Catalysis Letters 38 (1996) 95–99

Molybdenum based catalysts. I. MoO_2 as the active species in the reforming of hydrocarbons

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Received 17 October 1995; accepted 21 December 1995

The XPS spectra of bulk MoO_2 and MoO_3 are reported. Commercial MoO_2 reveals the presence of multilayers of MoO_3 covering bulk MoO_2. In situ reduction of bulk MoO_3 by H_2 at temperatures equal to 623 K and less than 673 K reduces the superficial layer(s) to mainly MoO_2. Such phase is characterised by a certain density of states in terms of the free 4d, 5s electrons localised mainly on the Mo atoms and observed in the valence band energy region at the Fermi-level in the XP spectrum of this system. Catalytic reactions on the MoO_2 phase of 2-methylpentane at atmospheric pressure using a mixture of the hydrocarbon (5 Torr) with hydrogen (755 Torr) yield 3-methylpentane and *n*-hexane as the main products in roughly equal amounts. These results are interpreted in terms of dual sites on the MoO_2 surface.

Keywords: molybdenum dioxide; XPS; argon ion bombardment; reforming of alkanes

1. Introduction

Transition metal carbides such as WC, W_2C and Mo_2C were expected to replace supported noble metals known for their bifunctional activity in hydrogenolysis and isomerization reactions [1–5]. It has been observed that the introduction of controlled amounts of oxygen at certain temperatures modifies completely the catalytic behaviour of these carbides in such a way that isomerization products become predominant [6–8]. This modified property has been attributed to a chemisorbed oxygen on WC surfaces [6], or to the formation of an oxycarbide species such as WO_xC_y [3] or MoO_xC_y [7].

Systematic studies using catalytic reactions in association with different spectroscopic techniques on WC, WO_3 and W(0) following oxidation and reduction under different experimental conditions led to the conclusion that the active species in terms of isomerization reactions for different hydrocarbon reactants is the WO_2 phase [8–10]. In a parallel study concerning the bulk molybdenum carbides and oxides, the catalytic behaviour of these systems was considered following different treatments such as oxidation and reduction as a function of the temperature and stability for different hydrocarbon reactants such as 2-methylpentane and *n*-hexane. XP spectra of these systems following different in situ treatments with H_2 at different temperatures and Ar^+ bombardment were recorded. It is important to note that the MoO_2 phase has a distorted rutile structure and exhibits a metallic electrical conductivity [11,12], while MoO_3 is an insulator. The electrical conductivity of the MoO_2 phase is attributed to a relatively high density of states in terms of the Mo 4d, 5s free electrons localised on Mo and can be observed in the valence band energy region. The presence of these free electrons contributes certainly to the catalytic activity of the Mo^{4+} in MoO_2 by comparison to Mo^{6+} in MoO_3, where all the valence electrons of Mo are involved in bond formation with the neighbouring oxygen atoms.

The purpose of this work is to follow the extent of in situ reduction of MoO_3 by H_2 to lower valence state(s) in function of the reduction temperature as characterised by the Mo 3d and valence band energy region structures. The catalytic behaviour of these systems obtained upon similar reduction treatments will be tested using different hydrocarbon reactants. A correlation between these results will be envisaged.

2. Experimental

Molybdenum trioxide (99.998%) and dioxide (99%) were obtained from STREM chemicals. The catalytic experiments were performed in the following way: the samples were maintained under a hydrogen flow (50 $cm^3\ min^{-1}$) at fixed temperatures (623 and 673 K) and atmospheric pressure. A dose of 5 μl of the reactant (partial pressure = 5 Torr) was injected periodically into the reactor at a flow rate of 140 $cm^3\ min^{-1}$. The reaction was completed very quickly, typically in a few minutes. The catalyst was then left under the hydrogen flow before another experiment was carried out. The temperature of all reactions was 623 K with 100 mg of the catalyst sample. In each run, a fraction of the reaction was analysed by gas chromatography over a capillary column (dimethyl siloxane, diameter 0.23 mm). The activity (conversion) α is defined as the ratio between the molecules which have reacted to those initially introduced.

The XP spectra were obtained using an ESCA III VG instrument with Al Kα radiation. All the spectral line binding energies were referred to the C 1s at 286.4 eV. Standard energy differences between the different molybdenum oxides and FWHM of the Mo 3d spectral lines were considered in the curve fitting process of the Mo 3d energy region of the systems studied in this work. Reductions under H_2 at atmospheric pressure were performed in a preparation chamber directly connected to the spectrometer. Argon ion bombardment (3 kV, 30 μA) was also employed as sputtering and reducing agent [13]. Binding energies are reported within an experimental error of ±0.2 eV.

3. XPS results and interpretation

3.1. Molybdenum trioxide

The XP spectrum is very similar to those reported previously by many authors [11–14]. The Mo 3d spin–orbit components are observed at 232.5 and 235.6 eV. In situ reduction of MoO_3 by H_2 at 623 K for 2h30 results in partial reduction of MoO_3 to two lower valence states with the $3d_{5/2}$ measured at 231.7 and 229.2 eV, fig. 1b. These values are attributed to the Mo_2O_5 and MoO_2 states respectively [15]. It is apparent from the curve fitting that the Mo_2O_5 phase is more abundant than MoO_2. Moreover, the valence band energy region shows a certain density of states at the Fermi-level which is characteristic of the MoO_2 phase and absent in MoO_3, figs. 2a and 2b. Further reduction by H_2 of the same sample for 5 h at the same temperature results in a considerable increase in the MoO_2 relative concentration as compared to Mo_2O_5 and MoO_3, figs. 1c and 2c. It is important to mention at this point that exposure of MoO_3 to H_2 at 623 or 673 K does not lead to the formation of the metallic Mo phase as observed in the XP spectrum. The in situ reduction of another sample of MoO_3 by H_2 at 723 K for 2h30 results in the presence of the Mo(0) metallic phase measured at 227.7 eV for the $3d_{5/2}$ besides the two Mo_2O_5 and MoO_2 states, figs. 1d and 2d. On the other hand, it was observed that Ar^+ bombardment of another MoO_3 sample leads to the formation of MoO_2 as a final stable state regardless of the exposure time of the sample to these energetic ions.

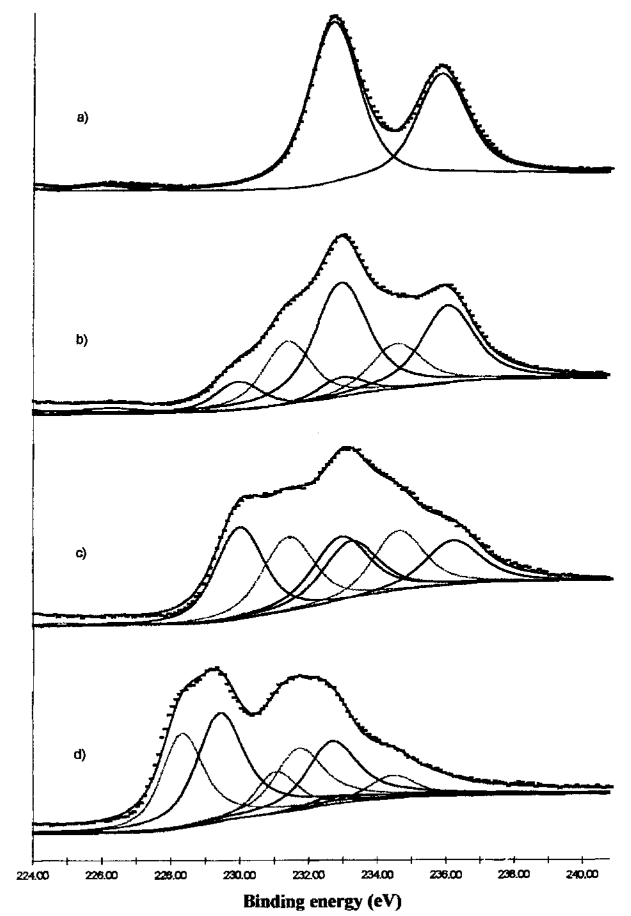

Fig. 1. The XPS of MoO_3 3d following different in situ treatments with H_2: (a) as received, (b) at 623 K for 2h30, (c) at 623 K for 5 h, (d) at 723 K for 2h30.

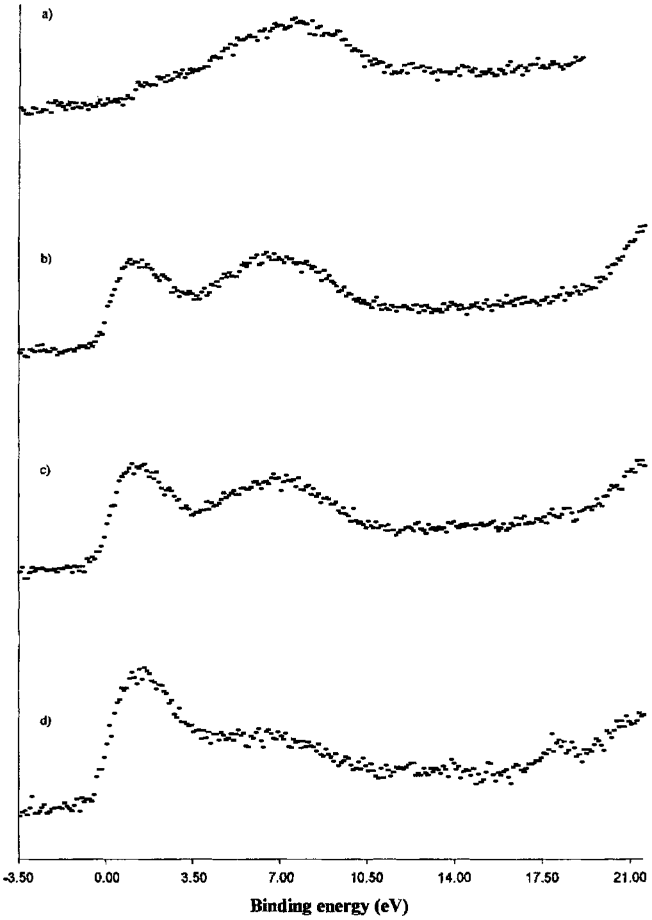

Fig. 2. The XPS of the valence band energy region of MoO_3 following different in situ treatments with H_2: (a) as received, (b) at 623 K for 2h30, (c) at 623 K for 5 h, (d) at 723 K for 2h30.

3.2. Molybdenum dioxide

The XPS of the MoO_2 sample as received shows the presence of three MoO_2, Mo_2O_5 and MoO_3 states, fig. 3a. It is apparent that exposure of MoO_2 to air results in its oxidation to the MoO_3 phase which constitutes the superficial layer(s) with "Mo_2O_5" as the interface between MoO_3 and MoO_2. The presence of MoO_2 can be observed in the valence band energy region, fig. 4a. The extent of MoO_2 oxidation to MoO_3 in air at atmospheric pressure depends on the exposure time of MoO_2 to air where a clear increase in MoO_3 relative concentration following a few weeks of MoO_2 exposure to air (figs. 3b and 4b) was observed. In situ reduction by H_2 of an MoO_2 sample at 623 K for 12 h results in a considerable decrease in the MoO_3 relative intensity in favour of MoO_2, as can be observed in figs. 3c and 4c. It is important to note that even after this relatively considerable time of reduction by H_2 at 623 K of the MoO_2 partially oxidized sample a small amount of MoO_3 is still present. Argon ion bombardment of sample c for 2 min results in the presence of an almost pure MoO_2 phase measured at 229.1 and 232.3 eV (fig. 3d). The band at 1.5 eV in the valence band energy region is attributed to the Mo 4d, 5s derived states, while the relatively broad band with a maximum at 7.2 eV is attributed to the O 2p states.

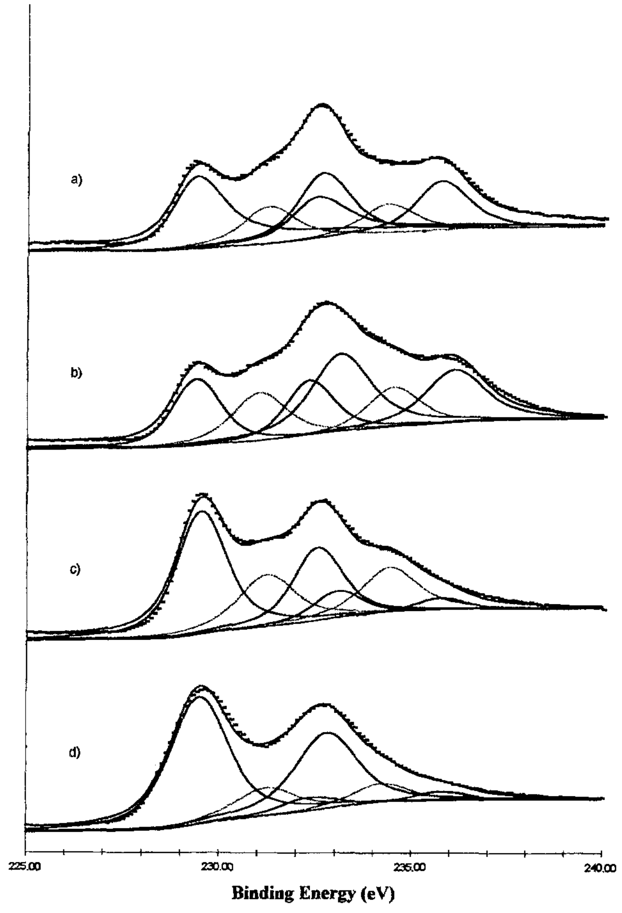

Fig. 3. The XPS of MoO_3 3d energy region of the commercial MoO_2 sample before and after H_2 reduction: (a) as received, (b) at 623 K for 2h30, (c) at 623 K for 12 h, (d) Ar^+ bombardment of (c) for 2 min.

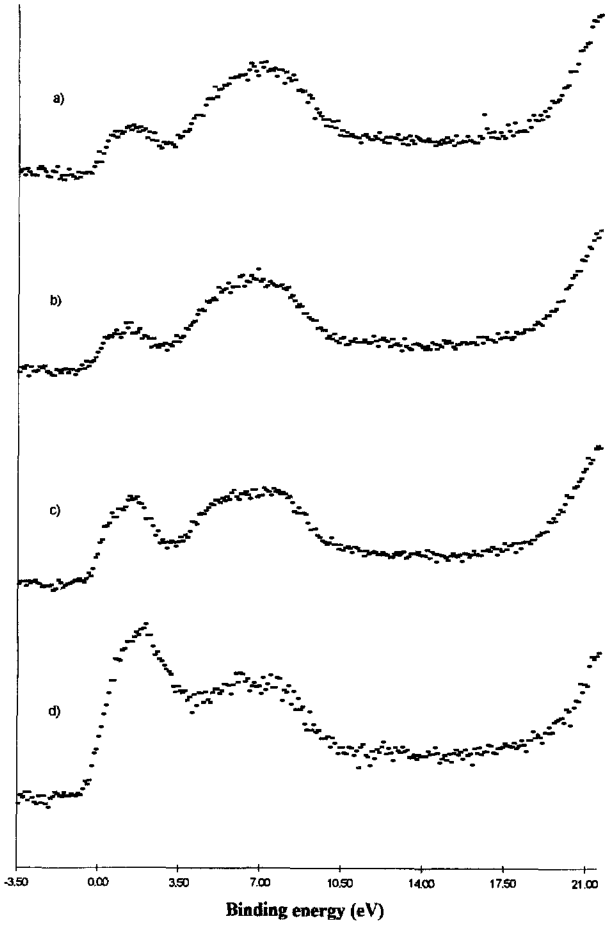

Fig. 4. The XPS of the valence band energy region of the commercial MoO_2 sample before and after H_2 reduction: (a) as received, (b) at 623 K for 2h30, (c) at 623 K for 12 h, (d) Ar^+ bombardment of (c) for 2 min.

4. Catalytic results

In the following study, the catalytic activities of bulk MoO_3 and partially oxidized MoO_2 samples will be studied using 2-methylpentane as reactant. Other reactants such as *n*-hexane and methylcyclopentane have also been studied but will not be discussed in this paper. Each catalytic reaction has been repeated several times in order to ensure reproducibility of results using the catalytic reactor mentioned in the experimental section. Having in mind the XPS results concerning the reduction of MoO_3 by H_2 as a function of the temperature and reduction time, we will report the catalytic results obtained using the two MoO_3 and MoO_2 samples mentioned previously.

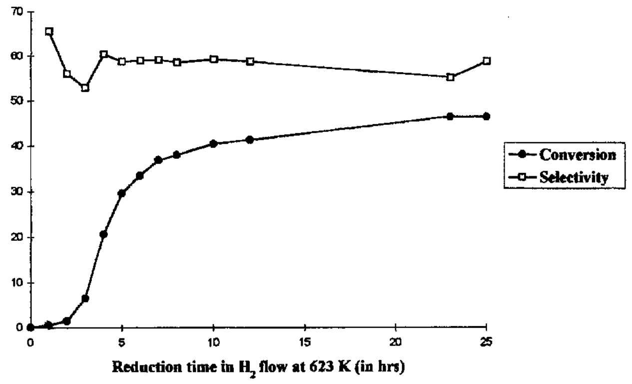

Fig. 5. The activity and selectivity of 2-methylpentane on MoO_3 as function of reduction time by H_2 at 623 K.

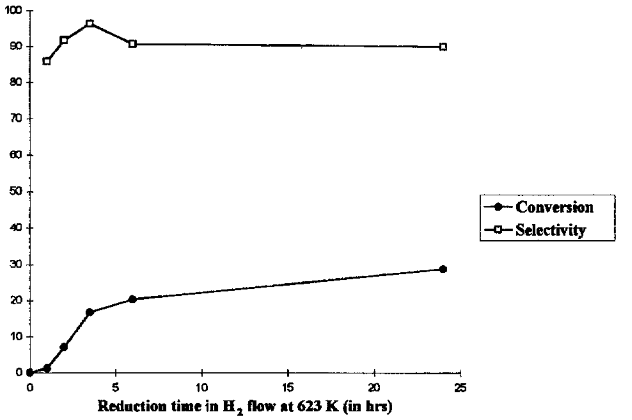

Fig. 6. The activity and selectivity of 2-methylpentane on MoO_2 as function of reduction time by H_2 at 623 K.

4.1. MoO_3

The temperature of the sample under the hydrogen flow was increased from 298 to 623 K at 10 K min^{-1}. An experiment was then performed but no activity was observed (point 0 of fig. 5). It required almost 1 h induction time to observe signs of activity and selectivity which reach a stable state within 10 h with an activity of 40% and a selectivity of 60% (fig. 5).

The values reported in fig. 5 were obtained by hourly injections of the hydrocarbon reactant while the catalyst was kept under H_2 flux at 623 K. The catalyst activity and selectivity were tested for a week without any noticeable change, neither in activity nor in selectivity. In order to verify the effect of the hydrocarbon reactant in modifying the chemical structure of the catalyst in terms of so-called oxycarbide species, we have carried out a separate experiment by maintaining the catalyst under H_2 flux at 623 K for 34 h, followed by a hydrocarbon injection. The catalyst activity and selectivity were very similar to those obtained by the previous experiment with repeated hourly injections of the reactant.

4.2. MoO_2

It is interesting that the catalytic behaviour of the partially oxidized MoO_2 catalyst is very similar to that observed previously in the case of MoO_3. However, it was observed that the induction time in order to reach a stable state in terms of activity and selectivity of MoO_2 catalyst is much less than that observed in the case of bulk MoO_3. Moreover, the selectivity of MoO_2 in terms of isomerization products is 90% with a conversion of $\sim$ 20% (fig. 6).

In the case of 2-methylpentane reactant, the major products were 3-methylpentane and *n*-hexane with a ratio of $\sim$ 1 at 623 K induction temperature in a similar way to that observed in the case of MoO_3 catalyst.

In order to determine the extent of the effect of reduction temperature on partially oxidized MoO_2 in terms of activity and selectivity, we have carried out separate experiments at intervals of 30 min after reduction at 673 K (fig. 7). Interestingly, a stable state in terms of activity and selectivity was reached rapidly with conversion of 35% and selectivity of 90%. The 3-methylpentane to *n*-hexane ratio was determined at 1.2.

5. Discussion

The XPS results reported in this work show that the reduction of MoO_3 to MoO_2 with Mo_2O_5 possibly located at the interface is a slow process even at 623 K. An important point is that no oxidation state lower than Mo(IV) was detected. The particular electronic properties of the MoO_2 phase with the free Mo 4d, 5s derived states localized mainly on the Mo atoms result in metallic conductivity of this system. This has certainly an influence on the catalytic behaviour in terms of the existence of dual sites, as already proposed [16]. No such an activity is expected in the case of Mo^{6+} in MoO_3 due to the absence of these free localised electrons. Defining MoO_2 as the active catalytic phase in these systems, it is

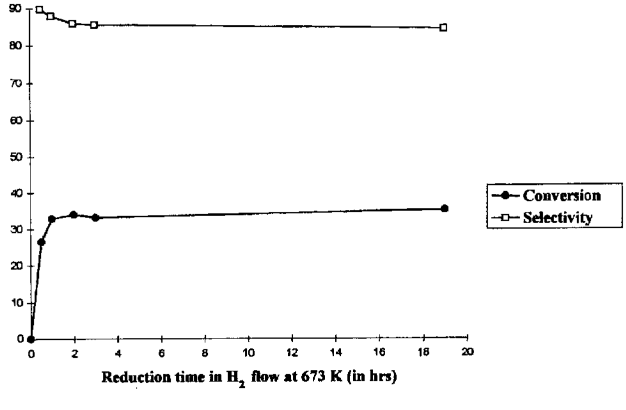

Fig. 7. The activity and selectivity of 2-methylpentane on MoO_2 at a reduction temperature of 673 K (reaction temperature: 623 K).

interesting to interpret the previously observed catalytic results on these grounds.

In the case of bulk MoO_3, it required about 1 h of exposure to H_2 at 623 K as an induction time to initiate the reduction of MoO_3 to MoO_2, as observed by XPS as well as catalytic activity. Apparently, a few atomic layers from the surface and below constitute the necessary requirement for a certain electronic stability of the system expressed in a stable catalytic activity and selectivity. However, further increase in the reduction temperature to equal or higher than 723 K leads to the partial reduction of MoO_2 to Mo(0). The presence of the metallic Mo on the surface of the catalyst would certainly favour the hydrogenolysis products [17].

In the case of bulk MoO_2, it was observed by XPS that this sample has been partially oxidized to MoO_3. Considering the limited number of MoO_3 layers surrounding the bulk of MoO_2, it was easier to reduce MoO_3 to MoO_2 in the case of this partially oxidised MoO_2, resulting in a much shorter induction time in activity and selectivity as compared to MoO_3. Moreover, no oxygen diffusion from bulk MoO_2 to MoO_2 surface layers is expected as it would be in the case of bulk MoO_3.

Considering the presence of carbon as a constituent element in the chemical structure of the active phase such as an oxycarbide MoO_xC_y species, we did not find any conclusive evidence for such a phase from the XPS of the samples studied in this work. Moreover, it was clearly observed that the catalytic results in terms of activity and selectivity are very similar in the case of repeated hourly injections of hydrocarbon reactant in the H_2 flow for 34 h and only one hydrocarbon injection after 34 h of H_2 flow over bulk MoO_3 catalyst at 623 K. Most probably, the only chemical species present at this point is the stable MoO_2 phase which we believe responsible for the catalytic behaviour of this system. It seems very unlikely that an oxycarbide phase could be formed on that phase especially if one considers that the contact time with the hydrocarbon was so short.

A complete study of these bulk and supported systems using different hydrocarbon reactants will be published elsewhere.

Acknowledgement

The authors would like to express their thanks to Mrs. P. Girard for her help in operating the catalytic reactor and associated instruments.

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