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Room-Temperature Oxidation of K_2CO_3/MoS_2 Catalysts and Its Effects on Alcohol Synthesis from CO and H_2

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Potassium-promoted MoS_2 is used as a catalyst for mixed alcohol synthesis from CO and H_2. This study investigates the room-temperature oxidation of the catalyst and its effect on the surface structure and catalytic activity in alcohol synthesis at 573 K and 1.5 MPa. Catalysts were stored in the atmosphere or in a vacuum oven for several weeks. The characterization of catalyst was performed using XRD, XPS, FT-IR, and TGA/DTA methods. The XPS data of K_2CO_3/MoS_2 stored in the atmosphere for extended periods indicated the oxidations of Mo(IV) (as sulfide) to Mo(VI) (as oxide) as well as S^{2-} (as sulfide) to S^{6+} (as sulfate) on the MoS_2 surface. The IR results showed that sulfate species first produced by oxidation had T_d symmetry, which was further transformed into C_{2v} (bidentate) upon a prolonged storage. The sulfate species formed on the catalyst surface were stable until they were decomposed above 1000 K. The oxidized K_2CO_3/MoS_2 catalyst showed enhanced catalytic activity and high selectivity to C_{2+} hydrocarbons, rather than forming alcohols as did fresh K_2CO_3/MoS_2. These modified catalytic properties were similar to those of fresh K_2SO_4/MoS_2.

INTRODUCTION

Molybdenum sulfides have been widely used as solid lubricants and as hydrotreating catalysts. In recent years attention has been focused on alkali-promoted molybdenum sulfides because they can be used as catalysts for mixed alcohols synthesis from CO and H_2 (*1–4*). In spite of the great commercial significance of these catalysts, the physical and chemical bases for the activity, selectivity, and stability of these catalysts are not yet understood. The preparation of the unsupported molybdenum sulfides employed for mixed alcohol synthesis is commonly based on ammonium thiosalts which are thermally split under inert atmosphere to yield poorly crystalline nonstoichiometric molybdenum sulfides (*1, 5, 6*). The catalytic properties of these molybdenum sulfide catalysts have been found to be significantly influenced by promoters such as alkali metal salts and CoS (*3, 4*).

Alkali metals are the most frequently used as promoters in heterogeneous catalysis because of their ability to modify activity and selectivity of the active catalytic components. Possible effects of alkali promoters include the activation of the reactants during the adsorption and the stabilization of one (or several) intermediate(s) during the reaction processes. In alcohol synthesis from CO and H_2 over alkali-promoted MoS_2, Santiesteban *et al.* (*4*) have proposed that the indispensable presence of the alkali promoter is due to the bifunctionality of the catalyst; namely, the alkali activates CO and MoS_2 activates H_2. For this reason, the addition of high concentration of alkali compounds to MoS_2 is necessary to effectively promote the alcohol formation. The motivation for this work was the observation that alcohol selectivity of K_2CO_3-promoted $MoS_2(K_2CO_3/MoS_2)$ stored in the atmo-

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sphere for extended periods was drastically reduced from that of fresh catalysts. Since transition metal sulfides were known to be sensitive to moisture and oxygen (*5–10*), it may be interesting to study the stability of alkali-promoted MoS_2 before use.

To the best of our knowledge, no work has been reported previously on the chemical behavior of K_2CO_3/MoS_2 catalysts after preparation (i.e., during storage or use as catalysts). In the present work, K_2CO_3/MoS_2 catalysts were stored in the atmosphere or in a vacuum oven, both at room temperature, for various periods, and the changes in surface structure and catalytic properties were investigated. XRD, XPS, FT–IR, and TGA/DTA were employed for catalyst characterization.

EXPERIMENTAL

The preparation of poorly crystalline molybdenum sulfide which is active for mixed alcohol synthesis from CO and H_2 has been widely studied (*1, 3, 11–13*). The MoS_2 samples used for the present study were prepared by the thermal decomposition of ammonium thiomolybdate $(NH_4)_2MoS_4$ in N_2 atmosphere. The $(NH_4)_2MoS_4$ was obtained by saturating an ammonium hydroxide solution of ammonium heptamolybdate (Alfa 99.9%) with H_2S at ambient temperature. The red-brown precipitate was filtered, washed with methanol, and dried under a vacuum. The structure of the $(NH_4)_2MoS_4$ obtained was confirmed by using powder X-ray diffraction. For MoS_2, $(NH_4)_2MoS_4$ was heated in a tube furnace with flowing nitrogen at 723 K for 2 h. The following reaction occurs under this condition:

$$(NH_4)_2MoS_4 \rightarrow 2NH_3 + H_2S + (3 - x)S + MoS_x \quad (x = 2\text{–}3).$$

XRD patterns were obtained with a Rigaku (Model DMax-B) diffractometer using Cu$K\alpha$ radiation. Elemental analysis of MoS_2 was carried out using the combustion gas chromatographic method. The specific surface area was measured with the BET method on a Micromeritics Accusorb 2100E. For the promoted catalysts, MoS_2 was impregnated with an aqueous solution of K_2CO_3 first, followed by drying at 383–393 K overnight. The K/Mo mol ratio was 0.4 for all the catalysts studied. After preparation, catalysts were stored for several weeks in a vacuum oven (ca. 20 Torr) or in the atmosphere at room temperature. K_2CO_3/MoS_2-A-*n* and K_2CO_3/MoS_2-V-*n* represent K_2CO_3-promoted molybdenum sulfides stored in the atmosphere and in a vacuum oven for *n* weeks, respectively. For example, K_2CO_3/MoS_2-A-0 and K_2CO_3/MoS_2-V-8 mean a fresh K_2CO_3/MoS_2 just exposed to air after preparation and a K_2CO_3/MoS_2 stored in a vacuum oven for 8 weeks, respectively.

The X-ray photoelectron spectra (XPS) were taken with a Perkin–Elmer PHI 5400 ESCA spectrometer equipped with an electrostatic analyzer and a position-sensitive detector. Powder samples were pressed into self-supporting wafers. The analyses were performed under a vacuum of at least 1×10^{-9} mbar. The X-ray source was the Mg$K\alpha$ radiation at 1254 eV. Binding energies were recorded for the Mo 3*d*, S 2*p*, K 2*p*, O 1*s*, and C 1*s* regions. In all cases, the peak position changes appearing on the XPS spectra were referenced to the carbon 285.0 eV line associated with hydrocarbon impurities present on the sample surface.

Infrared spectra were recorded with a Perkin–Elmer 1800 FT–IR double beam spectrophotometer on KBr pellets containing 0.5–1.0 wt% of catalyst sample powder, using reference beam screening to obtain suitable 100% baselines in all spectral ranges. All spectra were averages of 16 individual scans taken at room temperature with instrumental resolutions of 4.0 cm^{-1}.

Thermal analysis (TGA/DTA) was performed on a Perkin–Elmer 1700 system at a heating rate of 0.17 K s^{-1} in flowing N_2 (Kboc, 99.99%). The reactions between CO and H_2 were carried out in a tubular down flow fixed-bed reactor, which has been described in detail previously (*14*). Catalyst activities were determined at 573 K with synthesis gas with $H_2/CO = 1$, pressure =

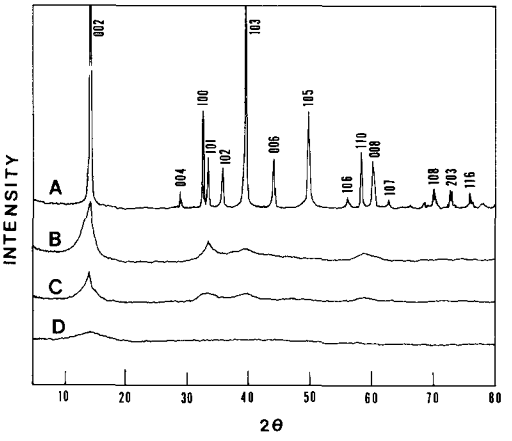


FIG. 1. X-ray diffraction patterns: (A) commercial crystalline MoS_2; (B) MoS_2 prepared at 723 K; (C) K_2CO_3-promoted "fresh" catalyst (K_2CO_3/MoS_2-A-0); (D) commercial MoS_3.

1.5 MPa, and contact time (W/F) = 8.0 g-catalyst h mol^{-1}. Carbon-containing reaction products consisted of methanol, alcohols heavier than methanol ($C_{2+}OH$), hydrocarbons, and carbon dioxide.

RESULTS

Characteristics of the Samples

The XRD patterns are shown in Fig. 1 for MoS_2 and K_2CO_3/MoS_2 immediately after preparation and for a commercial MoS_2 and MoS_3 (Alfa Co.). The MoS_2 produced by thermal decomposition of $(NH_4)_2MoS_4$ is characterized as poorly crystalline MoS_2 as shown by the positions of the broad peaks due to planes of (002), (100), (103), and (110) of MoS_2. It is similar to the XRD pattern reported by Ratnasamy and Leonard (*12*) and Chianelli and Dines (*15*) for MoS_2 prepared by the reduction of MoS_3. The peak at (103) indicates that the 2H (two-layer hexagonal) molybdenite stacking sequence is retained in some crystallites (*11*). The line-braodening analysis of the well-defined peaks carried out in the standard manner (*16*) resulted in an average crystallite size of about 36 Å in the *c*-direction (approximately five MoS_2 layers). The K_2CO_3/MoS_2 shows similar X-ray pattern and particle size to those of MoS_2. Chemical analysis of the sample yielded a nominal stoichiometry of $MoS_{2.3}$. The BET surface areas of MoS_2 and K_2CO_3/MoS_2 were 65 and 44 m^2 g^{-1}, respectively.

X-ray Photoelectron Spectroscopy Measurements

The Mo 3*d* and S 2*p* XPS spectra of powdered MoS_2 catalysts are shown in Figs. 2 and 3. The binding-energy (BE) values for Mo $3d_{3/2}$ and Mo $3d_{5/2}$ of MoS_2 are 232.3 and 229.0 eV, respectively. These binding

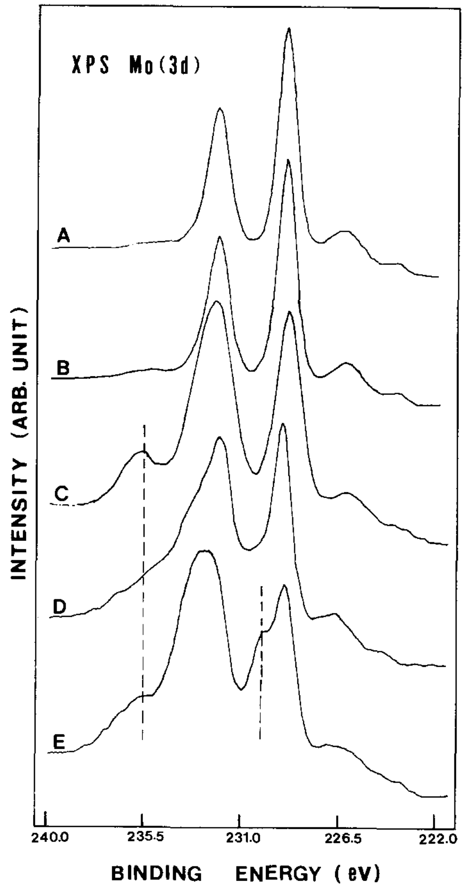


FIG. 2. Mo 3*d* photoelectron spectra: (A) MoS_2; (B) K_2CO_3-promoted "fresh" catalyst (K_2CO_3/MoS_2-A-0); (C) catalyst stored in a room air for 13 weeks (K_2CO_3/MoS_2-A-13); (D) catalyst stored in a vacuum for 6 weeks (K_2CO_3/MoS_2-V-8); (E) K_2CO_3/MoS_2-A-13 treated under 5%H_2S/H_2 mixture at 673 K for 3 h.

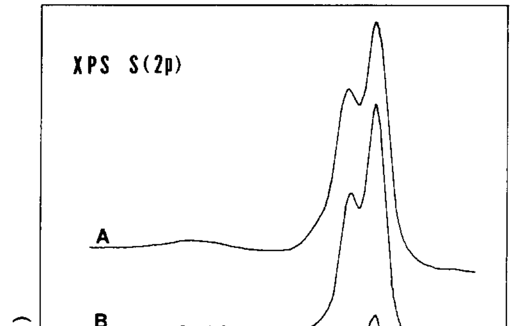


FIG. 3. S 2*p* photoelectron spectra: (A) MoS_2; (B) K_2CO_3-promoted "fresh" catalyst (K_2CO_3/MoS_2-A-0); (C) catalyst stored in a room air for 13 weeks (K_2CO_3/MoS_2-A-13); (D) catalyst stored in a vacuum for 6 weeks (K_2CO_3/MoS_2-V-8); (E) K_2CO_3/MoS_2-A-13 treated under 5%H_2S/H_2 mixture at 673 K for 3 h.

energies are consistent with the values reported by Stevens and Edmonds (*17*). The S 2*p* peak in Fig. 3 shows a doublet and suggests the presence of two types of S in MoS_2 (*17–19*). Liang *et al.* (*18*) proposed the presence of $(S\text{-}S)^{2-}$ and S^{2-} in amorphous MoS_3 using high-resolution X-ray radial distribution analysis and XPS. The fundamental nature of the poorly crystalline MoS_2 structure is not yet clear, although the question has been investigated elsewhere (*12, 13, 20*). In both cases of Mo 3*d* and S 2*p* XPS spectra, no significant difference was observed between fresh MoS_2 and K_2CO_3/MoS_2 (Spectra A and B in Figs. 2 and 3).

In contrast, the samples stored for long periods showed considerable changes in the XPS spectra for Mo 3*d* and S 2*p*. Spectrum C in Fig. 2 (spectrum 2C) and spectrum C in Fig. 3 (spectrum 3C) were obtained for a catalyst sample that had been stored in the atmosphere for 13 weeks. These catalysts showed new Mo 3*d* and S 2*p* peaks at 235.5 and 168.7 eV, respectively. The new Mo 3*d* binding energy value corresponds to the Mo $3d_{3/2}$ level of Mo(VI) (*21*). The slight shift in binding energy and broadening of the sulfur doublet peaks could be caused by the increased electrophilicity of Mo(VI) compared with that of Mo(IV) ions. Hence the spectrum 2C appears to be a combination of two spectra: one attributed to MoS_2 and the other to a Mo(VI) compound. The Mo $3d_{5/2}$ peak of the oxide seems to be masked by the large central peak of the Mo $3d_{3/2}$ of the sulfide. The new strong sulfur peak in spectrum 3C at the binding energy of 168.7 eV indicates the oxidation of S^{2-} to S^{6+} state.

For the sample stored in a vacuum oven (Figs. 2D and 3D), the relatively large Mo $3d_{3/2}$ peak and the slight broadening of the peak on the high-bonding energy side may be indicative of the presence of some other oxidation states of molybdenum, although the effect is not as extensive as that for the samples stored in the atmosphere. The peak at 168.7 eV in Fig. 3D indicates that S^{6+} complex species have been made on this sample as well. Clearly, the surfaces of these catalysts have been partially oxidized, regardless of the storing condition. Spectra 2E and 3E were obtained for the same sample as in spectra 2C and 3C, yet were treated in a 5% H_2S/H_2 mixture at 673 K for 3h. The Mo(VI) peak of Fig. 2C is reduced in intensity and a new peak appears at BE of 230 eV after the treatment. This indicates that the treatment under reduction environments resulted in the partial reduction of the sample from the Mo(VI) to Mo(V) state (*22*).

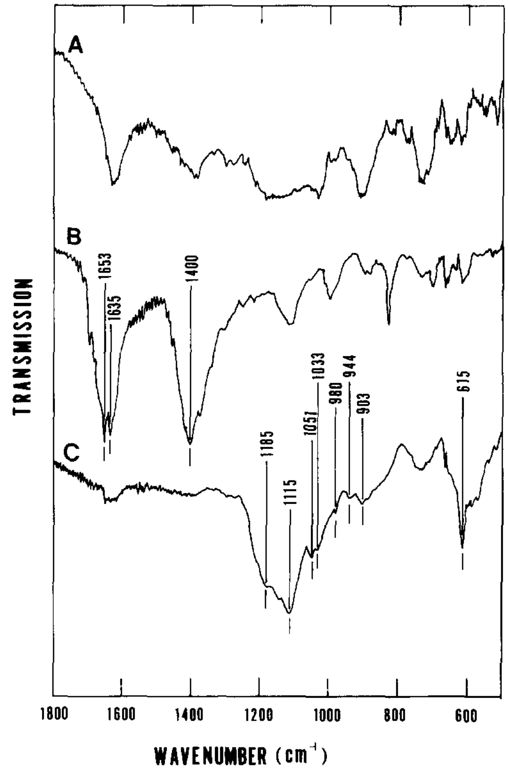


FIG. 4. IR spectra of MoS_2 catalysts: (A) MoS_2; (B) K_2CO_3-promoted "fresh" sample (K_2CO_3/MoS_2-A-0); (C) K_2SO_4-promoted "fresh" sample (K_2SO_4/MoS_2).

Furthermore the introduction of sulfur from H_2S appears to promote the formation of S^{6+} complex species as indicated by the enhanced intensity of the 168.7 eV peak (Fig. 3E).

Infrared Measurements

Additional information was obtained from the FT-IR spectra of MoS_2 catalysts. Figure 4 shows the spectra of the fresh samples (MoS_2, K_2CO_3/MoS_2, and K_2SO_4/MoS_2). When K_2CO_3 was added to MoS_2 (Fig. 4B), a pair of strong absorption bands appeared at 1400 and 1653 cm^{-1}. These bands are assigned to carbonate species. Similar bands due to carbonate species were reported in the spectral regions of 1700–1615 and 1450–1340 cm^{-1} upon CO_2 adsorption on α-Al_2O_3, η-Al_2O_3, or $MgAl_2O_4$ (*23–27*). These pair bands are attributed to monodentate species by the split between the symmetric and asymmetric stretching modes (*28*). Spectrum 4C of K_2SO_4/MoS_2 shows characteristic IR bands due to K_2SO_4 near 615 and 900–1200 cm^{-1}. Figure 5 shows the IR spectra of K_2CO_3/MoS_2 stored and treated under different conditions. The K_2CO_3/MoS_2 stored in the atmosphere for 5 weeks (K_2CO_3/MoS_2-A-5, Fig. 5A) and in a vacuum oven for 8 weeks (K_2CO_3/MoS_2-V-8, Fig. 5B) showed two new intense bands appearing in the regions of 614 and 1120 cm^{-1} together with very weak IR absorption bands in the 1034, 1190, and 933 cm^{-1} regions at the expense of the monodentate carbonate species found in the spectrum of

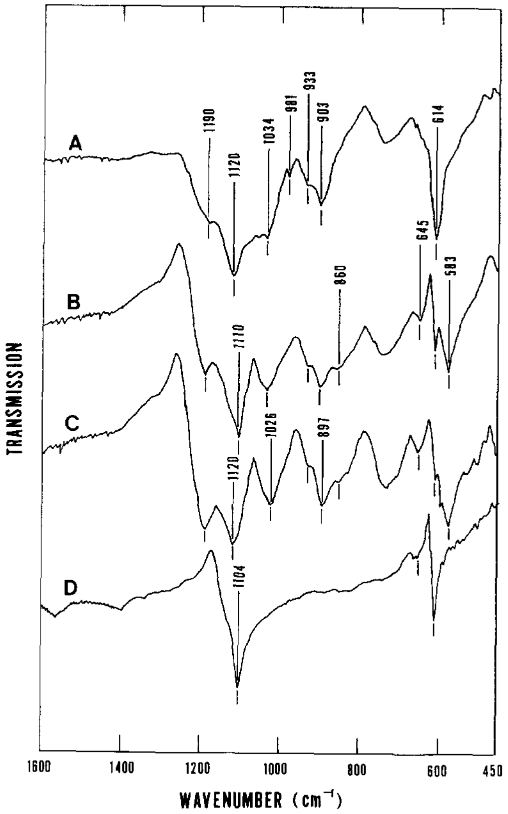


FIG. 5. IR spectra of MoS_2 catalysts: (A) catalyst stored in atmosphere for 5 weeks (K_2CO_3/MoS_2-A-5); (B) catalyst stored in a vacuum for 8 weeks (K_2CO_3/MoS_2-V-8); (C) catalyst stored in atmosphere for 13 weeks (K_2CO_3/MoS_2-A-13); (D) K_2CO_3/MoS_2-A-13 treated under 5% H_2S/H_2 mixture at 673 K for 3 h.

K_2CO_3/MoS_2 (Fig. 4B). In addition, IR bands in these regions are mainly associated with a sulfate group (*29–31*). Thus IR spectra for this catalyst are closer to the spectrum for K_2SO_4/MoS_2 (Fig. 4C) than that for fresh K_2CO_3/MoS_2 (Fig. 4B).

Free sulfate ion SO_4^{2-} and that in various crystalline environments, e.g., Na_2SO_4, belong to the same symmetry point group T_d and give rise to absorption bands at 1104(ν_3), 1140–1090(ν_3), and 610–670(ν_4) cm^{-1}, respectively. If the ion were coordinated to a metal, the symmetry is lowered and the splitting of the degenerate modes occurs. Thus, SO_4^{2-} complexes coordinated to one or two metal ions through two of its oxygens, called a chelating or a bridged bidentate complex, respectively, are formed. Both complexes belong to the same point group, C_{2v}. Recent works with infrared spectra of sulfate complexes have suggested that it is possible to distinguish between bidentate chelating and bridging sulfate groups (both C_{2v} symmetry) on the basis that the highest *SO* frequency of the bidentate groups lies above 1200 cm^{-1}, while the bridging complexes have frequencies below 1200 cm^{-1} (*29, 30*). A chelating bidentate complex has four adsorption bands at 1240–1230(ν_3), 1125–1090(ν_3), 1035–995(ν_3), and 960–940(ν_1) cm^{-1}, while the complex $(NH_3)_4Co(NH_2)(SO_4)Co(NH_3)_4$ examined by Nagamoto *et al.* (*32*) exhibits the bands at 1050(ν_3), 1170(ν_3), 1105(ν_3), and 950(ν_1) cm^{-1}. It is therefore concluded that the sulfate species formed in K_2CO_3/MoS_2 during storage for 5 weeks in the atmosphere have the structure of the point groups T_d and C_{2v}, with the latter in the bridged bidentate structure.

Figure 5C shows the IR spectrum of K_2CO_3/MoS_2 that has been stored for 13 weeks in the atmosphere. The IR absorption bands at 1191(ν_3), 1120(ν_3), 1026(ν_3), and 932(ν_1) cm^{-1} are assigned to the inorganic bridged bidentate complexes. The relative intensity of bands due to T_d and C_{2v} structure indicates that the sulfur species with T_d symmetry formed in the early stage on the oxidized surface of K_2CO_3/MoS_2-A-5 was transformed to a species with C_{2v} symmetry during further exposure to the atmosphere. It may be supported by the observation that the treatment of the catalyst with 5% H_2S/H_2 mixture caused a structural transformation from C_{2v} back to T_d (Fig. 5D). Both XPS and IR results indicate that the surface of the K_2CO_3/MoS_2 catalyst is oxidized by oxygen and/or water present in the atmosphere.

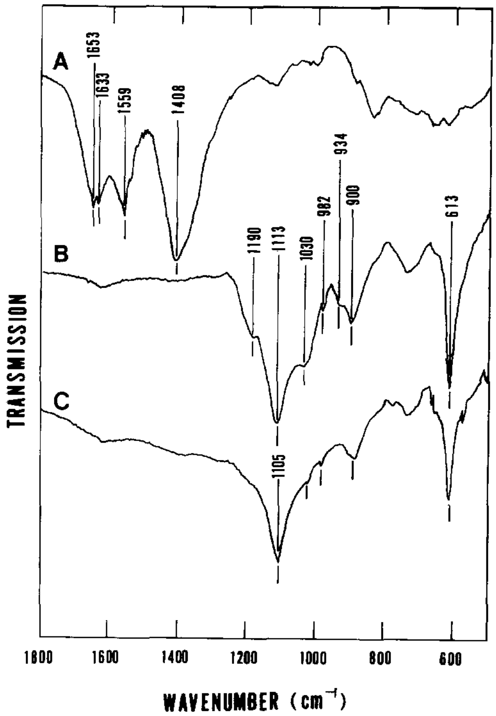


FIG. 6. IR spectra of MoS_2 catalyst: (A) K_2CO_3/MoS_2-A-0 after reaction; (B) K_2CO_3/MoS_2-A-5 after reaction; (C) K_2SO_4/MoS_2 after reaction.

The catalyst K_2CO_3/MoS_2-A-0 used for CO–H_2 reactions at 573 K, and 1.5 MPa for 5 h, provided the new band at 1559 cm^{-1} in addition to those due to monodentate carbonates species (Fig. 6A). It is difficult to determine the origin of this 1559 cm^{-1} band. Saussey *et al.* (*33*) proposed the band at 1546 cm^{-1} characterizing carboxylates reversibly adsorbed at room temperature. Hence, the new band may be due to an intermediate formed during CO–H_2 reaction. For K_2CO_3/MoS_2-A-5 and K_2SO_4/MoS_2, spectra obtained after CO–H_2 reactions (Figs. 6B and 6C) were similar to those obtained before the reaction (Figs. 5A and 4C). The only change was more intense bands at 1113(ν_3) and 614(ν_4) cm^{-1} due to the symmetry point group T_d of sulfate. This change after reaction is similar to that observed after the treatment of the sample with the 5% H_2S/H_2 mixture and indicates that some of C_{2v} sulfate structure is converted back to T_d due to the reducing environment by CO–H_2 reaction mixture.

Thermal Analysis

To examine the thermal properties of catalysts, TGA/DTA was carried out, and the results are shown in Fig. 7. The TGA/DTA curves in Figs. 7A and 7B indicate negligible changes for MoS_2 and K_2CO_3/MoS_2 samples. The gradual decrease in weight in the TGA curves is believed to be due to the volatilization of nonbridging sulfur ions present in the samples (*13, 34*). Both K_2CO_3/MoS_2-A-5 and K_2SO_4/MoS_2 samples showed similar TGA patterns. For these two catalysts, two maxima of endothermic peak in DTA appeared at 840 and 1065 K, respectively. The first peak in the range 820–850 K may be attributed to the transition of K_2SO_4 (from orthorhombic to hexagonal) (*35*), while the second peak in the range 1030–1100 K is due to the loss of sulfur as gaseous SO_3 or SO_2. It has been reported that sulfate species deposited on metal oxides decomposed to yield gaseous SO_3 (*36, 37*) or SO_2 (*38, 39*) above 770 K.

Catalytic Activity and Selectivity

The activity and selectivity of CO–H_2 reactions for catalyst described so far are given in Table 1. Unpromoted MoS_2 revealed a high catalytic activity for hydrocarbon synthesis, while very little alcohols were formed. The fresh K_2CO_3/MoS_2 catalyst tested immediately after preparation showed a high selectivity (>36%) for alcohols. These effects of K_2CO_3 addition to MoS_2 are well-established in CO–H_2 reactions at high pressures (*1–4*). Over the K_2CO_3/MoS_2-A-13 and K_2CO_3/MoS_2-V-8 catalysts the alcohol selectivity was drastically reduced, while CO conversion increased by a factor of ca. 2. The C_{2+}/C_1 ratio for hydrocarbons on these catalysts increased significantly compared to those on the fresh catalysts. The selectivities of K_2CO_3/MoS_2-A-13 and K_2CO_3/MoS_2-V-8 exhibited patterns similar to that of the fresh K_2SO_4/MoS_2 catalyst. It should be noted that K_2SO_4 is more thermally stable than any other potassium compound such as K_2CO_3, K_2S, and K_2O_2. The pretreatment of K_2CO_3/MoS_2-A-13 in the 5% H_2S/H_2 mixture led to a considerable increase in alcohol selectivity, with a decrease in CO conversion,

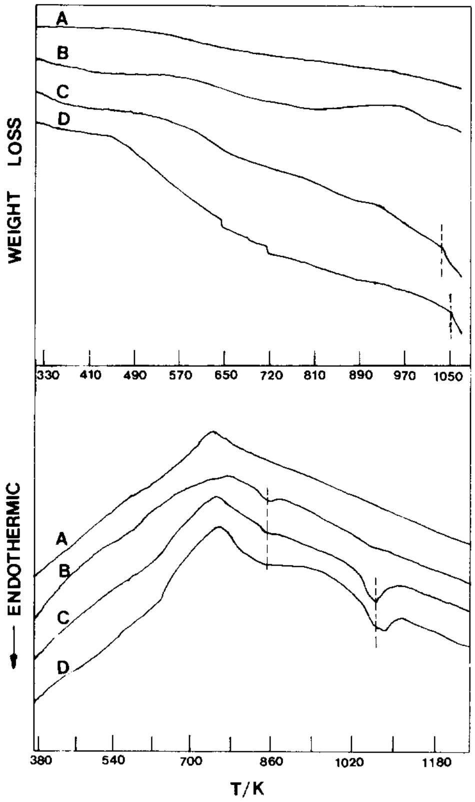


FIG. 7. TGA/DTA curves of MoS_2 catalysts: (A) MoS_2; (B) K_2CO_3/MoS_2-A-0; (C) K_2CO_3/MoS_2-A-13; (D) K_2SO_4/MoS_2.

TABLE 1

Activities and Selectivities of Various Catalysts[a]

Catalysts	CO conv. (%)	CO_2 yield (%)	Carbon atom selectivity (%)									C_{2+}/C_1 ratio	
			C_1	C_2	C_3	C_{4+}	Σ(HC)[c]	MeOH	EtOH	$C_{3+}OH$	Σ(Alc)[c]	HC	Alc
MoS_2	35.3	17.3	57.8	27.6	12.0	1.8	(99.2)	0.8	0.0	0.0	(0.8)	0.7	0.0
K_2CO_3/MoS_2-A-0	13.9	7.1	47.9	10.5	3.2	1.7	(63.3)	15.7	17.8	3.2	(36.7)	0.3	1.3
K_2CO_3/MoS_2-A-13	28.0	14.7	37.7	24.8	18.7	14.0	(95.2)	3.7	0.9	0.2	(4.8)	1.5	0.3
K_2CO_3/MoS_2-V-8	23.0	13.1	40.0	25.2	18.6	11.5	(95.3)	3.7	0.8	0.2	(4.7)	1.4	0.3
K_2SO_4/MoS_2	39.9	20.8	38.7	23.1	19.4	14.7	(95.9)	3.7	0.3	0.1	(4.1)	1.5	0.1
K_2CO_3/MoS_2-A-13[b]	8.7	3.7	40.4	15.9	8.6	4.1	(69.0)	20.5	8.4	2.1	(31.0)	0.7	0.5

[a] Reaction conditions: 573 K, 1.5 MPa, $H_2/CO = 1$, W/F = 8 g-cat h mol^{-1} and 300 min time-on-stream.

[b] Treated with 5% H_2S/H_2 mixture at 673 K for 3 h.

[c] Subtotal of each product components.

which recovered some characteristics of fresh K_2CO_3/MoS_2.

DISCUSSION

The results described so far unequivocally demonstrate that the oxidation of K_2CO_3/MoS_2 catalyst occurs in the atmosphere at room temperature. The XPS and IR spectra of the catalysts exposed to the atmosphere for extended periods indicate the formation of oxidized molybdenum, i.e., MoO_3, and oxidized sulfur, i.e., SO_4^{2-}. As mentioned earlier, transition metal sulfides are known to be sensitive to moisture and oxygen. The edge plane of single-crystal MoS_2 has been observed to be oxidized much more readily than the basal plane in the earlier work of Bahl *et al.* (*7*). They showed that when MoS_2 was heated in 10 Torr O_2 in the range 673–873 K, oxidation takes place preferentially at edge planes, or dislocation steps. Recently single-crystal studies also point out the reactivity of the edge planes toward oxygen by both optical and scanning Auger studies (*8, 9*). The rate of oxidation of commercial MoS_2 film at room temperature has been found to be much faster with moisture in wet than in dry air (*10*). Results of XPS analysis of samples in 100% relative humidity showed complete oxidation of Mo(IV) to Mo(VI) at the molybdenum disulfide surface, but there is no oxidation of sulfur to sulfite or sulfate. Lichtman *et al.* (*40*) in an XPS study of sulfur bonding in metal sulfides found that deeper oxidation in dry air led to SO_4^{2-} groups in the surface layers for a wide variety of sulfides. It is suggested that the sulfides of the fourth row elements seem especially susceptible to this sulfate formation. These results strongly suggest that the oxidation of the catalyst in this study has occurred by reactions with O_2 and H_2O present in the atmosphere. It is also observed that O_2 and H_2O are responsible for the oxidation of alkali-promoted MoS_2 by Karolewski and Cavell (*41*). They proposed that oxidation of the MoS_2 could involve direct Mo–O interaction, presumably with sulfur atom displacements (MoO_x^- or $MoSO_x^-$), or alternatively involve the formation of oxidative products of sulfur (sulfate, thiosulfate, etc.)

Possible reactions involved in the oxidation of potassium-promoted MoS_2 catalysts can be illustrated as follows:

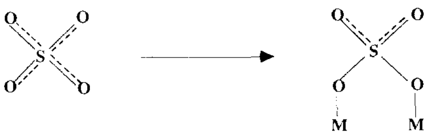
$$MoS_x + (3x/2)O_2 \rightarrow MoO_x + xSO_2 \qquad (1)$$

$$MoS_x + (x/2)O_2 + H_2O \rightarrow MoO_x + xH_2S \qquad (2)$$

$$MoSx + (5x/2)O_2 + xH_2O \rightarrow MoO_x + xH_2SO_x \qquad (3)$$

$$MoS_x + 2xO_2 \rightarrow Mo(SO_4)_x \qquad (4)$$

While reactions (1) to (3) represent oxidation of molybdenum from sulfides to oxides, reation (3) and (4) represent oxidation of S^{2-} to S^{6+}. In the oxidation of K_2CO_3/MoS_2, both sulfur and molybdenum are oxidized so that a mixture of oxidation products is produced on the surface. The extent of this oxidation is not clear, but XRD of the oxidized sample did not show any oxide or sulfate peaks, indicating that the oxidation was limited to a few surface layers or that the oxide and the sulfate are highly dispersed on the edge of MoS_2 with deeper oxidation. It is believed that water plays an important role in the formation of sulfate species. As mentioned earlier, the oxidation of MoS_2 film in dry air produces Mo(VI), but not S^{6+} (*10*). Hence, reaction (4) may not occur to a significant extent. Furthermore, there are no stable forms of $Mo(SO_4)_x$. Reaction (2) indicates the necessity for water vapor and the loss of sulfur during reaction. Such a reaction is consistent with the observed absence of any surface sulfates (*10*). Salomon *et al.* (*42*) have observed the formation of H_2S during wear tests on dry MoS_2 powders in humid atmosphere. In this study, the formation of sulfate appeared to have been enhanced by the H_2S/H_2 treatment (Fig. 3). Although the treatment itself was performed under a reducing environment, the water formed from the reduction of MoO_x might have contributed to the sulfate formation. Namely, the reduction of oxides by H_2S/H_2 and the oxidation of sulfidic sulfur by H_2O have occurred simultaneously. In this regard, K_2CO_3 may have also promoted sulfate formation during storage in the atmosphere by supplying moisture due to its hygroscopic nature. IR spectroscopy indicates that the sulfate species produced by oxidation is transformed from initial structure of the point group T_d(**I**) into the point group C_{2v}(**II**) of a bridged bidentate structure after a prolonged storage (Fig. 5).



(I) (II)

When 5% H_2S/H_2 mixture was introduced to potassium-promoted MoS_2, spectrum E of XPS spectra (Figs. 2E and 3E) indicated the reduction of Mo(VI) to a lower oxidation state, i.e., Mo(V) and the relative increase of S^{6+} intensity. The IR spectrum 5D indicates that the transformation of sulfate structure is partly reversible. Namely, the reduction treatment changed the symmetry point group of sulfate from C_{2v} back to T_d. The surface species found during exposure of K_2CO_3/MoS_2 to O_2/H_2O for extended periods seem to be quite stable. No significant structural change was observed during alcohol synthesis reaction at 573 K and 1.5 MPa of CO/H_2 except the transformation of some sulfate from C_{2v} to T_d. A loss of sulfur as gaseous SO_2 or SO_3 occurred only above 1030 K as confirmed by TGA/DTA measurements. This shows that sulfate species are thermally stable up to at least 1000 K. Also the transition point at 840 K present in DTA curves of oxidized catalysts and K_2SO_4/MoS_2 indicates the presence of sulfate species formed during the oxidation.

The $CO–H_2$ reactions after adding K_2CO_3 to MoS_2 showed that the product distribution shifts dramatically to the high yield of alcohols, while the activity was significantly reduced (Table 1). This is a well-established effect of alkali addition to MoS_2 to promote alcohol formation (*1–4*). Perhaps with this amount of alkali carbonate on the surface, the interactions of molecular CO with the catalyst surface become weaker and its direct hydrogenation without dissociation dominates other reaction channels occurring on MoS_2. Addition of K_2CO_3 can neutralize the surface acidity and may lead to the suppression of various unwanted side reactions such as dehydration and isomerization. The most interesting feature of K_2CO_3-promoted MoS_2 catalysts stored in the atmosphere for a prolonged period is their high selectivity and activity for C_{2+} hydrocarbons. This change in catalytic properties, depending upon the storage conditions, will lead the aftercare program of the catalyst before use, particularly for air-sensitive catalyst. Although the acidity of the oxidized catalysts was not measured, it can be considered that the high catalytic activity of these catalysts may be closely correlated with the increase in acid strength by the inductive effect of sulfate ion coordinated to Mo ions. This induction effect of sulfate ion is well documented to explain superacidity of sulfate-promoted Fe_2O_3, ZrO_2, and TiO_2 (*30, 36–39*). In any case, it should be noted that the modified catalytic properties of oxidized K_2CO_3/MoS_2 are very similar to fresh K_2SO_4/MoS_2 in accordance with their similarity in surface structure.

CONCLUSIONS

The oxidation of K_2CO_3-promoted MoS_2 occurs slowly at room temperature and produces oxides and sulfates on the catalyst surface. The surface oxidation reaction appears to proceed by reaction of MoS_2 with oxygen and/or water present in the atmosphere. The alkali salt of the catalyst may contribute to the oxidation of sulfur to the sulfate group indirectly. The sulfate species produced by oxidation assume the structure of T_d and then transform into C_{2v} (bidentate) symmetry after a prolonged storage and are thermally stable up to 1000 K. The oxidized K_2CO_3/MoS_2 shows high catalytic activity to C_{2+} hydrocarbons instead of alcohol formation mainly occurring on fresh catalysts. The shift in selectivity is closely related to the increase in acidic strength of the catalyst surface by the inductive effect of sulfate ion coordinated to Mo ions.

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