effect accompanied by the variation in reaction orders.

If this is the case, observed variation of activation energy must be explained by Eq. (3), whereas the verification of Eq. (3) encounters a difficulty in estimation of the heats of adsorption Δh_A° and Δh_B° under the reaction condition. In this respect the determination of heat of adsorption during the reaction will be helpful for the elucidation of the compensation effect.

REFERENCES

1. For example, BOND, G. C. "Catalysis by Metals." Academic Press, London, 1962.
2. CONSTABLE, F. H., *Proc. Roy. Soc.* (*London*) **A108,** 355 (1925); CREMER, E., AND SCHWAB, G. M., *Z. Phys. Chem.* (*Leipzig*) **A144,** 243 (1929); KEMBALL, C., *Proc. Roy. Soc.* (*London*) **A217,** 376 (1953); KWAN, T., *J. Phys. Chem.* **59,** 285 (1955).
3. VAN REIJEN, L. L., AND SCHUIT, G. C. A., *Bull. Soc. Chim. Belges* **67,** 489 (1958); *Advan. Catalysis* **10,** 243 (1958).
4. MORO-OKA, Y., AND OZAKI, A., *J. Catalysis* **5,** 116 (1966).

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The Role of a Metal–Oxygen Double Bond in the Activity of Molybdates in Oxidation Reactions*

We have studied the catalytic behavior of several molybdates in the oxidation of NH_3 and of propene. The kinetic measurements were made by a pulse microreactor with a chromatograph in series, in the range of temperature between 300° and 500°C. The data of activity are reported in Table 1. The same table reports the IR bands of the molybdates in the 900–1000 cm^{-1} region.

The table suggests that the molybdates studied may be classified depending on the nature of IR spectra:

(a) molybdates presenting bands between 940–970 cm^{-1}; these are molybdates of transition metals;

(b) molybdates presenting bands between 900–930 cm^{-1}; Al and Bi molybdates belong to this class;

(c) molybdates that do not present characteristic bands in the region between 900 and 1000 cm^{-1}; calcium, lead, and thallium molybdates belong to this class.

The characteristic spectra of the three classes are reported in Fig. 1.

The catalysts of the first and second class are active in the oxidation of propylene and ammonia, while those of the third class are practically inactive. Besides, the same catalysts that are active for the oxidation of ammonia and propylene are also active for the oxidation of methanol (*1, 2*).

It is known that in metal oxides and in mixed oxides, the presence of a band between 900 and 1000 cm^{-1} may be attributed to the presence of a metal–oxygen bond having properties of a double bond (*3, 4*).

From Table 1 it is seen that all the active molybdates have a metal–oxygen bond with double-bond character and the inactive ones have not this kind of metal-oxygen bond.

The greater activity of the molybdates with respect to the MoO_3 is accompanied by a shifting of Me=O to lower frequency.

Mars (*5*) had previously suggested that in the catalyst based on vanadium anhydride the most reactive oxygen is that bound to vanadium by a double bond. Subsequently (*6*) the promoting effect of

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TABLE 1

Index of Activity of Molybdates in the Oxidation of NH_3 and C_3H_6

P: 1200 mm Hg
Rate of He: 0.6 cc/sec
Catalyst: 0.4 g
Feed: NH_3 5% Air 95%
C_3H_6 5% Air 95%

Molybdates	Oxidation of NH_3[a]	Oxidation of C_3H_6[b]	IR between 900–1000 cm^{-1}
Fe[c]	350°	360°	960
Co	390°	390°	940
Ni	355°	350°	960–935
Mn	385°	385°	945
Cr[c]	348°	355°	968
Bi(Bi:Mo = 1:1)	300°	300°	928
Bi(Bi:Mo = 2:1)	395°	395°	920
Al[c]	425°	420°	910
Ca	>500°	>500°	—
Tl	>500°	>500°	—
Pb	>500°	>500°	—
MoO_3	420°	420°	985

[a] As index of activity we chose the temperature (°C) at which the conversion of NH_3 divided by surface area of catalyst was:

$$\frac{21.5 \text{ moles converted}}{100 \text{ moles fed} \times \text{m}^2 \text{ of catalyst}}.$$

[b] As index of activity we chose the temperature at which the conversion of C_3H_6 divided by surface area was:

$$\frac{10.7 \text{ moles converted}}{100 \text{ moles fed} \times \text{m}^2 \text{ of catalyst}}.$$

[c] In these molybdates there was an excess of MoO_3; for this case the IR band at 985 cm^{-1} for Mo = O of MoO_3 was omitted.

K and Mo on V_2O_5 was attributed to the labilization of the V=O bond, as could be observed from the shifting in the IR spectra of the V=O bond to lower frequency.

The correlation between the catalytic behavior of molybdates and the presence of a metal–oxygen bond with double-bond character, will be related to a certain mechanism of oxidative dehydrogenation, that can be considered as similar for all the studied molybdates. In the case of a different mechanism of oxidation this kind of bond can not be required.

The presence of lattice vacancies and defects, and of hydroxyl groups, connected with the method of preparation, and the irreversible adsorption of reaction products, will be further components determining the catalytic activity of molybdates. Moreover, from the results reported here, the presence of a metal–oxygen bond with double-bond character seems to be the necessary—if not sufficient—condition in order that the studied molybdates present catalytic activity.

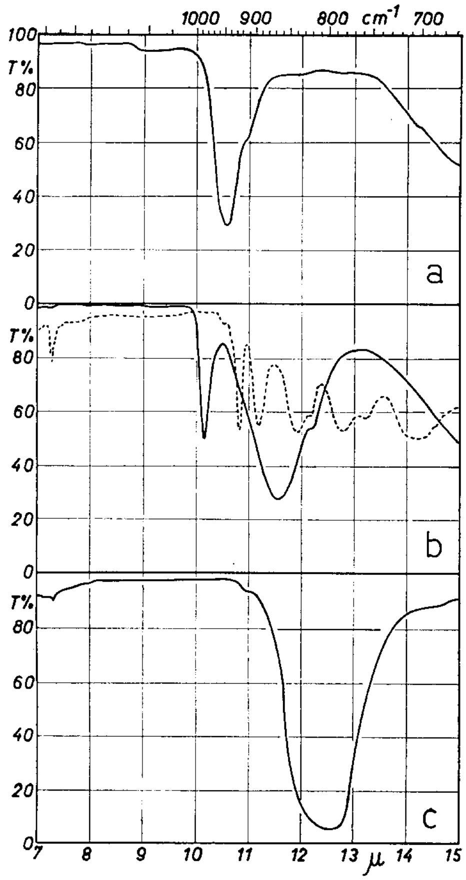

Fig. 1. Infrared absorption spectra (KBr disk method): (a) cobalt molybdate; (b) —, molybdic anhydride; ---, bismuth molybdate (Bi:Mo = 2:1); (c) lead molybdate.

From the suggestion of Clark *et al.* (*4*) and also taking into account the Me–O and Mo–O bond distances, known from the structure of cobalt molybdate and manganese molybates (*7*), the bond having the character of a double bond seems to be the Mo=O bond. In fact in the two molybdates the lowest lattice distance between metal and oxygen is that of the molybdenum–oxygen bond.

At this stage of experimentation we think that also for the other molybdates the metal–oxygen bond with double-bond character is that of molybdenum.

References

1. Jirů, P., Trifirò, F., Klisurshki, D., and Pasquon, I., Simposio di Dinamica delle Reazioni Chimiche, Padova, 1966.
2. Pernicone, N., Liberti, H., and Ersini, L., private communication.
3. Barraclough, C. C., Lewis, J., and Nyholm, R. S., *J. Chem. Soc.*, p. 3552 (1959).
4. Clark, G. M., and Doyle, W. P., *Spectrochim. Acta* **22**, 1441 (1966).
5. Mars, P., and Van Krevelen, D. W., *Chem. Eng. Sci.* **3**, 41 (1954).
6. Tarama, K., Teranishi, S., Yoshida, S., and Tannura, N., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, p. 282 (1965).
7. Abrahams, S. C., and Reddy, J. M., *J. Chem. Phys.* 43, (7), 2533 (1965).

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The Catalytic Activity and Selectivity of Unsupported Metal Sulfates for the Isomerization of *n*-Butenes

The rates and the selectivities of *n*-butene isomerization over a series of silica-gel-supported metal sulfates were discussed in correlation with the acid strength in a previous paper (*1*). In the present work unsupported metal sulfates have been investigated in comparison with silica-gel-supported metal sulfates.

Commercial metal sulfates of G. R. grade [$Al_2(SO_4)_3 \cdot 18H_2O$, $NiSO_4 \cdot 7H_2O$, $MgSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot 7H_2O$, and $CuSO_4 \cdot 5H_2O$] were calcined at various temperatures for 4 hr after the precalcination at 100°C overnight and were kept in vacuum desiccators. The same apparatus for the reaction was used as in the previous paper (*1*). The calcined metal sulfates were evacuated for 1 hr at the reaction temperature of 61.5°C just before the reaction. The acid strength of the calcined metal sulfates was measured after evacuation for 1 hr at about 60°C.

The effects of the calcination temperature on the catalytic activities and the selectivities of *cis*-2-butene isomerization over aluminum sulfate, nickel sulfate, and magnesium sulfate were obtained as shown in Fig. 1. The activities are given by the initial rate constants calculated by assuming first order reactions and the selectivities by the initial ratios of two isomerized butenes. It is of interest to note that the catalytic activity changed markedly with the calcination temperature for all catalysts, whereas the selectivity scarcely changed. The activity changes are not due merely to the surface area changes, because the surface areas (N_2 adsorption) of nickel sulfates were obtained as 16.8 m^2/g (calcined at 200°C), 9.9 (300°), and 7.8 (500°), whereas the rate constants of these catalysts were 2.3×10^{-4}, 1.7×10^{-3}, and 1.8×10^{-5} g^{-1} min^{-1}, respectively. The highest activity was displayed for each catalyst when its water content was intermediate between the monohydrated structure and the anhydrous one, as shown in Fig. 1. Takeshita *et al.* (*2*) proposed from the study of X-ray, ESR, acidity measurements, etc., that the acidity of nickel sulfate is associated with its metastable structure produced by the transition from the monohydrated structure to the anhydrous one. Their interpretation for nickel sulfate may be applicable to aluminum sulfate and magnesium sulfate as well.

The highest acid strength of metal sulfates calcined at several temperatures was measured by the use of the Hammett indi-