Effect of Mn Promoter on Structure and Performance of K-Co-Mo Catalyst for Synthesis of Higher Alcohols from CO Hydrogenation

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A series of Mn-doped K-Co-Mo catalysts were prepared by a sol-gel method. The catalyst structure was well characterized by X-ray diffraction, N\textsubscript{2} physisorption, NH\textsubscript{3} temperature-programmed adsorption,\textit{ in situ} diffuse reflectance infrared Fourier transform spectroscopy, and X-ray absorption fine structure spectroscopy. The catalytic performance for higher alcohol synthesis from syngas was measured. It was found that the Mn-doped catalysts exhibited a much higher activity as compared to the unpromoted catalyst, and in particular the C\textsubscript{2+} alcohol selectivity increased significantly. The distribution of alcohol products deviated from the Anderson-Schulz-Flory law. The portion of methanol in total alcohol was suppressed remarkably and the ethanol became the predominant product. Characterization results indicated that the incorporation of Mn enhanced the interaction of Co and Mo and thus led to the formation of Co-Mo-O species, which was regarded as the active site for the alcohol synthesis. Secondly, the presence of Mn reduced the amount of strong acid sites significantly and meanwhile promoted the formation of weak acid sites, which had a positive effect on the synthesis of alcohol. Furthermore, it was found that the incorporation of Mn can enhance the adsorption of linear- and bridge-type CO significantly, which contributed to the formation of alcohol and growth of carbon chain and thus increased the selectivity to C\textsubscript{2+}OH.

Key words: CO hydrogenation, Sol-gel method, Mo-based catalyst, Mn promoter, Higher alcohols synthesis

I. INTRODUCTION

In view of the increasing concerns over the environmental pollution and shortage of fossil fuel resources, the catalytic conversion of syngas into higher alcohols has drawn much attention for both industrial application and fundamental research in the past few decades [1–3]. Generally, the syngas, mainly composed of CO and H\textsubscript{2}, can be derived from various carbon sources, such as natural gas, coal, and renewable biomass, via gasification. Higher alcohols have high octane numbers, and this fact makes the most potential application of them as an additive for gasoline or replaces the methyl tert-butyl ether for the reduction of exhaust emission [4, 5].

Up to now, several catalyst systems for the conversion of syngas into higher alcohols have been developed. In general, the potential catalysts can be classified into two broad categories: noble metal-based and non-noble metal-based catalysts [6, 7]. Reportedly, as a significant noble metal-based catalyst, Rh-based catalysts have been found to be the most selective catalyst for the synthesis of higher alcohols from CO hydrogenation and show high selectivity to C\textsubscript{2+}OH (mainly ethanol). Nevertheless, rhodium is too expensive and sensitive to sulfur poisoning, which makes it difficult to realize the large-scale application in industry [8]. The non-noble catalysts for higher alcohol synthesis mainly include Cu-based catalysts and Mo-based catalysts. Cu-based catalysts exhibited a high selectivity to total alcohol, however the selectivity to C\textsubscript{2+}OH was fairly low and the dominant product was methanol [9]. Mo-based catalysts have shown high selectivity to C\textsubscript{2+}OH, and in some cases low selectivity to hydrocarbons. In particular, it has some advantages, such as low cost, excellent resistance to sulfur poisoning and coke deposition, etc.
Increasing attempts have been made to optimize the higher alcohol synthesis performances of Mo-based catalyst and to enhance the potential capability for application [10, 11]. Previous studies have shown that both the activity and selectivity for higher alcohol synthesis over Mo-based catalysts are strongly dependent on the type of promoters, the interaction between promoters and Mo species, the chemical state and dispersion of surface Mo species, and surface acidity of catalysts, etc. [13–17]. Unpromoted Mo catalysts produced mainly light hydrocarbons [18]. With the addition of alkali metal, such as potassium, the catalysts selectivity was greatly shifted from hydrocarbons to alcohols [19, 20]. The alkali metal promoters can neutralize the surface acidity of catalyst, enhance the adsorption and insertion of CO, as well as inhibit the hydrogenation rate to promote the growth of carbon chain [12, 21, 22]. Different alkali metals have different influences on the catalyst activity. The generally accepted order is Cs\(^+\) > Rb\(^+\) > K\(^+\) > Na\(^+\) > Li\(^+\), consistent with the sequence of decreasing basicity [23]. Some 3d transition metals, in particular Fischer-Tropsch (FT) elements such as Co or Ni, are effective promoters for improving the C\(_2\)OH selectivity as well as alcohol yield of Mo-based catalysts. The Co or Ni promoters acted as a synergistic system with the Mo species and promoted the growth of carbon chain. The structure, morphology of promoters, and their interaction with Mo species have significant impact on the promotional effects [24, 25].

As a potential element, Mn has been widely used as a promoter for CO hydrogenation. Morales et al. [26] investigated the electronic state and location of Mn in Co-based FT catalysts with a combination of EXAFS and STEM-EELS. They found that the presence of MnO phase in the catalysts can improve the percentage of higher hydrocarbons and increase the selectivity in the FT synthesis. For the silica-supported Co-Mn catalysts, the Mn promotion increased the rate of CO consumption, decreased the selectivity to methane, and increased the selectivity to C\(_2\)H\(_4\) products, and rationalized the promotion effects in terms of H availability and CO coverage [27]. More recently, Johnson et al. [28] reported that MnO would act as a Lewis acid to assist in CO dissociation as well as to increase the ratio of CO to H adsorbed on the Co catalyst surface. They demonstrated that active sites near the Co-MnO interface were responsible for the improved activity and C\(_2\)H\(_4\) selectivity. Over the K/Ni/Mo\(_2\)S\(_2\) catalysts, it was found that the addition of Mn significantly affected the dispersion of active components on the catalyst surface, improving the selectivity to C\(_2\)H\(_4\)OH [29]. For Mn-Fe-Cu catalysts, there existed a strong interaction between Mn and Fe components. The addition of Mn could improve the surface concentration of Fe and Cu species, leading to the increase of active sites for higher alcohol synthesis [30]. Zhang et al. [31] have employed density functional theory calculations to investigate the effect of Mn on ethanol formation on a Mn-promoted MnCu(211) surface. They suggested that with the addition of Mn, CH\(_3\) species were maximized and CH\(_3\)OH formation was suppressed. The C\(_2\) oxygenates formation via CHO insertion into CH\(_3\) was more favorable in both kinetics and thermodynamics when compared with the Cu(211) surface. Ojeda et al. [32] also compared the CO hydrogenation over Rh/Al\(_2\)O\(_3\) and Rh-Mn/Al\(_2\)O\(_3\) catalysts and found that higher activity of Rh-Mn/Al\(_2\)O\(_3\) catalyst was attributed to the decrease of the relative surface carbon coverage over the Rh particles.

So far, there are rare reports concerning the effects of Mn on the reduced Mo-oxide catalyst. Considering the unique structural and electronic effects of Mn oxide, it was proposed that the addition of Mn can play a positive impact on the catalytic performance of Mo-oxide catalysts. Herein, a series of Mn-doped K-Co-Mo catalysts were prepared by a sol-gel method. The activity of catalysts for the synthesis of higher alcohols from syngas was evaluated and their structures were characterized by means of X-ray diffraction (XRD), N\(_2\) physisorption, N\(_3\) temperature programmed adsorption (NH\(_3\)-TPD), in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and X-ray absorption fine structure spectroscopy (XAFS). Based on the characterization results, the promotional effects of Mn on the structure and performance of the Mo-based catalysts were discussed.

II. EXPERIMENTS

A. Catalyst preparation

The Mn-K-Co-Mo catalysts were prepared by a sol-gel method with citric acid as a complexant. A typical procedure is as follows: Firstly, an aqueous solution of Co(NO\(_3\))\(_2\) was added slowly to an aqueous solution of (NH\(_4\))\(_2\)Mo\(_7\)O\(_24\)6H\(_2\)O. Then an aqueous solution of Mn(NO\(_3\))\(_2\) was added into the above solution. Subsequently, a certain amount of citric acid aqueous solution was added slowly into the mixed solution under constant stirring. The molar ratio of citric acid to metallic ions was 0.4. Finally, the K\(_2\)CO\(_3\) aqueous solution containing a calculated amount of K was added dropwise to the solution. The pH value of the mixed solution was monitored using a pH meter and adjusted to 3.5 by addition of NH\(_4\)H\(_2\)O or HCOOH solution. The mixed solution was then kept in a water bath at 70 °C until the gel was formed. The as-prepared gel was dried at 120 °C for about 15 h and then calcined in flowing nitrogen at 400 °C for 4 h. The atomic ratio of K/Mo and Co/Mo were 0.1 and 0.5, respectively. The Mn content in the samples, expressed as Mn/Mo atomic ratio, ranged from 0.05 to 0.25. For comparison, the catalyst without Mn promoter was also prepared by the same procedure.
B. Catalyst characterization

The phase composition and crystalline structure of fresh catalysts were measured on a Rigaku TTR-III X-ray power diffractometer equipped with a Cu Kα (λ=0.15418 nm) radiation. Diffractograms were recorded at 2θ from 10° to 70° with a scan rate of 8°/min. The voltage and current were 40 kV and 200 mA, respectively.

The BET surface area, pore volume and average pore diameter of the catalysts were determined by nitrogen adsorption at −196 °C by means of a micrometerics TriStarII 3020 instrument. Prior to the measurement, all the samples were degassed under vacuum at 150 °C for 2 h to remove volatile adsorbates on the surface.

NH3-TPD was performed for determining the surface acid properties of the catalysts. Approximately 80 mg of the sample was loaded into a U-type quartz tube, which was mounted on the instrument. Then the sample was pretreated in He at 200 °C for 0.5 h (heating rate 10 °C/min). After cooling to room temperature, 0.5% NH3 in He was passed through the sample for 1 h, with subsequent flushing with helium at 100 °C for 1 h. The TPD analysis was carried out in flowing He from 100 °C to 850 °C at a heating rate of 10 °C/min.

In situ DRIFTS experiments were performed on a Bruker Vertex 70v FT-IR spectrometer equipped with a mercury cadmium telluride detector. A high temperature chamber fitted with CaF2 windows was utilized as the sample cell. The high-purity carbon monoxide was used as probe gas. Nitrogen and hydrogen were used as the flushing gas and reducing gas, respectively. All steps were carried out at atmospheric pressure. The catalysts were ex situ reduced in flowing pure H2 at 400 °C for 12 h. After cooling to room temperature under pure H2, the catalysts were passivated with 1%O2 in N2 for 2 h. The catalysts were then placed into the IR sample cell and reduced again in a H2 flow at 400 °C for 3 h to avoid the presence of any oxidized species produced by passivation or re-oxidation during sample handling. After the reductive pretreatment, the samples were then cooled down to room temperature in flowing pure H2. At this temperature, a background spectrum was collected. Next, CO gas was fed to the cell and the infrared spectra were taken at 4 cm−1 resolution with 32 scans. CO adsorption continued for about 40 min, with spectra being recorded about once every two minutes. After adsorption, the samples were flushed with nitrogen for 20 min (30 mL/min) to remove the gaseous carbon monoxide from the chamber, and then the IR spectra were collected again.

The X-ray absorption spectra at the Mo K-edge on catalysts and standard references were measured at the beamline of 1W1B of Beijing synchrotron radiation facility, China. The electron storage ring was operated at 2.5 GeV with an average current of 200 mA. A Si(111) double crystal was used as monochromater and the data of absorption samples were collected in transmission mode. The energy of the absorption spectra was calibrated by measuring the X-ray absorption near-edge spectroscopy (XANES) of a Mo metal foil. For each measurement, sample was ground into fine powders and brushed onto adhesive tapes. Thickness and homogeneity of the samples were optimized to obtain the best signal-to-noise ratio. The obtained data were processed by established methods with the ATHENA software package [33]. The normalized Extended X-ray absorption fine-structure spectroscopy (EXAFS) was converted from energy to k-space and weighted by k3. These data were then Fourier transformed to R-space. Due to the uncorrection for photoelectron phase shifts, distances in R-space are 0.3−0.5 Å shorter than actual bond distances.

C. Catalytic activity measurement

The catalytic performance testing was performed in a fixed-bed pressurized flow reaction system with a conventionally designed microreactor (600 mm length and 8 mm internal diameter stainless-steel tube). Feed gases were composed of 60%H2, 30%CO, and 10%N2 as an internal standard. The feed gas was purged into the reactor at a desired rate using high-pressure mass flow controllers. Temperature was monitored with a K-type thermocouple inserted in the catalyst bed. The samples (0.5 g, 40–60 mesh particle size) were diluted with a certain amount of quartz sand in order to maintain isothermal conditions and then charged into the fixed-bed reactor, which was housed in an electric furnace controlled by a temperature controller. Prior to the reaction, the catalysts were in situ reduced in pure H2 at a flow rate of 40 mL/min under atmospheric pressure for 12 h. Then the reactor was cooled down. When the reaction temperature rose to a desirable temperature, feed gas was introduced into the reactor. The effluent gas was cooled in an ice-water bath to separate into gas and liquid phases. Details on the product analytical procedure are described in our previous work [13]. For Mo-based catalysts, the higher alcohols synthesis reaction requires an introduction period to reach steady state. The activity data were measured after the reaction was performed for 24 h.

III. RESULTS AND DISCUSSION

A. XRD results

The XRD patterns of the catalysts with varying Mn amounts are shown in Fig.1. For the catalyst free of Mn, the XRD pattern exhibited three diffraction peaks at 2θ of 26.1°, 37.0° and 53.5°, corresponding to the (−111), (−211), and (−312) reflections of MoO2 crystalline phase. These reflections were very broad and weak, suggesting that the MoO2 phase had a low crys-
The formation of MoO$_2$ was attributed to the reduction effect of decomposition of citric acid in nitrogen. Besides, no diffraction reflections related to MoO$_3$ and Co-containing phases were observed, indicating that these species in this sample may exist in the form of amorphous state. After Mn was added, distinct changes occurred in the XRD profiles. At the lowest content of Mn, there appeared five new weak diffraction peaks with 2θ values of 18.2°, 35.7°, 52.1°, 56.3°, and 64.2°. They could be attributed to the contributions from CoMoO$_3$. When increasing the Mn contents, a series of new diffraction peaks appeared, which can be assigned to Co$_2$Mo$_2$O$_9$ phase. The intensities of the diffraction peaks assigned to Co-Mo species increased with an increase of Mn content. Meanwhile, the peak corresponding to MoO$_2$ became weaker. These results suggested that the interaction between Mo and Co became stronger with the addition of Mn promoter. It is noted that no peaks of Mn species were observed in the XRD patterns of the catalysts. The reason may be attributed that the Mn species were either amorphous or in the form of very small nanoparticles with a high dispersion over the catalysts.

### B. Nitrogen adsorption-desorption results

The nitrogen adsorption-desorption isotherms as well as pore size distribution curves for all samples are displayed in Fig.2. The unpromoted catalyst exhibited a type IV isotherm with a hysteresis loop of type H3 according to the Brunauer-Deming-Deming-Teller (BDDT) classification. The capillary condensation in pores occurred at a relative pressure ($P/P_0$ > 0.40), indicating the presence of a large amount of mesopores. The isotherms of the Mn-doped catalysts had a similar feature with that of the undoped sample. With an increase in Mn content, the hysteresis loop was shifted to the higher relative pressure, indicative of a larger pore size. These results indicated that the pore diameter increased with the increasing Mn content, which was further confirmed by the pore size distribution curves as shown in the inset of Fig.2.

Table I lists the textural properties of the samples. The BET surface area, pore volume, and average pore diameter of the unpromoted catalyst were 21.2 m$^2$/g, 0.07 cm$^3$/g, and 13.2 nm, respectively. The catalyst with Mn/Mo ratio of 0.05 exhibited higher BET surface area and pore volume as comparison to the unpromoted catalyst, which may be caused by the destruction of MoO$_2$ structure and formation of poorly crystalline CoMoO$_3$ phases. However, with further increasing Mn content, the BET surface area and pore volume of the catalysts began to decrease. This result may be ascribed to the formation of well crystallized Co-Mo-O species, leading to the decrease of BET surface area and blockage of the pores of the particle networks.

### C. NH$_3$-TPD results

The NH$_3$ desorption profiles of all catalysts are presented in Fig.3. It was generally accepted that the types of acid sites were related to the corresponding desorption temperature, whereas the area of desorption peak can reflect the amount of acid sites [34, 35]. Figure 3 the catalysts exhibited several NH$_3$ desorption peaks in the range of 200–850 °C. The low-temperature peak located at 200–400 °C corresponded to the desorption of NH$_3$ on the weak acid sites, whereas the high-temperature desorption between 400 and 850 °C were attributed to the NH$_3$ coordinated to the strong acid sites. For the unpromoted K-Co-Mo catalysts, the low-temperature desorption peak was very weak and three strong peaks at high temperature were observed, indicating that the strong acid sites were formed on the surface of unpromoted catalyst. After the addition of Mn, it was clearly observed that the high-temperature desorption peaks decreased sharply, while that of the low-temperature peaks inversely increased with the increment of Mn content. These results confirmed that

<table>
<thead>
<tr>
<th>Mn/Mo</th>
<th>$S_{\text{BET}}$(m$^2$/g)</th>
<th>$V$/(cm$^3$/g)</th>
<th>$D$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>21.2</td>
<td>0.07</td>
<td>13.2</td>
</tr>
<tr>
<td>0.05</td>
<td>33.4</td>
<td>0.12</td>
<td>14.7</td>
</tr>
<tr>
<td>0.10</td>
<td>31.7</td>
<td>0.12</td>
<td>14.9</td>
</tr>
<tr>
<td>0.15</td>
<td>25.7</td>
<td>0.10</td>
<td>16.1</td>
</tr>
<tr>
<td>0.20</td>
<td>19.6</td>
<td>0.08</td>
<td>15.6</td>
</tr>
<tr>
<td>0.25</td>
<td>17.6</td>
<td>0.06</td>
<td>13.7</td>
</tr>
</tbody>
</table>

Note: $V$ is total pore volume, $D$ is average pore diameter.
the addition of Mn had a significant impact on the surface acidity of K-Co-Mo catalyst. The strong acid sites were reduced significantly and weak acid sites were predominant. This effect may be due to the presence of a large amount of Co-Mo-O species in the Mn-promoted catalyst, as evidenced by XRD results.

D. In situ DRIFTS Results

Figure 4 shows the in situ DRIFTS spectra of CO adsorbed on the reduced catalysts. From the figure, two broad peaks centered at around 2173 and 2115 cm\(^{-1}\) have been attributed to the rotational/vibrational transitions of the residual gaseous CO [36]. For the unpromoted catalyst, the peak at around 2010 cm\(^{-1}\) can be assigned to linearly coordinated CO to Co\(^0\) species on the surface [36]. This low frequency band of CO linearly adsorbed on Co\(^0\) was attributed to low-index surface crystallographic planes or corners and step sites with low-coordinated surface sites [37]. The addition of Mn promoter induced a shift of this peak toward higher wavenumber so that the catalyst with Mn/Mo ratio of 0.25 had a peak position of 2035 cm\(^{-1}\). Blue shifting of the linearly adsorbed CO peak indicated that the binding of CO to the Co surface was weaker, which reflected a decrease in \(\pi^*\)-back bonding from the Co atoms to the carbonyl ligands. The reason may be attributed that the Mn promoter can act as an electronic promoter to withdraw electron density from Co\(^0\) phase. It has been reported that a decrease in surface electron-density resulted in decreasing the back-donation into the antibonding \(\pi^*\) orbital of CO and weakening the Co-carbonyl bond. Consequently, the C≡O triple bond gained strength, leading to a shift to higher CO stretching frequencies [38]. Morales \textit{et al.} reported the similar results [39]. They studied the CO adsorption onto Mn-promoted Co catalysts and suggested that the with-
FIG. 3 NH₃-TPD curves of the catalysts with different Mn/Mo molar ratio. (a) 0.00, (b) 0.05, (c) 0.10, (d) 0.15, (e) 0.20, and (f) 0.25.

FIG. 4 In situ DRIFTS spectra of adsorbed CO on reduced catalysts with different Mn/Mo molar ratio. (a) 0.00, (b) 0.05, (c) 0.10, (d) 0.15, (e) 0.20, and (f) 0.25.

drawal of electron density from the Co by the MnO promoter decreased the extent of \( \pi^* \) back-donation to the adsorbed CO and thus increased the carbonyl stretching frequency.

The bands in the range of 1950 to 1700 cm\(^{-1}\) were commonly assigned to two-fold, three-fold, and possibly four-fold bridge-bonded CO to Co\(^0\) species according to the literatures [39]. It was apparent that with the Mn content increase, these peaks intensities of CO adsorption both in the linear and bridge types increased, indicating that the presence of Mn created more active sites for the linear and bridge adsorption of CO.

The spectral region between 1700 and 1200 cm\(^{-1}\) was the characteristic frequencies of carbonate species [40]. Specifically, the peak at around 1675 cm\(^{-1}\) was assigned to the bidentate-bonded bicarbonate species. The peak at 1590 cm\(^{-1}\) and the shoulder at 1310 cm\(^{-1}\) corresponded to the bidentate-bonded carbonate species, and the peaks at 1540 and 1340 cm\(^{-1}\) can be attributed to monodentate-bonded carbonate species. For the unpromoted K-Co-Mo catalyst, the peaks related to carbonate species were very weak. When the Mn was added, the bands intensities of carbonate species increased significantly with increasing the Mn content, indicating that the addition of Mn promoted the formation of carbonate species, in accordance with the previous report [28].

E. XAFS Results

XANES spectra are sensitive to the local symmetry around center atom and useful in revealing the local coordination structure of center atom. The near-edge can provide much detailed information on the average valence and coordination geometry around center atom and the shift in the absorption edge can be used to identify the changes of valence state. The normalized Mo K-edge XANES spectra of the catalyst samples and two reference compounds MoO\(_3\) and MoO\(_2\) are shown in Fig. 5. A characteristic feature of pre-edge peak were observed for all the samples except for MoO\(_2\), which can be attributed to the so-called “1s–4d bound state transition”. The transition probability of the formally forbidden excitation depends on the local symmetry around the Mo atom. If a center of inversion symmetry in the molybdenum site is lost, the intensity of the transition probability from the 1s to 4d state will be increased. In the case of tetrahedral Na\(_2\)MoO\(_4\) structure, the \( p \) character in the final state becomes dominant by the effective mixing of metal \( d \)-states with ligand \( p \)-orbitals, resulting in an intense pre-edge feature [41]. Thermodynamic MoO\(_3\) crystallizes in a unique orthorhombic crystal structure, showing the layered structure. The Mo atom is located at the off-center position in a heavily distorted MoO\(_6\) octahedron that gives three crystallographically inequivalent oxygen sites [42]. This non-perfect octahedral surrounding of the central Mo atom slightly allows the 1s–4d transition to occur. As a result, a weak pre-edge peak was observed in the XANES spectra of MoO\(_3\). MoO\(_2\) shares a monoclinic structure closely related to that of rutile. Each Mo atom in MoO\(_2\) is coordinated by six oxygen atoms which have two distinct metal-oxygen bond lengths [42]. So MoO\(_2\) has a more regular octahedron in comparison with MoO\(_3\),

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TABLE II  Effect of Mn content on the catalytic performance toward higher alcohols synthesis from CO hydrogenation.

<table>
<thead>
<tr>
<th>Mn/Mo</th>
<th>CO conv./%</th>
<th>Alc. Sel./*/%</th>
<th>MeOH</th>
<th>EtOH</th>
<th>PrOH</th>
<th>BuOH</th>
<th>PeOH</th>
<th>MeOH/C2+OH</th>
<th>Alc. STY/(g/((kg h))</th>
</tr>
</thead>
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<tr>
<td>0.00</td>
<td>40.2</td>
<td>4.2</td>
<td>2.9</td>
<td>0.7</td>
<td>0.4</td>
<td>0.1</td>
<td>0.02</td>
<td>2.38</td>
<td>14.7</td>
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<tr>
<td>0.05</td>
<td>30.8</td>
<td>21.1</td>
<td>8.6</td>
<td>7.3</td>
<td>3.9</td>
<td>1.1</td>
<td>0.2</td>
<td>0.69</td>
<td>63.2</td>
</tr>
<tr>
<td>0.10</td>
<td>21.5</td>
<td>53.1</td>
<td>11.8</td>
<td>23</td>
<td>11.6</td>
<td>4.3</td>
<td>2.4</td>
<td>0.29</td>
<td>85.7</td>
</tr>
<tr>
<td>0.15</td>
<td>24.0</td>
<td>51.6</td>
<td>10.8</td>
<td>22.2</td>
<td>11.8</td>
<td>4.6</td>
<td>2.2</td>
<td>0.26</td>
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<tr>
<td>0.20</td>
<td>19.7</td>
<td>50.1</td>
<td>10.2</td>
<td>21.8</td>
<td>11.6</td>
<td>4.4</td>
<td>2.1</td>
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<tr>
<td>0.25</td>
<td>17.4</td>
<td>55.8</td>
<td>9.0</td>
<td>24.2</td>
<td>12.8</td>
<td>6.3</td>
<td>3.5</td>
<td>0.19</td>
<td>68.2</td>
</tr>
</tbody>
</table>

Note: Catalysts: K/Mo=0.1,Co/Mo=0.5, reduction condition: pure H2, T=400 °C, reaction condition: H2/CO=2/1, P=5.0 MPa, T=300 °C, GHSV=4800 h⁻¹.

* Alc. Sel. is based on a CO2-free basis.

and the pre-edge peak becomes nearly invisible in the XANES spectra of MoO2.

As shown in Fig.5, the XANES spectra of the unpromoted catalyst possessed the highest pre-edge peak and the absorption edge was close to that of MoO3. These results suggested that a less centro-symmetric surrounding was present around the Mo atom and not only octahedral coordinated Mo⁶⁺ species but also tetrahedral Mo⁶⁺ species were formed on the catalyst. It should be mentioned that no MoO3 diffraction peaks were observed in XRD pattern of the unpromoted sample, which may be attributed that the specie in this sample existed in the form of amorphous state. For the Mn-doped catalyst, at a low Mn content, the intensity of the pre-edge peak decreased to similar level to that of MoO3, and the absorption edge shifted to lower energy, indicating that there existed a fraction of octahedral coordinated Mo⁴⁺ species in the catalyst. With further increasing the Mn content, the pre-edge peak became weaker and the absorption edge shifted to lower energy, close to that of MoO2. The results indicated that the addition of Mn promoter promoted the transformation of the coordination environment of the Mo atom from tetrahedral to octahedral structure and the reduction of Mo⁶⁺ to Mo⁴⁺ species.

The Fourier transforms of the k³-weighted Mo K-edge EXAFS spectra of the catalysts and reference compounds MoO3 and MoO2 are displayed in Fig.6. It is observed that all samples exhibited coordination peaks at around 0.8–1.9 Å (without phase-shift corrections) due to the presence of the neighboring oxygen atoms (Mo−O). The peaks were slightly shifted to higher R values with the addition of Mn, implying that the bond length of Mo−O increased. This may be due to the change of coordination environment around Mo atom caused by the addition of Mn, as revealed by the XANES result. With regarding to the sample without Mn content, a weak peak ascribed to Mo−Mo bond was found at around 1.9–2.6 Å, which had a similar feature to the MoO2. This result confirmed the presence of MoO2 species, consistent with the results of XRD and

FIG. 6  Fourier transform of k³-weighted Mo K-edge EXAFS spectra of the catalysts with different Mn/Mo molar ratio and reference compounds. (a) 0.00, (b) 0.05, (c) 0.15, (d) 0.25, (e) MoO3, and (f) MoO2.

XANES. After Mn was added into the catalyst, besides the Mo−Mo peak at 1.9–2.6 Å, a new peak attributed to the Mo−Co coordination at around 2.6–3.0 Å was observed. Furthermore, the intensities of the two peaks increased with an increase in Mn content, suggesting a stronger Mo−Co interaction at higher Mn content.

F. Catalytic performance

The catalytic performance of the catalysts with different Mn/Mo ratio for higher alcohol synthesis were measured under the reaction conditions of 5.0 MPa, 300 °C, 4800 h⁻¹, and H2/CO molar ratio of 2. The measured CO conversion, total alcohols selectivity, total alcohols STY, alcohols distribution and MeOH/C2+OH ratio after reaction for 24 h are summarized in Table II. The unpromoted catalyst exhibited a very high CO conversion, but the selectivity and STY toward alcohols were extremely low. The predominant alcohol product was methanol. When the Mn promoter was added, the alcohol formation was enhanced significantly although the CO conversion decreased. The alcohol STY and selectivity increased with the Mn content increase and

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TABLE III Effect of reaction temperature on the catalytic performance toward higher alcohols synthesis from CO hydrogenation.

<table>
<thead>
<tr>
<th>Mn/Mo</th>
<th>CO conv./C%</th>
<th>Alc. Sel.*/C%</th>
<th>CnOH Sel./C%</th>
<th>MeOH/C2nOH</th>
<th>MeOH/C2n+OH</th>
<th>Alc. STY/(g/(kg-h))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MeOH</td>
<td>EtOH</td>
<td>PrOH</td>
<td>BuOH</td>
<td>PeOH</td>
</tr>
<tr>
<td>290</td>
<td>9.3</td>
<td>64.3</td>
<td>11.4</td>
<td>27.5</td>
<td>14.8</td>
<td>6.7</td>
</tr>
<tr>
<td>300</td>
<td>15.0</td>
<td>62.4</td>
<td>10.9</td>
<td>26.4</td>
<td>14.7</td>
<td>6.5</td>
</tr>
<tr>
<td>310</td>
<td>18.9</td>
<td>61.4</td>
<td>10.3</td>
<td>26.3</td>
<td>14.4</td>
<td>6.5</td>
</tr>
<tr>
<td>320</td>
<td>23.9</td>
<td>58.6</td>
<td>9.2</td>
<td>24.8</td>
<td>14.6</td>
<td>6.3</td>
</tr>
<tr>
<td>330</td>
<td>26.1</td>
<td>51.0</td>
<td>7.8</td>
<td>22.4</td>
<td>13.1</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Note: Catalysts: K/Mo=0.115, Co/Mo=0.5, Mn/Mo=0.15, reduction condition: pure H2, T=450 °C, reaction condition: H2/CO=2/1, P=5.0 MPa, GHSV=6000 h⁻¹.

Alc. Sel. is based on a CO2-free basis.

TABLE IV Catalytic performance of Mn-K-Co-Mo in comparison with similar catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T/K</th>
<th>P/MPa</th>
<th>GHSV/h⁻¹</th>
<th>CO conv./C%</th>
<th>Alc. Sel/C%</th>
<th>Alc. STY/(g/(kg-h))</th>
<th>MeOH/C2nOH C/C wt/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-K-Co-Mo</td>
<td>593</td>
<td>5.0</td>
<td>6000</td>
<td>23.9</td>
<td>58.6</td>
<td>148.3</td>
<td>0.19</td>
</tr>
<tr>
<td>K-Co-MoS2 [43]</td>
<td>599</td>
<td>10.0</td>
<td>5418</td>
<td>5.0</td>
<td>65</td>
<td>161.2</td>
<td>0.41</td>
</tr>
<tr>
<td>K-Co-Mo2C [44]</td>
<td>573</td>
<td>8.0</td>
<td>2000</td>
<td>51.0</td>
<td>39.6</td>
<td>105.8</td>
<td>0.66</td>
</tr>
<tr>
<td>K-Co-Mo/clay [45]</td>
<td>553</td>
<td>5.0</td>
<td>4800</td>
<td>27.7</td>
<td>48.3</td>
<td>102</td>
<td>0.66</td>
</tr>
<tr>
<td>Ce-K-Co-Mo2S    [46]</td>
<td>603</td>
<td>3.0</td>
<td>2225</td>
<td>18.6</td>
<td>73.3</td>
<td>85</td>
<td>0.55</td>
</tr>
<tr>
<td>Y-K-Co-Mo2S     [46]</td>
<td>603</td>
<td>3.0</td>
<td>2225</td>
<td>16.5</td>
<td>69.3</td>
<td>96</td>
<td>0.65</td>
</tr>
</tbody>
</table>

reached the highest level on the catalyst with Mn/Mo ratio of 0.15. Over the catalyst, the alcohol STY was 91.4 g/(kg-h), about 6.2 times more than that of the unpromoted sample. The alcohol selectivity also increased significantly from 4.2% to 51.6%. More interestingly, the addition of Mn promoted the formation of C2+ alcohol significantly. As shown in Table II, the MeOH/C2+OH ratio decreased from 2.38 to 0.19 when the Mn/Mo ratio increased to 0.25. The portion of methanol in total alcohol was suppressed remarkably and the ethanol became the predominant product. The distribution of alcohol products deviated from the Anderson-Schulz-Flory (ASF) law. Table III summarized the effect of reaction temperature on the catalytic performance of the Mn-promoted catalyst. With an increase in the temperature, the CO conversion increased while the selectivity to total alcohol showed a slight decrease. Furthermore, the ratio of MeOH/C2+OH decreased gradually, indicating that increasing temperature facilitated the formation of higher alcohols. The total alcohol STY reached the highest level at the reaction temperature of 320 °C. Under the reaction conditions, the alcohol STY and selectivity were 148.3 g/(kg-h) and 58.6%, respectively. Especially, the MeOH/C2+OH ratio decreased to 0.19. For comparison, the catalytic performance of some similar catalysts reported in the recent literatures are summarized in Table IV. Compared to the sulfided K-Co-MoS2 catalyst [43], the present Mn-K-Co-Mo exhibited a slightly lower alcohol selectivity. However, its STY of alcohol, in particular the C2+OH content in total alcohols were much higher. Furthermore, it should be noted that the reaction pressure for K-Co-MoS2 catalyst was much higher. It is well known that the higher pressure can enhance significantly the alcohol formation, especially the C2+OH selectivity. In comparison with the K-Co-Mo2C catalyst [44], the present catalyst showed a similar alcohol STY, but much higher alcohol selectivity and lower MeOH/C2+OH ratio. Furthermore, the Mn-K-Co-Mo catalyst also exhibited better activity, especially the C2+OH selectivity as comparison to the K-Co-Mo/clay and Ce, Y, and La doped Mo-based catalysts [45, 46]. To our best knowledge, the selectivity to C2+OH over the present catalyst is the highest level achieved to date for Mo-based catalyst.

Over the Mo-based catalysts for alcohol synthesis, the Co promoter is known to act synergistically along with Mo species, rather than acting independently. It was reported that in some similar catalysts, the presence of Co2Mo2C, Ni6Mo6C, Co-Mo-S, and Ni-Mo-S phases were responsible for the higher alcohol synthesis [44, 47, 48]. Liakakou et al. [17] studied CO hydrogenation reaction over K-Ni-Mo/AC catalysts. The formation of oxygenates was attributed to the Ni-Mo synergetic interaction and the Ni-Mo-O sites were suggested to be the active phase for CO activation.
the interaction between Co and Mo species can enhance the overall reactivity and promote the formation of higher alcohols over methanol [24]. A density functional theory study also indicated that Co atoms can be incorporated in the S-edge sites of MoS$_2$, which may generate the active Co-Mo-S species and increase the activity of catalyst [49]. For the present catalysts, as revealed by the XRD and XAFS results, the incorporation of Mn promoter enhanced the interaction between Co and Mo and thus led to the formation of Co-Mo-O species, which was suggested to be active for the alcohol synthesis. Furthermore, the good synergistic effect between Co and Mo was also conducive to enhance the promotional effect of Co.

The acidity of catalysts plays an important role in the alcohol formation. The surface acidity was favorable for the CO activation [17], but strong acid sites were also the active site for alcohol dehydration and thus decreased the alcohol selectivity [34]. Furthermore, reduced acidity can facilitate the aldol-type condensation reactions, which was regarded as the intermediate step for the production of higher alcohols [9]. A correlation between acid site concentration and CO conversion further revealed that decreasing the surface acidity of catalyst was conducive to the formation of higher alcohols [9, 34]. The NH$_3$-TPD results shown in Fig.3 clearly indicated that the presence of Mn reduced the amount of strong acid sites significantly and meanwhile promoted the formation of weak acid sites. The change trend was suggested to have a positive effect on the synthesis of higher alcohols from syngas according to the above discussion.

The CO adsorption property has a crucial impact on the CO hydrogenation reaction. The in situ DRIFTS results indicated that the incorporation of Mn can enhance the linear and bridge adsorption of CO on the surface of catalysts. Moreover, the formation of carbonate species was also enhanced. The bridge-type adsorbed CO was easily dissociated to carbon and oxygen [50]. The C–O bond cleavage led to the more frequent appearance of C$_1$ species that can scavenge H to promote the growth of carbon chain [28]. The linearly adsorbed CO was beneficial for the formation of oxygenated compounds, because a linearly-adsorbed CO molecule had a stronger C–O bond and thus can be less easily dissociated [39]. For the reduced Mo-based catalysts, the higher alcohol synthesis consists of several steps including the CO dissociation, hydrogenation and CO insertion, etc. The CO dissociation and hydrogenation promoted the formation of alkyl group and growth of carbon chain. The alkyl group was further transformed to the acyl species by the insertion of non-dissociative CO. Finally, the acyl species was hydrogenated to form the corresponding alcohol product. From these perspectives, the enhanced adsorption of linear- and bridge-type CO due to the incorporation of Mn contributed to the growth of carbon chain and formation of alcohol, leading to the increase of the selectivity to C$_2$+OH.

This work developed a highly active Mo-based catalyst for the synthesis of higher alcohols and provided some new insight into the promotional effect of Mn.

**IV. CONCLUSION**

The Mn-K-Co-Mo catalysts with different Mn content were prepared by a sol-gel method. It was found that the addition of Mn enhanced the interaction between Co and Mo, leading to the formation of active Co-Mo-O species. Meanwhile, the surface strong acidity of catalyst was reduced significantly and the amount of weak acid sites increased. Furthermore, the incorporation of Mn promoted the adsorption of linear- and bridge-type CO significantly. Benefit from these features, the Mn-doped catalysts exhibited an excellent catalytic activity for the alcohols synthesis from syngas. In particular, the selectivity to C$_2$+ alcohol increased greatly. The alcohol products distribution deviated from the ASF law. The formation of methanol was suppressed significantly and the ethanol became the predominant product.

**V. ACKNOWLEDGMENTS**

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