Supplementary Material

# A highly efficient Li-Cu/$MoO_x$ catalyst constructed by a precursor dispersion and alkali metal promotion stepwise regulation strategy for $CO_2$ hydrogenation to methanol reaction

Bin Kang[a], Yichi Zhang[a], Jian Sun[a], Hui Yang[a], Yue Su*[,b], Haiquan Su*[,a]

[a]Inner Mongolia Key Laboratory of Chemistry and Physics of Rare Earth Materials, School of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China

[b]School of Ecology and Environment, Inner Mongolia University, Hohhot 010021, China

E-mail addresses: haiquansu@imu.edu.cn (H. Su)

suyue@imu.edu.cn (Y. Su)

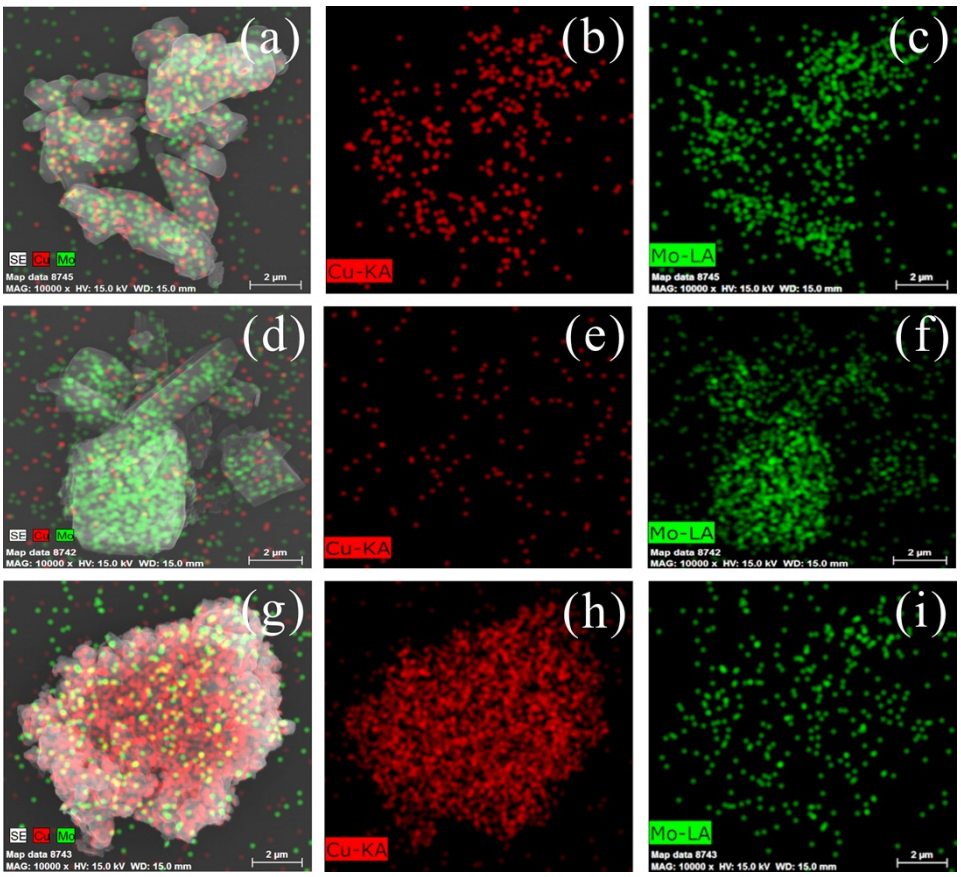


**Figure S1:** Mapping results of the Cu/$MoO_x$-spent (a-c) and Cu/$MoO_x$-mix-spent (d-i)

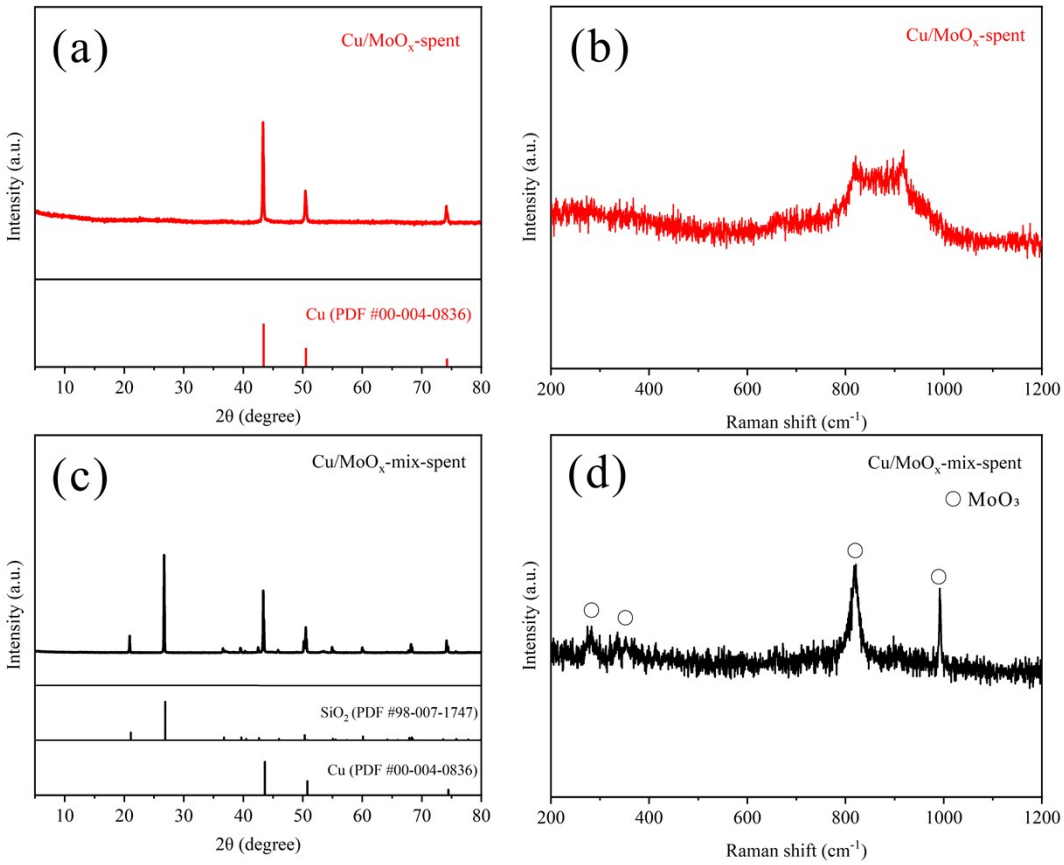


**Figure S2:** XRD patterns and Raman spectra of the Cu/MoO$_x$-spent (a, b) and Cu/MoO$_x$-mix-spent (c, d).

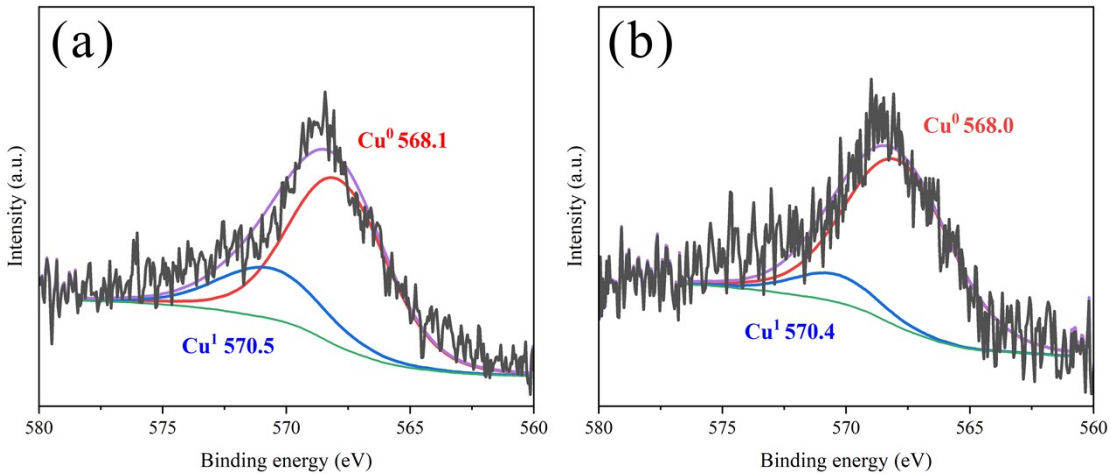


**Figure S3:** Cu LMM Auger spectrum of Cu/$MoO_x$-mix (a) and Cu/$MoO_x$ (b)

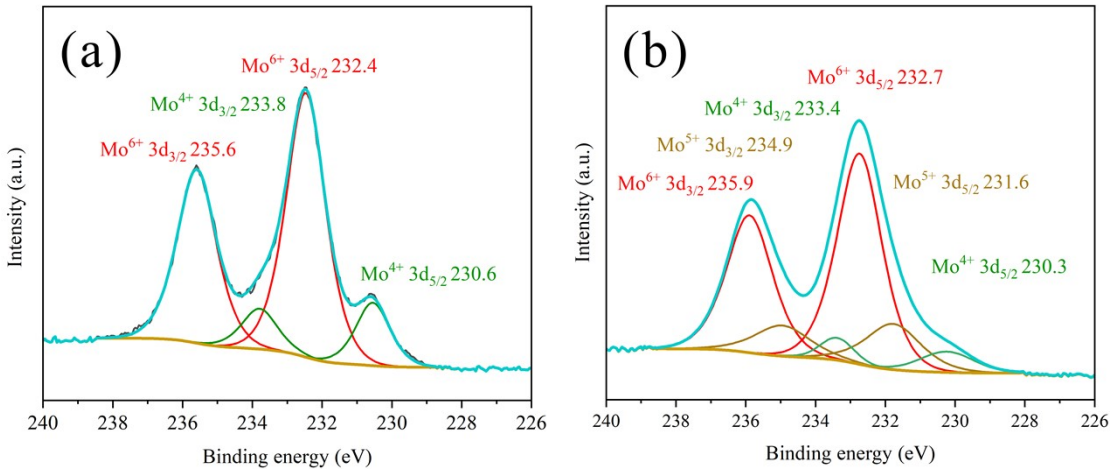


**Figure S4:** XPS spectra of Cu/$MoO_x$-spent (a) and Cu/$MoO_x$-mix-spent (b)

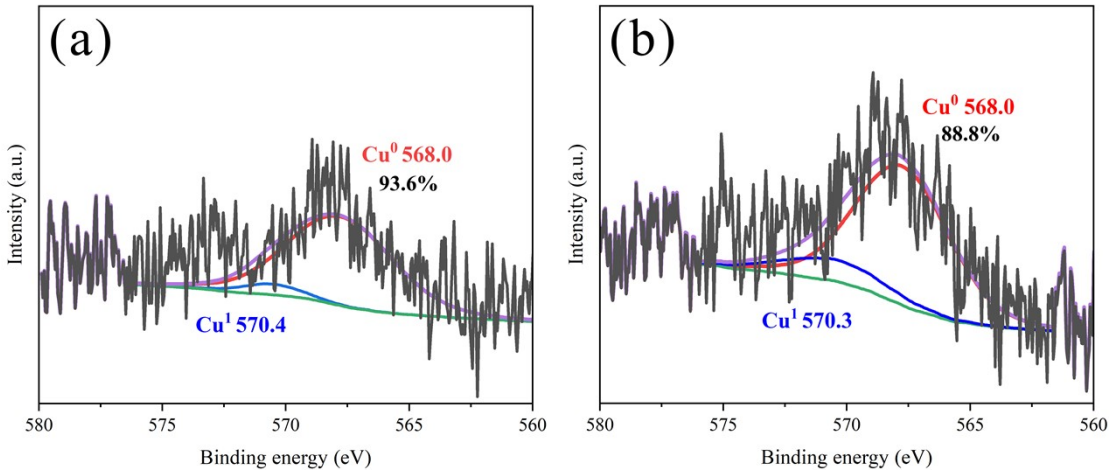


**Figure S5:** Cu LMM Auger spectrum of Cu/$MoO_x$-spent (a) and Li-Cu/$MoO_x$-spent (b)

**Table S1:** XPS data of Mo 3d for $Cu/MoO_x$-mix and $Cu/MoO_x$.

| Samples | $Mo^{6+}$ | | | $Mo^{5+}$ | | | $Mo^{4+}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $3d_{5/2}$ (eV) | $3d_{3/2}$ (eV) | Percentage (%) | $3d_{5/2}$ (eV) | $3d_{3/2}$ (eV) | Percentage (%) | $3d_{5/2}$ (eV) | $3d_{3/2}$ (eV) | Percentage (%) |
| $Cu/MoO_x$-mix | 232.8 | 235.9 | 84.5 | 231.5 | 234.6 | 15.5 | - | - | - |
| $Cu/MoO_x$ | 232.2 | 235.3 | 84.8 | - | - | - | 230.4 | 233.6 | 15.3 |

**Table S2:** Summary of Cu-based catalysts for $CO_2$ hydrogenation to methanol

| Catalysts | T (°C) | P (Mpa) | Space velocity ($h^{-1}$) | $X_{CO_2}$(%) | $S_{MeOH}$ (%) | Reference |
|---|---|---|---|---|---|---|
| Cu/ZnO | 180 | 2 | 9600 | 5 | 98 | 1 |
| $Cu/ZrO_2$ | 260 | 8 | 3600 | 15 | 86 | 2 |
| $Cu/CeO_2$ | 280 | 3 | 10000 | 10 | 74 | 3 |
| $Cu/SiO_2$ | 190 | 3 | 2040 | 5 | 79 | 4 |
| $Cu/Mo_2CT_x/SiO_2$ | 230 | 2.5 | / | 3 | 52 | 5 |
| $Cu/ZnO/ZrO_2$ | 270 | 5 | 4600 | 15 | 66 | 6 |
| $Cu/ZnO/Al_2O_3$ | 206 | 2 | 6000 | 11 | 75 | 7 |
| $Cu\text{-}Mo_2C$ | 150 | 2 | 7200 | 5 | 70 | 8 |
| $Cu/ZnO/Al_2O_3$ | 280 | 44.2 | 10000 | 90 | 95 | 9 |
| $Cu/ZnO/Al_2O_3/ZrO_2$ | 190 | 5 | / | 11 | 82 | 10 |
| $La_2CuO_4$ | 250 | 5 | 3600 | 9 | 65 | 11 |
| **Li-Cu/$MoO_x$** | **260** | **5** | **3000** | **13.4** | **88.8** | **this work** |

**Table S3:** Cu dispersion degree of the fresh catalysts and spent catalysts

| Samples | $d(Cu^0)$[a] (nm) | D (%)[b] |
|---|---|---|
| $Cu/MoO_x$-mix (fresh) | 70 | 1.43 |
| $Cu/MoO_x$-mix (spent) | 97 | 1.03 |
| $Cu/MoO_x$ (fresh) | 27 | 3.70 |
| $Cu/MoO_x$ (spent) | 60 | 1.67 |
| Li-$Cu/MoO_x$ (spent) | 37 | 2.70 |

[a] $d(Cu^0)$ was calculated from Scherrer's equation based on X-ray diffraction data.

[b] Cu dispersion degree: $D = 100/d(Cu^0)$, using the formula from the literature[12].

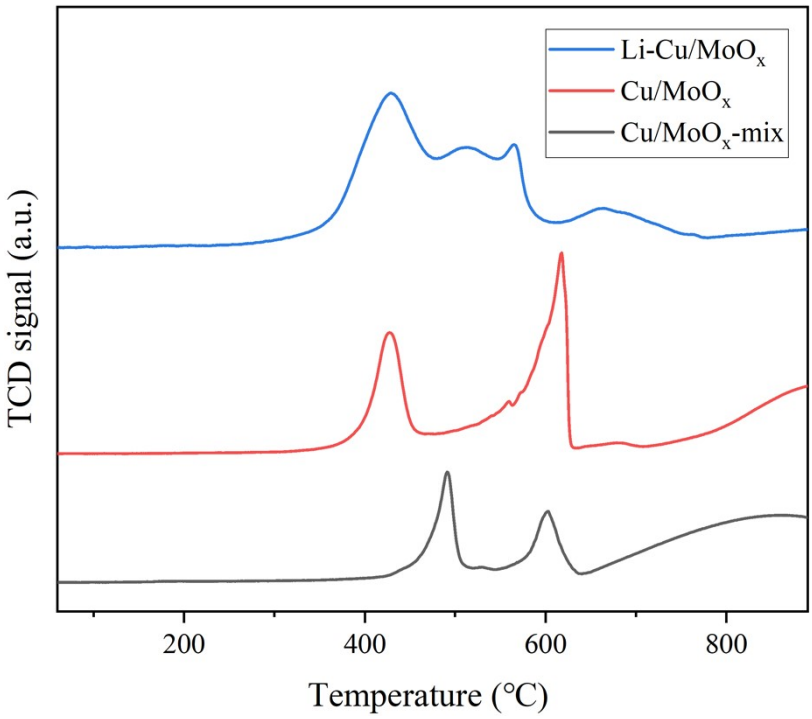


**Figure S6:** $H_2$-TPR profiles of Li-Cu/$MoO_x$, Cu/$MoO_x$ and Cu/$MoO_x$-mix

## References


1. T. Witoon, T. Permsirivanich, W. Donphai, A. Jaree and M. Chareonpanich, *Journal of Energy Chemistry*, 2013, **116**, 72-78.

2. K. Samson, M. Liwa, R. P. Socha, K. Góra-Marek and J. Soczyński, *ACS Catalysis*, 2016, **4**, 3730-3741.

3. W. Wang, Z. Qu, L. Song and Q. Fu, *Journal of Energy Chemistry*, 2019.

4. J. Yu, M. Yang, J. Zhang, Q. Ge, A. Zimina, T. Pruessmann, L. Zheng, J.-D. Grunwaldt and J. Sun, *ACS Catalysis*, 2020, **10**, 14694-14706.

5. H. Zhou, Z. Chen, A. V. López, E. D. López, E. Lam, A. Tsoukalou, E. Willinger, D. A. Kuznetsov, D. Mance and A. Kierzkowska, *Nature Catalysis*, 2021, **4**, 860-871.

6. D. Xiaosu, Z. Ning, L. Feng, X. Fukui and T. Yisheng, *Applied Catalysis B Environmental*, 2016, **191**, 8-17.

7. F. Gallucci, L. Paturzo and A. Basile, *Chemical Engineering&Processing: Process Intensification*, 2004, **43**, 1029-1036.

8. A. B. Dongil, Q. Zhang, L. Pastor-Pérez, T. Ramírez-Reina, A. Guerrero-Ruiz and I. Rodríguez-Ramos, *Catalysts*, 2020, **10**, 1213.

9. R. Gaikwad, A. Bansode and A. Urakawa, *Journal of catalysis*, 2016, **343**, 127-132. 10. S. Xiao, Y. Zhang, P. Gao, L. Zhong, X. Li, Z. Zhang, H. Wang, W. Wei and Y. Sun, *Catalysis Today*, 2017, **281**, 327-336.

10. S. Xiao, Y. Zhang, P. Gao, L. Zhong, X. Li, Z. Zhang, H. Wang, W. Wei and Y. Sun, *Catalysis Today*, 2017, **281**, 327-336

11. H. Zhan, F. Li, P. Gao, N. Zhao, F. Xiao, W. Wei, L. Zhong and Y. Sun, *Journal of power sources*, 2014, **251**, 113-121.

12. Zhenle, Yuan, and, Lina, Wang, and, Junhua, Wang, and and Shuixin, *Applied Catalysis B Environmental*, 2011.