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Effect of preparation method on the dispersion and activity of V_2O_5–Al_2O_3 catalysts

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Al_2O_3-supported 12 wt% V_2O_5 catalysts were prepared by physically grinding both the oxides (solid–solid wetting) and by wet impregnation techniques. The physical mixtures (PM) were treated under two different conditions – calcination in the presence of dry oxygen and wet oxygen. The catalysts were characterized by x-ray diffraction, scanning electron microscopy, electron spin resonance and oxygen and carbon dioxide chemisorptions. Vanadia dispersion of the physical mixture calcined in the presence of wet oxygen was found to be very similar to that of the V_2O_5/Al_2O_3 catalyst prepared by the standard impregnation method. Methanol partial oxidation activities of these catalysts were also comparable.

1. Introduction

V_2O_5 supported on Al_2O_3 has received much attention as a catalyst for selective oxidation, ammoxidation of hydrocarbons and for catalytic reduction of NO_x by ammonia [1–4]. The active phase–support interaction is mostly regarded as a prerequisite for catalyst reactivity. V_2O_5/Al_2O_3 catalysts are normally prepared by impregnation of the alumina support with an aqueous solution containing ammonium metavanadate, followed by drying and calcination steps. Preparation of the catalysts by this method results into two types of vanadyl species on the alumina surface, namely, the monomeric and polymeric forms. The nature of vanadia species formed on the support surface depends on the method of preparation, pH, drying and calcination conditions, etc.

Preparation of supported metal oxide catalysts by solid–solid wetting has been receiving considerable attention in recent years. In the case of alumina-supported molybdena catalyst, solid–solid wetting is reported to result in spontaneous spreading of the active species on the support [5–13]. Calcination in wet oxygen has resulted in the formation of polymeric molybdena species, whereas in dry oxygen the formation of agglomerates of MoO_3 are reported [5–13]. Similar studies have also been made on supported vanadia catalysts [4–18]. Hausinger *et al.* [14] reported that calcination in wet oxygen increases the mobility of the active species due to enhanced surface hydroxylation of TiO_2 when compared to that in dry conditions. Increased mobility leads to a higher degree of spreading and a corresponding decrease in the crystallinity of V_2O_5.

Sobalik *et al.* [15], in their ^1H and ^{51}V nuclear magnetic resonance (NMR) studies on alumina- and titania-supported vanadia catalysts prepared by ultra-high intensity grinding (UHIG), have shown that UHIG causes significant V_2O_5–support interaction changing the vanadium (V) environment. However, a simple method, such as gas adsorption, has not been reported to correlate the adsorption uptakes with the structure and reactivity of the V_2O_5/Al_2O_3 catalyst.

The objective of this work was to study the active oxide–support interaction by oxygen and carbon dioxide chemisorptions, as well as X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron spin resonance (ESR). The catalytic activity of the catalysts for methanol partial oxidation has been correlated with their physical characteristics.

2. Experimental procedure

2.1. Preparation

The materials used were γ-Al_2O_3 (Harshaw Al-111-61E; crushed to 200 mesh, BET surface area 204 $m^2\,g^{-1}$, precalcined at 500 °C for 12 h before use), V_2O_5 and ammonium metavanadate (both from Fluka). A 12 wt% V_2O_5 loading on γ-Al_2O_3 was chosen to prepare the catalysts using different preparation methods because this loading represents monolayer loading [19]. The physical mixtures (PM) catalyst of V_2O_5 and Al_2O_3 was prepared by first tumbling and then grinding the powders in an agate mortar for 30 min in order to obtain as homogenous a mixture as possible. To prepare the catalyst in the presence of dry oxygen (PMD), a portion of the PM catalyst was first heated in dry nitrogen at a rate of

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$10\,^{\circ}C\,min^{-1}$ to a temperature of 500 °C. Nitrogen was then replaced with oxygen flowing at a rate of $30\,ml\,min^{-1}$ and the process continued for 4 h, at the end of which the sample was again cooled in nitrogen to room temperature. To prepare the catalyst in wet oxygen (PMW), a similar heat treatment was given to another portion of the PM catalyst under wet oxygen conditions. For this purpose, a bubble flow saturator, filled with water maintained at ambient temperature, was used to generate water vapour. The catalyst obtained by the wet impregnation techniques (IMPR) was prepared by the standard wet impregnation method using aqueous ammonium metavanadate. The impregnated material was dried at 100 °C for 16 h and calcined at 500 °C for 12 h in an air circulation furnace. The V_2O_5 contents of the finished catalysts were determined by using an inductively coupled plasma (ICP) analyser (Labtam Instruments, Australia) which indicated no appreciable loss of V_2O_5 during the preparation and pretreatment of the catalysts, and the overall V_2O_5 loading was within the range of ± 0.05% variation.

2.2. Characterization

XRD patterns were recorded on a Philips PW-1051 instrument using nickel-filtered CuK_{α} radiation. The ESR spectra of the unreduced and reduced catalysts were recorded on a Bruker ER 200D-SRC X-band spectrometer with 100 kHz modulation at ambient temperature. The details of the experimental procedure followed were reported in an earlier paper [20]. Diphenyl picryl hydrazine (DPPH) was used for calibration. SEM studies were made on a Hitachi model S-520 microscope at an applied voltage of 10 kV. For this purpose, the catalyst samples were mounted on aluminium stubs and were gold-coated in a Hitachi HUS-5GB vacuum evaporator.

Carbon dioxide chemisorption uptakes of the catalysts at ambient temperature were measured in an all-glass high-vacuum system having a stationary background vacuum of 10^{-6} torr (1 torr = 133 Pa). In a typical experiment, about 0.5 g catalyst was evacuated to 10^{-6} torr for 2 h before CO_2 was adsorbed at increasing vapour pressure in the range 0–30 mm Hg.

After degassing for 2 h, a second adsorption isotherm was generated in an identical way. The carbon dioxide uptake was taken as the difference between the two parallel portions of the isotherms. The same vacuum apparatus, with an added facility to reduce the samples *in situ*, was used to carry out the low-temperature oxygen chemisorption experiments. The oxygen uptakes at − 78 °C were determined according to the procedure of Parekh and Weller [21] following the double isotherm method, as described earlier. Prior to the first isotherm, the catalyst sample (200 mg) was reduced for 3 h at 500 °C in a flowing purified hydrogen ($40\,cm^3\,min^{-1}$), degassed for 1 h at the reduction temperature and then cooled under vacuum (10^{-6}) to the temperature of adsorption. Between the first and second adsorption isotherms the sample was evacuated for 1 h at − 78 °C. BET surface areas were measured for all samples by adsorption of nitrogen at − 196 °C assuming $0.162\,nm^2$ as the area of cross-section of the nitrogen molecule.

2.3. Activity studies

Methanol partial oxidation reaction was carried out at 225 °C in a continuous flow isothermal microreactor, interfaced with a gas chromatographic unit through a six-way gas sampling valve. 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 catalyst was used and the reaction effluents were analysed by using a 10% carbowax 20M column (2 m long). The major products observed were dimethyl ether (DME) and formaldehyde (HCHO) along with some traces of methyl formate, carbon monoxide and carbon dioxide.

3. Results and discussion

XRD patterns of all the four V_2O_5/Al_2O_3 catalysts are shown in Fig. 1. In the case of the PM catalyst, sharp diffraction lines due to well crystallized orthorhombic V_2O_5 phase (JCPDS card 9–387) can be seen. A decrease in intensity of peaks due to the crystalline V_2O_5 phase can be noted in the case of PMD catalyst. Very weak diffraction lines due to the crystalline V_2O_5 phase could be seen in PMW catalyst. No crystallinity due to vanadia was seen in the IMPR catalyst. The background pattern of the γ-Al_2O_3 phase (JCPDS card 29–1486) is featured in all the catalysts. These observations show that the V_2O_5 dispersion is in the order IMPR = PMW > PMD > PM catalysts, which explains the phenomenon that the physical mixtures lose their crystallinity during heat treatment (calcination) in both dry and moist atmospheres [14]. No compound formation could be seen between vanadia and alumina.

Fig. 2 shows microphotographs of alumina, bulk V_2O_5 and of PM, PMD, PMW and IMPR samples. The porous nature of Al_2O_3 can be clearly seen. Bulk V_2O_5 appears as crystalline particles. Cleaved particles of crystalline vanadia can be observed in the PM catalyst. Calcination of PM in dry oxygen giving the PMD catalyst, resulted in the formation of fine needles of V_2O_5. In PMW and IMPR samples, vanadia was well spread on the support surface. Similar observations were made by del Arco *et al.* [12] in SEM characterization of molybdena catalysts. Those authors observed aggregates of MoO_3 at higher loadings and dispersed molybdena phase at lower loadings.

Figs 3 and 4 show the ESR spectra of the calcined (except the PM catalyst) and reduced V_2O_5/Al_2O_3 catalysts respectively, recorded at ambient temperature (25 °C). Clear hyperfine splitting (h.f.s.) patterns corresponding to $^{51}V^{+4}(I = 7/2,\ S = 1/2)$, could be seen in the PM sample which is contrary to the usual absence of h.f.s. in bulk vanadia. However, h.f.s. in the PM sample may be due to physical dispersion of V_2O_5 over the surface of Al_2O_3 [14] which can be attributed to strong mechanical forces experienced by

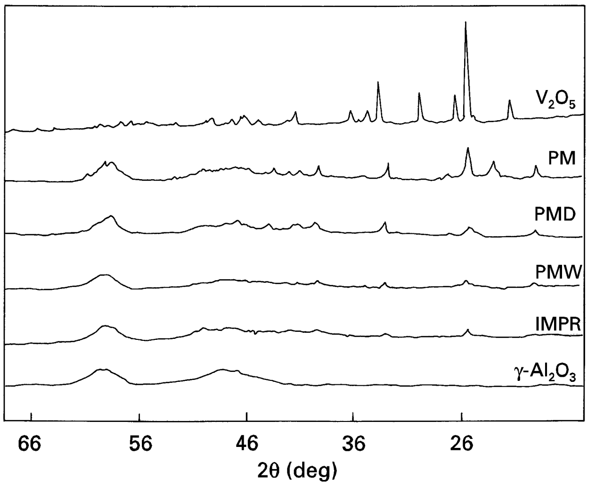

Figure 1 X-ray diffraction patterns of V_2O_5/Al_2O_3 catalysts.

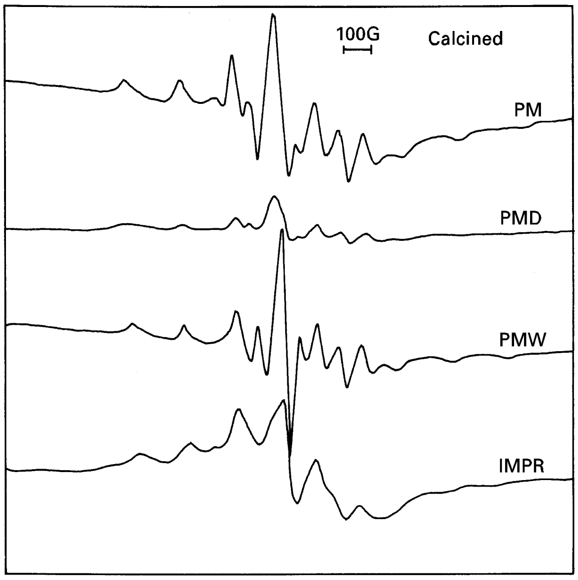

Figure 3 Electron spin resonance spectra of fresh V_2O_5/Al_2O_3 catalysts.

V_2O_5 crystallities during grinding. The broadening of the spectra in the PMD sample may be due to spin–spin interaction between adjacent V^{4+} ions indicating the presence of agglomerates of V_2O_5. Observation of well-resolved spectra in both oxidized and reduced conditions in PMW samples indicates the stabilization of a small fraction of V_2O_5 on the Al_2O_3 surface as V^{4+}. On the other hand, broadening of the spectra in the IMPR sample is due to short spin lattice relaxation times arising from the presence of V^{4+} in the undistorted environment of oxygen atoms.

Carbon dioxide uptake, BET surface area and apparent surface coverage derived from carbon dioxide chemisorption for various V_2O_5/Al_2O_3 catalysts, are

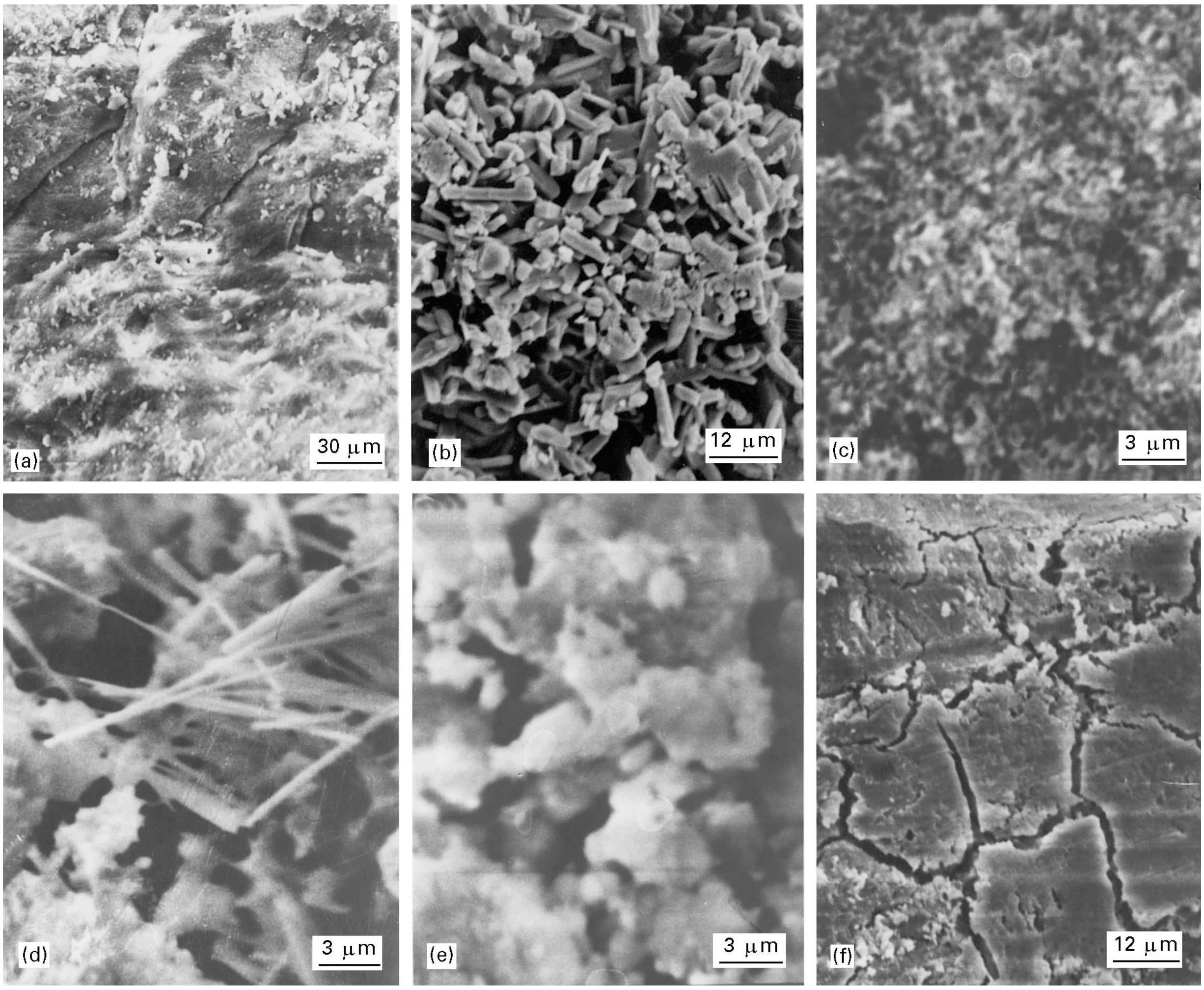

Figure 2 Scanning electron micrographs of the V_2O_5/Al_2O_3 catalysts. (a) Al_2O_3, (b) V_2O_5, (c) PM, (d) PMD, (e) PMW, (f) IMPR.

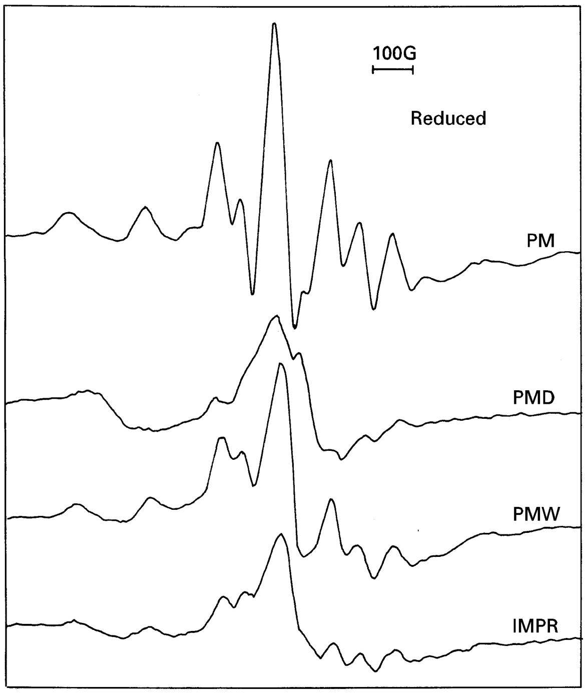

Figure 4 Electron spin resonance spectra of reduced V_2O_5/Al_2O_3 catalysts.

presented in Table I. It is worth mentioning here that uptake of carbon dioxide was not observed on pure V_2O_5. A maximum carbon dioxide uptake of 81.7 μmol g^{-1}, as observed on the Al_2O_3 support and the value is close to that (81.1 μmol g^{-1}) reported by Zimerczak *et al.* [22], for an Al_2O_3 with BET surface area of 194 m^2 g^{-1}. To calculate the apparent surface coverage by the adsorbed carbon dioxide on V_2O_5/Al_2O_3 catalysts, a conversion factor of 2.4 μmol CO_2/m^2 Al_2O_3 was used, taking into consideration the observed carbon dioxide uptake on Al_2O_3 support. The same value was used by Zimerczak *et al.* [22]. As can be seen in Table I, the apparent surface coverage gives meaningful information about the accessible support surface for carbon dioxide adsorption. In the case of PM catalyst, the calculated uncovered alumina surface is about 92%. This sample contains about 88 wt % Al_2O_3 and 12 wt % V_2O_5. In the case of PMD, about 56% of the alumina support is uncovered with vanadia. Accordingly, the IMPR catalyst contains about 16% free alumina uncovered by vanadia. In other words, the vanadia coverage on the alumina support surface is about 84%. A very similar surface coverage of vanadia can be seen in the case of PMW catalyst. The carbon dioxide chemisorption results clearly reveal that the dispersion of vanadia on PMW is comparable with that of IMPR catalyst.

Among the four catalysts, similar and optimum oxygen uptakes were observed on IMPR and PMW catalysts, indicating higher vanadia dispersion. This is in agreement with carbon dioxide chemisorption results where lower carbon dioxide uptakes were obtained. In the case of PMD, the oxygen uptake of 78 μmol g^{-1} indicates a decline in reducibility of V_2O_5 which may be due to the inaccessibility of all V_2O_5 units in the crystallites to the reducing gas. The oxygen uptake is the lowest in PM, indicating the presence of predominantly uninteracted V_2O_5. The carbon dioxide and oxygen chemisorption results are thus complementary to each other in assessing the effective V_2O_5 dispersion. In the case of the PMD catalyst, even though moderate V_2O_5 dispersion is expected, V_2O_5 has not lost its identity and, despite the fact that it is in a dispersed form, it probably is not interacting with hydroxyl groups of the Al_2O_3 support. However, in the case of PMW when V_2O_5/Al_2O_3 mixture is subjected to calcination in wet oxygen, the interaction between V_2O_5 and OH groups of Al_2O_3 appears to be on a par with V_2O_5/Al_2O_3 catalyst prepared by the impregnation method. On the basis of the above observations, we can say that the interaction of active oxide–support oxide is more in PMD and PMW than in a simple physical mixture. Hausinger *et al.* [14], in their studies on V_2O_5/TiO_2 catalysts prepared by grinding, have observed increased dispersion of the active component when treated in water vapour. This was attributed to hydroxylation of the TiO_2 surface in the presence of water vapour. On the other hand, cleaved planes of V_2O_5 that might have resulted during grinding, can also be hydrated affecting the dispersion. On the basis of UV–VIS studies, they have observed a stronger interband transition in the sample calcined in the presence of water vapour, whereas the absorption due to V_2O_5 near 500 nm was found to be less in the sample calcined under dry conditions.

Methanol conversion and selectivities to dimethyl ether (DME) and formaldehyde (HCHO) on various V_2O_5/Al_2O_3 catalysts are illustrated in Fig. 3. The activity results clearly indicate that formation of the main products, DME and HCHO, depends on the origin of the catalyst. Alumina support alone shows some conversion (3%) and total selectivity to DME under the experimental conditions employed in this study. The increase in conversion and HCHO formation, in addition to DME in the case of PM, can be

TABLE I Chemisorption and BET surface area of V_2O_5/Al_2O_3 catalysts

	Catalyst	Surface area (m^2 g^{-1})	Oxygen uptake (μmol g^{-1})	Carbon dioxide uptake (μmol g^{-1})	Apparent free surface[a] (%)
1.	Alumina	196	–	82	100
2.	IMPR	166	118	11	16
3.	PMW	163	107	10	15
4.	PMD	178	78	41	56
5.	PM	189	33	72	92

[a] Calculated from CO_2 uptakes.

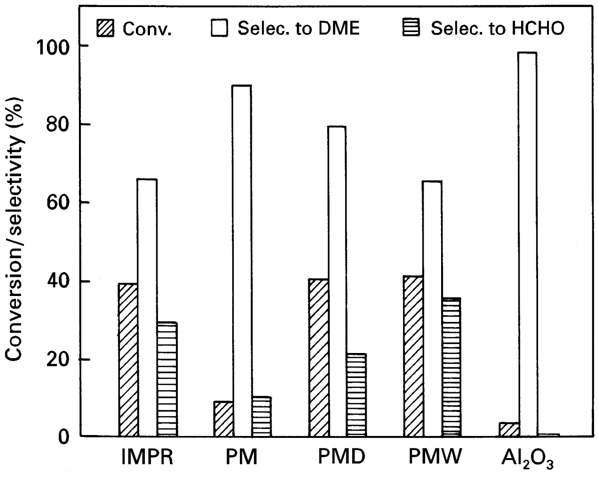

Figure 5 Product distribution in the methanol partial oxidation reaction.

attributed to the presence of V_2O_5. The activity of PM is only slightly better than on Al_2O_3 support. The DME selectivity on various samples follows the order $Al_2O_3 > PM > PMD > PMW = IMPR$, whereas the HCHO selectivity is in the order $PM < PMD < PMW = IMPR$. An interesting observation is that activity and selectivity trends are fairly similar, within experimental error, on both the impregnated and wet oxygen-treated physical mixture. The formation of HCHO in the catalysts prepared by solid–solid wetting shows that essentially interaction is taking place between active oxide (V_2O_5) and the support oxide (Al_2O_3) and it is in the order of $PMW > PMD > PM$. The feasibility of the reaction depends on the vanadia dispersion as well as the environment of vanadyl species. From the results it can be said that reducible vanadia sites which are titrated by oxygen chemisorption are responsible for HCHO selectivity. Further, it appears that well dispersed γ-Al_2O_3-supported V_2O_5 catalysts can be prepared by the solid–solid wetting method, provided they are calcined in wet oxygen.

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