JOURNAL OF CATALYSIS **113**, 256–258 (1988)

On the Valence State of Molybdenum Ions in Silica–Molybdenum Catalysts Photoreduced in Carbon Monoxide

We have shown earlier (*1, 2*) that UV irradiation of Mo^{6+}/SiO_2 samples (1 wt% Mo) in the CO atmosphere results in molybdenum ion reduction, mainly to Mo^{4+}. This conclusion was based on a comparison of the average oxidation state of molybdenum ions (4+) with UV–Vis optical and EPR data on the photoreduced samples. Later we found (*3*) that photoreduced samples exhibit a high catalytic activity at room or lower temperatures for propylene metathesis, which is likely associated with the presence of considerable amounts of Mo^{4+} in the catalysts. In particular, this was evidenced by the constancy of specific catalytic activities referred to Mo^{4+} ion (turnover numbers) (*3*) at approximately tenfold variation of the Mo^{4+} concentration in the catalyst.

Recently a number of papers (*5–7*) have been published, in which attempts were made to determine the valence state of molybdenum ions using IR spectra of CO chemisorbed on photoreduced ions. After UV irradiation of Mo^{6+}/SiO_2 in the presence of gaseous CO, principally two IR bands at 2075–2080 and 2125–2130 cm^{-1} were observed. However, there is strong disagreement in the interpretation of these bands: in (*5, 6*) they were assigned to dicarbonyl complexes of Mo^{2+} ions, whereas in (*7*) they were attributed to those of coordinatively unsaturated Mo^{4+} ions. After pumping off CO at room temperature, the bands of dicarbonyl complexes disappeared and a new IR band at 2035–2050 cm^{-1} appeared which was attributed either to $Mo^{2+}(CO)$ (*5, 6*) or to $Mo^{4+}(CO)$ (*7*) monocarbonyl complexes. In addition, a couple of bands at 2142 and 2109 cm^{-1} were detected (*7*), which were reversibly transforming into the band at 2021 cm^{-1} during evacuation of the sample. These coupled bands were attributed to di- and monocarbonyl complexes of Mo^{4+} ions, respectively, located in polymolybdate structures.

Thus, the valence state of the major part of photoreduced molybdenum ions still remains under discussion and more experimental data are necessary to make a choice in favor of this or that assumption. For instance, it seems worthwhile to compare quantitatively the number of CO molecules desorbing during the decomposition of $Mo^{x+}(CO)$ complexes (N_{CO}^{des}) and the number of CO_2 molecules (N_{CO_2}) formed during photoreduction of Mo^{6+}/SiO_2 (each CO_2 molecule corresponds to two electrons left behind in the sample after removal of one oxygen atom). No such comparison was made in the IR works. Indeed, if photoreduction proceeds up to the Mo^{4+} state and the observed IR bands actually belong to $Mo^{4+}(CO)$ complexes, then N_{CO}^{des} should be equal to N_{CO_2}. On the contrary, if photoreduction results mainly in Mo^{2+} formation, N_{CO}^{des} is expected to be equal either to $\frac{1}{2}N_{CO_2}$ (for $Mo^{2+}(CO)$ complexes) or to $\frac{1}{4}N_{CO_2}$ (for $Mo^{2+}–CO–Mo^{2+}$ complexes). In this note the results of such experiments are presented in Table 1.

Experiments were carried out with Mo^{6+}/SiO_2 (1 wt% Mo) samples prepared by impregnation of KSK-2-5 silica gel with an aqueous solution of ammonium paramolybdate. The procedure of sample preparation, their heat treatment, and photoreduction was described in our earlier work (*3*).

0021-9517/88 $3.00

TABLE I

Comparison of CO Amounts Adsorbed on and Desorbed from Mo/SiO_2 Samples Photoreduced in CO

Expt. No.	N_{CO_2} (10^{-18} molec/g(cat.))	$N_{CO}^{des}(1)$ (10^{-18} molec/g(cat.))	N_{CO}^{ads} (10^{-18} molec/g(cat.))	$N_{CO}^{des}(2)$ (10^{-18} molec/g(cat.))
1	11.2		10.2	9.6
			11.8	12.3
			10.7	10.7
2	13.9	14.4	13.9	11.8
3	15.0	13.4	13.9	12.8
4	7.0	9.1	5.4	8.0

Temperature-programmed CO desorption (TPD) curves were taken using a Pyrani gauge at the heating rate of 4.5 K/min. The amounts of adsorbed and desorbed CO molecules were measured with McLeod or Pyrani gauges. Diffuse reflectance spectra were recorded with a Hitachi M-340 spectrophotometer using a MgO pellet as a reference.

After photoreduction in CO of Mo/SiO_2 and outgassing of the samples at 293 K, i.e., under conditions when mainly monocarbonyl complexes of photoreduced molybdenum ions are on the surface (*5–7*), the diffuse reflectance spectrum, shown in Fig. 1b, was observed. The absorption bands in the 350–1000 nm range can be assigned to Mo^{4+}(CO) complexes (*1, 2*). These disappeared when the temperature is raised *in vacuo* to 473 K (Fig. 1c). Simultaneously some CO is evolved in the gas phase (see $N_{CO}^{des}(1)$ in Table 1). Two desorption maxima on the TPD curve (at 360 and 430 K, Fig. 2) are likely due to the decay of monocarbonyl complexes of polymolybdates and isolated tetrahedrally coordinated Mo^{4+} ions, respectively. After the temperature is raised to ~500 K, CO desorption is completed. Correspondingly, all the IR bands of chemisorbed CO disappear (*7*), while in the UV–Vis spectrum (Fig. 1c) there appear absorption bands at 350, 625, and 775 nm, which were assigned in (*1, 2*) to coordinatively unsaturated bare Mo^{4+} ions.

After CO readsorption at 293 K and outgassing of the sample at this temperature the spectrum of Fig. 1b was obtained; i.e., the desorption–adsorption cycle can be repeated many times. In Table 1 the amounts of CO molecules readsorbed at 293 K (N_{CO}^{ads}) and desorbed in the range 293–473 K ($N_{CO}^{des}(2)$) are compared with the amounts of

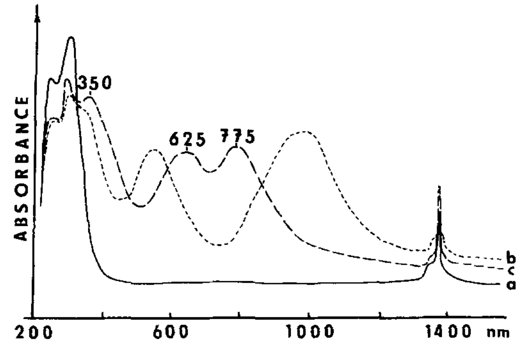

FIGURE 1

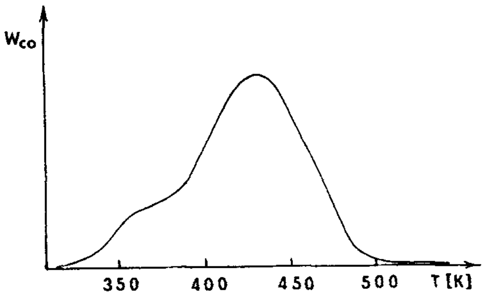

FIGURE 2

CO_2 (N_{CO_2}) produced during photoreduction of the sample. Although the accuracy and reproducibility of the measurements are only mediocre, nevertheless the data of Table 1 allow us to draw a qualitative conclusion that in each experiment $N_{CO}^{des}(1)$ or (2) $\simeq N_{CO}^{ads} \simeq N_{CO_2}$. This agrees well with our previous assumption that by photoreduction of Mo^{6+}/SiO_2 in CO mainly Mo^{4+} ions are produced, although because of the relatively poor accuracy of CO adsorption–desorption measurements possible formation of smaller amounts of molybdenum species in oxidation states lower than 4+ cannot be ruled out. The fraction of such species apparently increases in photoreduced samples with smaller Mo loadings (0.01–0.1 wt%), showing the average oxidation numbers in the range 2.6–2.8 (*8*).

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Received September 24, 1987; revised February 23, 1988

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