JOURNAL OF CATALYSIS 28, 489-505 (1973)

NOTE(S)

Mechanism of the Oxidation of Olefins on Mixed Oxide Catalysts

The mechanism of the selective oxidation of olefins on oxide catalysts has been extensively studied in recent years and the following facts have been established:

a. the first step of the reaction is the dissociative chemisorption of an olefin molecule with the abstraction of α-hydrogen and formation of a symmetric allylic species (*1*, *2*);

b. this chemisorption is the rate determining step (*3*, *4*);

c. in the case of the oxidative dehydrogenation of butene-1 to butadiene the rate of the reaction is equal to the initial rate of reduction of the catalyst with butene-1 in the absence of oxygen, which speaks in favor of the reduction–oxidation mechanism (*5*, *6*).

No data are available to decide with certainty whether the allylic species are adsorbed on a metal cation or on an oxygen anion of the surface. Experimental evidence indicates that all selective catalysts are composed of at least two oxide components, one of which is responsible for the selectivity and the other for the activity. This raises the question as to whether both cationic centers participate in surface processes or whether the role of the activating component consists only in modifying the oxygen bond strength of the catalyst. Many papers have been devoted in recent years to the problem of the correlation between the oxygen bond strength and the catalytic activity in oxidation reactions (*7–11*). A correlation is in fact observed in the case of total oxidation (*11*), but its existence for the selective oxidation of olefins may be seriously questioned. This may be taken as an evidence in favor of the hypothesis that different oxygen species are involved in partial and total oxidation.

We have recently investigated the mechanism of the interaction of hydrogen and lower olefins with some molybdate catalysts in the absence of gaseous oxygen (reduction of the catalysts) and in its presence (catalytic oxidation). In the course of these studies it occurred to us that some of our results, when compared with the abovementioned previously established facts, enable a hypothesis concerning the mechanism of the oxidation of olefins on molybdate catalysts to be formulated.

Table 1 summarizes the results of our measurements of the rates and activation energies of the oxidation of hydrogen, propylene and butene-1 on Bi_2O_3 and three bismuth molybdate phases in the absence of oxygen (reduction of the catalyst) and in its presence (catalytic reaction). The last column gives the selectivity to the main product in the case of propylene. The experiments are described elsewhere (*12*, *13*). In all cases the reaction was first order with respect to the reducing agent and it could be concluded that adsorption of the reducing gas is the rate determining step, in agreement with the earlier results obtained by Adams (*3*) and Batist, Lippens, and Schuit (*4*).

Let us now examine the behavior of the three bismuth molybdates. Bi_2MoO_6 (koechlinite) has a structure composed of layers of MoO_6 octahedra (*14*). As indicated in our earlier paper (*15*), $Bi_2Mo_2O_9$ may be considered as built of MoO_4 tetrahedra linked to layers of MoO_6 octahedra. Recently it was shown that $Bi_2(MoO_4)_3$ has a scheelite structure built of MoO_4 tetra-

TABLE 1

INTERACTION OF Bi–Mo–O CATALYSTS WITH HYDROGEN, PROPYLENE AND BUTENE-1 IN THE ABSENCE OF OXYGEN AND IN ITS PRESENCE[a]

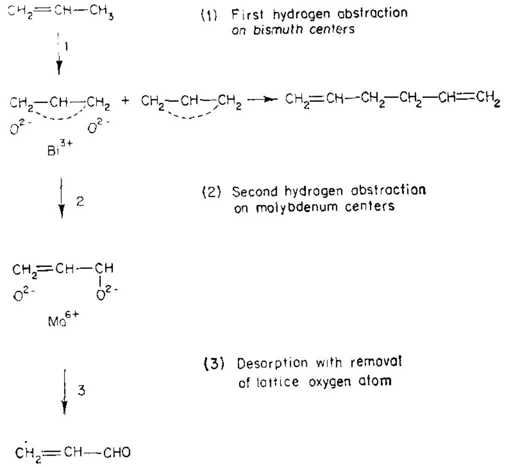
	Reduction with				Oxidation of		
	Hydrogen		Propylene		Propylene	Butene-1	Main product of interaction with propylene
Catalyst	v	E	v	E	E	E	
Bi_2MoO_6	1.48×10^{-2}	19.4	0.68	15.7	14	11	90% acrolein
$Bi_2Mo_2O_9$	0.92×10^{-2}	29.0	0.45	15.7	15	11	91% acrolein
$Bi_2(MoO_4)_3$	0.76×10^{-2}	32.6	0.36	15.6	17	11	89% acrolein
Bi_2O_3	3.5×10^{-2}	21.5					79% 1,5-hexadiene 20% benzene

[a] v = rate of the reduction of catalyst (mg O_2/m^2 min), activation energy E (kcal/mole).

hedra (*16*). Thus the three phases differ in the coordination of molybdenum ions; this offers a good opportunity for investigation of the structure-activity correlation. As shown in Table 1, the activation energies of reduction of the three molybdates with hydrogen differ considerably. As the adsorption is the rate determining step, these differences of the activation energy may reflect the differences in the heat of chemisorption of hydrogen, as given by the Polanyi relation. The heat of hydrogen chemisorption on the three molybdates may be different because of the different coordination of molybdenum. Indeed, as Bi_2MoO_6 is built of MoO_6 octahedra, its oxygen is less tightly bonded than in the other two molybdates. Thus the heat of adsorption of hydrogen on this molybdate should be the highest and hence the activation energy of reduction the smallest, as actually observed.

In contrast to the reduction with hydrogen, the activation energy of the reduction of the three molybdates with propylene and butene does not show much difference. By virtue of the same argument it may be concluded that the heat of chemisorption of hydrocarbon is approximately the same on all three molybdates. This, however, indicates that the allylic species formed on adsorption are bonded to the cationic centers, as the coordination of oxygen anions is different at the surface of the three molybdates. We arrive thus at the conclusion that two kinds of active centers exist at the surface of molybdates: O^{2-} centers involved in the adsorption of hydrogen, different at the surfaces of the different molybdates, and cationic centers, responsible for bonding of the allylic species and identical for the three molybdates.

Let us now consider the nature of the cationic active centers. During the reduction of bismuth molybdates with propylene, acrolein is formed as the main product, whereas on reduction of pure Bi_2O_3 with propylene we observed the formation of 1,5-hexadiene in large quantities. The formation of 1,5-hexadiene with a selectivity of the order of 70% on passing propylene over Bi_2O_3 was recently reported also by Swift, Bozik, and Ondrey (*17*). This observation has very important implications. The formation of 1,5-hexadiene can be easily explained if we assume that on adsorption of propylene on Bi_2O_3 allylic species are formed which are identical to those postulated as the first step of the oxidation of propylene. The recombination of two such allylic species gives 1,5-hexadiene directly. This leads us, however, to the conclusion that Bi–O polyhedra act as centers in the first hydrogen abstraction and formation of allylic species. If no other centers are present, these allylic species recombine giving 1,5-hexadiene. If, however, Mo–O polyhedra are also present at the surface, they act as centers for a second hydrogen abstraction, which results in the formation of an allylic fragment σ-bonded to the lattice oxygen ion; this is then desorbed together with the lattice oxygen as acrolein, leaving an oxygen vacancy. We therefore postulate the following mechanism for the partial oxidation of propylene:



MoO_3 is known to be a selective but nonactive catalyst for propylene oxidation. Apparently a large number of centers exist for the second abstraction of hydrogen, but the first step (formation of allylic species) is very slow. The role of bismuth is to provide rapid formation of allylic species. The fact that all three bismuth molybdates show comparable activity seems to indicate that the molybdenum active centers are not connected with any special configuration of molybdenum. It may well be the type B center of Matsuura and Schuit (*18*).

As supporting evidence we would like to mention some results of work function measurements made during the interaction of Bi_2O_3, MoO_3 and bismuth molybdates with oxygen and with vacuum as the reducing agent (*19*). The changes of the work function observed on desorption and adsorption of oxygen on bismuth molybdates resemble those observed in the case of Bi_2O_3, whereas MoO_3 shows a different behavior. This fact may be taken as an indication that not only do the parts of the surface composed of molybdenum polyhedra participate in surface redox processes, as usually assumed, but also those composed of bismuth polyhedra.

The role of cations having been discussed, a question may now be raised as to the type of oxygen species involved in partial oxidation. The data of Table 1 show that similar values of rates and activation energies are observed during the interaction of olefins with the catalysts both in the absence and in the presence of oxygen. This indicates that lattice oxygen is involved in partial oxidation. Examination of the oxygen exchange data in the literature not only supports this conclusion, but enables its further extension. Table 2 summarizes the available data on the activity in oxygen isotopic exchange of some double oxide systems known to be selective in partial oxidation as well as data for the single oxides, some of which are very active on total oxidation. We would like to emphasize the following points:

a. Very selective Bi/Mo catalysts show no activity in oxygen exchange, and Matsuura and Schuit (*18*) found no adsorption of oxygen on them;

TABLE 2
ACTIVITY OF OXIDES IN ISOTOPIC EXCHANGE

Catalyst	*T* (°C)	Rate (g O_2/m^2 hr)	Ref.
MoO_3	580–601	9×10^{-4}	(*20*)
Bi/Mo = 2/1	250–500	No exchange	(*21*)
Bi/Mo = 1/1	474–500	No exchange	(*22*)
Co/Mo = 1/1.7	599–634	1.8×10^{-4}	(*23*)
Co/Mo = 2/1	401–462	2.9×10^{-2}	(*23*)
Co_3O_4	125–250	12.7	(*24*)
Fe/Mo = 1/1.7	511–551	7×10^{-3}	(*23*)
Fe/Mo = 1/1	508–552	1×10^{-3}	(*23*)
Fe_2O_3	350–450	4×10^{-1}	(*24*)

b. Similarly, a selective Co/Mo catalyst of composition 1/1.7 shows a very slow exchange and we have found that no adsorption of oxygen takes place; the much less selective Co/Mo = 2/1 catalyst shows already a higher rate of exchange;

c. In the case of Co_3O_4, which is a good catalyst for total oxidation, the rate of exchange attains a high value, but only an amount of oxygen corresponding to less than one monolayer is exchanged (*25*). It was found by Boreskov, Popovskii, and Sazonow (*11*) that the surface of Co_3O_4 is covered by loosely bonded oxygen, the bonding energy strongly depending on the coverage;

d. Work function measurements carried out in our laboratory (*26*) have shown that the charge characteristic for adsorbed oxygen species appears at the surface of Co_3O_4 on contacting with oxygen.

Similar correlations may be found for the Fe/Mo and Fe/Sb systems. We may thus conclude that to be selective in allylic oxidation a catalyst should not contain adsorbed oxygen species at the surface. When such species are present, the olefin gives rise to a different active complex with breaking of the double bond, which then leads to total oxidation. We would like to formulate, therefore, a general conclusion: partial oxidation requires the activation of the olefin molecule, but no activation of oxygen should take place. Activation of oxygen leads to total oxidation.

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Received March 3, 1972