Phase transformation study of titania in V$_2$O$_5$/TiO$_2$ and MoO$_3$/TiO$_2$ catalysts by X-ray diffraction analysis

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Abstract

The effect of the presence of vanadia or molybdena and the thermal treatment on the phase transformation of titania in V$_2$O$_5$/TiO$_2$ and MoO$_3$/TiO$_2$ catalysts was investigated using X-ray powder diffraction (XRD) analysis. The titania support used was a commercial sample from Harshaw containing anatase together with a small quantity of graphite. The XRD results suggest that when the TiO$_2$ support is calcined at 973 K, anatase is partially transformed into rutile, whereas at 1273 K it is totally converted to rutile. In the presence of V$_2$O$_5$ the temperature of partial conversion is reduced to 813 K, and a total transformation is noted already at 973 K. MoO$_3$ also induces this transformation, but is less effective than V$_2$O$_5$. XRD results further show that when the V$_2$O$_5$/TiO$_2$ catalyst is subjected to calcination at 973 K, no crystalline V$_2$O$_5$ phase is present. The same is not true for MoO$_3$, which is present in a crystalline state at this calcination temperature. This study reveals clearly that vanadia and molybdena behave differently when impregnated on the same titanium dioxide support.

Introduction

Titania is an important catalytic material, not only because of its effectiveness in photoassisted reactions [1], but also because it enhances the activity and selectivity of transition and noble metals when used as a support [2–5]. The titania–vanadia combination is a classic example of support enhancement of the active phase, especially when the vanadium oxide is applied to the carrier surface as a monomolecular layer [5]. Titania-supported molybdena catalysts are reported to be highly active for the hydrodesulfurization of thiophene when compared with conventional alumina-supported molybdate catalysts [6]. Titania (anatase) supported vanadia and molybdena catalysts have also received much attention recently for use in the reaction of NO$_x$ reduction with NH$_3$ [7–10]. As pointed out by Wainwright and Foster [2], the most successful support in heterogeneous catalysis is titania, normally used in the form of anatase.

The preparation and characterization of vanadium and molybdenum oxide monolayer catalysts on various supports, including titania, has been the topic of numerous investigations [11–28]. All of these studies dealt with the structure of the active component below and above monolayer coverages and the influence of the support materials on these structures. It is well known

that vanadia supported on titania promotes the transformation of anatase into rutile during calcination, which is also coupled with the incorporation of V^{4+} into the rutile lattice [29]. According to Vejux and Courtine [30], the simultaneous reduction of V$_2$O$_5$ and transformation of anatase into rutile are topotactic reactions activated by the remarkable fit of the crystallographic patterns of V$_2$O$_5$ and the anatase phase of TiO$_2$. A remarkable fit has been found to exist between the structures of the cleavage plane (010) of V$_2$O$_5$ and the (001), (100) and (011) planes of anatase. Regarding MoO$_3$, Bodes et al. [31] reported that the (110) and (010) planes of MoO$_3$ can also be anchored on the (010) and (001) planes of anatase, thus suggesting that growth of reduced MoO$_3$ layers on these faces of TiO$_2$ crystallites would be facile. However, the MoO$_3$-induced phase transformation of anatase into rutile has not yet been fully studied. Both oxides, V$_2$O$_5$ and MoO$_3$, are known to form perfect layered structures. Therefore, it is very interesting to study the dependence of the phase transformation of anatase into rutile on the amounts of V$_2$O$_5$ and MoO$_3$, as well as on their thermal treatments. In this study, V$_2$O$_5$ and MoO$_3$ loadings were varied from 2 to 12 wt.%, with the calcination temperature varying from 813 to 1273 K. The primary objective was to determine the influence of V$_2$O$_5$ and MoO$_3$ on the phase transformation of anatase into rutile with samples of identical loadings on the same support material.

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Experimental

Materials and catalyst preparation

The TiO_2 support (Ti-0720, 1/8 in. thick, surface area 169 m^2 g^{-1}, pore volume 0.36 ml g^{-1}) used in this study was a gift sample from Harshaw (USA). The grey-coloured TiO_2 support in tablet form was ground to a fine powder (−200 BSS mesh fraction) for impregnating the active components as well as for X-ray diffraction analysis. Ammonium metavanadate (Fluka, Switzerland, AR grade) and ammonium heptamolybdate (Baker, England, AR grade) were used as the sources of V_2O_5 and MoO_3, respectively.

The V_2O_5 or MoO_3 loadings selected ranged from 2 to 12 wt.%. The V_2O_5/TiO_2 catalysts were prepared by a wet impregnation method, where the required amount of ammonium metavanadate was dissolved in a 2 M oxalic acid solution and mixed with the support. Excess water was slowly evaporated on a water bath with continuous stirring. The residue thus obtained was dried at 393 K for 16 h and calcined at 813 K for 6 h in an open-air furnace.

MoO_3/TiO_2 catalysts were prepared by the standard incipient wetness method. For this purpose a calculated amount of ammonium heptamolybdate corresponding to the desired MoO_3 loading on the support was dissolved in a volume of water that corresponded exactly to the total pore volume of the quantity of support used for impregnation. The support was then uniformly wetted by the solution, stirred well for 30 min and then allowed to stand for 2 h. The impregnated samples thus obtained were dried at 393 K for 16 h and then calcined in air for 6 h at 813 K.

For studying thermal effects, the oven-dried or finished catalysts were calcined in air at various temperatures. The rate of heating was always maintained at 10 K min^{-1}.

XRD and surface area measurements

X-ray powder diffraction patterns were recorded on a Philips PW 1051 diffractometer with monochromated Fe Kα radiation ($\lambda = 1.93597$ Å) and under standard conditions. The BET surface areas of various samples were measured on a volumetric high-vacuum system by N_2 physisorption at 77 K and by taking 0.162 nm^2 as the cross-sectional area of the N_2 molecule.

Results and discussion

The BET surface area of the commercial TiO_2 sample obtained by N_2 physisorption at 77 K was 161 m^2 g^{-1}. After calcination at 813 K the surface area dropped to 65 m^2 g^{-1}, which was further decreased to 22 and 8 m^2 g^{-1} after calcination at 973 and 1273 K, respectively.

The colour of the sample also turned from dark grey to pure white, typical of TiO_2, after calcination at 973 K. The colour remained unchanged on further calcination at 1273 K, indicating that there are no other colour-inducing impurities.

The BET surface areas of various V_2O_5/TiO_2 and MoO_3/TiO_2 catalysts calcined at 813 and 973 K are shown in Table 1. A consistently decreasing trend with increasing V_2O_5 or MoO_3 loading is noted in both series of samples. In general, the surface area of the support material decreases with increasing quantity of the active component until the monolayer coverage of the active component is completed [13]. This is primarily due to the penetration of the active component into the pores of the support during the preparation step itself, which in turn results in a high dispersion of the active component on the support.

The quantity of V_2O_5 or MoO_3 needed to cover the support surface as a monomolecular layer can be estimated using the literature. Bond *et al.* [23] suggested that theoretically a load of 0.145 wt.% per m^2 of surface is required in order to cover the surface of a titanium dioxide support with a compact single lamella of the vanadium pentoxide structure. In a similar fashion, Hengstum *et al.* [24] reported the theoretical monolayer capacity of MoO_3 on TiO_2 as 0.16 wt.% per m^2 of support surface. Hence, the amounts of V_2O_5 or MoO_3 needed to cover the TiO_2 support having a 65 m^2 g^{-1} surface area are 9.4 and 10.4 wt.%, respectively. However, Bond *et al.* [23], Baiker and co-workers [25,26] and Haber *et al.* [27] observed experimentally that the actual vanadia loading needed to cover the titania surface as a single monolayer was always less than the theoretical monolayer capacity and corresponded to about 70% of the theoretical value. Kim *et al.* [28] recently reported that for Degussa P-25 TiO_2 support, the required quantity of V_2O_5 or MoO_3 is 0.12 wt.%. Therefore, in the present study a range of compositions was used, and the maximum loading used was slightly in excess of the theoretical monolayer capacity based on the surface area of the support.

The XRD patterns of the TiO_2 support, uncalcined and calcined at various temperatures, are shown in Fig. 1. The commercial TiO_2 support appears to contain a small quantity of graphite (ASTM 25-284) in addition to the anatase phase of TiO_2 (ASTM 21-1272). The anatase phase is, however, in poorly crystalline form. Because of preferential orientation the characteristic line due to graphite is sharp. Graphite and some organic acids are normally added as binders to make the fine catalyst powders into the desired shapes (tables, extrusions, etc.).

Based on chemical, XRD and BET surface area measurements, it was inferred that the unusually high surface area (161 m^2 g^{-1}) and the dark grey colour

TABLE 1. N_2 BET surface areas of various V_2O_5/TiO_2 and MoO_3/TiO_2 catalysts calcined at 813 and 973 K

V_2O_5 or MoO_3 loading[a] (wt.%)	Calcination at 813 K		Calcination at 973 K	
	Colour	S.A. ($m^2 \ g^{-1}$)	Colour	S.A. ($m^2 \ g^{-1}$)
V_2O_5/TiO_2 series				
2	light grey	58	greyish white	22
4	light grey	55	white	21
6	grey	52	yellowish brown	19
8	light brownish grey	48	brown	18
12	brownish grey	46	dark brown	16
MoO_3/TiO_2 series				
2	light grey	57	white	23
4	grey	56	greyish white	21
6	grey	56	light grey	20
8	grey	51	grey	18
12	grey	49	grey	17

[a]Balance is TiO_2.
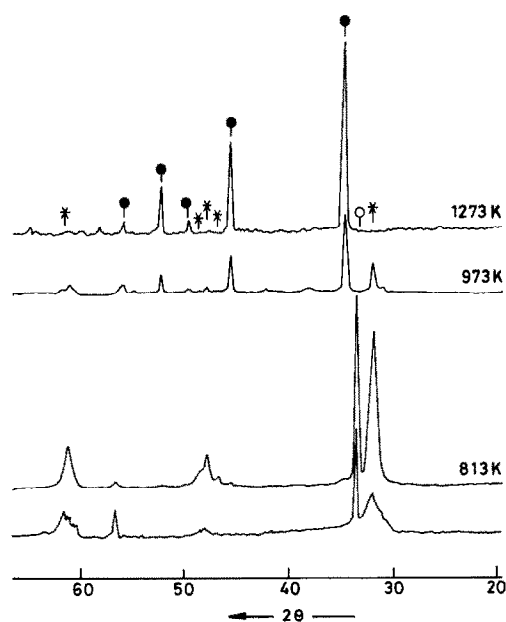
Fig. 1. X-ray diffraction patterns of TiO_2 sample calcined at various temperatures: (*) characteristic lines due to anatase phase; (●) lines due to rutile; (○) lines due to graphite.

are primarily due to the presence of graphite in the sample. When the sample was calcined in air at 813 K, a good improvement in the crystallinity of the anatase phase and graphite was noted. Upon further calcination at 973 K for 10 h, the carbon peak disappeared totally and the sample turned pure white. We also noted transformation of anatase phase into rutile phase (ASTM 21-1276) in good quantity, as evidenced by strong peaks due to rutile phase. Calcination of this sample at 1273 K for 4 h transforms anatase completely into rutile phase. This complete transformation of an-atase into rutile was also noted in an independent

experiment in which the starting TiO_2 support was directly heated in air at 1273 K for 6 h. Here also, the carbon binder disappeared as gaseous carbon dioxide during the calcination step.

XRD patterns of various V_2O_5/TiO_2 and MoO_3/TiO_2 catalysts calcined at 813 K are shown in Figs. 2 and 3, respectively. As can be seen in Fig. 2, prominent lines due to anatase phase of TiO_2 as well as that of graphite are seen in all the spectra. The intensity of the graphite peak decreases gradually with increasing V_2O_5 content. This loss in the intensity of the graphite line may be due to a real loss in the concentration of graphite with the addition of vanadia, or it may be due to enhanced gasification of carbon in the presence of V_2O_5. A rough estimation of the intensity ratios of graphite and anatase, however, support the latter pos-
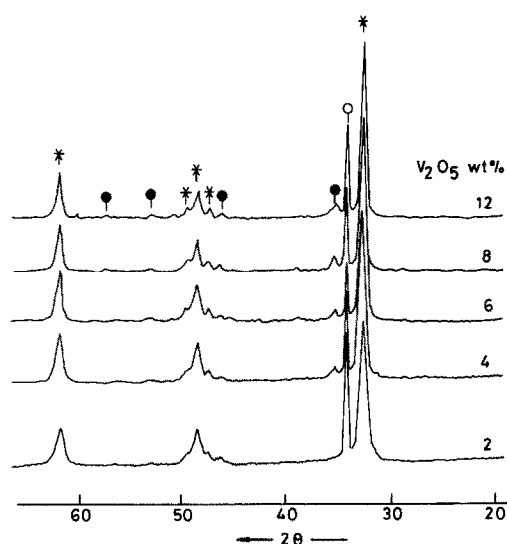

Fig. 2. XRD patterns of V_2O_5/TiO_2 catalysts calcined at 813 K; symbols as in Fig. 1.
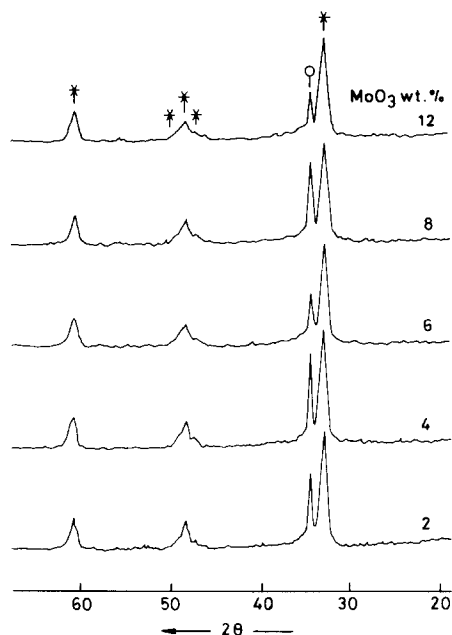
Fig. 3. XRD patterns of MoO₃/TiO₂ catalysts calcined at 813 K; symbols as in Fig. 1.

Fig. 4. XRD patterns of V₂O₅/TiO₂ catalysts calcined at 973 K: (△) characteristic lines due to V₂O₅; other symbols as in Fig. 1.

Fig. 5. XRD patterns of MoO₃/TiO₂ catalysts calcined at 973 K: (▲) characteristic lines due to MoO₃; other symbols as in Fig. 1.

sibility. Another important observation (from Fig. 2) is that rutile phase is present at V_2O_5 loadings of 4 wt.% and above. No lines due to either crystalline vanadium oxide phases or binary compounds of V_2O_5 and TiO_2 are noted even at the highest loading of V_2O_5. This unequivocally indicates either that vanadia is in a highly dispersed state or that the crystallites formed are too small to be detected by XRD, i.e., <4 nm in size. In fact, oxygen uptake and electron spin resonance measurements revealed that vanadium oxide is in a highly dispersed state [32]. In the case of $MoO_3/$ TiO_2 samples (Fig. 3) also, no XRD lines due to crystalline MoO_3 phase are observed. Here again, the anatase phase dominates in all the spectra and the intensity of the graphite peak diminishes with increasing molybdena content. Another important observation, contrary to that for the V_2O_5/TiO_2 series (Fig. 2), is the absence of lines due to rutile phase even at the highest loading of molybdena on TiO_2.

XRD patterns of V_2O_5/TiO_2 and MoO_3/TiO_2 catalysts calcined at 973 K are shown in Figs. 4 and 5, respectively. Notable differences can be observed in the spectra of these two series of samples. In the case of the $V_2O_5/$ TiO_2 series, both anatase and rutile phases are seen at 2 wt.% loading, with anatase phase dominating. On increasing the V_2O_5 loading to 4 wt.% and above, the anatase phase vanishes totally and rutile phase alone is manifested. A very weak pattern of crystalline V_2O_5 phase can be seen only at the highest vanadia loading. However, in the case of MoO_3/TiO_2 catalysts, a gradual transformation of anatase into rutile phase is observed with increasing MoO_3 loading. Here again, at the lowest

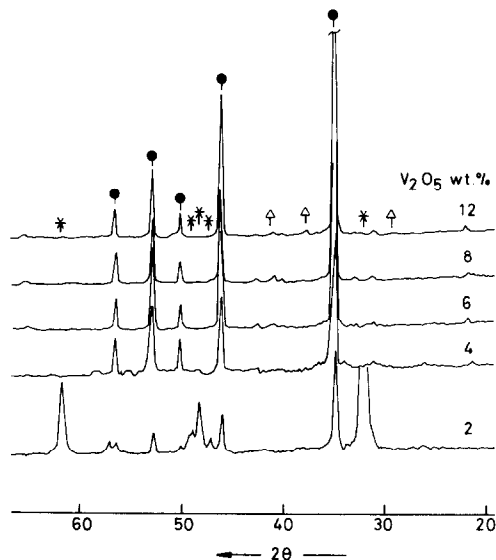(2 wt.%) MoO_3 content the dominant phase is anatase and at higher loadings it is rutile, but even at the highest loading (12 wt.%) some untransformed anatase phase persists. In addition, for loadings of 6 wt.% and above, characteristic lines of crystalline MoO_3 phase are also observed. It can therefore be concluded that vanadia and molybdena behave differently when incorporated on the surface of titanium dioxide (anatase).

A close look at the XRD patterns of V_2O_5/TiO_2 and MoO_3/TiO_2 samples calcined at different temperatures (Figs. 2–5) reveals at least two principal differences in their spectra. The first is that the transformation of anatase to rutile phase occurs at a much lower temperature than that generally expected for V_2O_5/TiO_2 catalysts [29]. The dispersed vanadia on the titania surface appears to lower the activation temperature of the anatase to rutile phase transformation, which is normally expected to be 973 K and above in impurity-free TiO_2 samples. The second observation is the presence of crystalline MoO_3 phase in addition to the unconverted anatase phase at higher MoO_3 contents in the case of MoO_3/TiO_2 catalysts calcined at 973 K (Fig. 5). No such crystalline phase is noted in the case of V_2O_5/TiO_2 samples calcined at 973 K. The absence of crystalline V_2O_5 phase even after calcination at 973 K may presumably be due either to a redispersion of vanadium oxide on the titania surface or to the formation of a glassy vanadia phase. The glassy vanadia phase can be formed by dissolution of titania into the vanadia melt, since this calcination temperature corresponds exactly to the melting temperature of V_2O_5 (the m.p. values of V_2O_5 and TiO_2 are 963 and 2123 K, respectively). Takasaki et al. [33] earlier reported the possibility of redispersion of cobalt particles on the TiO_2 support when the catalyst was calcined at the latter oxide's melting point. However, in the case of MoO_3/TiO_2 catalysts, such a phenomenon is apparently not taking place, owing probably to the high melting point of MoO_3 (1068 K). Hence, a fair amount of crystalline MoO_3 phase is leaching out.

As pointed out earlier, both V_2O_5 and MoO_3 are known to have layered structures, and the fit of various crystallographic planes of these oxides to the titania faces is also an established fact [29–31]. However, these two oxides appear to behave differently when impregnated on the surface of titanium dioxide and thermally treated at different temperatures. Even though both oxides have layered structures, there appears to be a slight difference in their behaviour, in that MoO_3 forms more regular structures than V_2O_5 [34]. Arco et al. [34] attempted to explain the differences between the V_2O_5/TiO_2 and MoO_3/TiO_2 catalysts on the basis of their surface areas and pore structures. They proposed that both oxides form supported phases interacting through the support hydroxyls. However, the growth of V_2O_5 crystallites does not take place uniformly, giving rise to islands of V_2O_5 and leaving part of the support surface uncovered, and this growth causes the sintering of different TiO_2 particles. Hence a considerable decrease in the surface area was noted in the case of V_2O_5/TiO_2 catalysts. MoO_3, on the contrary, grows epitactically on the TiO_2 crystallites, leaving the particles apart. Therefore, interparticle pores will not be de-

stroyed and no loss of surface area is noted. However, in the present study, no such difference in N_2 BET surface areas was observed (Table 1). From extended X-ray absorption fine-structure spectroscopy (EXAFS) studies, Kozlousky et al. [35] have proposed that the so-called epitactic model for the interaction between anatase and V_2O_5 is not applicable to V_2O_5/TiO_2 catalysts. An interpretation at the atomic level for the observed differences between the V_2O_5/TiO_2 and MoO_3/TiO_2 catalysts is lacking in the literature, but should obviously be related to the structure and chemistry of the supported phases formed during thermal treatments.

Conclusions

The following conclusions can be drawn from this study:

(1) Vanadia and molybdena behave differently when incorporated on the surface of titanium dioxide.

(2) Vanadia is more reactive than molybdena in transforming anatase into rutile.

(3) Crystalline vanadium oxide on titanium dioxide support does not exist when this catalyst is calcined at about 973 K.

(4) Crystalline MoO_3, however, is seen when MoO_3/TiO_2 catalyst is calcined at 973 K.

Finally, further study is needed in order to understand fully the microscopic mechanism of the transformation of anatase to rutile phase under the influence of V_2O_5 and MoO_3.

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