

# A highly active K-Co-Mo/C catalyst for mixed alcohol synthesis from CO + H<sub>2</sub>

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**A highly homogeneous and dispersed K-Co-Mo/C catalyst which prepared by a sol-gel method exhibits high alcohol yield, especially high C<sub>2+</sub>OH selectivity for mixed alcohol synthesis from CO + H<sub>2</sub>.**

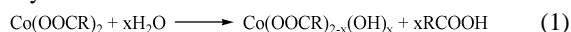
Mixed alcohol (MeOH and C<sub>2+</sub>OH) synthesis from CO + H<sub>2</sub> is of considerable interest because mixed alcohol can be used as additives in gasoline (usually 2–5 wt%) to increase the octane number and reduce air pollution.<sup>1</sup> In the field, alkali-promoted Mo catalysts are more attractive for commercial aspects because of their excellent sulfur-tolerance. Great efforts have been made in improving the alcohol yield, especially the C<sub>2+</sub>OH selectivity. The promoters, supports and catalysts structure have been studied extensively. It was found that Co and Ni are effective promoters for enhancing alcohol yield and C<sub>2+</sub>OH selectivity.<sup>2–4</sup> The interaction between Mo and promoters<sup>2,4</sup> and dispersion of catalysts<sup>5,6</sup> exert great influences on the catalytic activity.

From a practical point of view, it is necessary to further increase the alcohol yield as well as C<sub>2+</sub>OH selectivity. The traditional synthesis of promoted Mo catalysts is by impregnation or precipitation technique. These methods are difficult to produce homogeneous distributions of various components or highly dispersed catalysts, which limit the catalytic activity. The preparation of Mo-based catalyst with higher alcohol yield, especially higher C<sub>2+</sub>OH selectivity becomes a main challenge. In this study, we report a simple sol-gel synthesis of K-Co-Mo catalyst with high homogeneity and dispersion, its activity for alcohol synthesis is compared with similar catalysts reported.

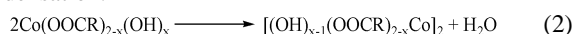
The preparation of catalyst is as follows: firstly, Co(NO<sub>3</sub>)<sub>2</sub> (AR) and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> (AR) aqueous solutions were prepared separately and then mixed (Co/Mo molar ratio = 0.5). Citric acid (AR) was added to the solution under constant stirring (citric acid/metallic ions molar ratio = 0.4). Finally, K<sub>2</sub>CO<sub>3</sub> solution was dropped slowly into the solution (K/Mo molar ratio = 0.1). The pH value of the mixed solution was adjusted to 3.5 by using HCOOH and NH<sub>4</sub>OH. The solution was kept in a water bath at 65 °C until the solution became a gel. During the gelation process, the solution kept homogeneous and no precipitation was formed. The as-prepared gel was dried at 120 °C for 15 h and calcined in Ar at 400 °C for 4 h.<sup>†</sup>

In the preparation process, citric acid was used as a complexing hydroxy acid. It reacted with cobalt ions to form cobalt citrate (Co(OOCR)<sub>2</sub>) and prevented the co-precipitation between Co and Mo. Then under appropriate conditions, the cobalt citrate hydrolyzed and formed sol. The sol-gel chemistry process can be described as below:

Hydrolysis:



Condensation:



The microstructure of the prepared sample was studied by high-resolution TEM-EDS analysis. The TEM image is shown in Fig. 1. It can be seen that the sample show a high

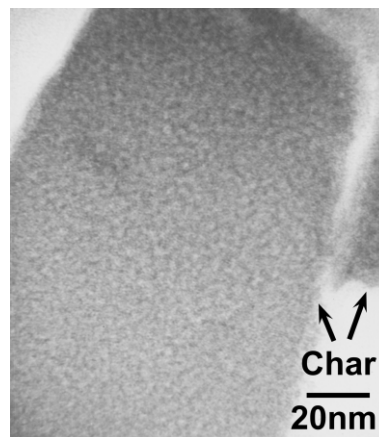


Fig. 1 TEM image of K-Co-Mo catalyst (×400K).

homogeneity, and the amorphous char is clearly observed. EDS analysis demonstrates that besides the K, Co, Mo, O, the element C also exists in the sample and its atomic concentration is ~40%. The formation of amorphous char is attributed to the decomposition of citric acid in Ar. It is noted that the catalytic active particles, which are composed of K, Co and Mo, almost cannot be observed in the TEM image even if the magnifying times are 400K. The pattern of electron diffraction is shown in Fig. 2. Only very weak ring is seen in the Figure, indicating the K-Co-Mo active particles are highly disordered. In general, the particle size in a type amorphous structure is < 2 nm. According to above results, the size of K-Co-Mo active particles in the sample is estimated about 2–5 nm, and they are homogeneously dispersed in the amorphous char.

The measured stable catalytic activity for alcohol synthesis after reaction for 24 h is shown in Table 1. Contact time is denoted by two means, GHSV (h<sup>-1</sup>) and W/F (g.cat.h mol<sup>-1</sup>). Entries 1–4 clearly show that the space-time-yield (STY) and selectivity of alcohol is improved at short contact time, suggesting a significant activity for the dehydration of alcohol to hydrocarbons under synthesis conditions.<sup>7</sup> Long contact time result in an increase of C<sub>2+</sub>OH/MeOH ratio, which can be

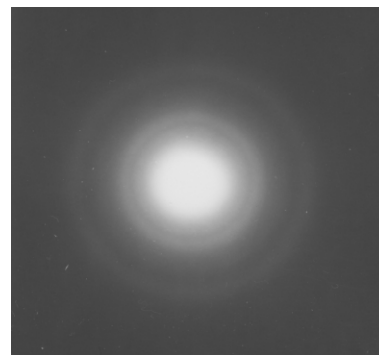


Fig. 2 Diffraction patterns of K-Co-Mo catalyst.

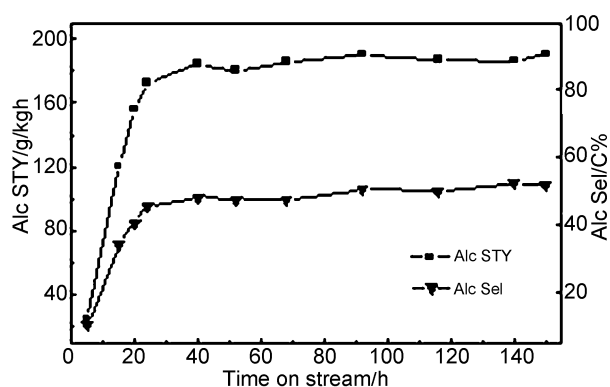
**Table 1** Catalytic results for mixed alcohol synthesis from CO + H<sub>2</sub><sup>a</sup>

| Samples | Temp. (°C)                             | Pressure (MPa) | GHSV (h <sup>-1</sup> ) | W/F (g.cat.h mol <sup>-1</sup> ) | CO Conv. (C%) | Alc.Sel. (C%) | Alc.STY. (g kg.h <sup>-1</sup> ) | C <sub>2+</sub> OH/MeOH (Wt.) | Ref. |    |
|---------|--|----------------|-------------------------|----------------------------------|---------------|---------------|----------------------------------|-------------------------------|------|----|
| 1       | K-Co-Mo/C                              | 230            | 6.0                     | 1200                             | 9.6           | 25.1          | 44.8                             | 105.6                         | 2.65 |    |
| 2       | K-Co-Mo/C                              | 230            | 6.0                     | 4800                             | 2.4           | 12.8          | 49.9                             | 208.1                         | 1.79 |    |
| 3       | K-Co-Mo/C                              | 230            | 6.0                     | 9600                             | 1.2           | 7.5           | 60.4                             | 296.5                         | 1.48 |    |
| 4       | K-Co-Mo/C                              | 230            | 6.0                     | 14400                            | 0.8           | 5.5           | 70.2                             | 375.4                         | 1.42 |    |
| 5       | K-Co-Mo/C                              | 230            | 3.0                     | 4800                             | 2.4           | 7.3           | 38.4                             | 95.4                          | 1.18 |    |
| 6       | K-Co-Mo/C                              | 230            | 5.0                     | 4800                             | 2.4           | 11.8          | 45.7                             | 172.1                         | 1.52 |    |
| 7       | K-Co-Mo/SiO <sub>2</sub>               | 250            | 5.0                     | —                                | 10            | 7.2           | 52.8                             | 31.2                          | 1.59 | 9  |
| 8       | K-Co-Mo/Al <sub>2</sub> O <sub>3</sub> | 343            | 10.45                   | 28000                            | —             | —             | 59.0                             | 370                           | 1.24 | 3  |
| 9       | K-Co-MoS <sub>2</sub>                  | 305            | 10.45                   | 1300                             | —             | 39.0          | 75.7                             | 115                           | 2.56 | 10 |

<sup>a</sup> Syngas is composed of CO 30%, H<sub>2</sub> 60%, and N<sub>2</sub> 10%. 0.5 g catalysts were used in each experiment. The catalysts were reduced in flowing H<sub>2</sub> at 400 °C for 12 h before use. Products were analyzed by GC. Details have been described in literature.<sup>6</sup> The CO conversion and alcohol selectivity is referred to that with CO<sub>2</sub>-free.

ascribed that the EtOH is produced also by way of homologation of MeOH directly produced by CO hydrogenation.<sup>8</sup> Entries 2, 5 and 6 show that raising the pressure, the STY of alcohol and C<sub>2+</sub>OH/MeOH ratio is greatly improved. For the purpose of comparison, the activities of similar catalysts systems in previous papers are collected in Table 1 (entries 7–9). Compared to the supported K-Co-Mo/SiO<sub>2</sub><sup>9</sup> (entries 1 vs entries 7), under similar reaction conditions, the STY of alcohol on the K-Co-Mo/C catalyst is about three times than those of the K-Co-Mo/SiO<sub>2</sub>, especially the distribution of C<sub>2+</sub>OH is much higher. For the optimized compositions K-Co-Mo/Al<sub>2</sub>O<sub>3</sub> (entries 8),<sup>3</sup> under the condition of 10.45 MPa, 28000 h<sup>-1</sup>, the STY of alcohol and the C<sub>2+</sub>OH/MeOH ratio are similar to those of the K-Co-Mo/C catalyst in entries 4. However, it should be noted that the reaction conditions for the K-Co-Mo/Al<sub>2</sub>O<sub>3</sub> is much more severe (entries 8 vs entries 4). Higher pressure and shorter contact time will greatly enhance the alcohol formation. The catalytic properties of patented sulfided K/Co/MoS<sub>2</sub> are also listed in the Table (entries 9).<sup>10</sup> Compared to the patented catalyst, the STY of alcohol of K-Co-Mo/C catalysts in entries 1 is slightly reduced, whereas the C<sub>2+</sub>OH/MeOH ratio is higher (entries 1 vs entries 9). It should be mentioned that the pressure in entries 9 is much higher than that in entries 1. In addition, in the activity measurement of the patented sulfided K/Co/MoS<sub>2</sub> catalysts, about 50 ppm of H<sub>2</sub>S was presented in the feed gas. It is well known that the incorporation of the H<sub>2</sub>S in the feed can remarkably increase the C<sub>2+</sub>OH selectivity,<sup>11</sup> but a large amount of sulfur compounds in the system is undesirable. One thing should be mentioned is that the compositions and reaction conditions (including reduction temperature and reaction temperature) are not optimized for the K-Co-Mo/C catalysts. So, the K-Co-Mo/C catalysts in this work are expected to perform better under appropriate conditions. A stability test of the K-Co-Mo/C catalyst at 230 °C, 5.0 MPa and 4800 h<sup>-1</sup> was conducted for about 150 h (Fig. 3). During the induction period of the reaction, the activity and selectivity for alcohol synthesis are very low, but gradually increase with time on stream and reach a steady state after about 24 h. It indicates that the catalyst is thermally stable under reaction conditions.

In summary, we prepared a highly homogeneous and dispersed K-Co-Mo/C catalyst by using a sol-gel method with citric acid as complexant. The catalyst exhibits much higher alcohol activity, especially higher C<sub>2+</sub>OH selectivity for alcohol synthesis from CO + H<sub>2</sub> than those of the previous catalysts reported. This suggests that the prepared K-Co-Mo/C catalyst is

**Fig. 3** Stability test of K-Co-Mo/C catalyst.

potentially a new catalytic material for mixed alcohol synthesis. Efforts of mechanistic studies are in process in our laboratory.

## Notes and references

† For safety, the dried-gel should be heat-treated in a flow of Ar, not in a closed system.

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