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The Role of Different MoO_3 Crystal Faces in Elementary Steps of Propene Oxidation

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Activity and selectivity of MoO_3 crystallites of different properties in the oxidation of allyl compounds were compared with those observed in the oxidation of propene in order to elucidate the role of different crystal faces in the elementary steps of oxidation. The yield of acrolein from allyl compounds was linearly dependent on the surface area of the basal (010) face, indicating that this face is responsible for insertion of oxygen into the activated hydrocarbon molecule. Product distribution from propene may be explained by assuming that its activation takes place at the side (100) and (101) faces, and the total oxidation at all faces.

Some time ago Tatibouët and Germain (*1*), using crystallites of MoO_3 prepared by sublimation and appropriate sieving, showed that on the basal (010) plane of MoO_3 methanol in the presence of oxygen becomes dehydrogenated to formaldehyde, whereas on the (100) and (101) faces it is dehydrated to dimethyl ether. This seemed to indicate that the (100) and (101) faces are characterized by acid–base properties usually considered responsible for the catalytic activity in elimination reactions, whereas the (010) plane contains centers active in redox processes. On the other hand Volta and co-workers (*2–4*) observed a reaction specificity of the MoO_3 crystal planes for propene, 1-butene, and isobutene oxidation on oriented MoO_3 samples obtained by intercalation of graphite. These authors conclude that selective oxidation of propene to acrolein proceeds mainly on the side faces (100) and (101) or ($\bar{1}$01), whereas its total oxidation to CO_2 occurs only on the basal (010) face. The two groups of results are not consistent, as it is generally assumed that the presence of acid–base centers at the surface of an oxide catalyst accelerates the total oxidation of hydrocarbon molecules and it could be thus expected that total oxidation of propene would take place on the (100) and (101) faces, and not on the (010) face as claimed by Volta *et al.* At variance with these authors, Ziółkowski (*5*) on the basis of a crystallochemical model, considers the side (101) face as responsible for the formation of acrolein. Finally it should be recalled that Gąsior and Machej (*6*) observed the selective oxidation of *o*-xylene to phthalic anhydride on plate-like crystallites of V_2O_5, but obtained total oxidation in the case of needle-shaped ones which indicates that it is the basal plane of V_2O_5 which is responsible for the formation of selective oxidation products.

It is now well established (*7*, *8*) that selective oxidation proceeds in a series of consecutive elementary steps of hydrogen abstraction and nucleophilic oxygen insertion. In the case of propene the first step consists in the abstraction of α-hydrogen and formation of an allylic species, which then undergoes the nucleophilic attack of oxygen to form acrolein. The question concerning the activity of different crystal faces in catalytic oxidation should be thus

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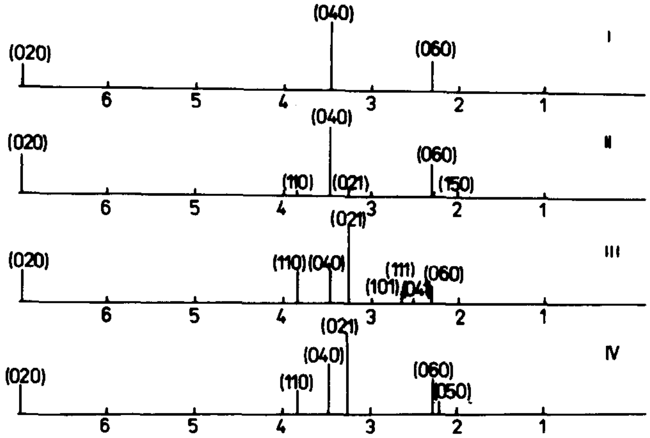


FIG. 1. X-ray diagrams of MoO_3 preparations used as catalysts.

rephrased to read: which is the role of surface geometry in separate elementary steps of the oxidation and whether these steps can take place on one crystal face or require active centers generated at different crystal faces. It seemed thus of interest to study the catalytic activity of MoO_3 samples of different crystal properties separately in the first step of oxidation, consisting in the activation of the propene molecule to form allylic species and in the subsequent nucleophilic insertion of oxygen to form acrolein. One of the ways by which these steps may be studied separately (*9*) is to compare the reaction of propene with that of an allyl compound such as allyl bromide, allyl iodide, or allyl oxalate, which readily decompose into allyl radicals. In the latter case, the first step of the selective oxidation is thus by-passed, making the examination of the conditions, which are necessary for the insertion of oxygen in the next step of the reaction possible.

EXPERIMENTAL

Materials

Four different preparations of MoO_3 were used in the experiments. Preparation I was prepared by sublimation of commercial MoO_3 at 1000 K and selection of larger plate-like crystallites. By carefully crushing these crystallites in a mortar, preparation IV was obtained. Preparation III was MoO_3 supplied by Climax Molybdenum Co., and annealing this preparation at 923 K resulted in considerable growth of plate-like crystallites, which, after appropriate sieving, were used as preparation II. Figure 1 shows the X-ray diffraction patterns of these preparations obtained using a DRON 2 diffractometer and Cu$K\alpha$ radiation. All diagrams show only the presence of the diffraction lines of MoO_3. Reflections from the $(0k0)$ planes show high intensity, whereas reflections from other planes have higher intensity only in diagrams of preparations III and IV and are absent from the diagram of preparation I. Indeed, scanning electron micrographs (Fig. 2) clearly show that preparation I is composed of very thin large plates. Also preparation II contains plate-like crystallites but some spherical particles are also present. Preparation III has the form of spherical grains, which are aggregates of smaller particles, and the picture of preparation IV reveals very small spherical crystallites. By microscopic analysis it could have been estimated that the basal (010) crystal plane accounts for 90% of the total surface area of preparation I and 80% of this area in the case of preparation II. In view of the observation that preparations

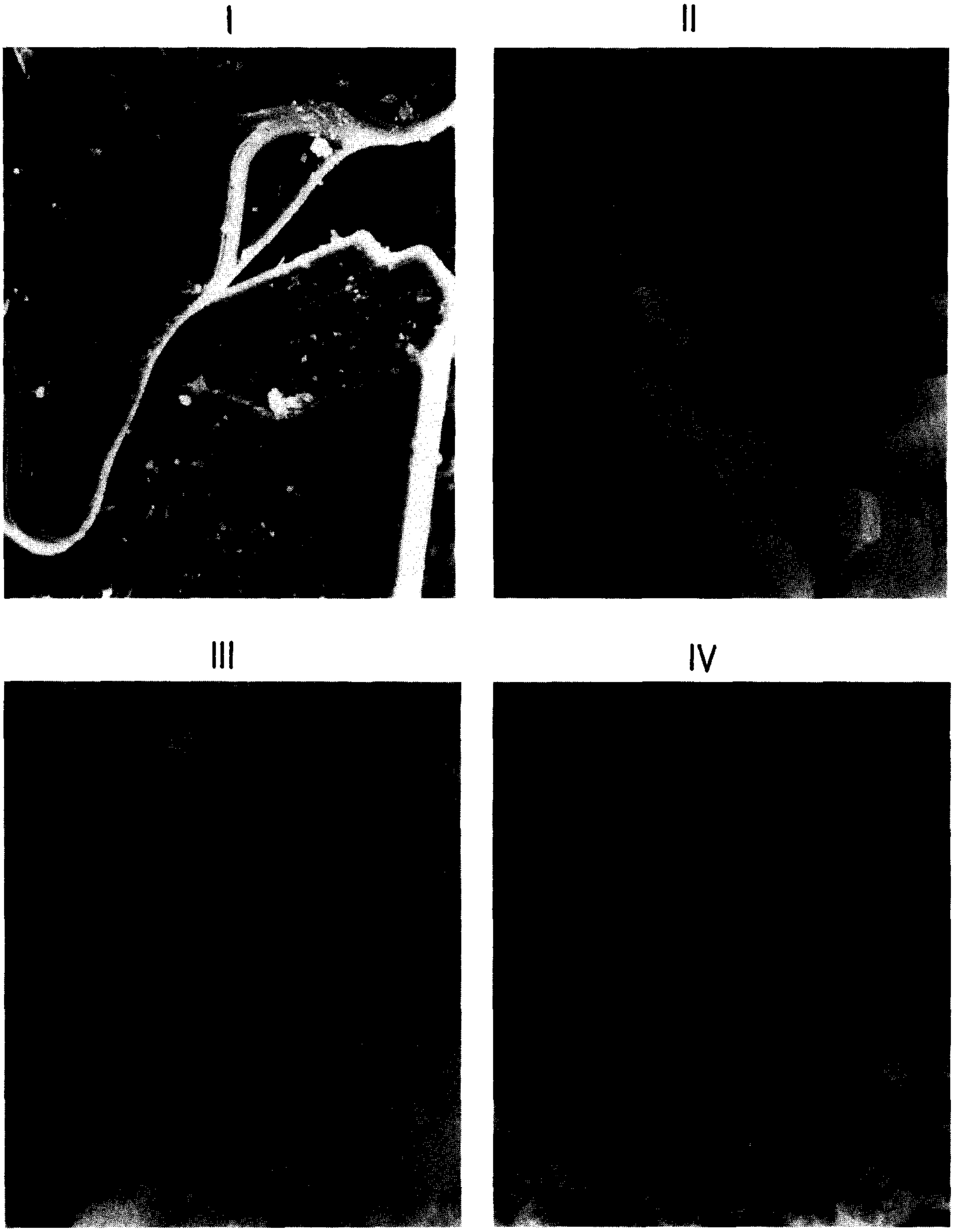


FIG. 2. Scanning electron micrographs for preparations I, II, III, and IV.

III and IV are composed of regular spherical particles it seemed plausible to assume that the contribution from the (010) face amounts to 33%. The total surface areas as determined by BET method from the adsorption isotherm of krypton are given in

TABLE 1

Catalyst (I)	Method of preparation (II)	BET surface area (m^2/g) (III)	Percentage of (010) face (IV)	Surface area of (010) face (m^2/g) (V)
I	Sublimed at 1000 K	0.015	90	0.0148
II	Climax annealed at 923 K	0.68	80	0.054
III	Climax	2.60	33	0.085
IV	Grinding of preparation I	4.60	33	0.153

column III of Table 1, and column V shows the results of the calculations of the specific surface area of the basal (010) face.

Procedure

The oxidation reactions of propene (Fluka purum) and of allyl compounds (Reakhim reagent, pure grade) were studied by means of the pulse method, introducing doses of reactants into a stream of helium, used as the carrier gas, passing through the catalyst bed at the flow rate of 30 ml/min. The samples of the catalyst were placed in a microreactor connected on-line to a series of gas chromatographs. The analysis of liquid products was performed using a 2-m Carbowax column and FID. The gaseous products were analyzed on a 4-m column with DMS and a 1-m column filled with molecular sieve, 13X, the TCD being used in this case.

As seen from Table 1 the preparations of MoO_3 differ considerably in surface area so that different conditions prevail in the pulse reactor when catalytic activity is determined. On the other hand, comparison of catalytic properties of different samples requires the calculation of the specific catalytic activity on the basis of experimentally determined total activity, which is permissible only when a linear relationship exists between activity and surface areas of the samples, i.e., the amounts of the catalyst in the reactor. In order to check whether this requirement is satisfied experiments were carried out, in which conversion of allyl iodide was determined as a function of the amount of catalyst placed in the reactor. Constant dynamic conditions in the reactor and in the GC analytical system were secured by mixing MoO_3 samples with appropriate amounts of inert silica support so that a catalyst bed of the same thickness was used in each run. Results of experiments in which the conversion of allyl iodide is plotted as a function of the amount of catalyst in the reactor are shown in Fig. 3 for preparations II and III. The results indicate that under our experimental conditions conversion is proportional to the amount of catalyst when the latter does not exceed about 0.2 g, i.e., if the conversion remains lower than about 30%. Thus, in further experiments samples of 0.1 g of catalyst were

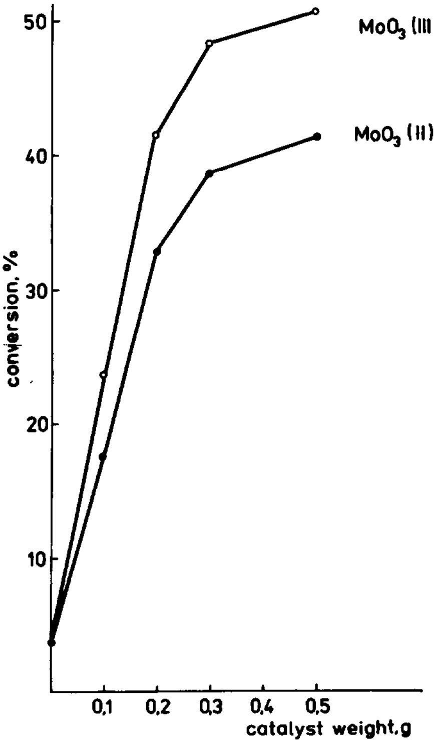


FIG. 3. Conversion of allyl iodide at 320°C as a function of the amount of catalyst for preparations II and III. (Results for the first pulse.)

TABLE 2

Activity of Different MoO_3 Preparations in the Reaction with Allyl Compounds

Preparation	Number of pulses	Allyl iodide				Allyl bromide				Allyl oxalate
		Conversion per unit surface area (%)	Yield		Selectivity (%) of acrolein	Conversion per unit surface area (%)	Yield		Selectivity (%) of acrolein	Yield of acrolein per unit surface area
			Propene	Acrolein			Propene	Acrolein		
I	1	16.3	5.1	11.8	72	15.4	3.9	11.9	77	
	2	13.2	1.5	11.7	89	14.6	3.4	11.5	79	
	3	14.5	2.8	11.7	81	15.0	2.8	11.7	78	
II	1	23.0	7.3	12.3	53					11.5
	2	20.0	6.2	11.1	56					
	3	16.0	5.0	10.2	64					
III	1	9.0	3.1	3.5	39					3.6
	2	7.4	2.2	3.3	45					
	3	6.9	2.4	2.7	39					
IV	1	10.2	3.4	3.7	36	5.5	0.5	4.1	75	
	2	8.9	2.5	1.6	18	5.4	0.4	3.9	72	
	3	8.4	3.1	1.1	13	4.4	0.4	3.6	82	

used for the determination of catalytic activity in the oxidation of allyl compounds, which were introduced in pulses of 0.6 μl. With temperature increasing from 320 to 450°C, the spectrum of products becomes broader and variable, and in addition to aerolein and propene some hexadiene and benzene also appear, as well as increasing amounts of CO and CO_2. At the same time total conversion of allyl compounds is attained, rendering any comparisons of activity meaningless. Therefore all experiments with allyl compounds were carried out at 320°C, at which the degree of conversion was not yet too high and the only products were acrolein and propene.

In the case of the oxidation of propene the conversion observed in the investigated temperature range was one order of magnitude smaller and no constraints existed as to the amount of catalyst used. Thus pulses of 0.6 ml of 1 : 1 propene : oxygen mixture were injected over samples of 0.5 g of the catalyst.

RESULTS AND DISCUSSION

Table 2 summarizes the results obtained when pulses of allyl iodide were passed over different preparations of MoO_3 at 320°C. Propene and acrolein were the only products formed at this temperature. The values of conversion and yields of propene and acrolein are recalculated per unit BET surface area (0.1 m^2). Only the initial three pulses were taken into consideration. The allyl compounds, on interaction with MoO_3, become oxidized at the expense of the lattice oxygen of MoO_3, the latter undergoing gradual reduction. This reduction is negligible in the first pulses and may begin to influence the catalytic properties only on prolonging the reaction. Simultaneously, coke deposition takes place in some cases and—as discussed later—results in a decrease of activity.

It may be noted from Table 2 that preparation I, which has the highest percentage of the total surface area composed of the basal (010) face, shows the highest yield of acrolein. This observation was taken as an indication that it is the (010) plane where the insertion of oxygen into the allylic species takes place. This preparation is characterized also by the highest selectivity of the reaction of allyl iodide to acrolein, which indicates that other observed reaction

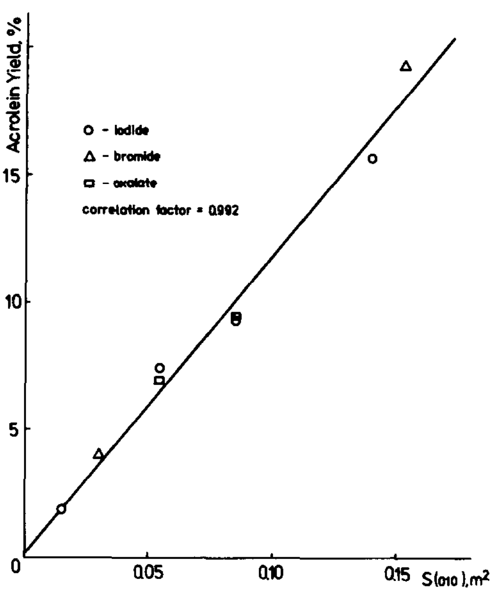


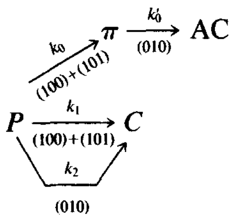
FIG. 4. The yield of acrolein in the reaction of allyl compounds at the surface of different MoO_3 preparations as a function of the surface area of the basal (010) face of the catalyst. (Results for the first pulse.)

paths, i.e., formation of propylene and coke deposition, proceed at other crystal faces. In order to check this assumption, the yield of acrolein obtained in experiments with allyl compounds was plotted (Fig. 4) as the function of the surface area of the (010) crystal faces as given in Table 1. A linear relationship is obtained, the straight line passing through the origin of the coordinate system with a correlation factor of 0.992. It may be thus concluded that the nucleophilic addition of oxygen into allylic species to form acrolein takes place at those parts of the MoO_3 surface where the (010) faces are exposed.

A question must be raised at this point as to how this conclusion can be made consistent with the results described by Volta *et al.* which led these authors to infer that oxidation of propene to acrolein takes place at the (100) and (101) faces of MoO_3 crystallites, whereas the (010) face is responsible mainly for total oxidation.

As already mentioned oxidation of propene proceeds through several consecutive steps, the first being the activation of propene to allylic species, followed by the nucleophilic addition of oxygen ions. In mixed catalysts these two steps are clearly separated; low-valent cations play the role of centers activating the hydrocarbon molecule, whereas nucleophilic attack is performed by oxygen ions from the lattice of the oxides of high-valent transition metals or from the anionic sublattice of their oxysalts, e.g., molybdates and tungstates (*10*). One of the elements whose ions are particularly efficient in activation of propene to form allyl species is bismuth. Therefore, preparations II and III were impregnated with bismuth ions. The method of preparation and results of surface analysis by XPS, SEM, and EDAX are described elsewhere (*11*). They revealed that Bi^{+3} ions are deposited selectively on the (100) and (001) crystal planes of MoO_3 crystallites, where OH groups are present, but not on the (010) plane, which remains bare. Table 3 shows the results of the determination of catalytic activity in the oxidation of propene at 450°C. As in experiments with the interaction of allyl compounds and pure preparations II and III, the yield of acrolein is proportional to the surface area of the (010) face, although in this case the allyl species are generated by the bismuth ions located on the side (100) and (001) faces. This confirms the conclusion that the second step in the process of the oxidation of propene, the nucleophilic addition of oxygen, takes place at the (010) face of MoO_3 catalysts. Therefore the presence of Bi^{3+} ions, deposited on the (100) and (001) faces, does not interfere with the addition of surface oxygen ions to the adsorbed allyl species (*11*).

Let us now assume that also in the case of pure MoO_3 these two steps are separated, taking place at two different crystal faces; activation of propene at the (100) or (101) face and nucleophilic addition of oxygen at the (010) face, as concluded above from the experiments with allyl compounds. Let us also assume that total oxidation of propene proceeds at all crystal faces, albeit with different rate constants. We postulate thus a following reaction scheme:



where P is propene, π is intermediate allyl species, AC is acrolein, C is carbon oxides, and k_0 is the rate constant of propene activation on the (100) and (101) faces, k_1 and k_2 are the rate constants of the total oxidation on the side (100) and (101) faces and the basal (010) face, respectively, k_0' is the rate constant of oxygen addition to intermediate allyl species.

The rate of the conversion of propene may be described by

$$-\frac{dC_p}{dt} = (k_0 + k_1 + k_2)C_p. \qquad (1)$$

Experimental results indicate (*9*) that as soon as the molecule of propene becomes activated to an allylic species, oxygen is very rapidly inserted and the molecule of acrolein desorbed, the activation of propene being always the rate-determining step. Thus, $k_0' \gg k_0$. From the same experiments it is also known that the rate of total oxidation on MoO_3 catalyst is comparable with the rate of acrolein formation. It follows that $k_0' \gg k_0, k_1, k_2$, and the observed selectivity of the catalytic reaction to acrolein amounts to

$$S_{AC} = \frac{k_0}{k_0 + k_1 + k_2}. \qquad (2)$$

The observed rate constants of elementary steps taking place at different crystal faces are proportional to the contributions of these faces, A_i, to the total surface area of the catalyst: $k_i = a_iA_i$; $\Sigma A_i = A$. Thus,

$$S_{AC} = \frac{a_0(A_{100} + A_{101})}{a_0(A_{100} + A_{101}) + a_1(A_{100} + A_{101}) + a_2A_{010}}$$
$$= \frac{A_{100} + A_{101}}{(1 + \beta)(A_{100} + A_{101}) + \alpha A_{101}} \qquad (3)$$

which can be transformed into a linear form

$$\frac{1}{S_{AC}} = 1 + \beta + \alpha \cdot \frac{A_{010}}{A_{100} + A_{101}}, \qquad (4)$$

where

$$\alpha = \frac{a_2}{a_0} \qquad \beta = \frac{a_1}{a_0}.$$

Experimental data concerning the catalytic properties of different preparations of MoO_3, quoted by Volta *et al.* (*3*), were thus recalculated according to Eq. (4) and the result is plotted in Fig. 5. It may be seen that the data fit perfectly to Eq. (4), the correlation factor being 0.995.

It may be thus concluded that both the observations described by Volta *et al.* (*2–4*)

TABLE 3

Activity of Different MoO_3 + 0.25 Bi Preparations in the Oxidation of Propene

Catalyst	Surface area (m^2/g)	Conversion (%)	Yield (%) per unit surface area		Yield of acrolein per unit surface area of the (010) face (%)
			Acrolein	CO_2	
MoO_3 + 0.25Bi (prep. II)	0.60	9.5	13.0	2.5	14.4
MoO_3 + 0.25Bi (prep. III)	2.60	16.9	5.1	1.3	15.4

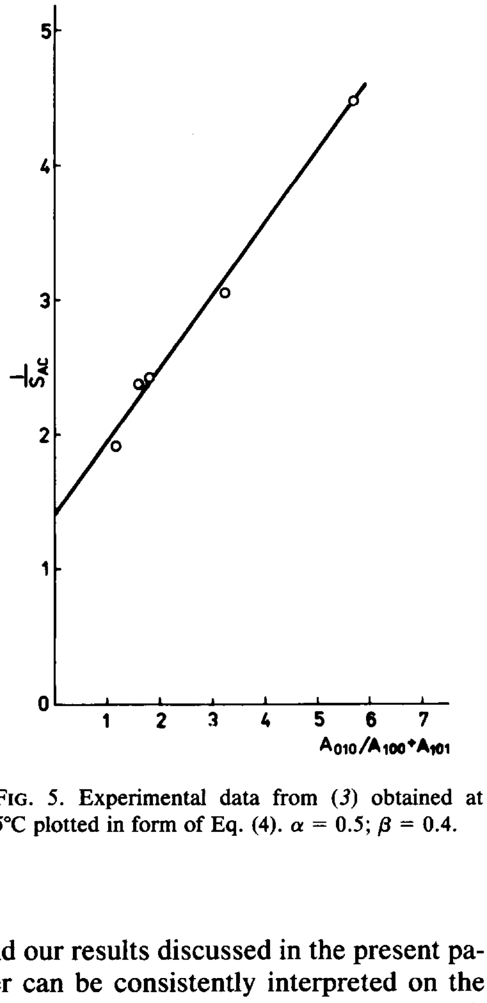


FIG. 5. Experimental data from (*3*) obtained at 375°C plotted in form of Eq. (4). $\alpha = 0.5$; $\beta = 0.4$.

and our results discussed in the present paper can be consistently interpreted on the basis of the model which assume that activation of propene molecule to an allyl intermediate takes place at the (100), (001) and/or (101) faces of MoO_3, whereas insertion of oxygen into this intermediate is performed by oxygen ions at the (010) face.

Strong evidence supporting this model is provided by ESR studies of MoO_3 in the course of its interaction with different atmospheres (*12*). Analysis of the situation at the surface of MoO_3 crystallites led to the conclusion that the value of the *g* tensor in the spectra of MoO_3, registered after exposing it to reducing atmosphere, indicates that the surface oxygen, bridging two adjacent octahedra in the double string of edge linked MoO_6 octahedra, is removed from the (010) face on interaction with a reducing agent.

It should be noted that—as revealed by the data summarized in Table 2—the yield of acrolein obtained on interaction of allyl compounds with MoO_3 decreases with the number of pulses injected on the catalyst. This decrease is well pronounced in case of preparations III and IV, in which the (100) and (101) side crystal faces constitute a large proportion of the total surface exposed to gaseous reactants, but is practically nonexistent in the case of preparation I. If the loss of selectivity were due to reduction of catalytic surface, one would expect it to take place in all preparations and to be most serious for preparation I because of the highest yield of acrolein. The alternative explanation is the deposition of coke which blocks the active centers where acrolein is formed. The fact that the decrease of selectivity is observed in the cases of preparations III and IV but not in I indicates that the active species, responsible for the deposition of coke, are generated at the (100) or (101) face. As already mentioned studies of methanol transformation on MoO_3 crystallites with different habit (*1*) led to the conclusion that the (100) and (101) faces are characterized by acid–base properties. This explains the activity of these faces in the generation of coke-forming species by the carbonium ion mechanism. In order to confirm this conclusion preparation IV was exposed in the reactor at first to pulses of pyridine in order to poison its Brönsted acid centers, and only then pulses of allyl iodide were injected into the carrier gas. The results of this experiment are shown in Table 4. It may be seen that after poisoning the catalyst with pyridine the yield of acrolein remains unchanged in several consecutive pulses of allyl iodide, whereas in case of fresh catalyst this yield drops dramatically in the course of first three pulses. We may thus conclude that indeed it is the Brönsted acid centers located at the (100), (001), and (101) faces

TABLE 4

Influence of Poisoning with Pyridine on Activity of Allyl Iodide Reaction with MoO_3 (Preparation IV)

Number of pulses	Fresh sample			After poisoning with pyridine		
	Conversion (%)	Yield (%)		Conversion (%)	Yield (%)	
		Propene	Acrolein		Propene	Acrolein
1	10.2	3.4	3.7	8.4	4.2	3.1
2	8.9	2.5	1.6	8.3	4.1	3.2
3	8.4	3.1	1.1	8.4	4.0	3.1
4				8.3	4.3	3.1

which are responsible for the generation of coke-forming species, although the deposition of coke probably takes place over the entire surface, so that the mechanism of the nucleophilic addition of oxygen from the (010) face becomes partially blocked. This is in line with the multistep mechanism of the oxidation of propene, discussed above, and the assignment of different elementary steps to different crystal faces. Namely, activation of propene by abstraction of α-hydrogen to form allylic species may be discussed in terms of the acid–base mechanisms:

$$CH_2{=}CH{-}CH_3 + O^{2-}\,(\text{latt.}) \rightarrow$$

proton transfer

$$[CH_2{=}CH{=}CH_2]^- + OH^-$$

$$[CH_2{=}CH{=}CH_2]^- + 2Me^{+n} \rightarrow$$

electron transfer

$$[CH_2{-}CH{-}CH_2]^+ + 2Me^{+(n-1)}$$

Acid–base properties of the (100) and (101) faces of MoO_3 may render these faces active in generation of allyl species in the first step of the oxidation of propene.

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