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NOTE

Reactivity of V_2O_5 with TiO_2–ZrO_2 Mixed Oxide: An X-ray Diffraction Study*

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The reactivity of vanadia with TiO_2–ZrO_2 mixed oxide support was investigated by the X-ray powder diffraction technique. TiO_2–ZrO_2 mixed oxide was prepared by the technique of precipitation from homogeneous solution. Ammonium metavanadate was used as a source of vanadia, and V_2O_5 contents varied from 2 to 16 wt%. Calcination of Ti- and Zr-hydroxides at 773 K result in the formation of an amorphous phase, and further heating at 873 K converts this amorphous phase into a crystalline $TiO_2 \cdot ZrO_2$ compound. This compound is quite stable in the absence of V_2O_5. Addition of V_2O_5 and heating of the samples beyond 873 K result in the formation ZrV_2O_7, with the simultaneous presence of TiO_2 rutile phase. Quantities of these phases increase with increasing in V_2O_5 content.

Introduction

Supported vanadium oxides are perhaps the most studied catalytic systems because of their industrial importance (*1, 2*). Vanadia is normally supported on different carriers depending on the nature of the reaction to be catalyzed: on silica support to oxidize naphthalene (*3*), on anatase phase of titania to oxidize o-xylene (*4*), on alumina to oxidize benzene (*5*), on zirconia to partially oxidize methanol (*6*), and so on. The critical parameters that determine the number of active surface sites and reactivity per site are the specific oxide support, catalyst composition, and calcination temperature (*7*).

The structural transformations of vanadia–titania catalysts have been extensively investigated by several workers using XRD, ESR, ESCA, and other techniques (*4, 7–14*). It is also well known that vanadia supported on titania promotes the anatase–rutile phase transformation during calcination, which is coupled with the incorporation of V^{4+} into the rutile lattice (*8–12*). It has been proposed by Vejux and Courtine (*13*) that the anatase-to-rutile transformation and the reduction of V_2O_5 are brought about by the fit of the crystallographic structures in the V_2O_5 and TiO_2 (anatase) interface. A remarkable fit has been found to exist between structures of the cleavage plane (010) of V_2O_5 and (001), (100), and (011) planes of anatase (*13, 14*). Zirconia is yet another interesting support. It can be prepared in many ways resulting in various modifications of it viz., monoclinic, tetrago-

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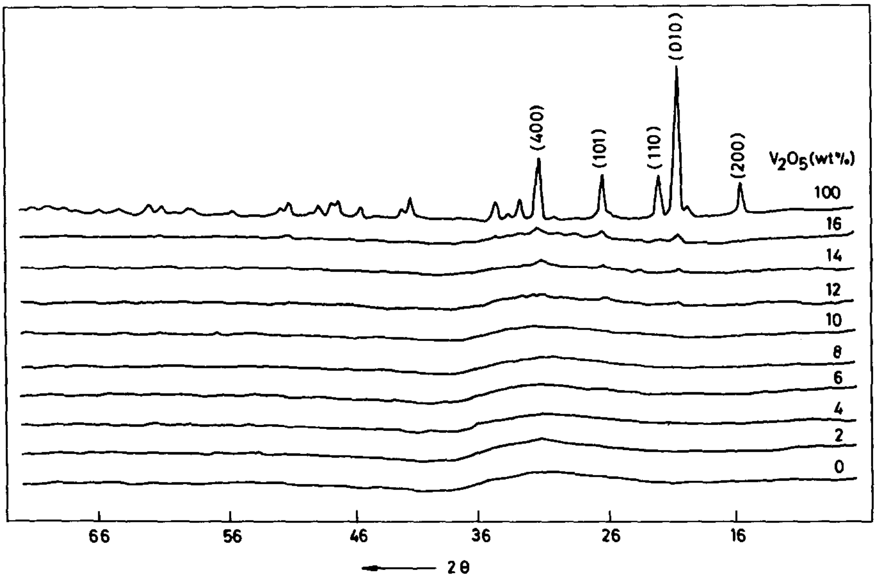

FIG. 1. X-ray diffractograms of TiO_2–ZrO_2 and V_2O_5/TiO_2–ZrO_2 samples calcined at 773 K.

nal, and cubic (*15*). ZrO_2 possesses acidic, basic, oxidizing, and reducing properties on the surface. The four surface properties including phase modifications change independently with the method of preparation and pretreatment temperature (*15*, *16*). Therefore, the combined mixed oxide support TiO_2–ZrO_2 is very interesting for structural study. In the present investigation the effect of vanadia content and the calcination temperature on the phase transformations of TiO_2–ZrO_2 binary oxide support were studied by the X-ray diffraction technique.

Experimental

Sample Preparation

The TiO_2–ZrO_2 (1 : 1 molar ratio) mixed oxide support was prepared by calcination of the coprecipitated hydroxides at 773 K for 6 h. The coprecipitated hydroxides were prepared by precipitation from homogeneous solution (PFHS) method using urea as hydrolyzing agent (*17*). An aqueous mixture solution containing the required quantities of $TiCl_4$ (Fluka, AR grade), $ZrOCl_2$ (Fluka, AR grade), and urea (Loba-Chemie, GR grade) was heated to 368 K with constant stirring. Precipitation was complete after 2 to 3 h, at which time the pH of the solution was approximately 7. The precipitate was then filtered off, washed several times with deionized water to remove chloride ions, dried over night at 393 K, and finally calcined at 773 K for 6 h. The resulting TiO_2–ZrO_2 support had a N_2 BET surface area of 160 m^2g^{-1}.

The TiO_2–ZrO_2 supported vanadia catalysts with various V_2O_5 loadings ranging from 2 to 16 wt% were prepared by wet impregnation of the carrier with stoichiometric aqueous solutions of ammonium metavanadate (Fluka, AR grade) and evaporation to near dryness with constant stirring. The impregnated samples thus obtained were dried at 393 K for 12 h and calcined in an open air furnace at 773 K for 4 h. Thus, finished catalysts were again treated at various temperatures, 873, 973, and 1073 K for 6 h in a closed electrical furnace in open air atmosphere.

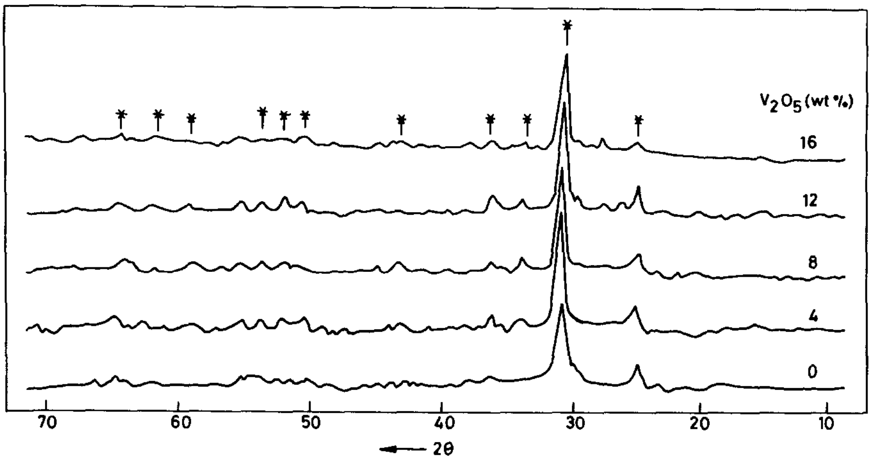

FIG. 2. X-ray diffractron patterns of V_2O_5/TiO_2–ZrO_2 samples calcined at 873 K; †, lines due to $TiO_2 \cdot ZrO_2$.

X-ray Diffraction

X-ray powder diffraction patterns were recorded on a Philips PW 1051 diffractometer using nickel filtered Cu*Kα* radiation and standard conditions.

Results and Discussion

XRD patterns of V_2O_5/TiO_2–ZrO_2 samples calcined at 773 K are shown in Fig. 1. Diffraction patterns of unsupported V_2O_5 and TiO_2–ZrO_2 support alone are also shown in Fig. 1 for comparison. According to its diffraction profile the TiO_2–ZrO_2 binary oxide support calcined at 773 K is an amorphous state. The V_2O_5/TiO_2–ZrO_2 samples calcined at 773 K with a vanadium content of 12 wt% and above show broad V_2O_5 reflections in the X-ray diffractograms. This suggests that V_2O_5 below 12 wt% loading is in a highly dispersed and amorphous state. Hence, it can be inferred that the monolayer capacity is below 12 wt% of V_2O_5, which is in agreement with earlier reports (*7, 18–20*). According to Bond *et al.* (*19*) the amount of vanadia needed per m^2 of the support for monolayer coverage is about 0.07 wt%. Therefore, for a TiO_2–ZrO_2 support of 160 m^2g^{-1} surface area the required quantity of vanadia to yield a single monolayer is about 11.2 wt%, i.e., below 12 wt% loading. So the present XRD results (Fig. 1) are in perfect agreement with this estimate.

In general, the maximum amount of vanadium oxide that can be formed in the two-dimensional vanadium oxide overlayer, i.e., monolayer coverage, depends on the support surface area and the concentration of reactive surface hydroxils (*7, 18–20*). Accordingly, composition of the catalyst determines the type of vanadium oxide species present in supported vanadium oxide catalyst. For vanadia contents less than monolayer coverage, the entire vanadium oxide component in the catalyst is normally present as a two-dimensional surface vanadium oxide overlayer on the oxide support. Quantities above monolayer coverage will have microcrystalline V_2O_5 particles present in the catalyst in addition to the surface vanadium oxide monolayer (*21*).

Calcined V_2O_5/TiO_2–ZrO_2 samples were again heated at various temperatures for 6 h in closed atmospheric conditions. X-ray diffractograms of the samples heated at 873 K are shown in Fig. 2. At least two new

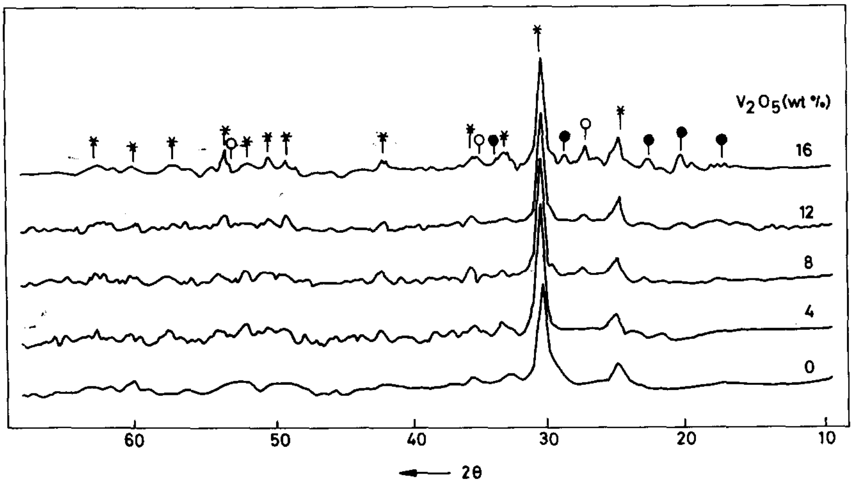

FIG. 3. X-ray diffraction patterns of $V_2O_5/TiO_2–ZrO_2$ samples calcined at 973 K; †, lines due to $TiO_2 \cdot ZrO_2$; ●, due to ZrV_2O_7; ○, due to TiO_2 (rutile).

effects can be noted in this figure: the appearance of diffraction patterns of $TiO_2 \cdot ZrO_2$ crystalline compound (*22*) and the disappearance of residual crystalline V_2O_5 phase. However, at higher V_2O_5 contents additional lines other than due to the $TiO_2 \cdot ZrO_2$ phase are observed. Because of the poor crystallinity of the phases formed, these lines are very broad. Therefore, these were not assigned to any particular phase.

On further heating at 973 K, more changes can be seen in the XRD patterns of the samples (Fig. 3). Here also at zero vanadium content only the $TiO_2 \cdot ZrO_2$ phase is present. Increase in the vanadium content induced few modifications in the XRD patterns of the $TiO_2 \cdot ZrO_2$ compound. At higher V_2O_5 loadings formation of zirconium divanadate, ZrV_2O_7 (*23*), and the rutile phase of TiO_2 (*24*) is manifested. Further improvement in the crystallinity of the ZrV_2O_7 and $TiO_2 \cdot ZrO_2$ compound can be seen from the diffractograms of the samples treated at 1073 K (Fig. 4). Here again, $TiO_2 \cdot ZrO_2$ is the only major observable crystalline phase in the absence of a vanadium oxide active component. However, formation of ZrV_2O_7 and rutile phases can be noted from 4 wt% V_2O_5 loading onward. An interesting observation is that the intensity of the ZrV_2O_7 patterns increases with increases in V_2O_5 content. At the same time the rutile reflections also become stronger.

A close look into the Figures 1, 2, 3, and 4 reveals that the heating temperature and concentration of V_2O_5 have two principle effects on $TiO_2–ZrO_2$ mixed oxide support: (i) Transformation of amorphous TiO_2 and ZrO_2 mixed oxide support into a definite crystalline $TiO_2 \cdot ZrO_2$ compound beyond 773 K temperature. Crystallinity of this phase increases with increasing temperature. This compound appears to be quite stable in the absence of vanadium oxide. This is evidenced by the absence of crystalline TiO_2 (rutile) and ZrO_2 phases in the absence of vanadia on the $TiO_2–ZrO_2$ support even after high temperature treatments. (ii) Disappearance of crystalline V_2O_5 phase and appearance of ZrV_2O_7 compound for calcination temperatures beyond 773 K. Both calcination temperature and the

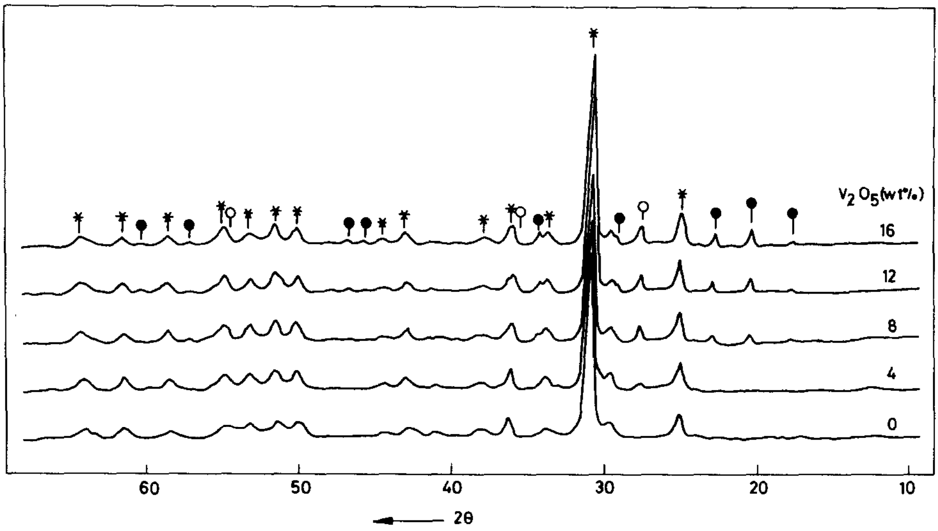

FIG. 4. X-ray diffraction patterns of V_2O_5/TiO_2–ZrO_2 samples calcined at 1073 K. Symbols as in Fig. 3.

amount of vanadium oxide appears to have a pronounced effect on this phase.

It is widely established that the transformation of anatase-into-rutile starts beyond 773 K temperature (*12, 25, 26*). Highly dispersed vanadia on the anatase phase is known to accelerate this transformation by lowering the activation temperature of this phenomena (*12, 13, 25–27*). Bond *et al.* (*8*) also reported that during the transformation of anatase-into-rutile, the vanadia phase was reduced and got incorporated into the rutile structure as $V_xTi_{(1-x)}O_2$ (rutile solid solution). However, in the present study the reactivity of vanadia toward the $TiO_2 \cdot ZrO_2$ compound appears to be different. It appears that vanadia reacts preferentially with the ZrO_2 portion of the $TiO_2 \cdot ZrO_2$ compound to form the ZrV_2O_7 phase, thus liberating the TiO_2 phase. The portion of TiO_2 released from the $TiO_2 \cdot ZrO_2$ compound appears as the crystalline rutile phase as shown in Eq. (1):

$$TiO_2 \cdot ZrO_2 + V_2O_5 \rightarrow ZrV_2O_7 + TiO_2\,(R). \quad (1)$$

An analogous reaction between V_2O_5 and $TiNb_2O_7$ was also reported earlier by Eon and Courtine (*28*). When V_2O_5–$TiNb_2O_7$ were heated together, formation of VNb_9O_{25} with the liberation of TiO_2 (rutile) was noted. The formation of the double compound $TiO_2 \cdot ZrO_2$ seems to have taken place at a much lower temperature in the present study than that reported in literature (*22*). Earlier, Coughanour *et al.* (*22*) reported the formation of definite $TiO_2 \cdot ZrO_2$ compound between 1073 and 1473 K temperatures when these two independent components were slowly heated together and cooled to room temperature. Formation of this compound even at 873 K reported in the present study may presumably be due to the preparation procedure adopted, which is entirely different from the earlier one.

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