React. Kinet. Catal. Lett., Vol. 22, Nos 3–4, 325–329 (1983)

INFLUENCE OF THE HETEROGENEITY OF MOLYBDENUM COMPOUNDS ON THE ACIDITY OF MOLYBDENA-ALUMINA CATALYSTS

En Khwa Kim, K. P. Zhdanova, B. V. Timashkova, N. V. Alekseeva,
L. P. Batasheva and F. K. Schmidt

Institute of Petroleum and Coal Chemistry Synthesis, Irkutsk, USSR

Received July 21, 1982
Accepted November 17, 1982

Electron acceptor properties of molybdena-alumina catalysts is shown to increase with increasing molybdenum content and to be independent of its configuration. Molybdenum compounds with octahedral configuration result in Brönsted acidity.

Электроноакцепторная способность алюмомолибденового катализатора растёт с увеличением количества молибдена, причём не зависит от конфигурации соединений молибдена. Соединения молибдена с октаэдрической конфигурацией образуют кислотность бренстедовского типа.

In previous studies of the acidity of molybdena-alumina catalysts (MA), the heterogeneity of their molybdenum compounds has not been taken into account. Molybdenum compounds in MA are known to have octahedral [Mo(O)], and tetrahedral [Mo(T)] configurations /1/.

We have made an attempt to study the influence of Mo(O) and Mo(T) on the acidity by using IR-spectroscopy.

Catalysts were prepared like in Ref. /2/ (Refer to Table 1). UV-Diffuse-reflection spectroscopy studies (interpretation according to Ref. /3/) indicate that the solubilities of Mo(O) and Mo(T) are different.

UV spectra of the diffuse reflection of MA catalysts are illustrated in Fig. 1. It is seen that for the sample washed with water (B), the band maximum shifts to the short-wave region (270 nm), relative to the initial maximum (sample A) (290 nm). Curves B and B′ are qualitatively similar. Sample B′ prepared like in Ref. /4/, does not contain Mo(O). Hence it is mainly Mo(O) that is washed out by water.

The formation of Mo(O) and Mo(T) sites on γ–Al_2O_3 is inherently different. Mo(T) is formed due to the exchange with basic OH^- groups of alumina /4/ and is soluble in ammonium hydroxide.

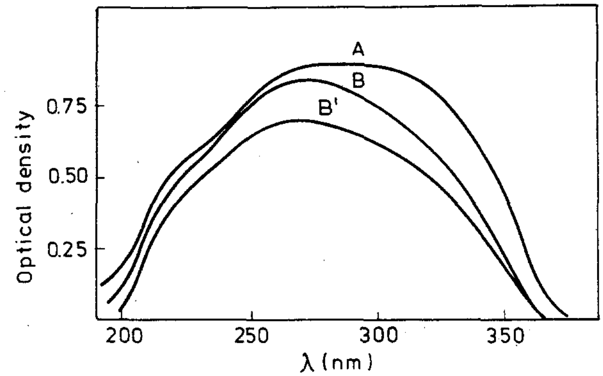

Fig. 1. UV-diffuse reflection spectra of molybdena-alumina catalysts. Designations in Figs 1 and 2 are the same as in Table 1

Table 1

Some characteristics of the samples

Sample	MoO_3 content (wt.%)	Preparation methods
A	11	Impregnated with APM* solution, calcined at 873 K for 3 h
B	9.3	From A, washed by water and dried
C	2.6	From A, washed by 3% NH_4OH and dried
D	17.5	Impregnated with APM, calcined at 873 K for 3 h. $C_{Mo(O)} = 0.075$ g/g_{cat}
B'	6.7	APM supported in a flow like in Ref. /4/.
L	–	γ–Al_2O_3 with surface area S = 200 m^2/g

*APM – ammonium paramolybdate

All samples were subjected to a vacuum-oxygen treatment at 773 K with further evacuation to 0.01 Pa at 393 K (Fig. 2) and 773 K (Fig. 4). Ammonia was used as a probe molecule to test the acidity of the catalyst. Spectra were interpreted according to Ref. /5/.

IR spectra of ammonia after its adsorption and desorption on samples A, B, C, D and γ–Al_2O_3 are illustrated in Fig. 2. The presence of L – ($\delta_{s, as}$ = 1240, 1605 cm^{-1}) and C-sites ($\delta_{s, as}$ = 1400, 1475 and 1690 cm^{-1}) is typical for alumina.

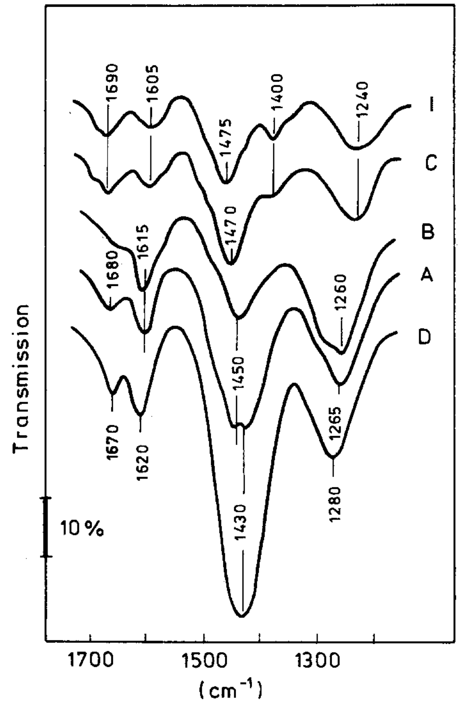

Fig. 2. IR spectra of NH_3 after adsorption-desorption at room temperature

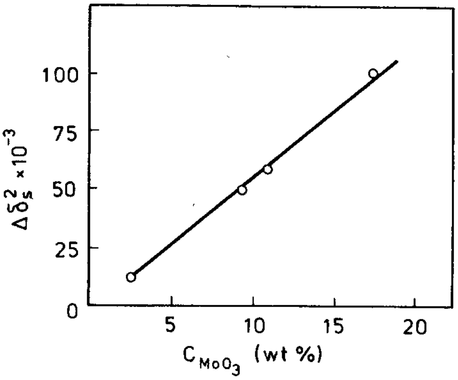

Fig. 3. The strength of aprotonic sites of molybdena-alumina catalysts vs. the concentration of supported MoO_3. $\Delta\delta^2 = \delta^2_{\text{sample}} - \delta^2_{Al_2O_3}$

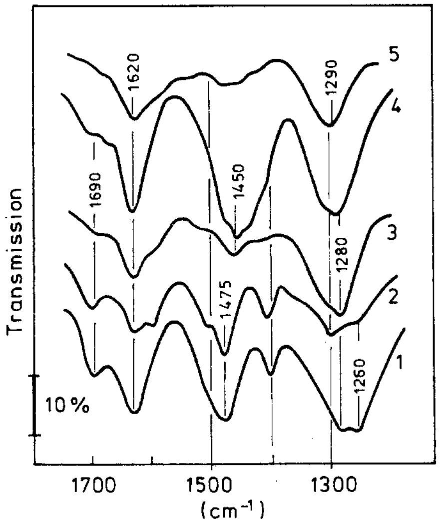

Fig. 4. IR spectra of NH_3 after desorption from γ–Al_2O_3 (1, 2) and of molybdena-alumina catalysts (3, 4, 5) at 373 K (1, 4) and 473 K (2, 3, 5); 4, 5 – sample A, 3 – sample B

After treating alumina with alkali, the bands at 1400, 1475 and 1690 cm^{-1} disappear, which fact confirms their association with C-sites. Mo-containing samples have C-sites characterized by lower frequency bands (1430, 1450 cm^{-1}) compared with that at 1475 cm^{-1}. The formation of C-sites is greatly influenced by the structure of the Mo(O) compounds, as is evidenced by the spectra of samples D, A, B. The Mo(O) content in these samples decreases in the sequence: $C_{\mathrm{Mo(O)}} > C_{\mathrm{Mo(O)_A}} > C_{\mathrm{Mo(O)_B}}$. In sample D, having high Mo(O) content, the number of C-sites is much greater than in γ–Al_2O_3. Under the same conditions of pretreatment, the C/L ratio in sample D is approximately twice as high as on γ–Al_2O_3. On the basis of the shift of the maximum from 1475 and 1690 cm^{-1} (Al_2O_3) to 1430 and 1670 cm^{-1} (sample D), the formation of new C-sites can be suggested. This is supported by both the spectrum of sample A (the bands at 1430 and 1450 cm^{-1}) and by the shoulder in the higher frequency region. For sample B, whose Mo(O) content is low, the band at 1430 cm^{-1} is almost absent and the intensity of the band at 1450 cm^{-1} decreases compared with sample A (C/L decreases approximately by a factor of 1.7). Sample C, containing no Mo(O) and Mo(T) gives only one band at 1470 cm^{-1} corresponding to the proton acidity of the carrier.

With increasing the Mo content in MA, the absorption band typical for the L-sites shifts from 1240 to 1280 cm^{-1} (Fig. 2). The same effect has been observed previously /6/. Assuming that the electron acceptability is proportional to δ_s^2 /7/, the increase in its intensity can be determined depending on the molybdenum concentration. As is seen from Fig. 3, in a given range of molybdenum concentrations the strength of L-sites increases linearly with increasing concentration of the molybdenum added independently of the type of its structure. The addition of molybdenum compounds to γ–Al_2O_3 enhances L-sites similarly to the effect of temperature rise during carrier pretreatment. Thus, γ–Al_2O_3 treated at 773 K for 6 h has stronger L-sites (δ_s = 1260–1280 cm^{-1}) than γ–Al_2O_3 trained at 393 K (δ_s = = 1240 cm^{-1}) (Figs 4 and 2) Besides, spectra recorded after ammonia desorption from γ–Al_2O_3 at higher temperatures (Fig. 4, sp. 2), exhibit a band at 1500 cm^{-1}. In Ref. /5/, this band is attributed to amide compounds. This band is almost absent in the spectra of Mo(O)-containing samples (Fig. 4, sp. 5). Hence, it can be suggested that a considerable amount of Mo(O) is formed on the sites of amide formation, i.e. on $Al_n^+ {-} O {-} Al_n / O^-$ -type sites (n is the coordination number of Al), and this Mo(O) forms C-sites (1430 cm^{-1}). We doubt that the band at 1450 cm^{-1} refers to certain molybdenum compounds. It can also be attributed to Mo(O).

REFERENCES

1. F. E. Massoth: In Advances in Catalysis and Related Subjects, New York, Academic Press, *27*, 265 (1978)
2. F. K. Schmidt, En Khwa Kim, B. V. Timashkova, S. M. Krasnopolskaya, N. E. Bauer, N. N. Orlova: React. Kinet. Catal. Lett., *14*, 283 (1980).
3. N. G. Asmolov, O. V. Krylov: Kinet. Katal., *11*, 1028 (1970).
4. B. A. Jannibello, F. Trifiro: Z. Anorg. Allg. Chem., *413*, 233 (1975).
5. A. V. Kiselev, V. I. Lygin: Infrared Spectra of Surface Compounds and Adsorbed Substances. p. 285, Nauka, Moskva 1972. A. A. Davydov, Yu. M. Shchekochikhin: Kinet. Katal., *10*, 163 (1969).
6. F. E. Kiviat, L. Petrakis: J. Phys. Chem., *77*, 1232 (1973).
7. V. N. Filimonov, Yu. N. Lopatin, D. A. Sukhov: Kinet. Katal., *10*, 458 (1969).