

INFLUENCE OF METAL OXIDE MODIFICATION OF ALUMINA ON THE DISPERSION AND ACTIVITY OF VANADIA CATALYSTS

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Alumina was modified with 10% MO_x ($MO_x = TiO_2, ZrO_2, La_2O_3$ or MgO) prior to its impregnation with 12 wt% vanadia. The catalysts were characterised by x-ray diffraction (XRD), electron spin resonance (ESR) 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 isopropanol. 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 more facile.

Keywords: modified alumina, vanadia, partial oxidation

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 adding small quantities of these oxides to relatively high surface area, thermally stable supports such as alumina the aforesaid problems can be obviated. Recently there are reports in the literature [7-11] on the support modification with additives like alkali/alkaline earth metals, halides, rare earth oxides, phosphates and sulphates, which enhance the acidic or basic character or impart thermal stability to the carrier. Shen et al. [7,8] in their investigations on Al_2O_3 support modification with additives such as K_2O , MgO , La_2O_3 , SnO_2 etc. have observed that these oxides influence the number and nature of acid sites on alumina support surface. Wei et al. [12] have observed increased reducibility of molybdena and higher hydrodesulphurisation activity on titania modified $\gamma-Al_2O_3$ supported hydroprocessing catalysts. 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. However, the influence of support modification on the redox and acid-base properties of V_2O_5/Al_2O_3 is not yet thoroughly understood.

The aim of the present investigation is to elucidate the role of modification of the Al_2O_3 support with TiO_2 , ZrO_2 , La_2O_3 or MgO on the dispersion and methanol partial oxidation activity of vanadia catalysts.

EXPERIMENTAL

Four different modified supports, namely, $TiAl$, $ZrAl$, $LaAl$ and $MgAl$ were prepared by impregnating the $\gamma-Al_2O_3$ (Harshaw, Gamma phase, S.A. 196 m²/g) support with 10 wt. % each of MO_x , ($MO_x = TiO_2, ZrO_2, La_2O_3, MgO$). The precursors used were Fluka A.R. grade $(C_{12}H_{28}O_4)Ti$ and $(C_{12}H_{28}O_4)Zr$ for TiO_2 and ZrO_2 respectively; and Loba Chemie, A.R. grade $Mg(NO_3)_2$, $6H_2O$ and $La(NO_3)_3$, $6H_2O$ for MgO and La_2O_3 , respectively. The organometallic precursors of titania and zirconia were dissolved in methanol prior to impregnation on Al_2O_3 . 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. VMA1 catalysts ($M = Ti, Zr, La, Mg$) were synthesized by

impregnation of aqueous solution containing a calculated amount of NH_4VO_3 (Fluka, A.R. grade), corresponding to 12 wt.% V_2O_5 , on modified supports. Drying and calcination procedures were similar to those described above. Following the same procedure a 12 wt.% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3(\text{VAI})$ was prepared as a reference.

XRD patterns were recorded on a Phillips PW 1051 diffractometer using Ni filtered CuK_α radiation. ESR spectra were recorded on a Bruker ER 200 D SRC X band spectrometer with 100 KHz modulation at ambient temperature. An all-glass high vacuum apparatus with a facility to reduce (at 500°C , in a flow of H_2) 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 [10]. BET surface area of the catalysts were determined by N_2 physisorption.

Activity studies for the partial oxidation of methanol were carried out in the temperature range $175\text{--}250^\circ\text{C}$ 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. After a steady-state period of 30 min the products were analyzed on-line with a 10% Carbowax 20 M column (2 m long) using a flame ionization detector. The product stream comprised mainly formaldehyde, dimethyl ether with some traces of methyl formate, CO and CO_2 . Oxidative decomposition of isopropanol 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

BET surface area, oxygen uptake, active site density and surface coverage values 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 (VAI), 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. Oxygen uptakes of the VMAI catalysts are more when compared to the VAI catalyst except in the case of VMgAl. Among the four catalysts VTiAl is showing 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 V_2O_5 is highly dispersed on the TiO_2 modified Al_2O_3 support. Generally the strength of interaction between the support and the active component governs the dispersion and hence oxygen uptake capacity [13]. The increased oxygen uptakes of VTiAl, VZrAl and VLaAl catalysts may be due to reduced strength of metal oxide-support interaction. Modification of alumina might have caused a decrease in interaction between the support and active phase enabling increased reducibility of V_2O_5 . Similar observations were made by Wei et al. in molybdena based hydroprocessing catalysts supported on TiO_2 modified Al_2O_3 [12].

The XRD patterns of the VAI and VMAI catalysts show that there are no lines corresponding to crystalline vanadia in all the catalysts. Vanadia may be existing as a highly dispersed 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 TiO_2 was observed in TiAl and lines corresponding to tetragonal and monoclinic phases of ZrO_2 were observed in ZrAl. LaAl and MgAl were x-ray amorphous.

Fig. 1 shows the ESR spectra of various catalysts recorded at ambient temperature. Clear hyperfine splitting (hfs) corresponding to V^{4+} can be seen in VTiAl and VZrAl indicating the isolation of vanadia species on the surface of the support. This is a significant observation since the hfs of vanadia species vanadia supported on unmodified Al_2O_3 has been reported to be recorded only at liquid nitrogen temperature [14]. The observance of hyperfine interaction only at -196°C implies that it is destroyed by spin-spin interaction at higher temperatures between neighboring V^{4+} ions. The resolution of peaks is not so discrete in the cases of VLaAl and VMgAl indicating possible agglomeration of V^{4+} ions leading to dipolar broadening.

The conversions and selectivities towards formaldehyde and dimethylether on various catalysts in partial oxidation of methanol (carried out at a reaction temperature of 200°C) are plotted in Fig. 2. The activities of 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 towards the dehydrogenation product, HCHO, has been improved over the VAl catalyst.

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 the activity. Our results indicate that the increased oxygen uptake capacities of vanadia on TiO₂, ZrO₂ and La₂O₃ modified alumina catalysts are a consequence of reduced strength of metal-support interaction. Interaction of V₂O₅ with MgO appears 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 partial oxidation activity.

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 have been examined by the isopropanol decomposition reaction. The results are incorporated in Table 1. Relatively higher decomposition rates have been obtained on VTiAl, VZrAl and VLaAl compared to VAl catalyst. But, when compared to VAl, the acetone selectivities of the above three catalysts have 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. [15]. Low oxygen uptake, a consequence of low reducibility, further supports this observation.

Hence, it may be concluded that 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.

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Table 1: Physico-chemical properties and the product distribution during the IPA decomposition on vanadia catalysts.

Catalyst	Surface area (m ² /g)	O ₂ uptake uptake (μmol/g)	Surface coverage (%)	Active site density (nm ⁻²)	IPA conv. (%)	Acetone sel. (%)	Propylene sel. (%)
1. VAl	168	56	9.9	0.40	7	100	--
2. VTiAl	122	133	32.3	1.21	23	74	26
3. VZrAl	129	89	20.4	0.83	19	83	17
4. VLaAl	153	58	10.8	0.44	12	98	2
5. VMgAl	115	22	5.7	0.28	4	99	1

¹ Surface coverage is defined as 100x active surface area/BET SA of reduced catalyst.

² Active site density is the number of 'O' atoms chemisorbed per unit area of catalyst.

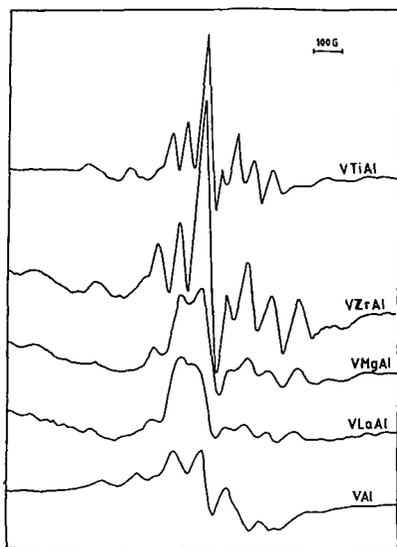


Figure 1. ESR patterns of the VAl and VMAl catalysts.

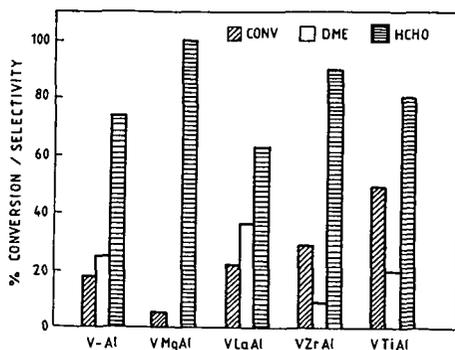


Figure 2. Methanol partial oxidation activity and selectivities on VAl and VMAl catalysts.