

Role of the Structural and Electronic Properties of Molybdenum Trioxide Catalysts on the Structure-Sensitive Oxidation of Methanol to Formaldehyde

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Summary. As catalysts for selective oxidation, molybdenum trioxide catalysts—prepared by two different methods—have been investigated. The results of vapor-phase oxidation of methanol are discussed on the basis of the acidic property, oxidizing functions, and the crystallographic structure of the catalysts. It was found that the acidic property is not the sole factor deciding the catalytic activity. Electrical conductivity measurements proved that molecular oxygen in the gas feed is necessary for maintaining the catalysts active. The difference in the catalytic activity and selectivity were reasonably interpreted in view of the structure sensitivity of those catalysts. A redox mechanism is also discussed in this paper.

Keywords. Molybdenum trioxide; Structure-sensitive oxidation of methanol.

Der Einfluß von strukturellen und elektronischen Eigenschaften von Molybdäntrioxidkatalysatoren auf die struktursensitive Oxidation von Methanol zu Formaldehyd

Zusammenfassung. Auf zwei verschiedene Arten hergestellte Molybdäntrioxidkatalysatoren wurden für selektive Oxidationen untersucht. Die Ergebnisse der Dampfphasenoxidation von Methanol werden auf Basis der sauren Eigenschaften, der oxidierenden Funktionen und der kristallographischen Struktur der Katalysatoren diskutiert. Es wurde festgestellt, daß die sauren Eigenschaften zur Erklärung der entscheidenden Wirksamkeit der Katalysatoren nicht alleine verantwortlich sind. Elektrische Leitfähigkeitsmessungen zeigten, daß molekularer Sauerstoff im zugeleiteten Gas zur Erhaltung der katalytischen Aktivität notwendig ist. Die Unterschiede in der Katalysatoraktivität und der Selektivität sind aus der Struktur der Katalysatoren zu erklären. Es wird ein adäquater Redox-Mechanismus diskutiert.

Introduction

MoO₃ is a very selective catalyst for the oxidation of methanol to formaldehyde [1] where it has been subjected to a number of important investigations [1–5]. Trifiro et al. [5, 6] postulated that the ability for the selective oxidation is connected with the double bond character of MoO₃, while others [7, 8] proposed the participation of acidic sites in the oxidative reaction. Recent studies provide several examples proving that the performance of molybdenum oxide catalysts through the oxidative dehydrogenation reaction depends on the kind of crystallographic plane preferentially exposed by the grains of polycrystalline sample [9–13].

According to these different views proposed by the above cited investigators and others, the present work is an attempt to gain more insight about the influence of different functions on the catalytic activity of molybdenum trioxide catalysts for methanol conversion to formaldehyde. Investigations are conducted by measuring the acidity, electrical conductivity, crystallographic structure as well as the dehydrogenation of methanol over two different samples of molybdenum trioxide.

Experimental

Reagent grade chemicals were used. Two samples A and B of molybdenum trioxide were prepared, sample A was obtained by the direct thermal decomposition of ammonium paramolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in an air flow at temperatures 300, 400 and 500°C for 5 h, the products were denoted as A-300, A-400 and A-500 respectively. Sample B was obtained by precipitating from 20% aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ with HNO_3 (1 : 1) at $pH \approx 2$. The precipitate was filtered, washed and annealed at the same conditions as sample A, the products are denoted as B-300, B-400 and B-500. Infrared spectra of the samples were obtained by the KBr disk technique in the range of 4000–200 cm^{-1} using a Perkin Elmer 599 B Infrared Spectrophotometer. The variation of the catalytic solid phase structure with temperature (TG and DTA) in an air atmosphere was carried out using an automatically recording thermobalance, type Li 160KS (Federal Republic of Germany). The X-ray diffraction patterns for the catalysts were carried out using the powder diffraction pattern technique at a value of 2θ between 2 and 60, using Philips Unit, type PW 2103/00, applying a Cu target and Ni filter. Their lattice parameters were accurately calculated using the well-known Cohen's least-squares method [14, 15] to minimise random as well as systematic errors. The normal equations were solved using a computer program, where the summations were taken over around twenty reflections.

The electrical conductivity measurements were carried out as described previously [16], while the calorimetric [17] titration method was used for the catalysts acidity determination.

Methanol oxidation was performed in an isothermal continuous flow fixed-bed reactor. Air was used as a carrier gas fed from a cylinder through a needle valve passing over silica gel and soda lime drying towers to the reactant container. The exit feed of the reaction products was analyzed using a Pye Unicam series 104 gas chromatograph and the iodometry titration method. Details of the analysis process have been reported elsewhere [18].

Results and Discussion

Characterization of the Catalysts

Informations concerning the presence of compounds and their possible structure were derived from infrared spectra and TG/DTA measurements.

Fig. 1 shows the ir spectra for the obtained catalysts. Absorption bands were assigned at 985 and 880 cm^{-1} which are attributed to $\text{Mo}^{6+}=\text{O}$ and $\text{Mo}^{6+}-\text{O}-\text{Mo}^{6+}$, respectively. This is in agreement with the reported data [19]. The absorption band at 1420 cm^{-1} , which is characteristic to sample B-300, is assigned to the OH groups [20]. The same band was observed also for sample B calcined at 350°C but it disappeared for sample B-400.

The structural modifications change of the prepared sample B was followed by TG and DTA. As seen in Fig. 2, a continuous loss of weight takes place in the range of 90–420°C, followed by a stable region up to $\sim 700^\circ\text{C}$. As elucidated from the ir spectra, the calcination products of sample B at 300 and 350°C still contain OH groups. Thus, the observed stepwise weight loss can be attributed to removal

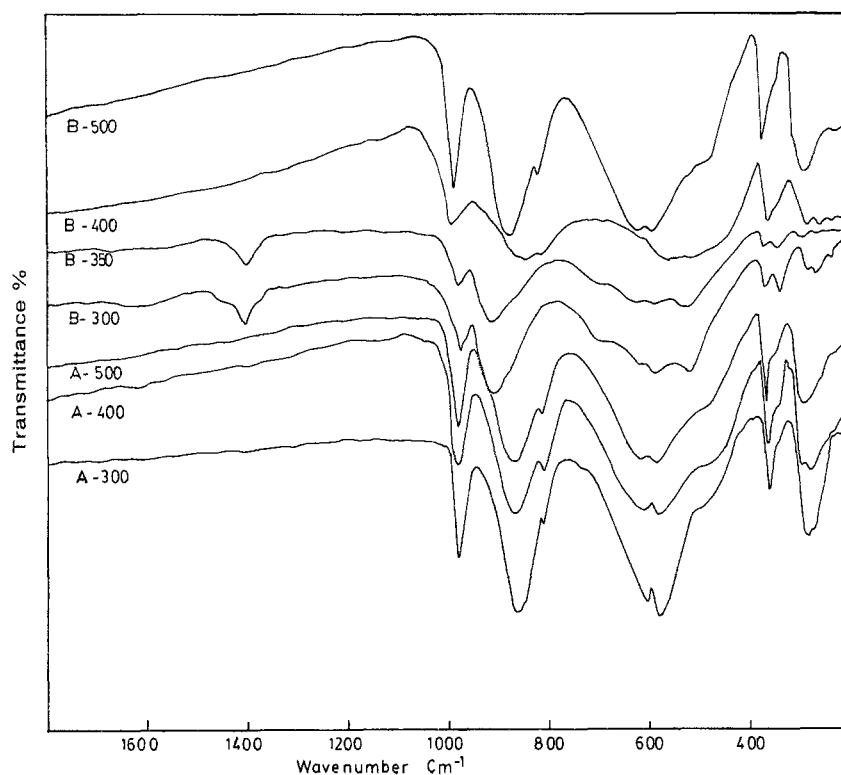


Fig. 1. IR spectra of the compounds A and B calcined at different temperatures for 5 h

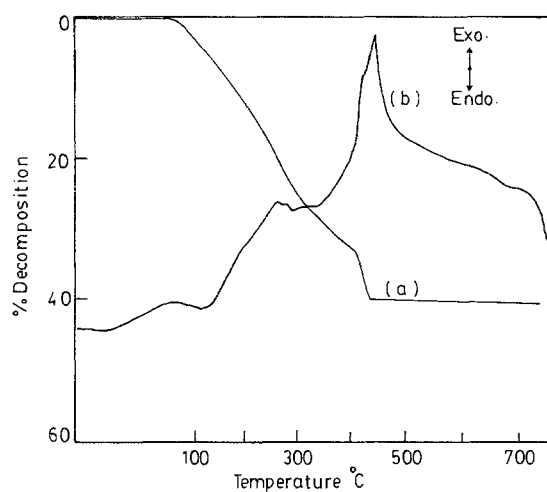


Fig. 2. TG and DTA curves (a and b, respectively) for the thermal decomposition of the parent sample B

of different types of volatile matters in the sequence of increasing the decomposition temperatures as: removal of adsorped water, removal of water resulting from combination of two OH groups leaving a chemisorped oxygen over the sample surface which appears to be removed at temperatures higher than 410 $^{\circ}\text{C}$. The DTA spectrum showed three major exothermic peaks (Fig. 2 b) with an additional exothermic peak located at 430 $^{\circ}\text{C}$ which corresponds to the recrystallization [21] of MoO_3 . Quantitative analysis of the TG curve predicts a structural formula of sample B to be $\text{MoO}_2(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$.

Catalytic Activity for Methanol Dehydrogenation

The catalytic activity of the two series of molybdenum trioxide (A and B) was tested using the vapor-phase dehydrogenation of methanol. The influence of calcination temperatures on the activity of these catalysts was studied at a reaction temperature in the range of 240–390°C. The experimental results, as shown in Fig. 3, show an increase of percentage conversion of methanol on increasing the calcination temperature from 300 to 400°C, then it declines to lower values at 500°C. Also, a maximum of the % conversion was attained at 390°C catalytic reaction temperature. The influence of methanol concentration in the gas feed as well as the contact time on the % conversion for the selected samples A-500 and B-500 were investigated. The results are tabulated in Table 1 and represented in Fig. 4. From the results depicted in Table 1, a remarkable increase of the catalyst activity and selectivity is observed with decreasing the methanol concentration in the gas

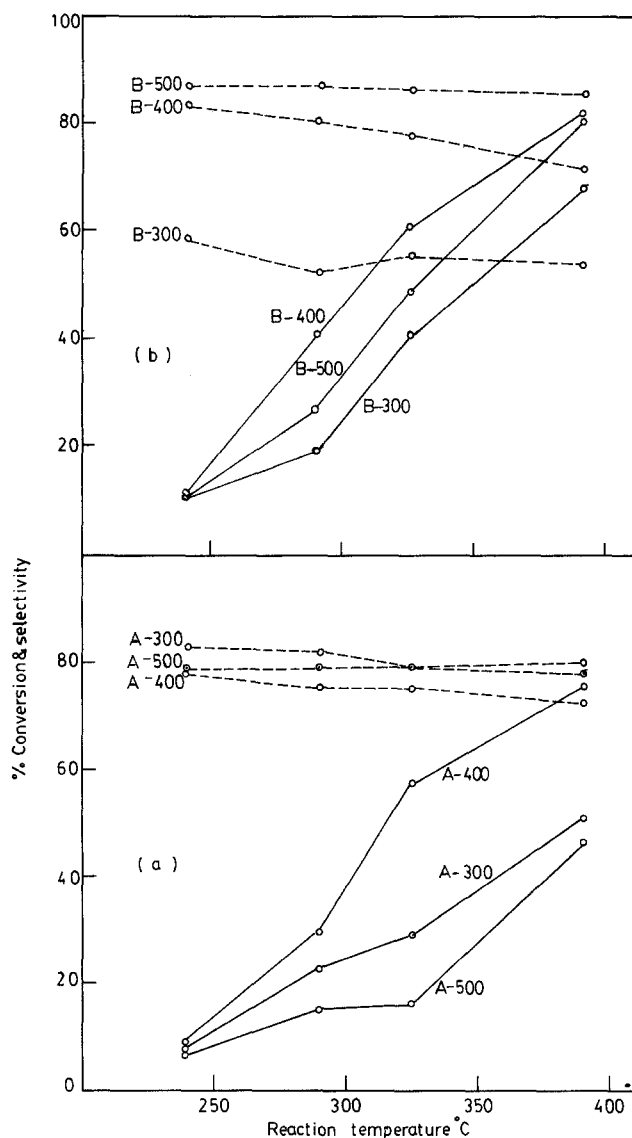


Fig. 3. Effect of the calcination temperatures of samples A and B on % conversion of CH_3OH (—) and selectivity of HCHO formation (---) in the range of reaction temperature 240–390°C

Table 1 a. Effect of methanol concentration in the gas feed on the catalytic decomposition over the two catalysts A-500 and B-500

mmol CH ₃ OH per liter feed	% Conversion		% Yield		% Selectivity	
	A-500	B-500	A-500	B-500	A-500	B-500
1.55	46.4	80.5	36.2	68.7	78.0	85.3
2.64	33.0	70.1	21.0	57.5	63.5	82.0
3.48	21.5	66.3	12.0	53.4	56.0	80.5
4.38	10.9	60.5	5.8	48.1	53.0	79.5
5.60	13.0	52.0	6.6	39.5	51.0	76.0

Table 1 b. Effect of contact time^a of the gas feed on the catalytic decomposition of methanol over the two catalysts A-500 and B-500

Contact time min × 10 ⁻³	% Conversion		% Yield		% Selectivity	
	A-500	B-500	A-500	B-500	A-500	B-500
3.0	38.3	64.1	31.6	59.7	82.4	93.1
5.3	46.4	80.5	36.2	68.7	78.0	85.3
10.0	55.6	83.9	21.7	43.9	39.1	52.3
15.0	62.7	92.3	13.9	38.0	22.1	41.2

^a 1/flow was taken as a measure for the contact time

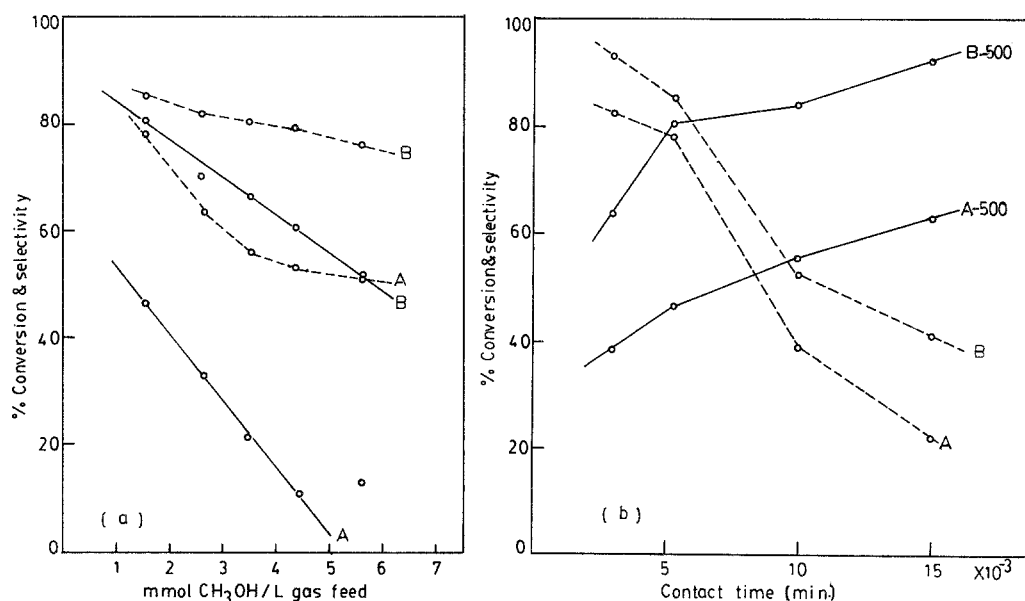


Fig. 4. Variation of % conversion of CH₃OH (—) and selectivity to HCHO formation (---) with concentration of CH₃OH in the gas feed and with the contact time of the reactant (a and b, respectively), for the samples A and B calcined at 500°C

feed. This activity increase is much higher for sample B-500 compared with sample A-500. Examination of the contact time effect over the two samples provides an important fact that the selectivity is largely dependent on the contact time value.

In order to reveal clearly the reasons for the obtained variations in both activity and selectivity rather than the mechanism by which the studied catalytic reaction is proceeding, it was necessary to recognize three different factors having an influence on the catalytic reaction process. Namely: the acidic property, the oxidizing functions and the structure sensitivity of these catalysts.

Acidity Determination

A representative set of differential heat of adsorption curves is shown in Fig. 5 for all catalysts. Assuming that chemisorption of *n*-butylamine on a stronger acidic site results in a higher heat of adsorption [17] and all acidic sites contributing in the catalytic activity and the relative contributions depend upon the strength of the acidic sites, the acidic strength of these catalysts can be arranged in the order A-400 > A-300 > A-500 and B-400 > B-300 > B-500. This indicates a general qualitative agreement between the relative activities and the acidity strength distributions. Although this assumption may be successful to explain the catalytic activity

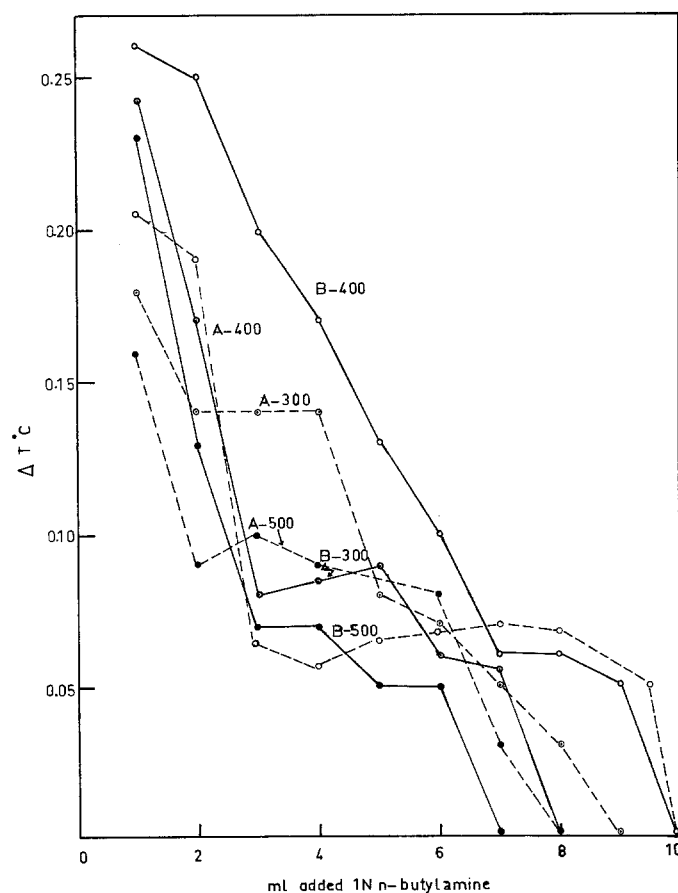


Fig. 5. Differential heat liberated with successive additions of *n*-butylamine to the catalysts A and B calcined at different temperatures

variation, it does not the same for the selectivity variation. Thus, the activation of methanol by acidic sites is not the sole factor deciding the catalytic process. Therefore, further studies concerning the influence of the electronic factors were done by in situ measurement of the electrical conductivity.

In situ Measurement of Electrical Conductivity

This measurement has been carried out for compounds of the two series A and B, the initial conductivities at 390°C in a flow of air are represented in Table 2. When methanol vapor was introduced (maintaining the same conditions as used for the catalytic studies), the conductivities increased and attained almost constant values after 30 min as in column 3 in Table 2. In case of successive exposure of the catalysts

Table 2. Conductivity values for the various catalysts as measured in air, after admission of methanol and after resubjection to air

Catalysts	σ in air $\times 10^{-8}$	σ after admission of methanol $\times 10^{-8}$	σ after admission of air $\times 10^{-8}$
A-300	3.4	22.2	5.7
A-400	4.0	32.3	5.1
A-500	11.1	294.0	20.0
B-300	183.0	855.0	67.0
B-400	1.6	60.6	2.7
B-500	8.0	308.0	23.0

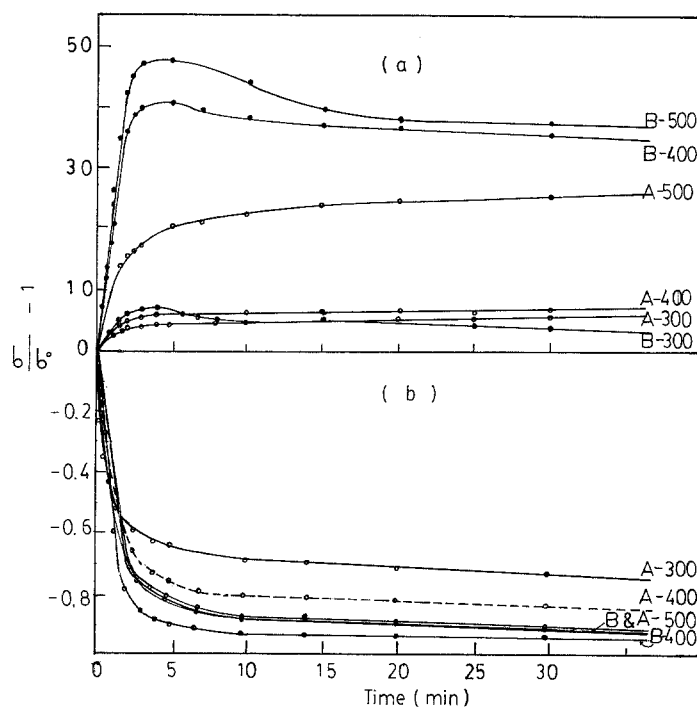
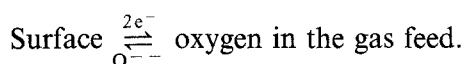


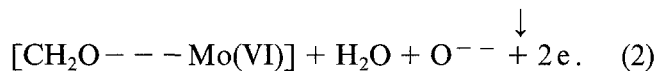
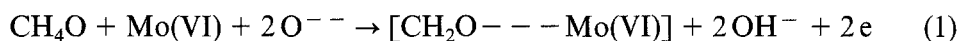
Fig. 6. Variation of $\sigma/\sigma_0 - 1$ vs. time for the catalysts A and B, calcined at 300, 400 and 500°C, during admission of gas feed containing CH_3OH as a reactant and during re-exposure to a stream of pure air (a and b, respectively)

to a flow of pure air the conduction values did not recover their initial state as shown in Fig. 6 (a and b), where $(\sigma_i/\sigma_0 - 1)$ is represented versus time (σ_0 is the initial conduction before admission of methanol and σ_i corresponds to the conduction at time t_i for both cases).

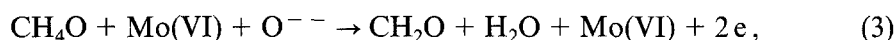
From these data it can be seen that the solid conduction order increases in the same sequence as the catalytic activity does. This indicates that a parallel relationship between the catalytic activity with the number of charge carries and/or their mobility exists. It shows also that the gaseous oxygen in the gas feed and the lattice oxygen of MoO_3 are contributing in the catalytic process. Our inference is in a complete accordance with that found gravimetrically by Niwa et al. [22]. It supports the view of dependence of the activity and selectivity, besides the acidity of the catalysts, on the ability of the catalysts to activate and incorporate gaseous oxygen into the crystal-lattice oxygen (O^{2-}) by electron transfer from the metal oxide [23]. Hence, the horizontal parts in Fig. 6 a appear to represent a steady state which can be considered as a result of activation of gaseous oxygen, sufficient to prevent the formation of electrical charge differences. Simultaneously a release of electrons (from the methanol molecule) to the surface of the catalyst occurs:



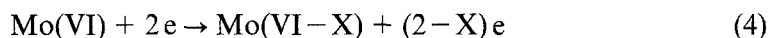
Taking into account the different opinions [3, 4, 24–27] concerning the mechanism of the oxidation over MoO_3 catalysts, our findings lead to the following mechanism:



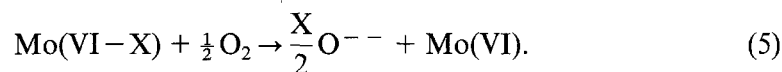
From (1) and (2):



where



and



Accordingly, the high selectivity which is associated with an increase of conductivity may be referred to a retardation of step (4) and consequently step (5) where, as soon as consumption of electron takes place, their contribution on the conductivity will be restricted [28]. This result is a clue for understanding the decrease in selectivity when the contact time or the concentration of alcohol is increased. At the same time it means that selectivity is greatly controlled by the activation of gaseous oxygen. However, when such activation exceeds the proper amount, the catalysts become too active and the reaction cannot stop at the step of formaldehyde formation but it oxidized to carbon oxides.

This result finds support from examining the structure sensitivity of the catalysis by means of X-ray diffraction.

X-Ray Studies of the Catalysts

The X-ray diffraction patterns of the various catalysts, shown in Fig. 7, were analyzed, giving following results:

1. The X-ray reflections are not broadened indicating that we have a well crystallized preparation.
2. The crystal lattice structure for series A is orthorhombic while for series B it starts in a hexagonal form and turns to orthorhombic upon annealing at temperature higher than 350°C.
3. For the orthorhombic crystals the relative intensities of the main reflections (020), (110), (040), and (021), on the average, are 23, 65, 44, and 100 respectively which is in agreement with the reported data [29].

The lattice parameters for both systems, as calculated using Cohen's least squares method, are tabulated in Table 3.

The pronounced difference which was found for the b values is in agreement with the knowledge that MoO_3 shows high anisotropy of thermal expansion [30],

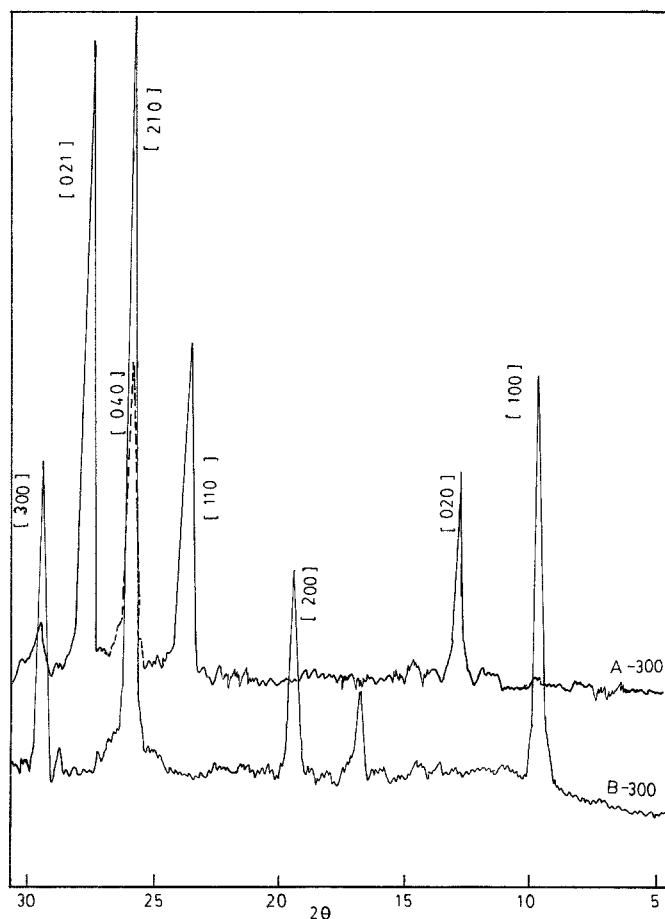


Fig. 7. X-ray diffraction patterns for the orthorhombic sample A-300 and the hexagonal sample B-300

Table 3. Lattice parameters for the various catalysts

Catalyst	Crystal symmetry	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
A-300	Orthorhombic	3.868	13.643	3.643
A-400	Orthorhombic	3.911	13.764	3.675
A-500	Orthorhombic	3.882	13.648	3.650
B-300	Hexagonal	10.660	–	2.168
B-400	Orthorhombic	3.913	13.771	3.671
B-500	Orthorhombic	3.851	13.551	3.625

^a $c/a = 0.203$ for sample B-300

the coefficient along *a*, *b* and *c* axes being respectively $(0.9 \pm 0.1) \cdot 10^{-5}$, $(18 \pm 2) \cdot 10^{-5}$, and 0 deg^{-1} . This means the interatomic distances along the *c* (and almost the *a*) axes remain practically unchanged on heating up to 400°C, while those along the *b* axis increase. It means also that for Mo–O bonds, situated along the *b* axis [11], their strengths would decrease as a result of their elongation upon heating up to 400°C. At temperature higher than 400°C a remarkable reduction of *b* values may be attributed to a recrystallization process [21].

In the view of our proposed mechanism in connection with the *b* values, i.e., Mo–O bond length, it appears that an increase of the Mo–O bond length render the dehydrogenation possibly by the easy abstraction of hydrogen as OH, with the tendency to oxidation to CO₂, by the weakly bonded oxygen which leads to more readily available lattice oxygen and therefore to more facile formation of carbon oxides. On the other hand, the decrease of the Mo–O bond length is associated with a preferential tendency of the acidic active sites to be attacked by the hydroxyl oxygen of methanol and then the abstraction of hydrogen may be caused by the activated “gaseous” oxygen.

Finally, our findings lead to the conclusion that the less selective sites for dehydrogenation of methanol to formaldehyde are those molybdenum cations associated with an easily ruptured long Mo–O bond which has a higher ability to activate the gaseous oxygen during the catalytic process, while the more selective sites are those associated with a short Mo–O bond with a double bond character rather than their relative lower oxidizing functions.

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