This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Targeted Design and Synthesis of a Highly Selective Mo-based Catalyst for the Synthesis of Higher Alcohols

Wei Xie,¹ Jilong Zhou,² Lili Ji,³ Song Sun,⁴ab Halbin Pan,³ Junfa Zhu,³ Chen Gao,⁴ab and Jun Bao*ab

Improving the C₂₅ alcohols selectivity is the most difficult challenge in higher alcohol synthesis (HAS) from syngas. Herein, three effective strategies were combined to develop a Mo-based catalyst for HAS. The sol-gel method produced a highly homogeneous distribution of components, which ensured an intimate and sufficient contact between different active sites. The incorporation of Mn oxide enhanced the interaction between Co and Mo and thus promoting the growth of alcohol chain. More importantly, the reduction degrees of Co and Mo can be tuned precisely. The prepared Mn/K/Co/Mo catalysts show unusual activity for HAS.

In the last few decades, the catalytic conversion of syngas to higher (C₂₅) alcohols has attracted significant research attention, owing to the relevance of higher alcohols as neat fuels, fuel additives and a feedstock for the synthesis of a variety of valuable chemicals.¹ The reaction is a typical example of those requiring synergetic effects between different catalytic sites with different functionality. Specifically, an active catalyst for the synthesis of higher alcohols from syngas should possess multiple active species corresponding to CO adsorption, dissociation, hydrogenation, and CO non-dissociative insertion etc., respectively.² Precise regulation of these active species to obtain a good synergy between each other is crucial to increase the catalyst activity. Due to this complex nature of the system, the development of solid catalysts displaying high selectivity for C₂₅ alcohols still remains the most attractive and difficult challenge and no commercial process exists today.

After decades of research, several catalyst families have been developed for producing alcohols from syngas.³ Among these, Mo-based catalysts have drawn special interest due to their excellent sulfur tolerance.⁴ Great efforts have been made to optimize the catalyst composition, regulate the catalyst structure and explore the structure-activity relationship as well as the reaction mechanism, etc.²,⁵ The addition of an alkali to a Mo catalyst increases alcohol production and suppresses hydrocarbon formation.⁶ Some 3d transition metals, especially Co, are found to be effective promoters for improving the C₂₅ alcohol selectivity because they can promote the formation of alkyl group (C₃H₇), which is recognized as the key intermediate for the synthesis of higher alcohols.⁷ Many factors, including the aggregation state of Mo species, the particle size, the interaction between promoters and Mo species, the reducibility of components as well as the distribution of different species etc. have significant influence on the catalytic performance.⁸ Simultaneously tuning these structure factors to achieve the positive effects on catalyst performance is still very difficult. For instance, the Mo⁹¹⁺⁻(1<δ<4) species are regarded as the adsorption site for non-dissociative CO and responsible for alcohol formation.²,⁹ However, under the reduction condition for producing Mo⁹¹⁺⁻(1<δ<4) species, most of Co species were often over-reduced to metal Co⁰, which was highly active for CO dissociative adsorption and hydrogenation and thus enhanced the hydrocarbons formation.

Herein, we combined three strategies to develop a highly efficient K and Co promoted Mo catalyst for the conversion of syngas to higher alcohols. First, a Mn oxide was introduced as the third promoter to tune the interaction between Co and Mo species, the reducibility of components as well as the aggregation state of Mo species based on the unique electronic and structural effects of Mn oxide. The related research has rarely been reported previously. Second, a modified sol-gel preparation method was employed to achieve a highly homogeneous distribution of components on the catalyst, ensuring an intimate and sufficient contact between promoters and Mo species. More importantly, a two-steps activation approach for catalyst activation was used to tune and match the reduction degree of Co and Mo species. Based on these targeted design, synthesis and activation strategies,
the obtained Mn/K/Co/Mo catalyst showed unusual activity 
for higher alcohol synthesis from syngas.

The citric acid was used as a complexing agent during 
the sol-gel process for the preparation of catalyst. The as-prepared 
dried gel was heat-treated in nitrogen to form the fresh 
catalyst powder. The decomposition of citric acid in nitrogen 
atmosphere reduced the Mo species and meanwhile inhibited 
the growth of particle size. Before reaction, the catalyst 
underwent the second reduction step using pure H₂, XRD 
patterns (Fig. S1, ESI†) show that for the sample without Mn 
promoter, only three diffraction peaks at 2θ = 26.1°, 37.0° 
and 53.5° were observed, corresponding to the (-111), (-211) and 
(-312) facets of MoO₃ crystalline. The formation of MoO₂ can 
be attributed to the reduction effect of the decomposition 
of citric acid in nitrogen atmosphere. The weak diffraction 
intensities indicated a low degree of crystallization. Besides it, 
no peaks assigned to other Mo or Co species were detected.

The doping of Mn promoter led to a significant change in XRD 
patterns. At a low Mn/Mo ratio of 0.05, five new weak peaks 
appeared at 2θ values of 18.2°, 35.7°, 52.1°, 56.3° and 64.2°. 
They could be attributed to the poorly crystalline CoMoO₄ 
phases. When further increasing the Mn content, a series of 
new diffraction peaks assigned to Co₂MoO₄ phase were observed. 
It can be seen that with an increase in the Mn content, the diffraction intensities of Co-Mo phases became stronger, while that of the MoO₂ decreased. The results indicated that the doping of Mn promoter significantly enhanced the interaction between Co and Mo species and improved the degree of crystallization. It is noted that no any 
peaks of Mn oxides were detected even at a relatively high Mn 
content, which may indicate that the Mn species were either 
amorphous or present in the form of very small nanoparticles 
with a high dispersion on the catalysts.

The morphology and microstructure of the catalysts were 
investigated by TEM technique. For the sample without Mn 
(Fig. S2a, ESI†), the large-size particles with irregular shape 
were the amorphous char, which was produced by the 
decomposition of citric acid in nitrogen. The catalyst particles 
had a size of about 5 nm and were homogeneously dispersed 
in the char. The pattern of electron diffraction further 
confirmed that the particle had an amorphous structure. After 
incorporating Mn promoter (Fig. S2b and S2c, ESI†) the 
catalyst particle had a regular plate-like structure, indicating a 
high degree of crystallization, which was further proved by the 
electron diffraction pattern. The clear and uniform lattice 
fringes observed in high-resolution TEM image (Fig. S3, ESI†) 
confirmed that the plate-like particles were highly crystallized 
Co₃Mo₆O₁₉, consistent with XRD results. The EDS mapping (Fig. 
S4, ESI†) indicated that the Co, Mo and Mn elements were 
distributed uniformly on the surface of the catalysts.

The distribution of Mo species of the catalysts derived 
from high-resolution X-ray photoelectron spectroscopy (Fig. 
S5, ESI†) are summarized (Table S1, ESI†). For the fresh Mn-
free sample, besides the characteristic binding energies of 
Mo⁶⁺ 3d₅/₂ (232.4 eV) and Mo⁶⁺ 3d₃/₂ (235.6 eV), two new 
peaks assigned to Mo⁷⁺ 3d₅/₂ (230.6 eV) and Mo⁷⁺ 3d₃/₂ (238.8 eV) 
were also observed, indicating the formation of Mo⁷⁺ 
species.⁹⁵ When incorporating the Mn promoter, the binding 
energies of Mo species did not change. However the surface 
content of Mo⁶⁺ species decreased whilst that of Mo⁷⁺ species 
increased significantly, indicating that the incorporation of 
Mn promoter promoted the reduction of Mo⁶⁺ to Mo⁷⁺ species 
during the decomposition of citric acid in nitrogen. The reason 
may be due to the fact that the doping of Mn facilitated the 
formation of two new phases CoMoO₄ and Co₂MoO₄, in which 
the valence state of Mo was +4. From the Co 2p core-level 
spectra, the binding energy of 780.9 eV and satellite peak at 
786.7 eV indicated the presence of Co²⁺ species in the fresh 
catalysts (Fig. S6, ESI†).¹⁰ For the Mn-doped fresh sample, 
the appearance of binding energy of Mn 2pₓᵧ/₂ (641.2 eV) and Mn 
2pₓᵧ/₂ (653.2 eV) confirmed the existence of Mn²⁺ species (Fig. 
S7, ESI†).¹¹ These results indicated that the decomposition 
of citric acid in nitrogen cannot reduce the Co and Mn species.

The in-situ synchrotron radiation XPS was employed for 
investigating the surface chemical compositions of the reduced 
catalysts. As shown in Fig. 1, after reduction in pure H₂ under 
673 K, new Mo species with lower valence state were formed 
on the surface of catalysts. For the catalyst without Mn, 
besides the Mo⁴⁺, the peaks at 227.4 eV and 228.4 eV can be 
attributed to the metal Mo⁰ and Mo⁴⁺ (2<x<3) species, 
respectively.¹² After incorporating with Mn, a new peak at 
228.9 eV was observed, corresponding to the Mo phase with a 
valence state of +y (3<y<3.5),¹² higher than that of the Mo⁴⁺ 
(2<x<3) species. Besides it, no peak assigned to metallic state 
Mo was observed on the reduced Mn-doped catalyst. These 
results demonstrated that the presence of Mn inhibited the 
reduction of Mo⁴⁺ species during the H₂ treatment. From the 
Co 2p spectra, it is evident that after reduction a large amount 
of metallic state Co⁰ (Co 2pₓᵧ/₂ peak at 777.9 eV) were formed 
on the sample without Mn.¹⁰,¹³ The Mn-doped catalyst 
exhibited a rather broad Co 2pₓᵧ/₂ peak at about 781.0 eV, 
which suggested the coexistence of several oxidation states,
predominantly Co$^{2+}$ and some Co$^{3+}$. Compared with the Mn-free catalyst, the fraction of metallic Co species decreased significantly when Mn was added, indicating that the reducibility of Co species was also suppressed by the addition of Mn. The chemical state of Mn species did not change significantly after reduction (Fig. S8, ESI†).

The normalized Mo K-edge XANES spectra of the fresh and reduced catalysts and two standard compounds MoO$_3$ and MoO$_2$ are shown in Fig. 2a. The absorption edge position provides the information about the chemical valence of central metal atoms, and the pre-edge peak intensity is sensitive to the symmetry of the absorbing atom.$^{14}$ The fresh Mn-free catalyst exhibited an obvious pre-edge peak higher than that of MoO$_3$, indicating that the central Mo atoms existed in not only octahedral but also tetrahedral coordination. The absorption edge was lower than that of MoO$_2$, suggesting that the Mo atoms were mainly present in octahedral coordination. The Co K-edge XANES spectra of the fresh and reduced catalysts are shown in Fig. 2b. The fresh undoped sample showed similar absorption edge energy as that of CoO. After reduction, the absorption edge shifted to lower value, close to that of Co foil, indicating the formation of metal Co$^0$. For the Mn-doped sample, the position of absorption edge did not show obvious change, suggesting the reduction of Co was inhibited.

The catalytic performance of the catalysts for the synthesis of higher alcohols was tested under the conditions of reaction temperature of 593 K, the catalyst showed the best activity. The total alcohol STY reached 148.3 g·kg$^{-1}$ with a high selectivity of 58.6%.

### Table 1. CO hydrogenation over the catalysts as a function of Mn contents.$^{a,b,c}$

<table>
<thead>
<tr>
<th>Sample (Mn/Mo)</th>
<th>CO conv. (%)</th>
<th>Alc. Sel. (%)</th>
<th>$C_2$/C$_1$</th>
<th>Alc. STY. (g·kg$^{-1}$·h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>40.2</td>
<td>4.2</td>
<td>0.4</td>
<td>14.7</td>
</tr>
<tr>
<td>0.05</td>
<td>30.8</td>
<td>21.1</td>
<td>1.5</td>
<td>63.2</td>
</tr>
<tr>
<td>0.10</td>
<td>21.5</td>
<td>53.1</td>
<td>3.5</td>
<td>85.7</td>
</tr>
<tr>
<td>0.15</td>
<td>24.0</td>
<td>51.6</td>
<td>3.8</td>
<td>91.4</td>
</tr>
<tr>
<td>0.20</td>
<td>19.7</td>
<td>50.1</td>
<td>3.9</td>
<td>78.3</td>
</tr>
<tr>
<td>0.25</td>
<td>17.4</td>
<td>55.8</td>
<td>5.2</td>
<td>68.2</td>
</tr>
</tbody>
</table>

$^a$Catalysts: K/Mo=0.1, Co/Mo=0.5. $^b$Reduction conditions: catalyst 0.5 g, T=673 K, pure H$_2$; reaction conditions: P= 5.0 MPa, T=573 K, GHSV=4800 h$^{-1}$, H$_2$/CO=2. $^c$Conv.=conversion, Alc.Sel.=alcohols selectivity, Alc.STY.= space-time-yield of alcohols. Both CO conversion and alcohols selectivity are calculated on a CO$_2$-free basis. $C_2$/OH/MeOH is based on moles of carbon.
Furthermore, the ratio of $C_2$OH/MeOH increased to 5.4. The mass fraction of $C_2$OH in the total alcohols approached 80% (Fig. 3b). To our best knowledge, the selectivity to $C_2$OH in total alcohol is the highest value achieved to date for Mo-based catalyst system.

For the Mo-based catalyst, the methanol is directly formed by the hydrogenation of non-dissociatively adsorbed CO, while the higher alcohols are generally formed via a CO insertion mechanism.\textsuperscript{26,30,38} First, the adsorbed CO was dissociated and then hydrogenated to form CH\textsubscript{2}, followed by the growth of the alkyl chain via CH\textsubscript{2} insertion. Then the non-dissociatively adsorbed CO inserted into an alkyl group to form an acyl species, which was hydrogenated to the corresponding alcohol or to a longer alkyl group via CH\textsubscript{2} insertion. The hydrocarbons were produced by the hydrogenation of the alkyl groups. For the activated Co-Mo catalyst, the Mo\textsuperscript{6+} (1<δ<4) species are the main adsorption site for non-dissociative CO and favors the CO insertion into alkyl species to produce alcohol, while the metal Co\textsuperscript{0} and metal Mo\textsuperscript{0} are highly active for hydrogenation. Too strong hydrogenation ability is conducive to the formation of hydrocarbons and thus inhibiting the synthesis of higher alcohols.

From the characterization results, the incorporation of Mn oxide combining the two-steps activation approach tuned the reduction degrees of Co and Mo species and optimized the distribution of different active sites. During the process of decomposition of citric acid in nitrogen, the incorporation of Mn promoted the reduction of Mo\textsuperscript{6+} to Mo\textsuperscript{4+}, whilst the Co species remained in the +2 oxidation state. In the second stage of H\textsubscript{2}-reduction, the presence of Mn conversely suppressed the reduction of Mo\textsuperscript{4+} to metal Mo\textsuperscript{0}, leading to the enrichment of Mo\textsuperscript{6+} (1<δ<4) species. The transformation of Co\textsuperscript{0} to metal Co\textsuperscript{0} was also suppressed to some extent by the addition of Mn. Consequently, the strong capabilities for hydrogenation were inhibited reasonably, and meanwhile the CO insertion ability was enhanced significantly. The good synergies between CO dissociation, hydrogenation and CO insertion played a crucial role in the formation of higher alcohols and growth of carbon chain. Second, the strong interaction between Co and Mo species caused by the addition of Mn was suggested to enhance the promotion effect of Co for the growth of alcohol chain as well as alcohol production because the presence of Co is conducive to the formation of intermediate alkyl group.\textsuperscript{7,16} Furthermore, the highly homogeneous distribution of components, derived from the sol-gel method, ensured an intimate and sufficient contact between different active sites and thus made it easier for the migration of reaction intermediates from one site to another, such as the migration of alkyl species from Co to Mo species for further CO insertion. These results demonstrated that by combining these strategies, some key structural properties of Mo-based catalyst for HAS can be tuned simultaneously to exert positive impact on the catalytic performance and thus improve significantly the selectivity to higher alcohols.

In summary, we demonstrated that the combined three strategies, related to design, synthesis and activation, respectively, are very effective for developing a Mo-based catalyst for higher alcohol synthesis from syngas. The catalyst, derived from these strategies, had a highly homogeneous distribution of components, strong interaction between promoters and Mo species, and especially the tuned reducibility of Co and Mo. These structural characteristics, to a large extent, promoted the formation of active sites and ensured good synergies between different active sites with different functionality. Benefited from this, the catalyst exhibited a very high selectivity for $C_2$ alcohol formation. The work offers a successful example of targeted design and synthesis of complex multifunctional catalysts.

This work was supported by the National Nature Science Foundation of China (11179034, 11205159), National Basic Research Program of China (973 Program, 2012CB922004).

### Notes and references


5  (a) V. P. Santos, B. van der Linden, A. Chojecki, G. Budroni, S.
Corthals, H. Shibata, G. R. Meima, F. Kapteijn, M. Makkee
and G. Gascon, ACS Catal., 2013, 3, 1634-1637; (b) H. Shou
and R. J. Davis, J. Catal., 2011, 282, 83-93; (c) Z. R. Li, Y. L. Fu,
155-161; (d) Y. Avila, C. Kappenstein, S. Pronier and J.
6  (a) H. C. Woo, I.-S. Nam, J. S. Lee, J. S. Chung and Y. G. Kim, J.
Catal., 1993, 142, 672-690; (b) J. S. Lee, S. Kim, K. H. Lee, I.-S.
Nam, J. S. Chung, Y. G. Kim and H. C. Woo, Appl. Catal., A,
7  (a) D. A. Storm, Top. Catal., 1995, 2, 91-101; (b) Z. R. Li, Y. L.
A, 2001, 220, 21-30; (c) K. Y. Yin, H. Shou, D. Ferrari, C. W.
8  (a) M. Jiang, G. Z. Bian and Y. L. Fu, J. Catal., 1994, 146,
144-154; (b) M. T. Claure, S. H. Chai, S. Dai, K. A. Unocic, F. M.
Alamgir, P. K. Agrawal and C. W. Jones, J. Catal., 2015, 324,
88-97; (c) Y. Yang, Y. D. Wang, S. Liu, Q. Y. Song, Z. K. Xie and
Heracleous, K. S. Triantafylolidis and A. A. Lemonidou, Appl.
Catal., B, 2015, 165, 296-305. (e) J. Bao, Y. L. Fu and G. Z.
9  (a) M. M. Zhang, W. Zhang, W. Xie, Z. M. Qi, G. M. Wu, M.
269-275; (b) M. M. Lv, W. Xie, S. Sun, G. M. Wu, L. R. Zheng,
2925-2934; (c) X. G. Li, L. J. Feng, LL. J. Zhang, D. B.
2010, 273, 229-235.
Chem., 2012, 22, 19190-19195; (b) D. P. Dubal, D. S.
12  O. Marin-Flores, L. Scudiero and S. Ha, Surf. Sci., 2009, 603,
2327-2332.
13  L. Ovari, S. K. Calderon, Y. Lykhach, J. Libuda, A. Erdohelyi,
C. Papp, J. Kiss and H. P. Steinruck, J. Catal., 2013, 307,
132-139.
1990, 45, 2639-2646; (b) T. Y. Park, I. Nam and Y. G. Kim,
16  (a) G. Z. Bian, Y. L. Fu and Y. S. Ma, Catal. Today, 1999, 51,
187-193; (b) M. L. Xiang, D. B. Li, W. H. Li, B. Zhong and Y H.
Graphical Abstract

Three effective strategies were combined to develop a Mo-based catalyst for higher alcohol synthesis. The catalyst had good synergies between different active sites with different functionality. Benefited from this, the catalyst exhibited a very high selectivity for C$_2$+ alcohol formation.