

## Electronic Supplementary Material

### Modified iron-molybdate catalysts with various metal oxides by a mechanochemical method: enhanced formaldehyde yield in methanol partial oxidation

Xue Liu, Lingtao Kong (✉), Shengtao Xu, Chaofan Liu, Fengyun Ma (✉)

Key Laboratory of Coal Clean Conversion & Chemical Engineering Process of Xinjiang Uyghur Autonomous Region, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China

E-mails: [lingtao\\_kong@hotmail.com](mailto:lingtao_kong@hotmail.com) (Kong L); [ma\\_fy@126.com](mailto:ma_fy@126.com) (Ma F)

Table S1 EDS analysis of Fe-Mo catalysts with metal oxide modification

Sample	Mo/Fe	O/Mo	Me/Mo	$T_{Me/Mo}$
Fe-Mo	3.01	5.72	0.00	0.00
Fe-Mo-Bi	2.31	4.43	0.03	
Fe-Mo-Co	2.68	4.71	0.06	
Fe-Mo-Ni	3.43	5.78	0.07	0.05
Fe-Mo-Al	2.44	4.84	0.13	
Fe-Mo-Kaolin	2.08	4.88	0.09	

Surface element distributions of Fe-Mo catalysts doped with different metal oxides are listed in Table S1. The theoretical mole ratio of Me/Mo is 0.05, and the experiment values for all Fe-Mo catalysts are within the range of 0.03~0.13. In addition, the mole ratios of Mo/Fe for all samples are within the range of 2.08~3.43. It is noted that the metal oxide modification could change the distribution of  $\text{MoO}_3$  and  $\text{Fe}_2(\text{MoO}_4)_3$  from the surface. Moreover, the experimental Mo/Fe mole ratio of

Fe-Mo-Kaolin (2.08) is clearly lower than that from the reference sample and theoretical value, which could have an influence on the catalytic performance in methanol to HCHO.

Table S2 Texture data of Fe-Mo catalysts with metal oxide modification

Sample	BET m <sup>2</sup> /g	total pore volume cm <sup>3</sup> /g	Pore Size /nm
Fe-Mo	6.957	0.0519	29.86
Fe-Mo-Bi	3.277	0.0184	22.52
Fe-Mo-Co	7.222	0.0548	30.35
Fe-Mo-Ni	8.576	0.0626	29.19
Fe-Mo-Al	10.01	0.0625	24.99
Fe-Mo-Kaolin	6.114	0.0506	30.02

N<sub>2</sub> adsorption result of Fe-Mo catalysts with different metal oxides modification are presented in [Table S2](#). The specific surface areas for all metal-modified samples are within the range of 3~10m<sup>2</sup>/g, which have no obvious difference compared with the reference sample. Moreover, the total pore volumes and pore sizes for all metal-modified samples also show slight change.

Table S3 Texture data of Fe-Mo catalysts modified by different Co/Mo mole ratios

Sample	Specific surface m <sup>2</sup> /g	total pore volume cm <sup>3</sup> /g	Pore Size /nm
S-0.00	6.96	0.050	29.86
S-0.01	5.43	0.047	34.33
S-0.03	6.28	0.046	27.33
S-0.05	7.22	0.055	29.47
S-0.07	6.00	0.044	28.41
S-0.11	6.86	0.046	25.66

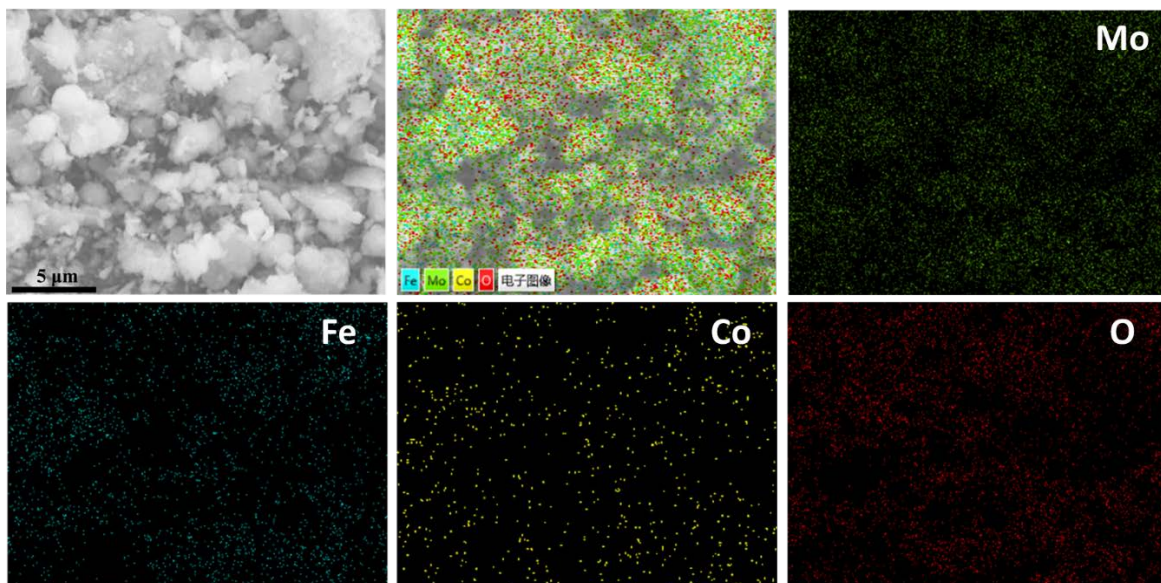


Figure S1 SEM-EDS Mapping of Fe-Mo catalyst modified with  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (S-0.05)

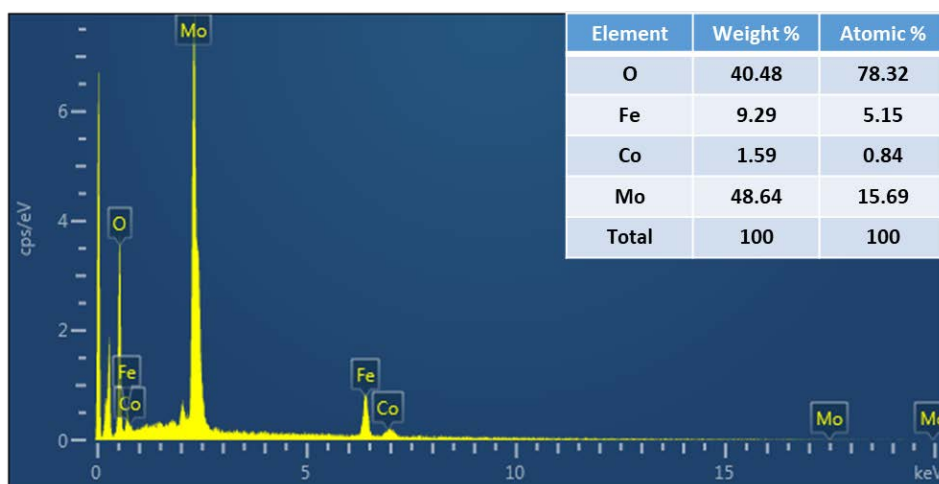


Figure S2 Element content distribution for S-0.05 based on SEM-EDS Mapping

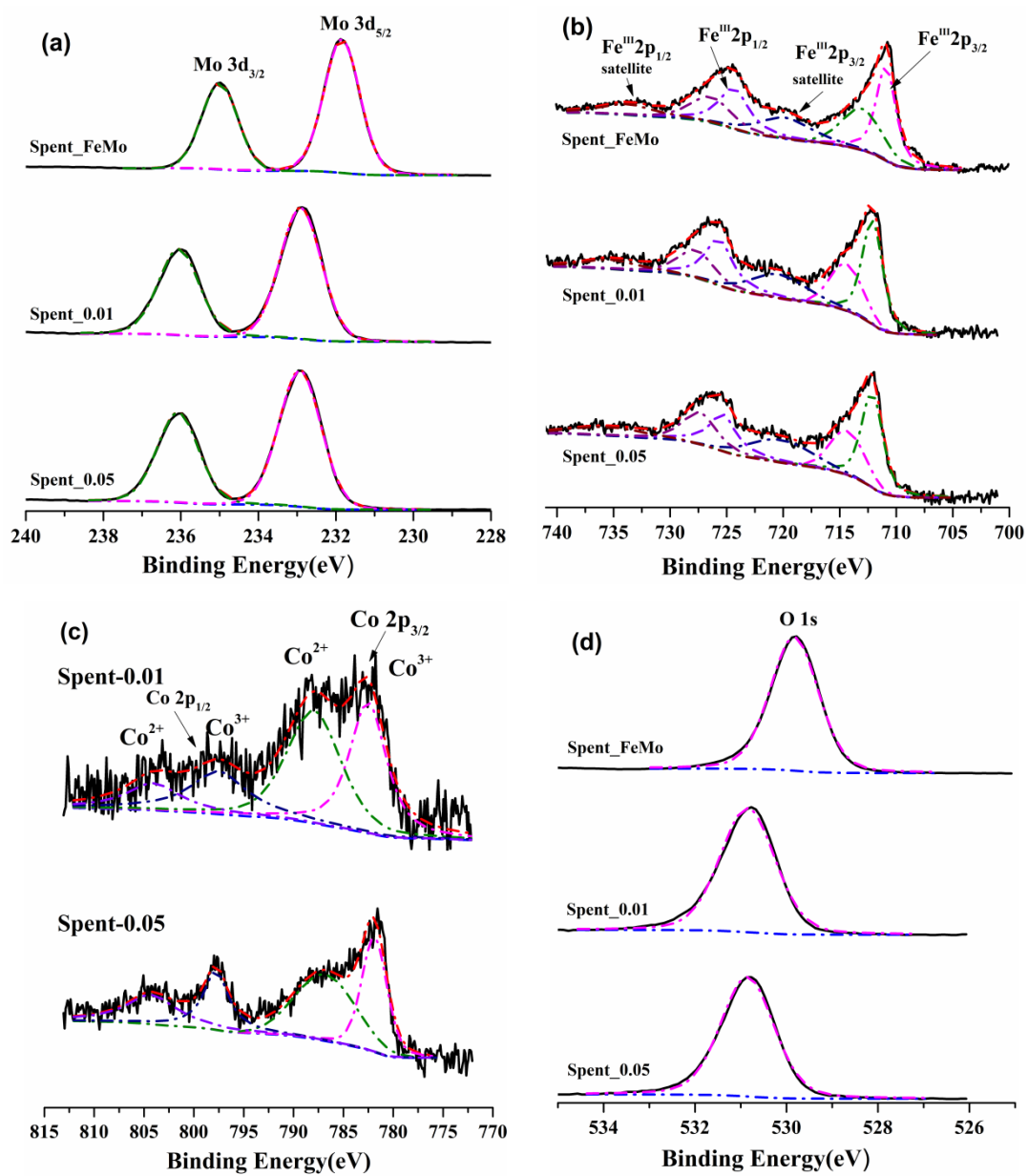


Figure S3 XPS results of the spent Fe-Mo catalysts modified with cobalt oxides