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Oxidized K_2CO_3/MoS_2 as a novel sulfur-resistant catalyst for Fischer–Tropsch reaction

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Potassium-promoted MoS_2 is an active catalyst for mixed alcohol synthesis from CO and H_2. When K_2CO_3/MoS_2 is oxidized, however, it produces mostly hydrocarbons, of which 40–50 wt% are C_2–C_4 alkanes. The reaction rates also substantially increase. Since oxidized K_2CO_3/MoS_2 can tolerate a high level (up to 300 ppm) of H_2S in the CO–H_2 feed, it could serve as a novel sulfur-resistant Fischer–Tropsch catalyst.

Keywords: Oxidized molybdenum sulfides; potassium-promoted; CO hydrogenation; sulfur resistance

1. Introduction

Molybdenum catalysts have long been recognized as being effective for methanation [1,2]. Recently, molybdenum sulfide catalysts were found to be active for the synthesis of mixed C_1–C_6 alcohols, which was significantly influenced by the presence of group VIII metals and alkali metal salts [3,4]. In the hydrogenation of CO over MoS_2 catalysts for mixed alcohol synthesis, it is essential that a certain amount of an alkali salt should be present on the catalyst [5–7]. Addition of potassium to the MoS_2 has a marked impact on its catalytic properties: CO conversion is lowered and the dominant products shift from alkanes to alcohols [6,7].

Recently it has been found that alcohol selectivity for K_2CO_3-promoted MoS_2 (K_2CO_3/MoS_2) stored in the atmosphere for an extended period after preparation

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is reduced to negligible level [8]. Instead, it produces hydrocarbons of C_1–C_{10} range (mainly paraffins) at higher rates of CO conversion. In this paper, it is described how the oxidation of K_2CO_3/MoS_2 under ambient conditions affects its structure and catalytic properties for CO–H_2 reactions. With MoS_2 as a base component, the catalyst could serve as a novel sulfur-resistant Fischer–Tropsch catalyst.

2. Experimental

Unsupported MoS_2 was prepared by thermal decomposition of $(NH_4)_2MoS_4$ in flowing nitrogen at 773 K for 2 h [9]. Addition of K_2CO_3 was accomplished by the mechanical mixing of MoS_2 powder in a glass mortar. The catalyst right after this preparation is called the *fresh* catalyst. The oxidized catalysts were prepared by exposing the fresh catalyst to the atmosphere for 3–11 weeks. The bulk and surface structure of the samples were determined by means of X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS), respectively.

The catalytic CO–H_2 reactions were carried out in a tubular down flow fixed-bed reactor at $CO/H_2 = 1.0$, 573 K, 1.5 MPa and a contact time (W/F) of 7.2 g-cat h mol^{-1}. Premixed CO, H_2 and N_2 (3 vol% as an internal standard) was continuously fed to the reactor through a charcoal trap to eliminate carbonyl impurities. Concentrations of CO, CO_2, CH_4, and N_2 in the product stream were determined by a thermal conductivity detector after being separated through a 4 m activated carbon-packed column. Organic compounds such as hydrocarbons and oxygenates were separated through a 50 m PONA capillary column and analyzed by a flame ionization detector. Procedures to test catalyst performance have been described in more detail elsewhere [10]. For oxidized catalyst, 2% H_2S in hydrogen was also fed with gaseous reactants to maintain its concentration at 300 ppm.

3. Results

The XRD patterns of MoS_2 produced by thermal decomposition of $(NH_4)_2MoS_4$ were characterized as poorly crystalline. These XRD results were also reported by Xie et al. [5] and Chianelli and Dines [11]. Fresh and oxidized K_2CO_3/MoS_2 showed similar X-ray pattern and particle size to those of MoS_2. The physical properties of the catalysts including X-ray patterns have been reported elsewhere [8].

XPS spectra were examined for the catalysts exposed to atmosphere during different periods of time after preparation. The Mo 3d and S 2p XPS spectra of powdered K_2CO_3/MoS_2 catalysts are shown in figs. 1 and 2. Spectrum (a) was observed for the fresh catalyst. Spectra (b)–(d) were recorded for oxidized catalyst by exposing the fresh catalyst to the atmosphere for 3, 9 and 11 weeks, respectively. The

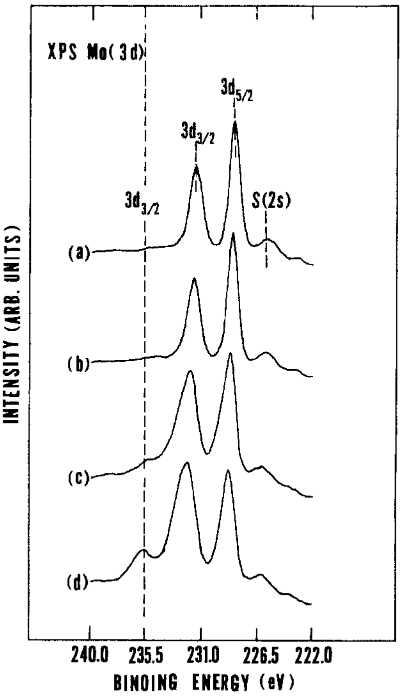

Fig. 1. Mo 3d photoelectron spectra: (a) fresh K_2CO_3/MoS_2 (K/Mo = 40 mol/mol); (b) K_2CO_3/MoS_2 exposed to atmosphere for 3 weeks; (c) K_2CO_3/MoS_2 for 9 weeks; (d) K_2CO_3/MoS_2 for 11 weeks.

binding energy values for Mo $3d_{3/2}$ and $3d_{5/2}$ of MoS_2 were 232.3 and 229.0 eV, respectively. These binding energies are consistent with those of Mo(IV) reported by Stevens and Edmonds [12]. The oxidized samples showed a considerable change in the XPS spectra for Mo 3d and S 2p. As the oxidation proceeded, a new Mo 3d binding energy appeared at 235.5 eV corresponding to the Mo $3d_{3/2}$ level of Mo(VI) [13]. Hence the spectrum (fig. 1 (d)) 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 Mo(VI) species seems to be masked by the large central peak of the Mo $3d_{3/2}$ of the sulfide. The new strong sulfur peak in the spectrum (fig. 2 (d)) at the binding energy of 168.7 eV indicates the oxidation of S^{2-} to S^{6+} state. In summary, the XPS data of K_2CO_3/MoS_2 stored in the atmosphere for extended periods of time reveal the oxidation of Mo(IV) to Mo(VI) as well as S^{2-} to S^{6+} on the MoS_2 surface.

The influence of aging time on CO conversion, the selectivities to alcohols and hydrocarbons, and C_{2+}/C_1 ratio over fresh K_2CO_3/MoS_2 (K/Mo = 0.40 mol/mol) at 573 K and 1.5 MPa are illustrated in fig. 3. As the oxidation of the catalyst progressed, the catalyst gained higher activity toward CO hydrogenation and the selectivity shifted from alcohol formation to hydrocarbons production. The

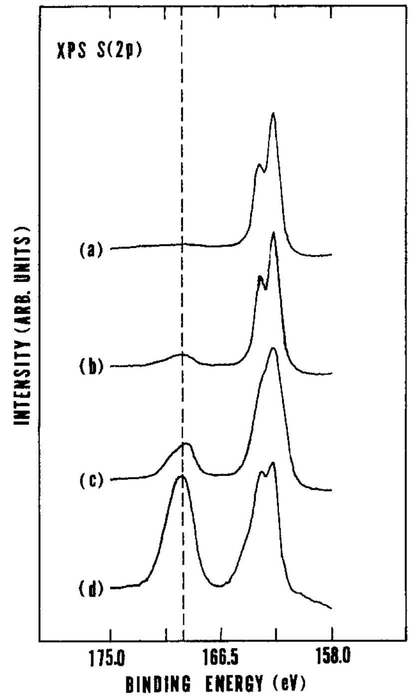

Fig. 2. S 2p photoelectron spectra: (a) fresh K_2CO_3/MoS_2 (K/Mo = 40 mol/mol); (b) K_2CO_3/MoS_2 exposed to atmosphere for 3 weeks; (c) K_2CO_3/MoS_2 for 9 weeks; (d) K_2CO_3/MoS_2 for 11 weeks.

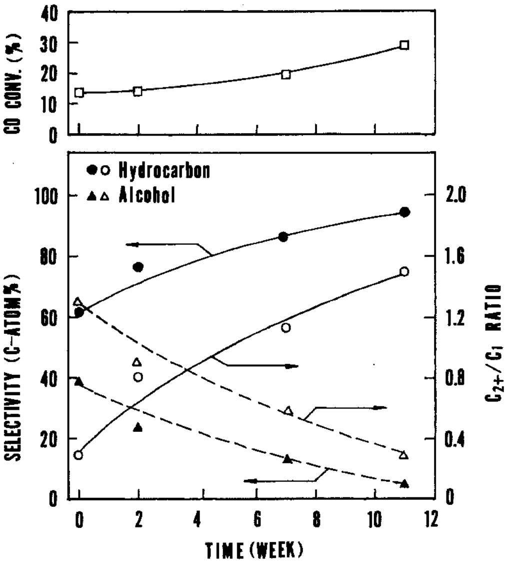

Fig. 3. The effect of aging time on the CO conversion, selectivity and C_{2+}/C_1 ratio for the hydrocarbons and alcohols over fresh K_2CO_3/MoS_2 (K/Mo = 0.40 mol/mol) at 573 K and 1.5 MPa.

C_{2+}/C_1 ratios of hydrocarbons and alcohols in product stream also changed systematically as their selectivities did.

Table 1 compares the product distributions over various MoS_2 catalysts. Unpromoted MoS_2 revealed a high catalytic activity for hydrocarbon synthesis, while very little alcohols were formed. As expected, a fresh K_2CO_3/MoS_2 showed a high selectivity (>65 at% C) for alcohols. In contrast, the oxidized K_2CO_3/MoS_2 catalyst gave high selectivity (>90 at% C) as well as the high C_{2+}/C_1 ratio for hydrocarbons. The hydrocarbons produced by all oxidized K_2CO_3/MoS_2 catalysts contained alkanes of ca. 80 wt%. In contrast to unpromoted MoS_2, which produced mostly C_1–C_3 hydrocarbons, the oxidized K_2CO_3/MoS_2 gave a significant amount of heavier hydrocarbons with the suppressed production of methane. The fraction of C_2–C_4 alkanes was 40–50 wt%. Although sulfide-based catalysts are naturally resistant to sulfur poisoning, the effect was examined for the oxidized K_2CO_3/MoS_2. Table 1 shows the variation in the selectivity of products with and without H_2S in the feed. In order to accelerate the effect of H_2S, if any, a very high level (300 ppm) of H_2S in the feed was deliberately employed as shown in fig. 4. The addition of H_2S to the feed reduced somewhat both CO conversion and C_{2+}/C_1 ratio for hydrocarbons. However, no serious deactivation was observed for 10 h on stream. With H_2S in the feed, the portion of C_2–C_4 alkanes was still maintained about 38 wt%. The deactivation is not simply due to H_2S in the feed as illustrated in fig. 4. It will be closely examined for further study.

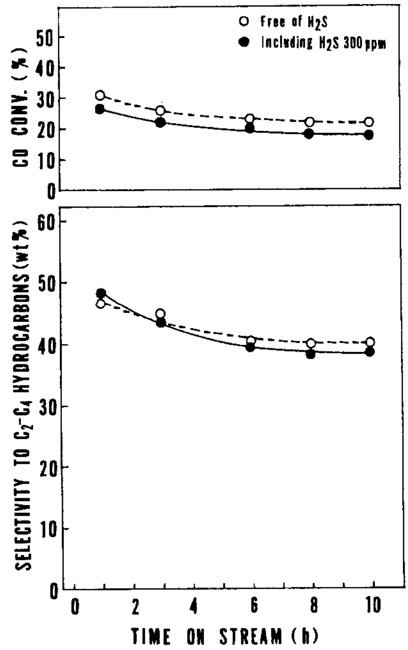

Fig. 4. The effect of H_2S addition on CO conversion and C_2–C_4 hydrocarbons with time on stream over K_2CO_3/MoS_2 (K/Mo = 0.40 mol/mol) exposed to atmosphere for 11 weeks.

Table 1
Activities and selectivities of various MoS_2 catalysts[a]

Catalysts	CO conv. (%)	CO_2 yield (%)	Carbon atom selectivity (%)								C_{2+}/C_1 ratio	
			C_1	C_2	C_{3+}	$\sum$(HC)[b]	MeOH	EtOH	$C_{3+}OH$	$\sum$(Alc)[b]	HC	Alc
MoS_2	38.7	19.3	58.9	27.5	12.9	(99.3)	0.7	–	–	(0.7)	0.69	0.0
fresh K_2CO_3/MoS_2[c]	8.4	3.5	31.0	5.5	2.3	(38.8)	36.0	22.0	3.2	(61.2)	0.25	0.70
oxidized K_2CO_3/MoS_2[c]	23.2	12.6	38.2	21.7	33.2	(93.1)	5.4	1.2	0.3	(6.9)	1.44	0.30
oxidized K_2CO_3/MoS_2[c] –H_2S 300 ppm	18.1	7.8	45.2	19.7	26.5	(91.4)	5.8	2.2	0.6	(8.6)	1.02	0.48

[a] Reaction conditions: 573 K, 1.5 MPa, $H_2/CO = 1$, $W/F = 7.2$ g-cat h/mol and 350 min time on stream.

[b] Subtotal of each product component.

[c] K/Mo = 0.40 mol/mol.

For the oxidized K_2CO_3/MoS_2 catalysts, carbon number distribution of the products followed a Schulz–Flory type distribution for hydrocarbons (fig. 5). The probability of the chain growth was found to be ranging from 0.30 to 0.41 for C_1–C_{10} hydrocarbons. All catalysts tested in this study produced considerable amounts of CO_2 as shown in table 1, which is commonly observed for CO hydrogenation over MoS_2 catalysts.

4. Discussion

The oxidation of K_2CO_3/MoS_2 catalyst occurs in the atmosphere at room temperature. The X-ray photoelectron spectra (XPS) of K_2CO_3/MoS_2 clearly indicate the oxidation of Mo(IV) to Mo(VI) as well as S^{2-} to S^{6+} states.

An interesting change in catalytic properties is accompanied by the oxidation. As shown in table 1, the addition of K_2CO_3 to MoS_2 shifts the product distribution of CO–H_2 reactions dramatically to the high yield of alcohols, while the activity is significantly reduced. It is a well-recognized effect of alkali metal on MoS_2 to promote alcohol formation [6,7,9].

The oxidation of K_2CO_3/MoS_2 catalysts by exposure to the atmosphere for a prolonged period of time results in high selectivity of C_{2+} hydrocarbons and enhanced activity for CO hydrogenation. In particular, the high selectivities for C_2–C_4 alkanes (40–50 wt%) over these oxidized catalysts approach the maximum predicted by the Schulz–Flory distribution [14]. This result is worthy of notice because ethane and propane most efficiently crack to valuable ethylene [15]. An extensive surface characterization study is under way to elucidate the reason why the same K_2CO_3 promotes alcohol synthesis on fresh K_2CO_3/MoS_2 catalyst and C_{2+} hydrocarbon formation on the oxidized catalyst. It has been proposed that the addition of K_2CO_3 to MoS_2 causes weaker interaction of molecular CO with the

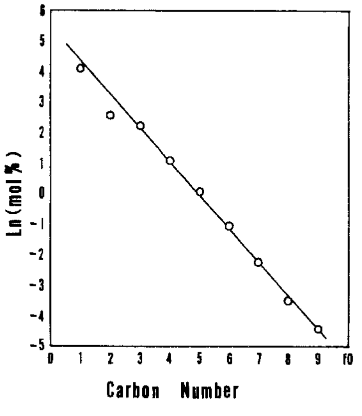

Fig. 5. Typical Schulz–Flory distribution of hydrocarbons produced on K_2CO_3/MoS_2 (K/Mo = 0.40 mol/mol) exposed to atmosphere for 11 weeks.

alkali overlayers, and thus its direct hydrogenation dominates other reaction paths involving dissociation of CO [5]. Thus the reaction to form alcohols might occur on the alkali overlayer instead of MoS_2. Addition of K_2CO_3 can also neutralize the surface acidity and may lead to suppression of various unwanted side reactions such as dehydration and isomerization [16]. Although details are unknown, the oxidation of K_2CO_3/MoS_2 alters the role of K_2CO_3, possibly by modifying its structure on MoS_2 surface. The oxidized K_2CO_3/MoS_2 in this study shows enhanced catalytic activity and high selectivity (> 58 at% C) for C_{2+} hydrocarbons in product (table 1). Superficially the results are similar to those observed for potassium modified iron foil [17] and nickel crystal [18]. Praliaud et al. [19] have proposed that potassium acts as an electronic modifier causing an electron enrichment of the metallic phase on the catalyst surface. The K_2CO_3 on oxidized K_2CO_3/MoS_2 is also believed as an electronic promoter which is often observed for group VIII metal catalysts.

In the conversion of syngas ($CO+H_2$) to hydrocarbon fuels, a number of transition-metal catalysts have been used, including Ni, Fe, Co, and Ru [20]. However, these metals suffer from certain operating limitations because of their susceptibility to the deactivation by surface carbon and sulfur [21]. Thus, in the case of coal-derived syngas, the H_2/CO feed ratio has to be adjusted to values greater than two, and the sulfur impurities must be reduced to lower levels (0.01–0.1 ppm) in the feed stream [15]. As mentioned earlier, molybdenum sulfide is resistant to sulfur poisoning and a good catalyst for the water–gas shift reaction. Although the selectivity to methane was increased by about 7 at% C in the presence of H_2S of the feed, the deactivation with time on stream was very similar to the case without H_2S. Since 300 ppm of H_2S in syngas is a very severe condition, it is believed that the oxidized K_2CO_3/MoS_2 can perform well for practical sulfur-containing syngases. The reason for the slight increase in methane selectivity is unclear yet. However, it is reported that unpromoted MoS_2 also promotes the methanation of $CO–H_2$ with high concentration of H_2S [22]. The incorporation of sulfur in excess of the stoichiometric composition proceeds readily with the catalyst surface and it yields a p-type semiconductor. The MoS_2 catalyst obtained from this process may have electronic hole carriers, which may enhance the dissociative chemisorption of hydrogen. Hence, the selectivity pattern of oxidized K_2CO_3/MoS_2 with H_2S could be elucidated by the promotion of methanation due to the enhanced dissociative chemisorption of hydrogen [22].

In summary, K_2CO_3/MoS_2 oxidized by the exposure to atmosphere for an extended period of time was found to be a unique catalyst for the Fischer–Tropsch reaction. In contrast to conventional group VIII metal catalysts, it performs well with syngas of low H_2/CO ratio even containing sulfur. Under the identical reaction conditions the selectivity pattern of the oxidized K_2CO_3/MoS_2 is distinct from the fresh K_2CO_3/MoS_2 (hydrocarbons versus alcohols) or unpromoted MoS_2 (C_{2+} hydrocarbons versus methanation).

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