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Structure and Catalytic Activity of $MoO_3 \cdot SiO_2$ Systems

II. Catalytic Activity in the Oxidation and Disproportionation of Propylene

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The role and nature of active species in the catalytic reaction of propylene over $MoO_3 \cdot SiO_2$ catalysts were established in the absence and presence of oxygen, i.e., under depletive and heterogeneous conditions. At $T = 400°C$, under depletive conditions and in the absence of water, only disproportionation occurs (maximum at 10 wt% MoO_3); this activity is ascribed to bis-molybdenyl-type species. In the presence of water, heterogeneous oxidation over samples containing over 10 wt% MoO_3 leads to acrolein, acetaldehyde, CO and CO_2, as well as minor amounts of propionaldehyde, acetone, and acetic acid. Acrolein, acetaldehyde, and part of CO_x appear to be primary reaction products. At higher conversion levels, CO_x is also formed via oxidation of intermediates. Catalytic results are accounted for by the presence of superficial polymolybdates which display polyfunctional characteristics, thus explaining formation of acrolein and acetaldehyde. Whiskers of MoO_3 are also present on the solid but contribute little to catalytic activity.

INTRODUCTION

The catalytic oxidation of olefins over molybdates has received considerable attention in the past. On the contrary, much less work has been devoted to the effects of inert supports. The present paper attempts to elucidate these aspects with regard to MoO_3 supported on a high surface microspheroidal SiO_2 gel; recently we have reported on solid-state properties of this same system (*1*). It was shown that impregnation (up to 25 wt% MoO_3) and activation (at 500°C) leads to a complex distribution of compounds due to physical and chemical interaction processes. Summarizing we may state that: (i) In the region up to 10% MoO_3, isolated Mo(VI) tetrahedral species are present together with silico-molybdic acid (SMA); (ii) in the upper region ($>10\%$ MoO_3) the surface is covered with polymolybdate species having Mo(VI) in an octahedral oxygen coordination; in addition, free MoO_3 is present in the form of whiskers, increasing drastically as the formal MoO_3 content increases. Products of more profound interaction (Mo^{6+} in the SiO_2 lattice) are also found.

In this paper we attempt to elucidate the role of each of these species in the heterogeneous oxidation of propylene and to discover the origin of acrolein and byproducts (acetaldehyde, CO, CO_2, etc.). Mechanistic aspects related to these reactions will be dealt with in more detail in a forthcoming paper (*2*). In addition, results of experiments performed under depletive conditions (pulse technique) are presented to elucidate aspects of disproportionation activity, also in comparison with results of our previous studies on the $MoO_3 \cdot Al_2O_3$ system (*3–5*).

EXPERIMENTAL

The catalyst samples used were the same as those described previously (*1*); the notations *A* and *V* refer to samples activated in air or in air/water vapor, respectively.

Apparatus and Experimental Procedure

Experiments to determine catalytic activity were carried out in the flow microreactor described elsewhere for studies on the $MoO_3 \cdot Al_2O_3$ system (*3*).

Conditioning of the catalysts before use, gas-chromatographic analysis, and data evaluation were also as before. Variants in the experimental conditions with respect to former work (*3*) were: (i) in pulse experiments, 0.5 g of catalyst (40–150-mesh size) at a He flow rate of 40 cm^3/min; pulse volume was 0.5 cm^3 of propylene; (ii) in tail experiments, reactants were fed in the ratio propylene:air = 1:12, at a total flow rate of 55 cm^3/min; the catalyst (150–270-mesh size) was located in the central part of the microreactor between two layers of inert Al_2O_3. Experiments were performed: (a) at $T = 440°C$ and contact times τ from 0.12 to 1 sec made to vary by modifying the amount of catalyst; (b) at $\tau = 1$ sec and $T = 360–440°C$. In addition, blank experiments were performed with the empty reactor or with packing of inert Al_2O_3.

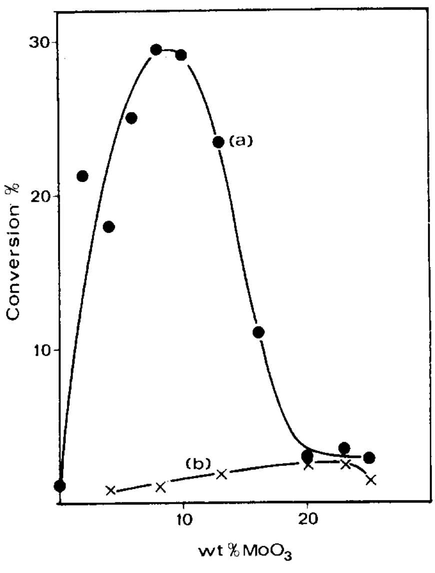

FIG. 1. Conversion of propylene as a function of the composition, for runs in the absence (a; mode 1) and presence of water (b; mode 2) at $T = 400°C$.

RESULTS

Pulse Experiments

As preliminary runs had indicated very low conversion of propylene under the conditions of the reference work (*3*), the temperature of the experiment was set at 400°C. Figure 1 shows the variation of catalytic activity, as a function of the composition, for experiments in the absence (mode 1) and presence (mode 2) of water. Under the former conditions, Fig. 2 illustrates variations in the selectivity and shows products of disproportionation (ethylene + butenes) in the lower MoO_3 region as opposed to oxidation to acrolein and CO_2 in the higher region. On the contrary, in the presence of water the disproportionation activity is severely reduced (Fig. 1) in accordance with expectations. The fraction of chemisorbed propylene was found to be very low for compositions up to MoO_3-16; at higher compositions it increases steeply, exceeding by an order of 1.5 the conversion to detectable products in case of the MoO_3-25 sample.

Tail Experiments

Results for runs at $T = 440°C$ and $\tau = 1$ sec are exemplified in Fig. 3. Catalytic activity, low in the lower MoO_3 region,

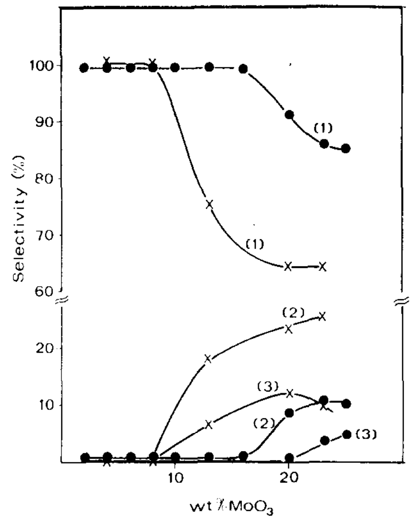

FIG. 2. Product distribution in the absence (mode 1, ●) and presence of water (mode 2, ×) at 400°C: (1) summation of selectivities to products of disproportionation; (2) selectivity to CO_2; (3) selectivity to acrolein.

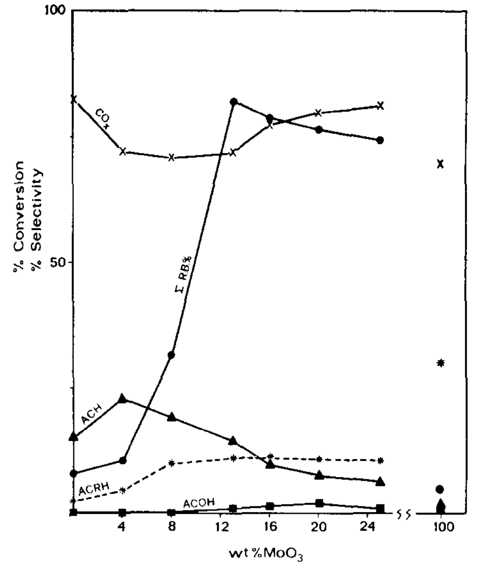

FIG. 3. Conversions and selectivities in oxidation of propylene, as a function of the composition, for runs at 440°C, t_c = 1 sec and the ratio air:propylene = 12:1. ACH, acetaldehyde; ACRH, acrolein; ACOH, acetic acid; ΣR.B., product yield.

increases sharply from MoO_3-8 to MoO_3-13 and then decreases; under comparative conditions, conversion on pure MoO_3 is ~5%. Further, a series of experiments performed to establish the dependence of catalytic activity upon the reaction temperature T_R has given the results illustrated in Fig. 4 with reference to the MoO_3-16 sample: Acrolein, acetone, and acetic acid are constant throughout, acetaldehyde, and propionaldehyde diminish with increasing T, and CO_x increases (CO_x is here meant to imply a mixture of CO and CO_2, mostly in a 1:1 ratio). Apparent activation energies were of the order of 28 kcal/mol for the 360–400°C range and 16 kcal/mol for 400–440°C. Other characteristic features of $MoO_3 \cdot SiO_2$ catalysts are shown in Fig. 3, namely, higher selectivities to CO_x and acetaldehyde prevailing in the low MoO_3 region and a slight increase of acrolein with higher MoO_3 contents up to a selectivity of about 30% for pure MoO_3.

To illustrate better the general performance of the $MoO_3 \cdot SiO_2$ system, Figs. 5 and 6 show the dependence of the selectivities upon conversions: in addition to data taken from Fig. 3, the plots include results from runs at τ from 0.12 to 1 sec as well as from

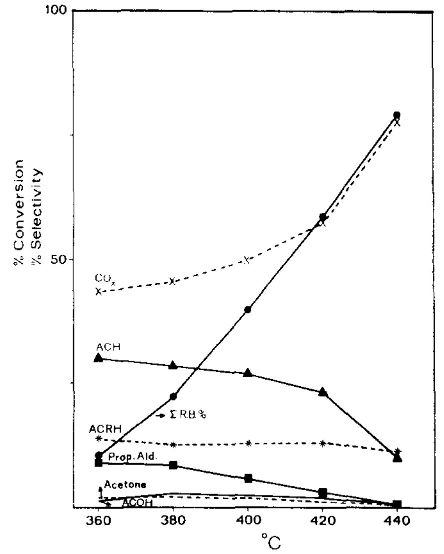

FIG. 4. Influence of reaction temperature on conversions and selectivities in oxidation of propylene, for MoO_3-16-500 (V series); t_c = 1 sec, C_3^-/air = 1/12. For abbreviations, see Fig. 3.

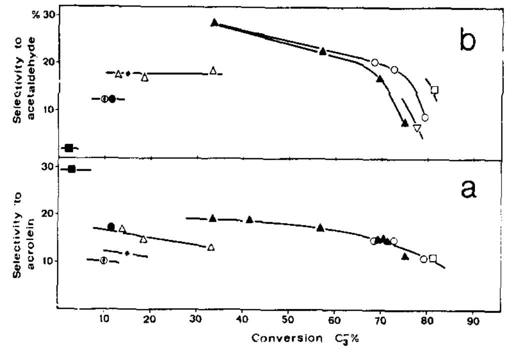

FIG. 5. Conversion vs selectivity to acrolein (a) and acetaldehyde (b) for $MoO_3 \cdot SiO_2$ catalysts (*V* series). SiO_2 (Φ); MoO_3-4-*V* (✳); MoO_3-6-*V* (●); MoO_3-8-*V* (△); MoO_3-13-*V* (□); MoO_3-16-*V* (○); MoO_3-20-*V* (▽); MoO_3-25-*V* (▲); MoO_3 (■). T = 440°C, τ from 0.13 sec to 1 sec.

experiments on MoO_3-25 catalysts activated under different conditions (see below). The comparison indicates higher selectivities to acrolein at the highest MoO_3 levels (Fig. 5a), particularly at the lowest conversions, i.e., at the lowest τ. Higher τ counteracts the effect of composition, and decay of acrolein occurs more rapidly on the MoO_3-richest samples. Acetaldehyde behaves similarly (Fig. 5b) but decay with τ occurs at a still higher rate. By-products (acetone, propionaldehyde, and acetic acid) behave similarly to acrolein and acetaldehyde in decay with τ; an account of their distribution as a function of various parameters will be given in a forthcoming paper (*2*). As to the influence of different modes of activation of catalysts, results presented in Figs. 6a and b show the influence of annealing in air (*A*), with respect to samples mechanically treated in a conventional attrition resistance apparatus (*B*) or leached chemically with NH_4OH (*C*). As described previously (*1*), the *B* and *C* samples were prepared to provide information on activity of catalysts freed from MoO_3 whiskers; as a result of these treatments, the catalysts present a structure composed mainly of octahedral polymolybdates (*B* type) and of tetrahedral Mo(VI) species (*C* type) with little or no residual free MoO_3 in both cases. The comparison of catalytic activity with respect to both *A* and *V* type (compare Figs. 5 and 6) shows interesting features, among which is a low catalytic activity of the NH_4OH-treated sample as opposed to the mechanical treatment which has little effect.

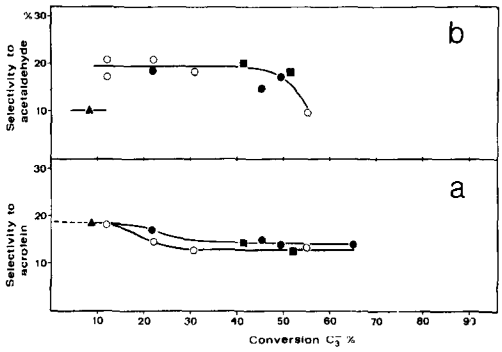

FIG. 6. Conversion vs selectivity to acrolein (a) and acetaldehyde (b) for $MoO_3 \cdot SiO_2$ catalysts (*A* series). MoO_3-25-*A*, 420°C (○); MoO_3-25-*A*, 440°C (●); MoO_3-25-*B* (■); MoO_3-25-*C* (▲). For experimental conditions see Fig. 5.

Moreover, in considering results of conversion vs selectivities to acrolein (Figs. 5a and 6a) and acetaldehyde (Figs. 5b and 6b), one can conclude that acrolein and acetaldehyde are both primary reaction products. In this respect, judging from the results of the *V* series, the system appears divisible into three groups: (a) catalysts containing up to 10% MoO_3; (b) catalysts in the range 13–25% MoO_3; (c) pure MoO_3. At any conversion level distinctive features are: (i) higher selectivities to acrolein at increasing percentages of MoO_3 (a < b < c); (ii) selectivites to acetaldehyde passing through a maximum at MoO_3-13, decreasing afterwards until they are extremely low in case of pure MoO_3; (iii) selectivities of the *V* series not too different from those of the other series, which thus seem to share some common characteristics (cf. Figs. 5a, b and 6a, b).

DISCUSSION

Disproportionation

Results of pulse experiments (Figs. 1 and 2) undoubtedly prove the existence of two distinct regions active in the disproportionation to olefins and in the oxidation of propylene to CO_x and acrolein. From a quantitative comparison it appears evident that the only reaction occurring in the absence of water (mode 1) is disproportionation, the depletive oxidation being almost nil. This behavior is analogous to that already reported for the $MoO_3 \cdot Al_2O_3$ system (*3*) which also displays a maximum disproportionation activity in that same composition range. By analogy with the $MoO_3 \cdot Al_2O_3$ system, the product distribution is close to the thermodynamic values with the butene-1/Σ butenes ratio equal to 0.26 (calcd value = 0.25) and the *trans*- to *cis*-butene-2 ratio equal to 1.37 (calcd value = 1.42). Main differences in the case of $MoO_3 \cdot SiO_2$ comprise: (i) a much broader volcano-shaped activity curve, with MoO_3-2 already being in the range of the highest activity; (ii) attainment of the same conversion levels as in $MoO_3 \cdot Al_2O_3$ but at higher reaction temperatures. The latter observation agrees well with literature information (*6*, *7*), which has indicated a temperature in the range 315–540°C to reach equilibrium conversions of propylene over $MoO_3 \cdot SiO_2$ systems. On the contrary, Al_2O_3-based catalysts usually require the temperature to be in the range 160–205°C to attain the same conversion levels.

An explanation for the differences may be deduced from the nature of the active species. In previous work on $MoO_3 \cdot Al_2O_3$ (*3–5*), disproportionation has been related to Mo(V) pairs as bis-molybdenyl species, which are formed via initial reduction of tetrahedral Mo(VI) to tetrahedral Mo(V) followed by intramolecular dehydration at the neighboring sites. Evidence has also been presented for the role of acid–base characteristics of the support in relation to the formation of the active oxycationic species. These concepts, together with information derived from studies of solid-state properties of the SiO_2-based system (*1*), make it possible to give a tentative explanation for the observations. First of all, tetrahedral Mo(VI), though present in both systems, is less abundant on SiO_2- than on Al_2O_3-based catalysts and is confined to the lowest MoO_3 region, thus accounting for the high activity already at the lowest compositions. Further, in accordance with the literature (*8*), outgassing or reduction is expected to yield Mo(V) with greater difficulty on SiO_2 than on Al_2O_3 systems. Finally, studies on the strength of acid sites of solids (*9*) indicate lower acidity of SiO_2, implying a smaller tendency to stabilization of molybdenum in the oxycationic form. On the assumption of a similar mechanism of formation of active sites and course of the reaction itself, the lower activity in case of SiO_2 is thus no longer surprising.

In view of the analogy with $MoO_3 \cdot Al_2O_3$, we deem it unlikely that silicomolybdic acid (SMA), also present in the region of disproportionation on $MoO_3 \cdot SiO_2$ catalysts (*1*), is responsible for the catalytic activity. In the Al_2O_3-based system, the corresponding alumina–molybdic acid has never been observed; moreover, the variation with composition of SMA [Fig. 6 of Ref. (*1*)] is not consistent with the observed volcano-shaped form of catalytic activity (Fig. 1). Also, exploratory runs on pure SMA at T between 150 and 400°C systematically failed to show any appreciable disproportionation activity.

Oxidation

Oxidation is confined to compositions higher than 10% MoO_3, as indicated by the steep increase of activity (Fig. 3) and differences in the product distribution (Figs. 5a and b). Combining the observations with those from studies of solid-state properties (*1*), it is concluded that highly dispersed MoO_3 or polymolybdates are the active sites for acrolein formation: Higher selectivities to acrolein occur in fact at those composition levels at which octahedral Mo(VI) becomes increasingly relevant. Bulk MoO_3, although quite selective to acrolein ($\sim$30%) can be ruled out due to the low conversion level under given conditions. This is in accordance with other reports (*10–17*): A survey shows that conversions do not surpass 20% whereas selectivities to acrolein vary from 30 to 70% within a wide range of experimental conditions. In connection with the observation that selectivities to acrolein are lower than that of bulk MoO_3, this can be ascribed to the presence of various oxymolybdenum species among those discussed previously (*1*) or to a polyfunctional character of polymolybdates. In the first event a competition may be envisaged between propylene undergoing allylic oxidation to acrolein over polymolybdates and side reactions occurring on other sites. As to the identification of the latter, we notice the absence of acetaldehyde over pure MoO_3; this compound is thus not specific. The lower selectivities to acetaldehyde at the smallest MoO_3 concentrations also rule out the tetrahedral species. The question is settled by considering the results of samples after mechanical treatment (*B* type) or leaching with NH_4OH (*C* type). Comparison with the original samples (*V* and *A* type) (Figs. 5 and 6) shows that, under equal conditions of T, τ, etc., activity and selectivities of the *B* type are not different from those of the *A* type, notwithstanding the decrease of MoO_3 from 25% (*A* type) to 20% (*B* type) (*1*). This observation proves that whiskers of MoO_3 do not contribute to the catalytic activity. As to the NH_4-OH-leached sample which displays the lowest residual MoO_3 content (8%), it has also the lowest catalytic activity: Selectivities to either acetaldehyde and acrolein are much like the equivalent untreated sample (MoO_3-8-*A*) thus proving that removal of polymolybdates by leaching with NH_4OH restores the activity proper of the tetrahedral Mo(VI) region. Available information thus indicates a common origin for acrolein and acetaldehyde as we observe: (a) parallel increase of the two products with composition; (b) selective removal of polymolybdates is equally selective towards both compounds. On this basis, the present results are better interpreted by a mechanism implying a polyfunctional character of polymolybdates, as will be illustrated in detail in a forthcoming paper (*2*). Though our investigations do not allow further deductions on the origin of by-products other than acetaldehyde, apparently there exists a strong similarity between its origin and that of propionaldehyde, acetone, and acetic acid; thus we assume that the same sites are involved, under the constraints of a similar mechanism. As to CO_x, these products may originate from: (a) direct attack of propylene; (b) consecutive oxidation of acrolein and/or other by-products (acetaldehyde). Both routes appear to coexist in our case; thus, from the balance to the sum of acetaldehyde and acrolein (Figs. 5 and 6) it results that CO_x, at conversion levels tending to zero, originates mostly from direct attack of propylene. This route is preferred in the tetrahedral region, also in accordance with results on NH_4OH-leached samples. On the other hand, consecutive oxidations become important at high conversion levels.

Having established the sites of catalytic activity, it remains to consider the mechanism which most adequately explains the observed behaviour with regard to the specific properties of different active sites. These aspects will be discussed in a forthcoming paper (*2*).

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