indicated an enhanced number of reducible vanadia sites, i.e., redox sites in the modified catalysts. Metal oxide modification is found to influence significantly the surface coverage and the methanol partial oxidation activity of vanadia supported on alumina. With proper MO_x modification enhanced reducibility of vanadia could be attained, which in turn makes the partial oxidation reaction of methanol more facile.

Introduction

Vanadia supported on high surface area carriers like Al_2O_3 , SiO_2 , etc., has been widely studied for catalyzing a great variety of reactions such as partial oxidation, selective catalytic reduction of NO_x , and oxidative dehydrogenation of light alkanes.^{1–5} The oxides like TiO_2 and ZrO_2 when employed as supports for partial oxidation and hydroprocessing catalysts were found to exhibit enhanced activities and selectivities in comparison with Al_2O_3 supported catalysts.^{2,6} The disadvantages with these carriers are their low surface area, high surface acidity, low volume activity, and phase transition at high temperatures, making them unsuitable for industrial applications. By addition of small quantities of these oxides to relatively high surface area, thermally stable supports such as alumina the aforesaid problems can be obviated. Support modification is said to influence the nature of active sites by way of increasing the reducibility of the transition metal oxide, resulting in enhanced activity and selectivity of the catalysts. The addition of Zn^{2+} and Sn^{2+} was found to increase the dispersion of platinum on alumina.⁷ The acidification of $\gamma\text{-Al}_2\text{O}_3$ with titania resulted in enhanced dispersion of copper.⁸ Jehng and Wachs⁹ have investigated a series of V_2O_5 catalysts supported on TiO_2 modified SiO_2 by employing the in situ Raman spectroscopic technique and the methanol partial oxidation reaction to determine the structure–activity relationships of the catalysts. They observed from these Raman studies the formation of small TiO_x species on the SiO_2 support surface at low titania loadings while at higher TiO_2 concentration they identified bulk TiO_2 particles; vanadia was assumed to be interacting with both of

these species formed on the support surface. They concluded from this study that the presence of bulk TiO_2 particles in the catalyst enhances the methanol partial oxidation activity and HCHO selectivity due to the predominance of redox sites.

Mastikhin et al.^{10,11} have employed ^{51}V and ^1H NMR to characterize $\text{V}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$ catalysts with various titania contents. They showed that there is a nonuniform surface coverage of SiO_2 with TiO_2 and that only a small part of vanadia interacts with TiO_x . They also observed in their ^1H NMR studies that supported vanadia interacts with the terminal Si–OH groups as well as with Ti–OH groups. Similar observations were made earlier by Rajadhyaksha et al.¹² in their studies on titania modified silica supported vanadia catalysts. They suggested the presence of two types of surface vanadates, namely, a polyvanadate species anchored on the silica surface which was uncovered and a second vanadia species interacting with the dispersed titania. According to Reardon and Datye,¹³ the addition of titania to γ -alumina prevents the formation of an inactive $\text{Al}_2(\text{MoO}_4)_3$ phase due to the titration of unwanted hydroxyl groups bound to tetrahedrally coordinated alumina. They also observed that α -alumina supported molybdena is more active than γ -alumina supported MoO_3 because of the more efficient utilization of active phase which was attributed to the absence of tetrahedrally coordinated Al^{3+} at its surface. $\gamma\text{-Al}_2\text{O}_3$ was found to have both octahedral and tetrahedrally coordinated Al^{3+} , and therefore on reaction with molybdena was found to form an inactive $\text{Al}_2(\text{MoO}_4)_3$ phase. Wei et al.¹⁴ also observed increased reducibility of molybdena and higher hydrodesulfurization activity on titania modified $\gamma\text{-Al}_2\text{O}_3$ supported hydroprocessing catalysts. Thus, with the addition of specific molecules or dopants as overlayers on Al_2O_3 with desirable properties such as high surface area and pore structure, one can design more efficient supports in order to achieve high disper-

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TABLE 1: Physicochemical Properties and the Product Distribution during the IPA Decomposition on Vanadia Catalysts

catalyst	bulk anal V ₂ O ₅ /MO _x , wt %	surface area, m ² /g	O ₂ uptake, μmol/g	% surface coverage ^a	active site density ^b (nm ⁻²)	% conv	% selectivity ACE/PROP
VAl	12.3/—	168	56	9.9	0.40	7	100/—
VTiAl	8.9/5.1	122	133	32.3	1.21	23	74/26
VZrAl	10.5/5.7	129	89	20.4	0.83	19	83/17
VLaAl	10.7/6.6	153	58	10.8	0.44	12	98/2
VMgAl	7.9/7.2	115	22	5.7	0.28	4	99/1

^a Surface coverage is defined as 100 × active surface area/BET SA of reduced catalyst. ^b Active site density is the number of "O" atoms chemisorbed per unit area of catalyst.

sion and activity. However, the influence of support modification on the redox and acid–base properties of V₂O₅/Al₂O₃ is not yet thoroughly understood.

The aim of the present investigation is to elucidate the role of modification of the γ-Al₂O₃ support with TiO₂, ZrO₂, La₂O₃, or MgO on the nature and dispersion of vanadia species and methanol partial oxidation activity of vanadia catalysts.

Experimental Section

Four different modified supports, namely, TiAl, ZrAl, LaAl, and MgAl, were prepared by impregnating the γ-Al₂O₃ (Harshaw, Gamma phase, S.A. 196 m²/g) support with 10 wt % each of MO_x (MO_x = TiO₂, ZrO₂, La₂O₃, MgO). The precursors used were Fluka A.R. grade (C₁₂H₂₈O₄)Ti and (C₁₂H₂₈O₄)Zr for TiO₂ and ZrO₂, respectively, and Loba Chemie, A.R. grade Mg(NO₃)₂·6H₂O and La(NO₃)₃·6H₂O for MgO and La₂O₃, respectively. The metalloorganic precursors of titania and zirconia were dissolved in methanol prior to impregnation on Al₂O₃. Lanthanum and magnesium hydroxides were precipitated by ammonia hydrolysis of their aqueous nitrate solutions. The excess solutions were evaporated to dryness on a water bath, and the catalyst masses were further dried in an air oven at 110 °C for 12 h. The modified supports were calcined at 550 °C for 5 h. The amount of metal oxides in the modified supports was determined by inductively coupled plasma (ICP) analysis on a Varian Liberty 100-OES spectrometer after calibrating the instrument with NIST traceable standards. A weighed sample was digested in an acid mixture of nitric acid, sulfuric acid, and perchloric acid until the dissolution was complete, and then the solution was diluted to a specific volume prior to analysis. VMAI catalysts (M = Ti, Zr, La, Mg) were synthesized by impregnation with an aqueous solution containing a calculated amount of NH₄VO₃ (Fluka, A.R. grade), corresponding to 12 wt % V₂O₅ of the modified supports. Drying and calcination procedures were similar to those described above. Following the same procedure, a 12 wt % V₂O₅/Al₂O₃ (VAl) was prepared as a reference. The vanadia contents of the calcined catalysts were estimated by ICP analysis.

XRD patterns were recorded on a Phillips PW 1051 diffractometer using Ni filtered Cu Kα radiation. ESR spectra were recorded on a Bruker ER 200 D SRC X band spectrometer with 100 kHz modulation at ambient temperature. The microwave frequency was 9.71 GHz. Raman spectra were recorded on a Bruker FRA 106 FT-Raman module interfaced to a Bruker IFS-66 FTIR bench. All Raman spectra were recorded at room temperature and under ambient conditions using a 80 mW power setting for the incident radiation at 943.4 nm from a Nd:YAG laser; samples were held in glass vials. Wide-line ⁵¹V NMR spectra were obtained on a Bruker ASX 200 MHz spectrometer, operating at 52.6 MHz for vanadium, equipped with a wide-line probe and a 10 mm insert. A 2 μs pulse was applied following a 2 s relaxation delay; typically 1400 scans were

acquired for these samples. Chemical shifts were referenced to external VOCl₃. An all-glass high-vacuum apparatus with a facility to reduce (at 500 °C, in a flow of H₂) the samples in situ was used to carry out the low-temperature (–78 °C) oxygen chemisorption experiments. The details of the experimental procedure are described elsewhere.¹⁵ BET surface areas of the catalysts were determined by N₂ physisorption using the same equipment.

Activity studies for the partial oxidation of methanol were carried out in the temperature range 175–250 °C, taking 200 mg of the catalyst (0.5 mm size) packed in a fixed bed tubular glass reactor of 6 mm i.d. Purified air at a flow rate of 60 mL/min, saturated with methanol (by passing through a saturator maintained at 25 °C), was introduced into the reactor. The low amount of catalyst and low feed rate were chosen to keep the conversions below 20%. Comparisons of activities and selectivities were made at a reaction temperature of 200 °C, at which both were moderate. After a steady state period of 30 min the products were analyzed on-line with a 10% Carbowax 20M column (2 m long) using a flame ionization detector. The product stream comprised mainly formaldehyde and dimethyl ether, with some traces of methyl formate, CO, and CO₂. Oxidative decomposition of 2-propanol was carried out in the same reactor under similar reaction and analysis conditions at a constant temperature of 175 °C and at atmospheric pressure, using about 200 mg of catalyst. The products observed consisted mainly of propene and acetone with traces of diisopropyl ether.

Results and Discussion

The metal oxide and vanadia contents of the calcined supports and catalysts, BET surface areas, oxygen uptake, active site density and surface coverage values, and product distribution during the IPA decomposition are shown in Table 1. It can be seen that the surface areas of the vanadia catalysts supported on MO_x modified alumina (VMAI) are significantly lower than vanadia on unmodified alumina (VAl), which in turn is lower than the alumina support itself. This observation is expected due to the blockage of pores in the alumina as a result of the addition of the metal oxide as well as the active component. Except in the case of VMgAl, oxygen uptakes of the VMAI catalysts are more when compared to the VAl catalyst, indicating an increase in the number of redox sites. Among the four catalysts, VTiAl shows the highest oxygen uptake, which may be due to a greater number of reducible vanadia sites. Both active site density and the surface coverage are high in VTiAl, indicating that the V₂O₅ is highly dispersed on the TiO₂ modified Al₂O₃ support. Generally, the strength of interaction between the support and the active component governs the dispersion and hence oxygen uptake capacity.¹⁶ The increased oxygen uptakes of VTiAl, VZrAl, and VLaAl catalysts may be due to an increase in the number of labile oxygen atoms on the catalyst surface, in other words an increase in the number of redox sites.

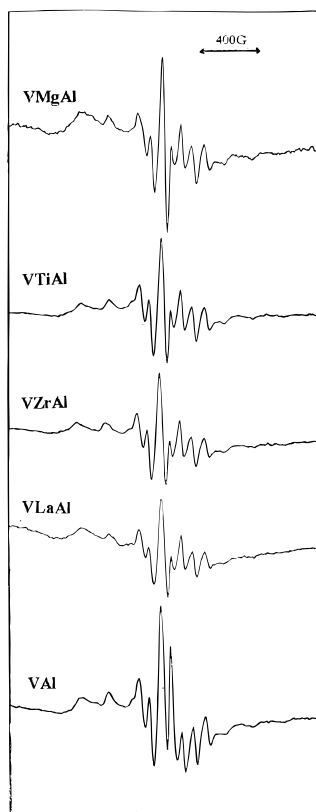


Figure 1. ESR patterns of the VAl and VMAl catalysts recorded at ambient temperature.

Modification of alumina appears to have increased the reducibility of vanadia due to V–O–M bond formation. Similar observations were made by Jehng and Wachs⁹ in their studies on titania modified silica supported vanadia catalysts. They attributed the increased activity of their catalysts to the increased number of redox sites. Another reason for the observed increased activity might be the expected improved dispersion due to a thermal spreading of V precursors after calcination at 550 °C, as reported, for example, by Knözinger and Taglauer.¹⁷

The XRD patterns of the VAl and VMAl catalysts show that there are no lines corresponding to crystalline vanadia in all the catalysts. Vanadia may thus be existing as a highly dispersed amorphous phase. However, the presence of microcrystalline particles with size less than 40 Å cannot be ruled out. The modified supports exhibited the peaks corresponding to their respective oxides with low intensities. The anatase phase of TiO₂ was observed in TiAl, and lines corresponding to tetragonal and monoclinic phases of ZrO₂ were observed in ZrAl. LaAl and MgAl were X-ray amorphous.

ESR spectroscopy is a very sensitive method for detecting the presence of V⁴⁺ environments in vanadia surface species. Hyperfine splitting (hfs) can arise for isolated V⁴⁺ sites because the unpaired electron associated with V⁴⁺ ($S = 1/2$) interacts with the large nuclear magnetic moment of ⁵¹V ($I = 7/2$) to give rise to eight parallel and eight perpendicular components. Several previous investigations^{18–23} showed that such hfs exists for V₂O₅ dispersed on alumina and other supports, with the occurrence of V⁴⁺ sites being effected by reduction methods or simply calcination. Broad signals with unresolved fine structure, as observed for V₂O₅ itself,²⁴ are expected if exchange of the electron can occur with neighboring V⁴⁺ sites, which is the case at higher temperatures and/or higher vanadia concentrations. Figure 1 shows the ESR spectra of the calcined catalysts recorded at ambient temperature. DPPH was used as an external reference. Well-resolved similar spectra, independent of the

TABLE 2: Spin-Hamiltonian Parameters of V⁴⁺ in the VAl and VMAl Catalysts

catalyst	$g_{ }$	g_{\perp}	$A_{ }$	A_{\perp}	A_{iso}	B ($\Delta g_{ }/\Delta g_{\perp}$)	β_2^{*2}
VAl	1.942	1.988	185	67	106	4.2	0.69
VLaAl	1.938	1.987	185	70	108	4.3	0.64
VZrAl	1.936	1.984	185	69	108	4.1	0.66
VTiAl	1.934	1.986	184	66	105	4.1	0.67
VMgAl	1.934	1.988	185	61	102	4.7	0.68

modifier oxide, showing clear hfs of isolated V⁴⁺ sites, were observed. Inomata and co-workers²³ have already indicated that at most only a few percent of reduced vanadium sites are expected for supported vanadia catalysts. Following earlier workers,^{18–23} we attribute the observed spectra to the presence of an axially symmetric ligand field. The derived ESR parameters, $g_{||}$ and g_{\perp} , and hyperfine coupling constants, $A_{||}$ and A_{\perp} , are given in Table 2. The values compare very closely to those reported in the earlier studies^{18–23} for surface vanadia species; usually C_{4v} symmetry arising from either square-pyramidal or axially distorted octahedral geometry has been involved for the V⁴⁺ ion environment. However, the presence of a tetrahedral geometry is not easily distinguished since $g_{\perp} > g_{||}$ and $A_{||} > A_{\perp}$ in all the cases, as Davidson and Che¹⁹ indicate in their tabulation of much literature data, though A_{iso} is smaller (80–100 G) in the tetrahedral case. Some authors have changed their assignment of geometry after reducing the same V₂O₅/Al₂O₃ samples at a lower temperature, though the ESR parameters were virtually identical.^{21,22} In the present catalysts, since the ⁵¹V and Raman data (vide infra) verify that only tetrahedral sites are common to all the species, we deduce that these sites give rise to the observed axially symmetric V⁴⁺ environments. We also measured the ESR spectra after evacuation of the samples at 250 °C in vacuum. Since the patterns remained identical to those observed at ambient temperature, though more intense due to the presence of more V⁴⁺ sites as a result of the reducing conditions, we conclude that the observed V⁴⁺ sites at ambient temperature are not due to hydration of tetrahedral environments. Since the ESR spectra remained virtually invariant as the modifying oxide changed, in contrast to the differences in the observed activities for methanol partial oxidation (vide infra), we also calculated two ESR parameters that relate to the V=O bond strength. Baiker and co-workers¹⁸ showed that B ($\Delta g_{||}/\Delta g_{\perp}$) and β_2^{*2} , which indicates the degree of delocalization, are useful parameters to monitor the effect of different supports on the strength of the V=O bond. Our observed values of B are moderately large, being more comparable to that observed ($B = 5.1$)²⁰ for an evacuated (720 K) VO²⁺/H–ZSM-5 sample than those reported by Baiker et al. for preparations of V₂O₅ on Al₂O₃, SiO₂, and MgO ($B = 2.1, 2.4$, and 1.3 , respectively). Since B decreases with tetragonal distortion of the ligand field symmetry, the estimated B values indicate that the V=O bond remains strong and little changed from that in VAl itself (i.e., without modifying oxides). Though β_2^{*2} parameters for the catalysts signify significant electron delocalization, their constancy again contrasts with the observed appreciable differences in activity as MO_x varies. One possible conclusion is that V⁴⁺ sites only occur in V–O–Al (not V–O–M) sites, whereas catalysis occurs at V–O–M sites.

Raman spectroscopy has been extensively used by researchers to study the coordination structure of supported vanadia catalysts.^{9,25–28} FT-Raman spectra of the various catalysts recorded at ambient temperature are shown in Figure 2. Among the modified supports, TiAl exhibited peaks corresponding to the anatase phase of TiO₂ at 640, 515, 396, 282, 198, and 144 cm^{−1}. The ZrAl, LaAl, and MgAl supports did not show any

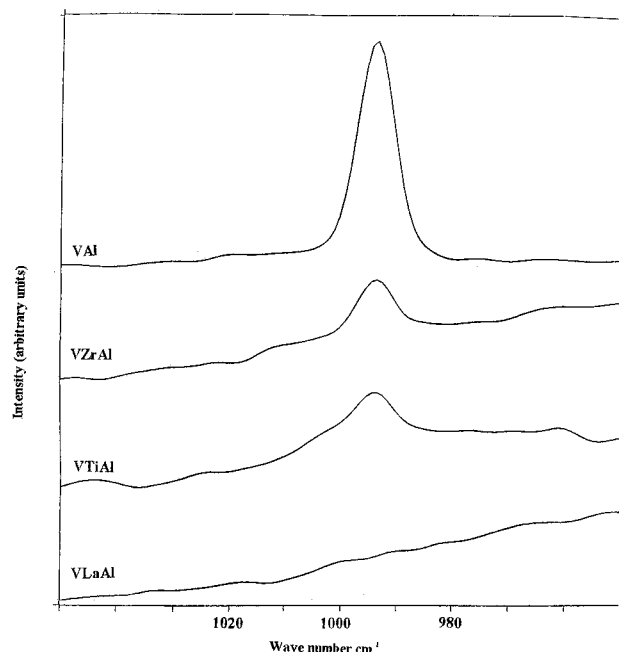


Figure 2. Raman spectra of the catalysts.

peaks. The catalysts VAl, VTiAl, and VZrAl showed a broad peak at $\sim 994\text{ cm}^{-1}$ corresponding to the presence of octahedral polyvanadate species.²⁸ In the case of VMgAl and VLaAl no such peak was present, however a broad band (also evident in VZrAl and VTiAl) was observed at about 900 cm^{-1} corresponding to tetrahedrally coordinated vanadia species in these samples.⁹

Solid state ^{51}V NMR spectroscopy has been demonstrated to be a powerful tool for determining the local vanadium coordination environment on various support surfaces.^{29–33} Major factors influencing the type of supported vanadia surface species are the pH of the impregnating solution, the concentration of supported vanadia, and the treatment temperature. In general, lower vanadia concentration results in broad often multicomponent ^{51}V NMR lines in the -300 to -800 ppm range, assignable to tetrahedral environments. In contrast, higher vanadium concentrations lead to the occurrence of a line with an axial anisotropy of the chemical shift tensor with a major peak near -300 ppm and a minor peak in the -900 to -1300 ppm range; V_2O_5 itself has -280 and -1250 ppm peaks.²⁹ Species showing such ^{51}V peaks can be assigned as having octahedral vanadia sites if $\Delta\delta$ is greater than 600 ppm.^{32,33} Wideline solid state ^{51}V NMR spectra of the catalysts recorded at 25°C are shown in Figure 3. The chemical shifts are tabulated in Table 3. The catalysts VAl, VTiAl, and VZrAl with chemical shifts at -332 , -532 ; -335 , -549 ; and -332 , -564 ppm, respectively, indicate the presence of both tetrahedral and octahedral vanadia species. In the samples VLaAl and VMgAl single peaks at -633 and -577 ppm, respectively, correspond to the presence of only tetrahedrally coordinated polymeric vanadia species on the support surface. In the case of VLaAl the peak is sharper, indicating the presence of vanadium in a more symmetric coordination environment. Formation of polymeric clusters is indicated by an increase in the width of the NMR peaks. The catalyst VAl was evacuated at 10^{-3} Torr for 2 h at 200°C , resulting in broadening of the peak at -532 ppm, which can be explained on the basis of removal of water molecules from the coordination sphere of the surface species.³⁴ ^{51}V and ^1H MAS NMR studies by Lapina et al.¹¹ on titania modified silica supported vanadia catalysts indicated that vanadia interacts with hydroxyl groups on both

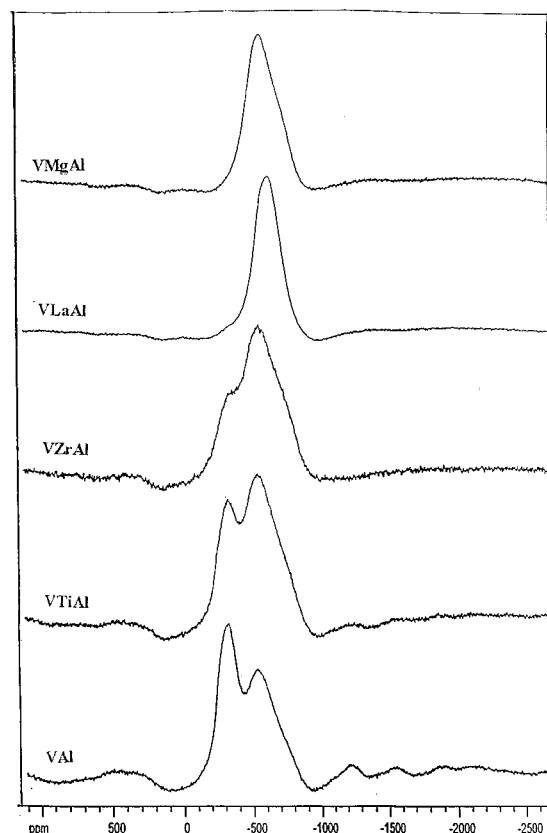


Figure 3. ^{51}V solid state NMR spectra of the catalysts.

TABLE 3: ^{51}V Solid State NMR Wide-Line Chemical Shifts for the Peak Maxima Assigned to Tetrahedrally and Octahedrally Coordinated Vanadia Species for Various Catalysts

catalyst	chemical shift (ppm)	
	tetrahedral	octahedral ^a
VAl	-532	-332
VTiAl	-549	-335
VZrAl	-564	-332
VLaAl	-633	
VMgAl	-577	

^a At higher gain a weak absorption was also observed near -1200 pm.

titania and silica. Therefore, in the present study there is likely an interaction of vanadia with both the modifier and the alumina support, as implied by the ESR and activity data.

The activities of the catalysts were tested with methanol partial oxidation as a model reaction because of its ability to differentiate the nature of surface sites depending on the product formed. The formation of dehydrated product dimethyl ether is a measure of acid sites, whereas formaldehyde and methyl formate formation indicates the presence of redox sites; basic sites can be evaluated by CO and CO_2 formation. The conversions and selectivities toward formaldehyde and dimethyl ether of the various catalysts in the partial oxidation of methanol (compared at a reaction temperature of 200°C) are plotted in Figure 4. The activities of these VMAI catalysts are in the order $\text{VTiAl} > \text{VZrAl} > \text{VLaAl} > \text{VMgAl}$. The O_2 uptakes of the catalysts also varied in a similar manner, indicating that the active sites titrated by oxygen molecules are responsible for the observed activities of the catalysts. Active sites are the vacancies created by removal of labile oxygen atoms (by reduction) upon which the dissociative chemisorption of oxygen takes place. Selectivity toward the dehydrogenation product,

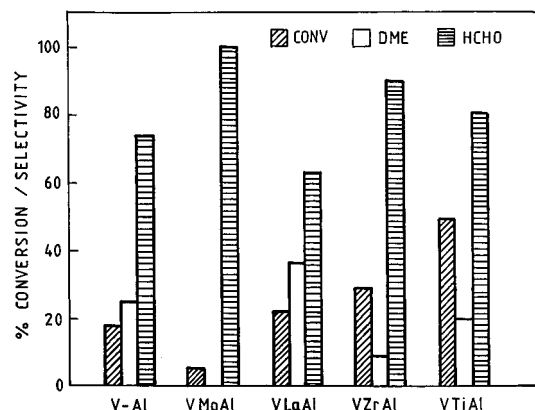


Figure 4. Methanol partial oxidation activity and selectivities on VAl and VMAl catalysts. Comparative results are shown at reaction conditions of 200 °C, with conversions being less than 20%.

HCHO, has been improved over the VAl catalyst in all the modified catalysts.

Deo and Wachs [2] in their investigation on partial oxidation activity on supported vanadia catalysts have reported that, instead of the weakening of the V=O bond, it is the weakening of the vanadium–oxygen–support bridging bond that is responsible for greater activity. Our results indicate that the increased oxygen uptake capacities of vanadia on TiO₂, ZrO₂, and La₂O₃ modified alumina catalysts may also be a consequence of a larger number of active sites being created by the formation of weaker V–O–M bonds, which are involved in the partial oxidation of methanol rather than the V–O–Al bonds. In contrast, interaction of V₂O₅ with MgO is expected to be stronger compared to the oxide support interaction in the cases of VAl and the other VMAl catalysts, which leads to reduced oxygen uptake and hence the lower partial oxidation activity of the VMgAl catalyst.

Supported vanadia catalysts exhibit bifunctional character since they possess both acid–base and redox sites. The influence of MO_x modification on the acid–base properties of the catalysts has been examined by the 2-propanol decomposition reaction. The results are incorporated in Table 1. Relatively higher decomposition rates have been obtained on VTiAl, VZrAl, and VLaAl compared to the VAl catalyst, but when compared to VAl, the acetone selectivities of the above three catalysts decreased by 15–25%. However, the sustained predominance of selectivity to acetone over selectivity to propylene indicates that in these catalysts the redox property is more dominant than their acid–base character. However, in the case of VMgAl, the lower decomposition activity associated with maximum dehydrogenation selectivity could be mainly due to the generation of acid–base paired sites which act in a concerted manner as proposed by Bond et al.³⁵ Low oxygen uptake, a consequence of low reducibility, further supports this observation for the VMgAl catalyst.

Conclusions

ESR, FT-Raman, and ⁵¹V NMR spectroscopic data are consistent in indicating the formation of tetrahedrally coordinated vanadia species in VLaAl and VMgAl catalysts and the presence of both tetrahedrally and octahedrally coordinated

polymeric vanadia species in VTiAl, VZrAl, and VAl catalysts. The methanol conversion/selectivity results show that VTiAl gave the greatest activity. Therefore, by choosing a suitable MO_x for the modification of γ -alumina, the desired redox property could be achieved which enhances the partial oxidation activity of the vanadia catalyst. The 2-propanol decomposition study indicates that redox reactivity dominates over the acid–base properties of these catalysts.

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