INFLUENCE OF THE FORMATION OF ALUMINIUM SPINEL, AlVO₄, ON THE CATALYTIC ACTIVITY OF V₂O₅ SUPPORTED ON γ-ALUMINA

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Vanadium pentoxide catalysts supported on γ-alumina (1 – 50 mole %) were prepared by impregnation method and calcined at 400 and 680 °C for 4 h. The structure of the original and calcined samples was characterized by DTA and X-ray diffraction. The electrical conductivity measurements of the calcined samples reveal that the conductance increases while the Fermi potential decreases on increasing V_2O_5 content up to 50 mole %. The catalytic dehydration of isopropanol was carried out at 250 °C using a flow system. The results showed an observable increase in the extent of catalytic dehydration of the alcohol on increasing V_2O_5 content from 5 mole % to 50 mole % with the samples calcined at 400 °C. The catalysts calcined at 680 °C were found to exhibit maximum activity at the composition of 20 mole % V_2O_5. Above the maximum a sharp decrease in the conversion and the yield towards propylene was found due to formation of aluminium vanadate, i.e. AlVO₄ spinel. The low activity associated with the existence of this spinel was correlated with the sharp decrease in the Fermi potential.

Metal oxides are often supported on suitable solids as industrial catalysts. Vanadium pentoxide supported on alumina is one of the most important type of solid catalysts[1–5]. A number of studies have been undertaken on supported V_2O_5 to study the structure of loaded vanadium species[6,7] and interaction between the vanadium oxide and its support[8,9]. In certain cases and under certain conditions, solid state reactions can occur during thermal treatment, by which cations of the active component may be incorporated into the support.

Our previous paper[10] has indicated that the surface site, V=O, is strongly affected by the presence of Al_2O_3 support and that an interaction between V_2O_5 and the support takes place at 660 °C, yielding the well crystallized aluminium vanadate, AlVO₄. Mutual solid–solid interactions between V_2O_5 and Al_2O_3 might, however, affect the activity and selectivity of the produced solid catalysts. The present work was undertaken to

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study the influence of the catalyst structure produced during thermal treatment of ammonium metavanadate (AMV) supported on γ-alumina on the conversion of isopropanol.

EXPERIMENTAL

Materials

The starting materials were Analar grade chemicals. γ-Alumina precalcined in air at 500 °C (S_{BET} ≈250 m^2 g^{-1}) was impregnated with different proportions of ammonium metavanadate dissolved in twice distilled water. The samples were dried in an oven at 100 °C for 24 h before being calcined at 400 and 680 °C for 4 h in air. The V$_2$O$_5$ content was 1, 3, 5, 10, 20, 30, and 50 mole %. Analytical grade isopropanol (IP, BDH Ltd) was refluxed with sodium and distilled before use. Its purity was determined by GC analysis.

Apparatus and Techniques

Differential thermal analysis (DTA) and thermogravimetry (TG) of AMV supported on γ-Al$_2$O$_3$ were carried out using a Shimadzu thermal analysis system (DT-40). The rate of heating of the samples was kept at 10 °C min^{-1} using an air flow of 40 ml min^{-1}. α-Alumina for DTA standard was applied as a reference. X-Ray diffraction (XRD) of the thermal products of AMV supported on γ-alumina was recorded using a Philips diffractometer (Model PW 1710) applying a copper target and a nickel filter.

The catalytic reactions of isopropanol were carried out in a conventional fixed-bed flow type reactor. The exit feed was analyzed by direct sampling of the gaseous products into a Pye Unicam gas chromatograph, which allowed to determine the alcohol together with its decomposition products. All the reaction measurements were made after a steady state activity level had been established.

The electrical conductivity measurements were carried out using a conductivity cell as described previously[12].

RESULTS AND DISCUSSION

Thermal Analysis

DTA and TG curves of AMV (*a*) and the metavanadate supported on γ-Al$_2$O$_3$ (30 and 50 mole % AMV, (*b* and *c*, respectively) are shown in Fig. 1. The curves in Figs 1*b* and 1*c* exhibit four endothermic peaks. The first peak with minimum at 190 °C indicates the decomposition of AMV to the intermediate ammonium bivanadate (ABV), (NH$_4$)$_2$V$_4$O$_{11}$. The second peak located at 224 °C corresponds to the decomposition of ABV to the intermediate ammonium hexavanadate (AHV), (NH$_4$)$_2$V$_6$O$_{16}$. The third peak centered at 304 °C corresponds to the decomposition of AHV to V$_2$O$_5$ (ref.[13]). The last one located at 660 °C is not followed by any change in weight and it may be ascribed to a phase transition of γ-Al$_2$O$_3$ or to a solid–solid interaction between V$_2$O$_5$ and Al$_2$O$_3$. It is worthnoting that DTA of all the other compositions containing less

than 30 mole % V_2O_5 is not accompanied by any peak on heating above 500 °C. In this case, identification of structure changes has been made by XRD (see below).

XRD Investigation of Thermal Products of AMV Supported on γ-Al₂O₃

The XRD lines of AMV supported on γ-Al_2O_3 (30 and 50 mole % AMV) calcined at 400 and 680 °C are represented graphically in Fig. 2. By matching the lines obtained with the corresponding ASTM cards[14] it can be seen that the samples calcined at 400 °C are mainly a mixture of V_2O_5 and γ-Al_2O_3. New lines are obtained when the calcination temperature is raised to 680 °C. These lines which are located at d (Å) = 1.92, 3.11, 2.46, and 3.20 are due to formation of crystalline aluminium vanadate[10,14], $AlVO_4$. Moreover, the lines corresponding to V_2O_5 and γ-Al_2O_3 are still present, indicating that solid–solid interaction between V_2O_5 and γ-Al_2O_3 is not completed. Therefore, an endothermic peak at 660 °C in DTA (Fig. 1) is due to solid–solid interaction between V_2O_5 and γ-Al_2O_3, giving[12] $AlVO_4$.
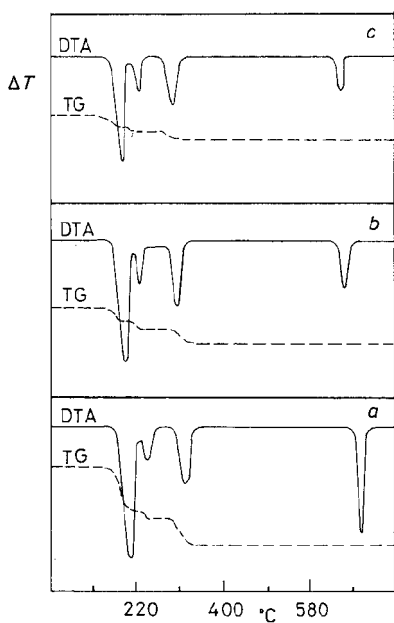

FIG. 1

DTA and TG curves of pure AMV (*a*), 50 mole % AMV (*b*) and 30 mole % AMV (*c*)
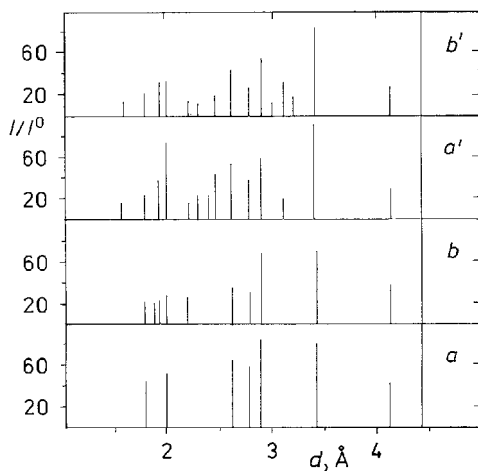

FIG. 2

X-Ray diffraction patterns of thermal products of AMV supported on Al_2O_3: 30 mole % AMV (*a*, *a'*), 50 mole % AMV (*b*, *b'*); calcined at 400 and 680 °C, respectively

Electrical Conductivity Measurements

The electrical conductivity measurements of V_2O_5 supported on γ-Al_2O_3 were carried out under air flow of 150 ml min^{-1}. Figure 3 shows the variation of log σ with the percentual content of V_2O_5 for the samples calcined at 400 and 680 °C. Curve *1* documents that log σ for the samples calcined at 400 °C increases gradually with increasing V_2O_5 content up to 30 mole %. Below the temperature of the interaction of these two oxides, some kind of solid solution between Al_2O_3 and V_2O_5 can exist, which is not easily detected by a simple X-ray diffraction analysis. The ionic radii of Al^{3+} and V^{5+} ions are 0.50 and 0.59 Å, respectively[15]. Therefore, some of Al^{3+} ions could be dissolved in the V_2O_5 lattice through location in interstitial position and/or cationic vacancies, according to the following doping mechanism using Kröger's notations[16].
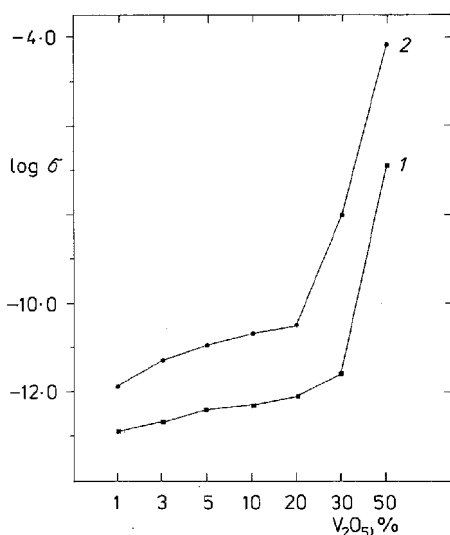
$$Al_2O_3 \ + \ 3 \ V^{5+} \ \longrightarrow \ 2 \ Al \ \boxed{\triangle} \ + \ 3 \ V^{3+} \ \ 3/2 \ O_2 \ (g) \qquad (A)$$

$$Al_2O_3 \ + \ 6 \ V^{5+} \ \longrightarrow \ 2 \ Al \ \boxed{\triangle} \ + \ 6 \ V^{4+} \ \ 3/2 \ O_2 \ (g) \qquad (B)$$

$$Al_2O_3 \ + \ 2 \ V^{3+} \ + \ O_2 \ (g) \ \longrightarrow \ 2 \ Al \ (V^{5+}) \ + \ 2 \ V^{5+} \qquad (C)$$

Fig. 3

Variation of log σ with V_2O_5 content in air for the samples calcined at 400 (*1*) and 680 °C (*2*)

Al $\triangle$ represents Al^{3+} located in an interstitial position or in a cationic vacancy, and Al (V^{5+}) denotes trivalent aluminium ion located in the position of host V^{5+} cations present in the V$_2$O$_5$ lattice. Thus, the formation of V^{4+} together with V^{5+} is responsible for the increase observed in electrical conductivity of the solid catalysts (Fig. 3). Further increase of V$_2$O$_5$ content to 50 mole % results in a sharp increase in the conductance. However, the results obtained from DTA show that the decomposition of the supported samples containing 30 or 50 mole % AMV follows decomposition processes of the pure AMV. This suggests that semiconducting properties of these samples approach those of the pure V$_2$O$_5$. It is known[17] that V$_2$O$_5$ contains some V^{4+} ions via the release of the lattice oxygen on calcination of ammonium metavanadate up to 500 °C, according to the following mechanism:

$$V_2O_5 \longrightarrow V\,|\,V\,|\,' \;+\; V_2O_5 \;+\; 1/2O_2 \;+\; 2e\;,\qquad (D)$$
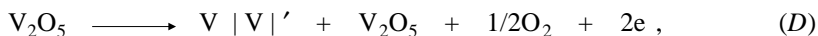
where V | V |′ are V^{4+} ions replacing V^{5+} in its normal lattice positions. The increase of electrons in the lattice together with the formation of V^{4+} by incorporation of Al^{3+} should increase the conductivity, as demonstrated experimentally.

Moreover, a similar behaviour was observed with the samples calcined at 680 °C (Fig. 3, curve *2*). In comparison with those calcined at 400 °C they exhibit, however, higher conductance values. An increase in the conductance in the presence of V$_2$O$_5$ up to 20 mole % can be attributed also to the increase of the conducting electrons according to the mechanisms suggested above. Above 20 mole %, the sharp increase in conductance may be attributed to formation of a new compound, AlVO$_4$, most likely characterized by a high conductivity value. Since activation energy provides the better understanding of conductivity changes, log σ values were plotted against reciprocal of the absolute temperature, and the conduction activation energies (E_σ) were determined from the slope of the obtained lines[18], where

$$\sigma \;=\; \sigma_0 \, \exp\,(-E_a/\boldsymbol{R}T)\;.\qquad (1)$$

The calculated E_σ's were 1.15, 0.50, and 0.06 eV for the samples containing 20, 30 and 50 mole % V$_2$O$_5$ and calcined at 680 °C, respectively. The sharp decrease in E_σ with increasing V$_2$O$_5$ content indicates the upward deviation of conduction band nearest to the surface, which is responsible for the observed increase in σ values. The latter may play a significant role in accounting for relation between electronic properties of the catalyst and its catalytic activity.

Catalytic Activity

The catalytic decomposition of isopropanol was carried out over the catalysts calcined at 400 and 680 °C for 4 h. The measurements of the conversion and yield (in %) were made after 2 h to achieve the steady-state conditions. The W/F ratio was 0.25 g catalyst $mol^{-1} h^{-1}$, where W refers to the catalyst weight and F is the total flow rate. The amount of isopropanol in the gas feed was 2 per cent, and the reaction temperature was 250 °C.

The conversion and yield of IP dehydration over V_2O_5 on γ-alumina catalysts of different composition are shown in Fig. 4. The results show that propylene is the only product of the decomposition. Curve *1* (Fig. 4) shows that the samples calcined at 400 °C exhibit a noticeable increase in IP conversion to propylene on increasing V_2O_5 content from 3 to 10 mole %, followed by a continuous increase up to 50 mole %. This indicates that the introduction of 10 mole % V_2O_5 to γ-alumina increases the conversion from 17 to 69%, and the yield of propylene from 15 to 66%. On the other hand, the low activity observed on addition of 1 or 3 mole % AMV may be due to the dispersion capacity of the high surface γ-Al_2O_3. It was found[8,9,19,20] that the structure of loaded vanadium species, the morphology of catalysts, and the interaction between vanadium oxide and its support all play a significant role in the catalytic activity and selectivity of V_2O_5. In addition, it was reported[10,21] that the vanadium oxide coverage of the support surface depends on the type of the support and the percentage loading of V_2O_5. Further, V_2O_5 on Al_2O_3 loses its $V = 0$ active sites until a multilayer is formed. Therefore, an increase in the catalytic activity of supported V_2O_5 in the presence of 5 mole % V_2O_5 may be attributed to the formation of a monolayer and of the active sites respon-
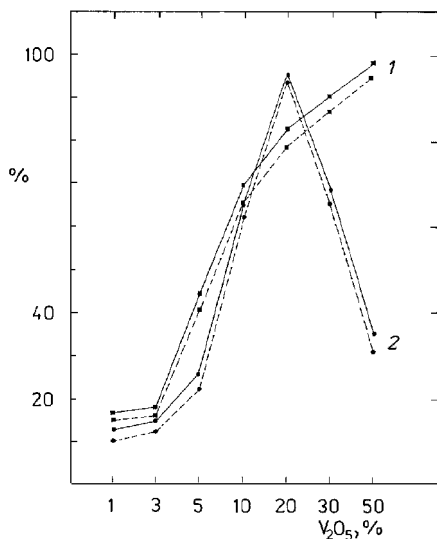

FIG. 4

Variation of IP conversion (full lines) and propylene yield (broken lines) in % with V_2O_5 content for the samples calcined at 400 (*1*) and 680 °C (*2*) for 4 h during the reaction of IP at 250 °C

sible for the dehydration of IP. Moreover, the increase in the catalytic activity and the yield of propylene with increasing V$_2$O$_5$ loading up to 10 mole % is due to formation of multilayers, associated with the increase of the amount of active surface sites, $V = 0$. Curve *2* in Fig. 4 shows the dehydration of IP over the samples calcined at 680 °C. It can be seen that the increase in IP conversion and propylene yield reaches maximum at 20 mole % V$_2$O$_5$, then being followed by a sharp decrease on further increase in the V$_2$O$_5$ content up to 50 mole %. We reported previously[22] that the catalytic activity of the unsupported V$_2$O$_5$ decreases sharply with increasing calcination temperature above 400 °C. This decrease was attributed to the sharp decrease in S_{BET} of V$_2$O$_5$ (from 9.0 to 1.0 m^2 g^{-1}). In this work the high activity obtained with the supported samples calcined at 680 °C may be attributed to the presence of γ-alumina which has high S_{BET}. Moreover, the best content of V$_2$O$_5$ which gives the highest IP conversion and propylene yield is 20 mole %. The sharp decrease in the catalytic activity above this maximum for the samples containing 30 and 50 mole % can be attributed to the formation of AlVO$_4$ spinel. This result is very important because spinel formation is accompanied with the low catalyst activity. Thus, the formation of the spinel is undesirable in the catalytic process. However, the sharp decrease in the catalytic activity associated the existence of this spinel may relate to its semiconducting properties. The electronic theory of chemisorption on semiconducting materials[23] postulates a close relation between the electronic properties of a catalyst and its catalytic activity. The width of energy gap is important in controlling the number of molecules which can be chemisorbed in the course of a catalytic reaction on the catalyst surface. These factors control both the catalyst activity and mechanism of the catalytic reaction. According to the electrical conductivity values obtained, the Fermi potential, E_σ, for the samples containing 30 and 50 mole % V$_2$O$_5$ decreases sharply as the AlVO$_4$ spinel is formed. This indicates that the decrease in the Fermi potential could increase the number of electrons coming from the conduction band to the catalyst surface. However, the increase of the electrons on the catalyst surface may retard chemisorption of IP molecules, being thus likely responsible for the decrease in the IP conversion and propylene yield with the samples in which formation of AlVO$_4$ has occurred.

CONCLUSIONS

The following conclusions can be drawn based on the results obtained:

1. V$_2$O$_5$ supported on γ-alumina is the active and selective catalyst when calcined at temperatures not exceeding 680 °C.

2. The best composition of the V$_2$O$_5$ on γ-alumina catalyst with respect to propylene formation is 20 mole % V$_2$O$_5$.

3. The formation of AlVO$_4$ spinel as a result of the solid–solid interaction between V$_2$O$_5$ and Al$_2$O$_3$ is undesirable, because it leads to a sharp decrease in the IP conversion.

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Translation revised by J.Hetflejs.