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Evidence from XPS for the Stabilization of High-Valent Molybdenum by Addition of Potassium in Mo/Al_2O_3 Catalysts

It has been found that alkali and molybdenum are important components of catalysts which convert synthesis gas into higher alcohols (*1, 2*). In general, these catalysts are reduced under relatively mild conditions (e.g., 673 K). The purpose of this study is to determine the oxidation state of molybdenum in reduced, potassium-promoted Mo/Al_2O_3 samples as a function of the alkali loading.

A series of Mo(x)/Al_2O_3 samples was prepared (x = wt% of molybdenum present) with 3, 6, 12, and 15 wt% molybdenum, using ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) and an incipient wetness impregnation technique. Aqueous solutions of the molybdenum salt were prepared at the desired concentrations to yield catalyst samples with the proper molybdenum loadings. The alumina used was a Norton, gamma type, No. 6375 (40-mesh) with a surface area of 216 $m^2\ g^{-1}$ and a pore volume of 1.1 $ml\ g^{-1}$. After impregnation with molybdenum, the samples were dried at 393 K for 16 h and calcined under flowing air at 773 K for 3 h.

Potassium was deposited on the Mo/Al_2O_3 samples from aqueous potassium carbonate (K_2CO_3) solutions. Samples of the Mo(3)/Al_2O_3 material were prepared with 0.5, 1.0, 3.0, and 6.0 wt% potassium to yield the K(y)–Mo(3)/Al_2O_3 catalysts. Samples of the Mo(12)/Al_2O_3 material were loaded with 0.5, 1.0, 3.0, 4.5, and 6.0 wt% potassium to yield the K(y)–Mo(12)/Al_2O_3 catalysts. The potassium-loaded materials were dried at 393 K for 16 h.

XPS analyses were carried out on a Leybold–Heraeus (LH) LS-10 instrument, equipped with a hemispherical analyzer. Catalyst samples were mounted on slides coated with adhesive tape or pressed into self-supporting wafers. The results obtained were identical with both sample preparation procedures. The analyses were performed under a vacuum of at least 1×10^{-8} mbar. Aluminum (1486.6 eV) or magnesium (1253.6) X-rays of 100 w power were used as the incident beam. Spectra were obtained by accumulating 100 scans for the self-supporting wafers, or 500 scans for the adhesive tape-supported samples. Binding energies were recorded for the Al 2*p*, Mo 3*d*, O 1*s*, K 2*p*, and C 1*s* regions after calibration to the Al 2*p* signal at 74.5 eV. Mo 3*d*/Al 2*p* and K 2*p*/Mo 3*d* ratios were used as a measure of the molybdenum and potassium coverages.

Reductions were performed *in situ* using a commercial (LH) temperature probe. The samples were moved from the analysis chamber to a reaction chamber and contacted with flowing hydrogen (100 ml min^{-1}, 1 atm) at 673 K for 2 h. After reduction, the materials were moved back into the analysis portion of the spectrometer, without exposure to air, and reanalyzed.

Deconvolutions of the Mo 3*d* regions were performed using the LH-supported software. The Mo(6+), (5+), and (4+) 3*d*5/2 binding energies used in curve analysis were 232.9, 231.5, and 229.4 eV, respectively. These can be compared to the binding energies of several standard compounds in Table 1: the resolution of this spectrometer was such that Mo(6+), Mo(4+), Mo(2+), and Mo(0) could be distinguished. The distance between 3*d*5/2 and 3*d*3/2 peak maxima was taken to be 3.1 eV in the curve fit analyses, for all molybdenum oxidation

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TABLE 1

X-Ray Photoelectron Spectroscopy Data Obtained for Some of the Alumina-Supported Molybdena and Alkali–Molybdena Samples

Sample[a]	Binding energy (eV)				Mo 3*d*/Al 2*p* (×100)	K 2*p*/Al 2*p* (×100)
	O 1*s*	K 2*p*	C 1*s*	Mo 3*d*[b]		
Mo(3)	531.8	—	285.4	233.1	1.8	—
Mo(3)-R[c]	531.7	—	286.1	233.0	1.6	—
Mo(12)	531.5	—	285.3	233.1	7.7	—
Mo(12)-R	531.5	—	284.9	232.3	6.8	—
K(0.5)–Mo(3)	531.7	293.8	285.4	233.0	1.8	0.4
K(0.5)–Mo(3)-R	531.7	293.8	285.2	233.0	1.6	0.2
K(3)–Mo(3)	531.7	293.7	285.5	232.9	1.4	4.4
K(3)–Mo(3)-R	531.5	293.8	285.5	233.0	1.4	5.3
K(0.5)–Mo(12)	531.5	294.0	285.2	233.1	6.8	0.0
K(0.5)–Mo(12)-R	531.4	293.4	285.0	232.6	6.3	0.4
K(3)–Mo(12)	531.2	293.2	285.3	232.9	5.6	2.2
K(3)–Mo(12)-R	531.1	293.6	285.2	232.6	6.2	4.8
Mo foil	531.7	—	285.2	227.7		
$(Mo(C_2H_3O_2)_2)_2$	531.2	—	284.6	228.6		
MoO_2	530.6	—	284.6	229.7		
MoO_3	530.8	—	284.1	232.9		

Note. Mo 3*d*5/2 binding energies of several standard compounds are also included at the end of the table.

[a] All molybdena and alkali–molybdena samples are supported on alumina.

[b] The Mo 3*d* binding energy is reported as the maxima of the 3*d*5/2 signal.

[c] R indicates that the material has been reduced (H_2, 673 K, 2 h, 1 atm, flow conditions).

states. The Mo 3*d*3/2 : 3*d*5/2 ratio was assumed to be 0.70. The full width at half maximum for the Mo 3*d*5/2 and 3*d*3/2 signals was between 2.3 and 3.1 eV, depending on the molybdenum and potassium loadings. Deconvolution of the Mo 3*d* region was accomplished using Gaussian functions to fit the data. The software compensated for sloping baselines by constructing a tangent from the start-to-finish of the fitted region. The parameters used here are similar to those used by Patterson *et al.* (*3*).

XPS data for the "as prepared" Mo(*x*)/Al_2O_3 samples reveal that molybdenum is only in the 6+ oxidation state (Table 1, Fig. 1A). The binding energies of the O 1*s* and C 1*s* signals are given in Table 1 and can be used to relate the calibration of these data to work reported previously (*3, 4*). Reduction of the Mo(*x*)/Al_2O_3 samples by hydrogen at 673 K resulted in reduction of a portion of the Mo(6+) to lower oxidation states. Curve analyses of the reduced materials reveal that molybdenum exists in the 6+, 5+, and 4+ oxidation states. The Mo(4+) is evident in samples of 6 wt% Mo or greater (Fig. 1C). Both the percentage of Mo(4+) and the extent of total molybdenum reduction are higher in the more highly loaded catalysts. Previous studies agree with the findings that molybdenum is reduced only to Mo(5+) and Mo(4+) (*3, 4*).

The reducibility of both the K(*y*)–Mo(3)/Al_2O_3 and the K(*y*)–Mo(12)/Al_2O_3 samples was also monitored by XPS. Again, reduction led to the formation of only Mo(5+) and Mo(4+) species (Tables 1 and 2). The extent of reduction was less on the alkali promoted systems: for example, the average molybdenum oxidation state in Mo(3)/Al_2O_3 was 5.61 compared to 5.81 in K(6)–Mo(3)/Al_2O_3 and the average oxidation

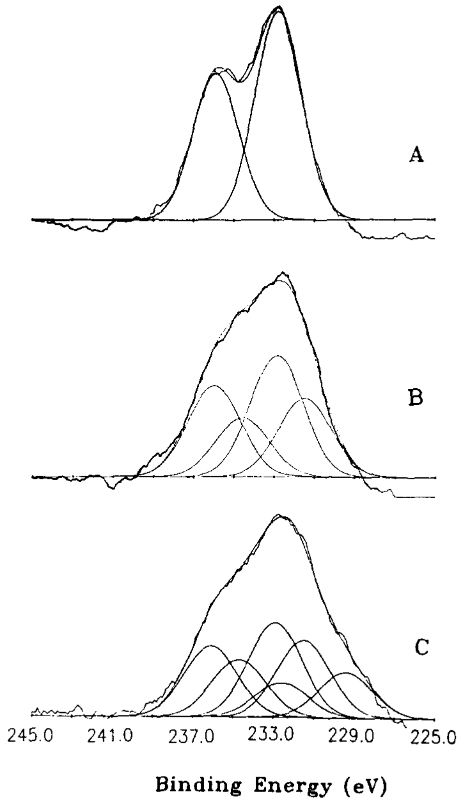

FIG. 1. X-ray photoelectron spectroscopy data showing the molybdenum 3*d* region in instances where (A) Mo (6+) is present—an "as prepared" Mo(12)/Al_2O_3 sample; (B) Mo (6+) and (5+) are present—a reduced K(1)–Mo(3)/Al_2O_3 sample; and (C) Mo is present in (6+), (5+), and (4+) oxidation states—a reduced Mo(12)/Al_2O_3 material.

TABLE 2

Percentages of Molybdenum in the Various Oxidation States, after Reduction of the Samples

Sample	Mo oxidation states 6+	5+	4+	Ave. oxidation state
Mo(3)	61.2	38.8	0.0	5.61
Mo(6)	47.5	45.4	7.1	5.40
Mo(12)	26.1	52.5	21.4	5.05
Mo(15)	26.5	47.5	26.0	5.01
K(0.5)–Mo(3)	61.1	38.9	0.0	5.61
K(1)–Mo(3)	64.1	35.9	0.0	5.64
K(3)–Mo(3)	68.8	31.2	0.0	5.69
K(6)–Mo(3)	81.3	18.7	0.0	5.81
K(0.5)–Mo(12)	38.1	45.0	16.9	5.21
K(1)–Mo(12)	38.3	44.9	16.8	5.22
K(3)–Mo(12)	39.0	42.9	18.1	5.21
K(4.5)–Mo(12)	54.5	27.7	17.8	5.37
K(6)–Mo(12)	69.3	8.4	22.3	5.47

state in the Mo(12)/Al_2O_3 sample was 5.05 compared to 5.47 in the K(6)–Mo(12)/Al_2O_3 material.

The extent of reduction is inversely proportional to the percentage of alkali on the material. Comparisons of the average molybdenum oxidation state with potassium content are shown in Fig. 2. It is noted that the potassium has a much greater effect on the oxidation state in the K(*y*)–Mo(12)/Al_2O_3 materials than in the lower molybdenum-loaded samples, as evidenced by the larger slope of this line (Fig. 2). In the 3 wt% Mo materials, addition of an equimolar amount of potassium to the system changes the oxidation state of the molybdenum by 0.08 *e*/Mo, while addition of equimolar amounts of potassium in the K(*y*)–Mo(12)/Al_2O_3 materials leads to a change of 0.32 *e*/Mo.

Previous work has suggested that K_2CO_3 could interact with a Ni–Mo/Al_2O_3 catalyst and destroy the surface polymolybdate phase (*5*). The molar ratio of potassium to

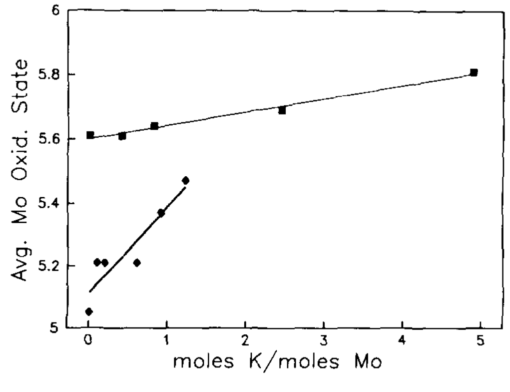

FIG. 2. Comparison of the average oxidation states in the reduced catalyst samples with the molar ratios of potassium to molybdenum: (■), data for the K(*y*)–Mo(3) samples; (◆) data for the K(*y*)–Mo(12) materials.

TABLE 3

X-Ray Photoelectron Spectroscopy Data Obtained for the K(1)–Mo(12)/Al_2O_3 Material: K 2*p* and C 1*s* Regions

Sample	C 1*s*(total)/Al 2*p* (×100)	C 1*s*(289.0)/Al 2*p* (×100)	K 2*p*/C 1*s*(289.0) (×100)
K(1)–Mo(12)	8.89	2.85	0.31
K(1)–Mo(12)-R	7.16	1.64	6.82

molybdenum in this study was 2.5. An argument was advanced that since the molar ratio of potassium to molybdenum was similar to that of certain potassium molybdates, these species could be forming on the catalyst surface. Also, it is known that alkali species do form bronzes with molybdenum (*6*). XPS data was obtained on K_2MoO_4 during this study. This material was found to be nonreducible in hydrogen at 673 K: all the molybdenum remained in the 6+ oxidation state. Extrapolating the lines shown in Fig. 2 will yield the following results: (A) the K(*y*)–Mo(3)/Al_2O_3 samples would become theoretically nonreducible when the K/Mo ratio is equal to 10; and (B) the K(*y*)–Mo(12)/Al_2O_3 samples would reach this state when the K/Mo loading equaled about 2.5. Apparently the data obtained for the K(*y*)–Mo(12)/Al_2O_3 series of samples is consistent with the conclusions of Kantschewa *et al.* (*5*). We have, however, no direct evidence that surface potassium molybdates have formed on these samples.

It is not unexpected that the potassium ions have less of an effect on the Mo(3)/Al_2O_3 reducibility. It is likely that the Mo in these systems is mostly present as isolated tetrahedral species (*7*). If the reduction that occurs here is of the small amount of polymolybdate that is present on the alumina, and if potassium deposition on the material is random, then large amounts of potassium will be needed to affect the molybdenum.

During reduction of the K–Mo/Al_2O_3 materials, a percentage of the potassium carbonate decomposes. Infrared studies have shown that some carbonate remains on catalysts after reduction (*5*). The C 1*s* XPS regions of the K–Mo/Al_2O_3 materials were examined both before and after the 673-K reduction (Table 3). Reduction results in an increase in the K 2*p*/Al 2*p* XPS signal ratio, especially evident in the K(*y*)–Mo(12)/Al_2O_3 catalyst series. There is also a decrease in the C 1*s* band at approximately 289.0 eV. This signal is due to carbonate and, perhaps, to other oxygenated carbon species. It is possible to approximate the change in oxygenated species, on the sample surface, as a function of reduction: the data in Table 3 reveal a 40% decrease in CO_x species (C 1*s*(289)/Al 2*p*) in the K(1)–Mo(12)/Al_2O_3 material. Also, the K 2*p*/Al 2*p* XPS ratio increases after reduction due to removal of surface carbonate groups, and perhaps also because of migration of alkali species into more uniform dispersions on the alumina.

In conclusion, it has been shown by XPS that potassium inhibits the reducibility of molybdenum species in Mo/Al_2O_3 samples. The effect was more apparent in the K(*y*)–Mo(12)/Al_2O_3 materials where addition of alkali to molybdenum in equimolar amounts resulted in a decrease in Mo reducibility of 0.32 *e*/Mo. Under the relatively mild reducing conditions employed here, only Mo 6+, 5+, and 4+ species were observed.

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STEPHEN J. DECANIO[1]
MAURICE C. CATALDO
ELAINE C. DECANIO
DAVID A. STORM

Texaco, Inc.
P.O. Box 509
Beacon, New York 12508

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[1] To whom correspondence should be addressed.