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An XPS Study of the Surface Oxidation States of Metals in Some Oxide Catalysts[1]

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Calcined samples of chromia supported on Al_2O_3, ZnO, or SnO_2 show both Cr(VI) and Cr(III) on the surface, Cr(VI) being preponderant in the case of Al_2O_3-supported catalysts. The proportion of Cr(VI) decreases with increase in Cr content of the calcined catalysts. Reduction of the supported chromia catalysts in H_2 at 720 K for 1 hr gives rise to Cr(III) and Cr(V). On carrying out the dehydrogenation of cyclohexane on the chromia catalysts a higher proportion of Cr(V) is found than after treatment with hydrogen. Vanadia supported on Al_2O_3 or MoO_3 shows significant proportion of V(IV) on carrying out the oxidation of toluene on the catalysts. Calcined MoO_3 (10%)/Al_2O_3 shows only Mo(VI) on the surface at 300 K, but on heating to 670 K in vacuum shows the presence of a considerable proportion of Mo(V) which on cooling disproportionates to Mo(IV) and Mo(VI). Mo(V) is noticed on surfaces of this catalyst on reduction with hydrogen as also on carrying out dehydrogenation of cyclohexane. While Bi_2MoO_6 shows only Mo(VI) on the surface at 300 K, heating it to 670 K in vacuum changes it entirely to Mo(V) which then gives rise to Mo(IV) and Mo(VI) on cooling.

INTRODUCTION

X-Ray photoelectron spectroscopy (XPS) is being effectively employed in the characterization of catalysts in recent years. We considered it interesting to investigate the surface oxidation states of transition metals in some important oxide catalysts by employing XPS in the light of detailed studies carried out by us on transition metal oxides in this laboratory (*1*, *2*). For this purpose, we have chosen the study of chromia catalysts supported on Al_2O_3, ZnO, and SnO_2, vanadia catalysts supported on Al_2O_3 and MoO_3, MoO_3 supported on Al_2O_3, and bismuth molybdate. In the case of chromia/silica catalysts Cimino *et al.* (*3*) have found only Cr(III) and Cr(VI) on the surface, while Cr(V) has been shown as an important species by Okamoto *et al.* (*4*) in reduced chromia/alumina catalyst. We have examined the relative proportions of Cr(III), Cr(V), and Cr(VI) on three types of chromia catalysts, a special feature being the study of the catalyst surfaces after carrying out the dehydrogenation of cyclohexane. Our study on the vanadia catalysts was aimed at finding the different oxidation states of vanadium present on the catalyst surface after carrying out an oxidation reaction.

The study of molybdena catalysts was particularly interesting to us. It has been reported (*5*) that MoO_3 can be readily reduced to metallic Mo by hydrogen at 670 K while MoO_3/Al_2O_3 or MoO_3/SiO_2 cannot be reduced below Mo(IV). Presence of Mo(IV), Mo(V), and Mo(VI) on surfaces of calcined MoO_3/SiO_2 catalysts has been suggested, the proportion of Mo(V) becoming significant on reaction with carbon monoxide (*6*). In view of the likely importance of the Mo(V) species in catalysis by molybdena catalysts (*7*), we have carefully investigated the Mo(IV), Mo(V), and Mo(VI) species by subjecting the catalyst to different treatments. For the purpose of comparison we have also studied bismuth molyb-

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date catalyst under similar conditions; it may be noted that reduction occurs at the molybdate group in this catalyst as well (*8*).

EXPERIMENTAL

Preparation of catalysts. Al_2O_3 was prepared by the hydrolysis of Analar $Al(NO_3)_3$ with aq.NH_3, subsequent drying of the gel at 400 K for 24 hr, and calcining the sample at 800 K for another 24 hr (*9*). Pure samples of ZnO and SnO_2 were commercially available. V_2O_5 was prepared by heating pure ammonium metavanadate at 720 K for 24 hr in air. MoO_3 was prepared by heating pure ammonium paramolybdate at 720 K for 24 hr in air. Bismuth molybdate was prepared by the method given by Grzybowska *et al.* (*10*).

Chromia/alumina catalysts (1.5, 5, 10, and 20% by weight of chromia) were prepared by the impregnation method. Al_2O_3 was treated with required amounts of $Cr(NO_3)_3$ solution and made into a slurry; the slurry was carefully evaporated to dryness and the samples dried at 400 K followed by calcination at 720 K for 24 hr. Chromia/ZnO and chromia/SnO_2 samples (with 5 and 10% by weight of chromia) were also prepared in a similar manner.

Supported vanadia (10%) catalysts were prepared by impregnating the support with ammonium metavanadate solution followed by slurrying and drying. The catalysts were then calcined at 720 K for 24 hr. MoO_3 (10%)/Al_2O_3 catalyst was prepared by impregnation of Al_2O_3 with ammonium paramolybdate. This catalyst was also calcined at 720 K for 24 hr.

Catalytic reactions. Dehydrogenation of cyclohexane was carried out on supported chromia, supported molybdena, and bismuth molybdate catalysts. Oxidation of toluene was carried out over supported vanadia catalysts. All the reactions were carried out at a constant weight hourly space velocity of 10 (i.e., grams of reactant per gram of catalyst per hour) at a temperature of 720 K usually for about an hour. The reaction conditions were such that the conversion in each case could be limited to less than 10%. It was found that cyclohexane dehydrogenates to predominantly benzene with traces of cyclohexane. In the case of toluene oxidation, the major product was benzaldehyde. At the end of the reaction, the catalysts were cooled in flowing dry N_2 and rapidly transferred to the spectrometer chamber taking care to ensure minimum contact with air.

XPS studies. X-Ray photoelectron spectra of the catalyst samples were recorded using an ESCA 3 Mark II spectrometer of V.G. Scientific Ltd. (U.K.). The base pressure in the analyser chamber was 10^{-9} to 10^{-10} Torr. Charging effect of the catalyst sample was corrected for by monitoring the C(1s) peak at a binding energy of 284.4 eV. Also internal checks were made using Al(2p), Zn($2p_{3/2}$), Sn($3d_{5/2}$); and O(1s) levels in the respective cases where these bands could be unambiguously assigned. In the case of Bi_2MoO_6 and MoO_3 (10%)/Al_2O_3 binding energies were carefully checked with the binding energies of Bi(4f) as well as Al(2p) levels, respectively, bearing in mind that the C(1s) line is not a good reference.

Decomposition of Cr(2p), V(2p), and Mo(3d) bands were carried out assuming that the peaks are gaussian. We have used fwhm values of 3.6 and 2.8 eV, respectively, for Cr(III) and Cr(VI) as given by Okamoto *et al.* (*4*). In the case of Cr(V) for which a literature value is not available, a value of 2.8 eV, identical to that of Cr(VI), was assumed in view of the depleted d-band and the fact that the spin-orbit splitting for both Cr(VI) and Cr(V) are the same (*4*). For V(2p) bands of V(V) and V(IV) the fwhm has been taken as 2.1 eV based on the spectra (*1*) for pure V_2O_5 and VO_2. For Mo(VI) as well as Mo(V) it is known (*5, 11*) that the binding energy as well as the linewidth of the Mo(3d) band change depending on the coordination which is determined by the nature of the support and calcination temperatures. Gajardo *et al.* (*12*) have reported that for the Mo(3d) band in MoO_3 (15%)/Al_2O_3 calcined at 773 K the fwhm is

2.2 eV. Our own value for the MoO_3 (10%)/Al_2O_3 calcined at 723 K is 2.1 eV. We have assumed the same value 2.1 eV as fwhm for Mo(V) as well as Mo(IV). We estimate that a change of 0.2 eV in fwhm leads to an error of about ±5% in the relative amounts of the species obtained by the decomposition of the spectra.

Okamoto *et al.* (*4*) have discussed in some detail the variation in the $Cr(2p_{3/2})/Cr(2p_{1/2})$ intensity ratio for a large number of compounds. For the decomposition of the spectra, we have ued a ratio of 1.66 for Cr(III) and 2.33 for both Cr(VI) and Cr(V). A ratio of 1.5 for V(V) and V(IV) has been used from data available for pure V_2O_5 and VO_2 (*1*). We find the $Mo(3d_{5/2})/Mo(3d_{3/2})$ intensity ratio for Mo(VI) to be 1.54 from the spectra for MoO_3(10%)/Al_2O_3 and Bi_2MoO_6 in agreement with the value given by Gajardo *et al.* (*13*). The same ratio was assumed for Mo(IV) and Mo(V) species. In the case where only Mo(V) species was identified on Bi_2MoO_6 surface, this ratio was actually observed. Relative amounts of the different oxidation states of Cr, V, and Mo were obtained from the areas of the respective $(2p_{3/2})$ or $(3d_{5/2})$ peaks in the decomposed curves.

RESULTS AND DISCUSSION

Supported Chromia Catalysts

In Fig. 1 we have shown the Cr(2p) band of chromia (5%)/alumina catalyst (a) after calcination at 720 K for 20 hr, (b) after reduction with hydrogen at 720 K for 1 hr, and (c) after carrying out dehydrogenation of cyclohexane at 720 K for 1 hr. We see that the calcined sample (Fig. 1a) has predominantly Cr(VI) on the surface with a small proportion of Cr(III) as characterized

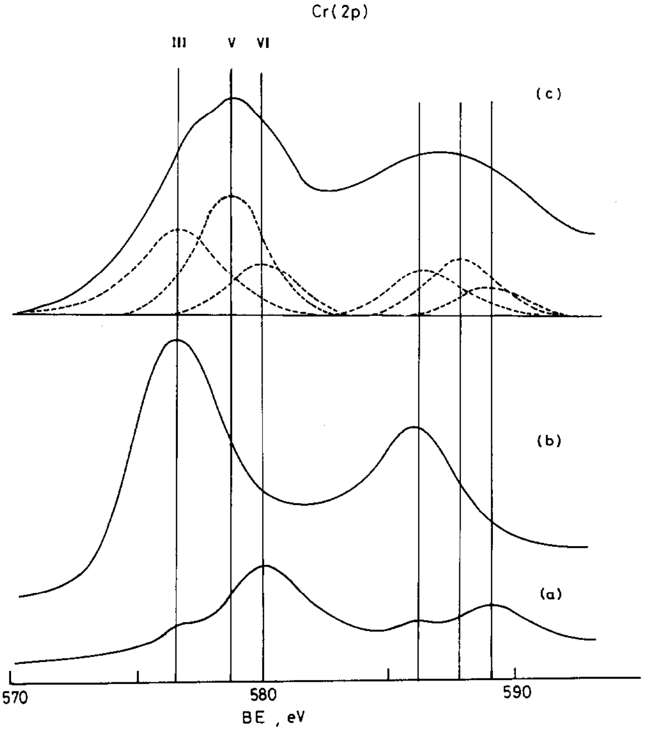

FIG. 1. Cr(2p) bands in chromia (5%)/alumina catalyst: (a) calcined at 720 K for 20 hr; (b) after reducing with H_2 at 720 K for 1 hr; (c) after carrying out dehydrogenation of cyclohexane at 720 K for 1 hr. Deconvoluted peaks due to Cr(III), Cr(V), and Cr(VI) are shown by broken curves. Positions of both the peaks due to spin-orbit splitting are shown by vertical lines.

by the Cr($2p_{3/2}$) signals at 580.0 and 576.6 eV, respectively, the corresponding spin-orbit splitting values being 9.1 and 9.8 eV. These results of the calcined catalysts are similar to those of Cimino *et al.* (*3*) on chromia/silica catalysts. Reduction of the calcined catalysts in hydrogen at 720 K for 1 hr gave predominantly Cr(III) on the surface (Fig. 1b). There is, however, evidence for a species in between Cr(III) and Cr(VI) with a binding energy of 578.8 eV and a spin-orbit splitting of 9.1 eV which we ascribe to Cr(V) in accordance with the assignment of Okamoto *et al.* (*4*).

On carrying out the dehydrogenation of cyclohexane on this catalyst, we find interesting changes in the surface composition of the oxidation states of chromium (Fig. 1c). Thus, we see all the three species, namely, Cr(III), Cr(V), and Cr(VI) on the surface. By decomposition of the Cr(2p) band, the proportions of these species are found to be 35, 45, and 20%, respectively.

We have similarly studied surfaces of chromia/alumina catalysts with different chromia content subjected to treatments similar to the chromia (5%)/alumina catalyst discussed above and the results are shown in Fig. 2. We see from Fig. 2a that the proportion of Cr(VI) decreases with increase in chromia content. This may be because of the crystallization of Cr_2O_3 on the surface as suggested by Cimino *et al.* (*3*). On catalysts reduced in hydrogen the proportion of Cr(III) increases with increase in chromia content while the proportion of Cr(V) decreases (Fig. 2b). On carrying out the dehydrogenation of cyclohexane on these surfaces, the proportion of Cr(III) increases with the chromia content on the surface. The proportion of Cr(V) is a maximum when the chromia content is less than 10% (Fig. 2c). At any one chromia composition, Cr(V) is higher after carrying out the dehydrogenation reaction rather than after hydrogen reduction.

The Cr(2p) band of chromia (5%)/ZnO was also studied (a) after calcination at 720 K for 20 hr, (b) after reduction with hydrogen at 720 K for 1 hr, and (c) after dehydrogenation of cyclohexane at 720 K for 1 hr (Fig. 3). In the calcined catalyst the proportion of Cr(III) is greater than Cr(VI) unlike

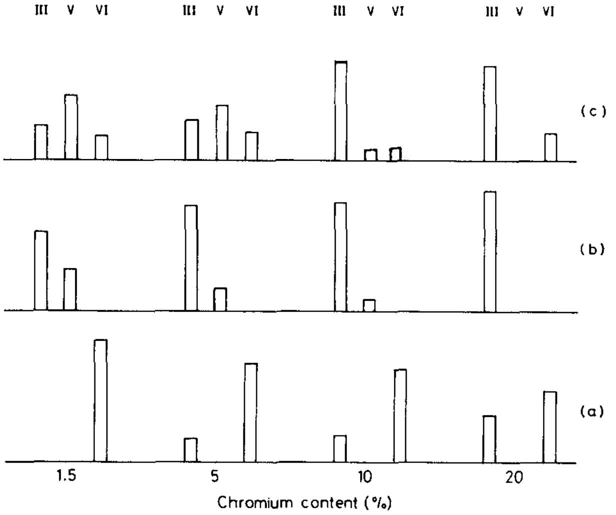

FIG. 2. Variation in the proportions of Cr(III), Cr(V), and Cr(VI) with weight percent of chromium in chromia/Al_2O_3 catalysts. (a), (b), and (c) are the same as in Fig. 1. This bar diagram has been prepared normalizing with respect to the chromium content (taking the total Cr content as unity for each composition); that is, the sum of the heights of the bars is constant.

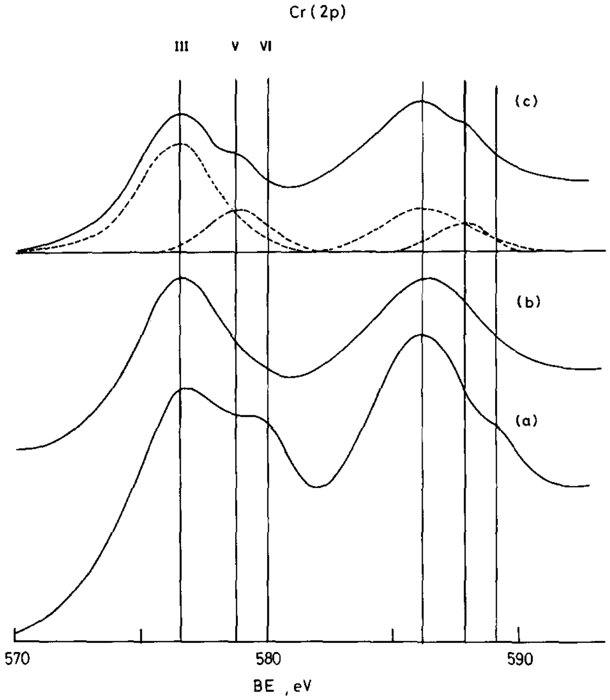

FIG. 3. Cr(2p) bands of chromia (5%)/ZnO catalyst. (a), (b), and (c) are the same as in Fig. 1.

in the case of chromia/alumina catalysts. On reduction with hydrogen we mainly see Cr(III) and Cr(V) species. The catalyst surface after dehydrogenation of cyclohexane gives rise to only Cr(III) and Cr(V) species; here again, proportion of Cr(V) is more after the dehydrogenation reaction than after hydrogen reduction. These results are summarized for two different chromia/ZnO catalysts in Fig. 4.

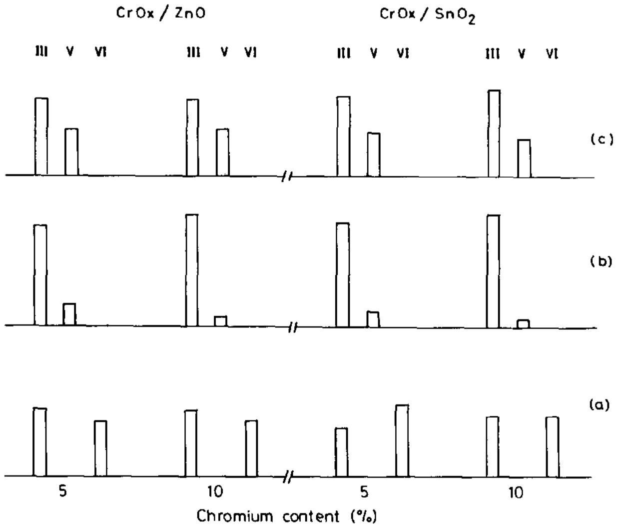

FIG. 4. Variation in the proportions of Cr(III), Cr(V), and Cr(VI) in chromia/ZnO and chromia/SnO_2 catalysts. (a), (b), and (c) are the same as in Fig. 1.

The results of our studies on chromia/SnO_2 catalysts are essentially similar to those of chromia/ZnO catalysts except that in the initially calcined catalysts the proportion of Cr(VI) is greater than Cr(III). The results on chromia/SnO_2 catalysts are summarized in Fig. 4.

In all three types of chromia catalyst, we found no changes in the binding energies of the metals of the supporting oxides (Al, Zn, and Sn). What is interesting is that in all three types of catalyst, Cr(V) is an important surface species when the catalysts are subjected to hydrogen reduction or after carrying out dehydrogenation of cyclohexane, the proportion of Cr(V) being generally higher in the latter case. When ZnO or SnO_2 is used as support, we find only Cr(III) and Cr(V) on the catalyst surfaces both after hydrogen reduction and after the dehydrogenation of cyclohexane, the proportion of Cr(VI) being negligible. The importance of Cr(V) as a reactive species in chromia catalysts has been pointed out in the literature (*4*, *14*). It may be noted that the presence of Cr(V) has also been found on copper chromite catalysts by Schreifel *et al.* (*15*).

Supported Vanadia Catalysts

In Fig. 5 we show the V(2p) band of the vanadia (10%)/alumina catalyst before and after reaction with toluene. The V(2p) band of pure V_2O_5 is also shown (Fig. 5a) for purpose of comparison. We see that the calcined catalyst (Fig. 5b) shows the presence of a small proportion of V(IV) in addition to V(V), as characterized by the $V(2p_{3/2})$ signals at 515.6 and 516.5 eV, respectively (the spin-orbit splitting for both these states is 7.5 eV). The decomposition of the V(2p) band shows that the proportion of V(IV) to V(V) is 40 : 60. On carrying out the reaction with toluene (Fig. 5c) we find an increase in the proportion of V(IV).

The V(2p) band of calcined vanadia (10%)/MoO_3 catalyst (Fig. 5d) shows that the proportion of V(IV) is less than V(V) (33 : 67) compared to vanadia (10%)/alumina catalyst. On reaction with toluene, however, the proportion of V(IV) appears to increase (Fig. 5e).

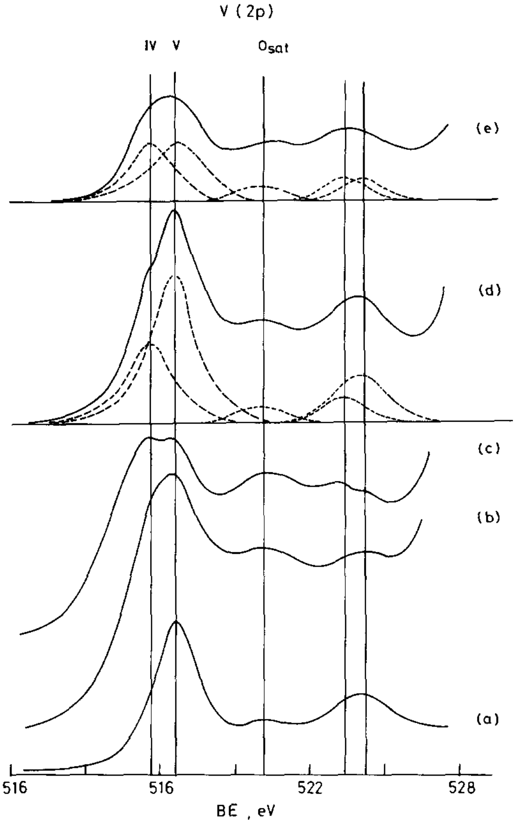

FIG. 5. V(2p) bands in supported vanadia catalysts: (a) pure V_2O_5; (b) calcined vanadia (10%)/Al_2O_3; (c) vanadia (10%)/Al_2O_3 after reaction with toluene; (d) calcined vanadia (10%)/MoO_3; (e) vanadia (10%)/MoO_3 after reaction with toluene.

In both the vanadia catalysts studied, we find no significant changes in the binding energies of the metal core levels of the supporting material (Al or Mo). This is particularly noteworthy in the case of vanadia (10%)/MoO_3 where the Mo(3d) binding energies show no changes on carrying out an oxidation reaction; this is unlike the case of molybdena catalysts to be discussed in the next section. All the vanadia catalysts show a small feature next to the $V(2p_{3/2})$ band around 519.5 eV. We attribute this to the Al$K\alpha_{3,4}$ satellite of the intense O(1s) band occuring at 529.8 eV.

MoO_3 (10%)/Al_2O_3 *Catalyst*

The calcined MoO_3 (10%)/Al_2O_3 catalyst shows a simple Mo(3d) band due to Mo(VI) at 300 K with a characteristic spin-orbit splitting of 3.2 eV (see Fig. 6a). On heating the sample to 670 K under the ambient vacuum conditions (10^{-9}–10^{-10} Torr) for 3 hr, the 3d band shows clear evidence for the formation of Mo(V) (Fig. 6b). On cooling this sample from 670 to 570 K, there appears to be a slight decrease in the proportion of Mo(V) (Fig. 6c), but on cooling to 300 K, the proportion of Mo(V) decreases significantly accompanied by the formation of Mo(IV) (Fig. 6d). A spectrum of this sample maintained at 300 K for 20 hr (Fig. 6e) shows a considerable increase in the proportion of Mo(IV), the other species being Mo(V) and Mo(VI).

Treatment of the MoO_3 (10%)/Al_2O_3 catalyst with hydrogen at 670 K for 1 hr shows mainly the presence of Mo(IV) and Mo(VI) on the surface with a small proportion of Mo(V) (Fig. 7a). On carrying out the dehydrogenation of cyclohexane on this catalyst, we find Mo(V) to be the preponderant species (Fig. 7b). We have summarized our results on the molybdena catalyst in Table 1 where we have given the approximate percentages of Mo(IV), Mo(V), and Mo(VI) under different conditions. It appears from our studies that Mo(V) is a very important species in determining the activity of molybdena catalysts, as suggested by several workers (*7*, *16*). It has indeed been pointed out by Maggiore *et al.* (*7*) that Mo(V) is an active species in the conversion of cyclohexane to benzene. Best *et al.* (*6*) have found evidence for Mo(V) on treatment of MoO_3/SiO_2 catalysts with carbon monoxide.

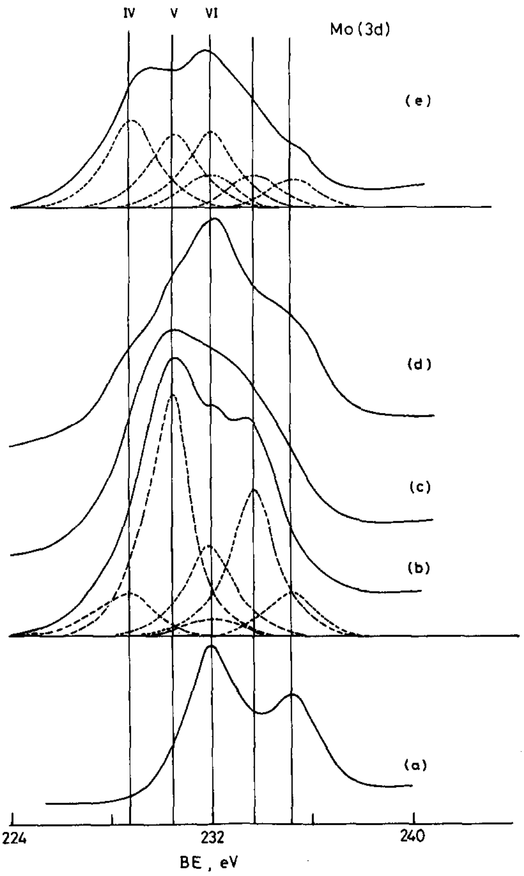

FIG. 6. Mo(3d) bands of the MoO_3 (10%)/Al_2O_3 catalyst: (a) calcined sample at 300 K; (b) calcined sample heated to 670 K in vacuum; (c) sample (b) cooled to 570 K; (d) sample (c) cooled to 300 K; (e) sample (d) maintained for 20 hr at 300 K.

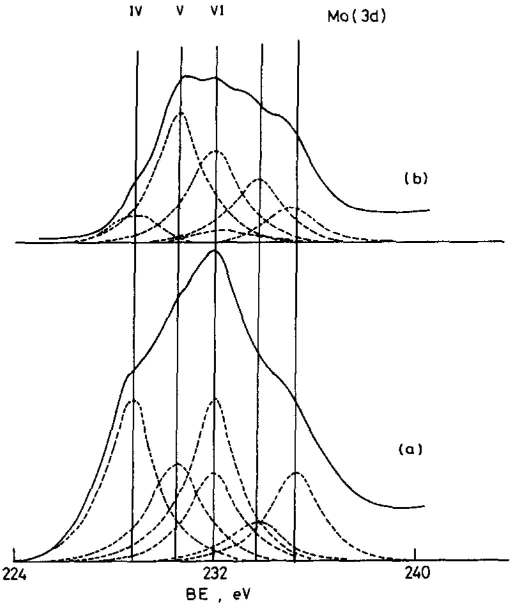

FIG. 7. Mo(3d) band of the MoO_3 (10%)/Al_2O_3 catalyst: (a) reduced in H_2 at 670 K for 1 hr; (b) after reaction with cyclohexane at 720 K for 1 hr.

TABLE 1

Surface Oxidation States of Molybdenum in Molybdena and Bi_2MoO_6 Catalysts

Treatment	$MoO_3(10\%)/Al_2O_3$[a]			Bi_2MoO_6[a]		
	%Mo(IV)	%Mo(V)	%Mo(VI)	%Mo(IV)	%Mo(V)	%Mo(VI)
1. Calcined sample	—	—	100	—	—	100
2. (a) Sample heated to 670 K in vacuum (10^{-9}–10^{-10} Torr) for 3 hr	10	65	25	—	100	—
(b) Sample cooled to 570 K	25	50	25	—	100	—
(c) Sample cooled to 300 K	30	40	30	10	80	10
(d) Sample after 20 hr in vacuum at 300 K	40	30	30	20	45	35
3. Sample 1 reduced in H_2 at 670 K for 1 hr	40	20	40	—	—	—
4. Sample 1 treated with cyclohexane at 720 K for 1 hr	10	50	40	—	100	—

[a] The $3d_{5/2}$ binding energies of Mo(IV), Mo(V), and Mo(VI) are 228.8, 230.6, and 232.0 eV, respectively; the spin-orbit splitting in all these cases is the same, namely, 3.2 eV.

Praliaud and co-workers (*11, 17, 18*) have shown in the case of supported MoO_3 catalysts that Mo(VI) species is present both in tetrahedral and octahedral environments (when Mo concentration is greater than 2%), the extent of occupancy depending both on the Mo content as well as the calcining temperature. In MoO_3/Al_2O_3 calcined at lower temperatures than 723 K, they find (*11*) that octahedral Mo(VI) concentration is only minor, as it is the calcination itself which leads to the octahedral Mo(VI). Above calcination temperatures of 823 K, octahedral Mo(VI) is predominant even at low Mo concentrations. After reduction, it is claimed that the Mo(V) species have both O_h and T_d symmetries even in cases with no octahedral Mo(VI) in the original samples. The Mo(V) O_h/Mo(V) T_d ratio is generally high in catalysts with Mo content greater than 10%. In view of these findings we feel that in our sample of MoO_3 (10%)/Al_2O_3 calcined at 723 K, the Mo(VI) species as well as Mo(V) are predominantly in O_h sites.

The Al(2p) band of the MoO_3 (10%)/Al_2O_3 catalyst showed some changes on heating to 670 K and then cooling it back to 300 K; the change was in terms of the appearance of a shoulder on the lower binding energy side of the Al(2p) band (73.5 eV). Hydrogen reduction as well as hydrogenation reaction with cyclohexane seem to lower the Al(2p) binding energy slightly. While we were tempted to relate these changes to changes in the environment of Al^{3+}, we decided against it since the changes are minor and shifts are within experimental uncertainty (±0.5 eV).

Bismuth Molybdate Catalyst

In view of our results on the MoO_3/Al_2O_3 catalyst, we considered it interesting to study the Bi_2MoO_6 catalyst subjected to similar treatments. The Mo(3d) band of Bi_2MoO_6 shows only the presence of Mo(VI) at 300 K (Fig. 8a). Heating the sample to 670 K under the ambient vacuum conditions (10^{-9}–10^{-10} Torr) seems to result almost entirely in Mo(V) on the surface (Fig. 8b) with no change in the Bi(4f) peak. Cooling this sample to 570 K does not result in any changes (Fig. 8c); on cooling to 300 K, however, we see evidence for the formation of Mo(VI) as well as Mo(IV) as shown by the broadening of the peaks (Fig. 8d). On keeping the sample for 20 hr at 300 K in vacuum, we see the formation of

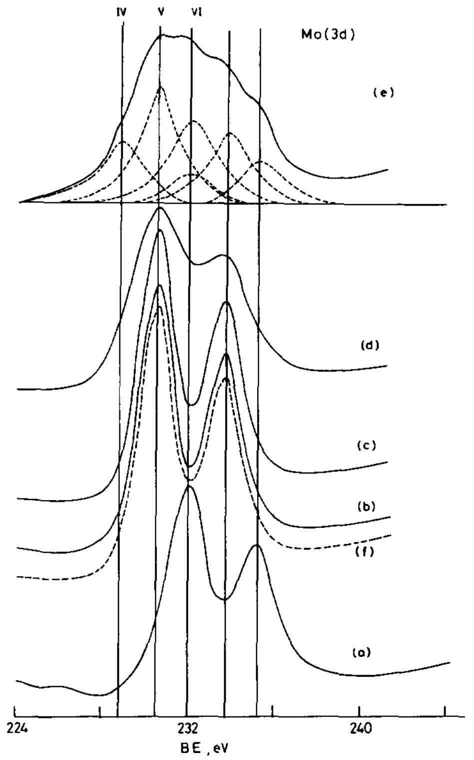

FIG. 8. Mo(3d) bands of Bi_2MoO_6 catalyst: (a) at 300 K; (b), (c), (d), and (e) are the same as in Fig. 6; (f) after reaction with cyclohexane at 720 K for 1 hr.

Mo(VI) and Mo(IV) with a small proportion of Mo(V) (Fig. 8e). The results of our studies on Bi_2MoO_6 are also summarized in Table 1 along with those on MoO_3 (10%)/Al_2O_3 catalyst. We see that the behavior of these two samples is remarkably similar except that Bi_2MoO_6 shows almost entirely Mo(V) in the temperature range 670–400 K while the molybdena/alumina catalyst shows the presence of Mo(V) along with Mo(VI). With a view to comparing the behavior of Bi_2MoO_6 with that of MoO_3 (10%)/Al_2O_3, we studied the Mo(3d) band of the former after reaction with cyclohexane. Surprisingly, the (3d) band shows the presence of only Mo(V) on the surface (Fig. 8f) just as the catalyst did at 670 K. In all these studies of Bi_2MoO_6, the O(1s) band was not affected except for a slight broadening.

It appears that Mo(V), which is the reactive species, is formed as an intermediate which then disproportionates to Mo(IV) and Mo(VI), the disproportion being more facile in the molybdena/alumina catalysts than in the case of Bi_2MoO_6. The present results for Bi_2MoO_6 differ from those of Grzybowska *et al.* (*19*) who find only Mo(IV) and Mo(VI) on the surface after heat treatment of the sample. Considering the relatively large concentration of Mo in the Bi_2MoO_6 and the observed fwhm of 2.2 eV for the Mo(3d) band (Fig. 8a), it is possible that Mo(VI) is octahedrally coordinated here as well (*11, 20*). From Fig. 8f where we see a single peak for the Mo(V) species, the fwhm has the same value as for Mo(VI).

Some workers have pointed out that bismuth in bismuth molybdate also undergoes changes in its oxidation state during catalysis (*21, 22*). Thus, Bi(IV) or Bi(V) has been suggested to play an important role in this catalyst. Our studies of the Bi(4f) bands show that the only Bi species is Bi(III) under all the conditions studied by us. It appears that the surface oxidation state of bismuth does not undergo changes as pointed out by Sleight and Linn (8).

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