

Supporting Information

Remarkable enhancement to the catalytic performance of molybdenum sulfide catalysts via in situ decomposition method for higher alcohols synthesis from syngas

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1. Syntheses

1.1 Synthesis of K-MoS₂-E(330) and K-Ni-MoS₂-E(330)

K-MoS₂-E(330) and K-Ni-MoS₂-E(330) catalysts (K/Mo molar ratio = 0.7:1) were prepared by *ex situ* method. A typical procedure was as follows: Firstly, MoS₂ was obtained by thermal decomposition of the (NH₄)₂MoS₄ at a temperature rate of 5 °C/min to 330°C and holding for 1 h under argon atmosphere. Ni-MoS₂ catalyst precursor was formed by mechanically mixed (NH₄)₂MoS₄ with Ni(CH₃COO)₂·4H₂O (Ni/Mo molar ratio = 1:3) in a mortar and pestle in ether for 1h, the resulting mixture was dried. The decomposition procedure of Ni-MoS₂ catalyst precursor was the same as MoS₂. Then, K-MoS₂-E and K-Ni-MoS₂-E catalysts were prepared by grinding K₂CO₃ together with MoS₂ or Ni-MoS₂ catalyst precursor in a mortar and pestle, respectively.

1.2 Synthesis of MoS₂-I

(NH₄)₂MoS₄ was decomposed *in situ* by syngas at 10MPa pressure with WHSV of 3000 h⁻¹ and 330 °C for 12 h, which was labeled as MoS₂-I.

2. Characterization

X-ray photoelectron spectroscopy analysis (XPS) was performed using an XSAM800 XPS spectrometer, operated at 12 kV and 15 mA with monochromatic Al K α radiation (1486.6 eV), and the binding energies (BE) were corrected taking C 1s (284.8 eV) as reference.

3. XPS analysis

To further verify the formation of K₂SO₄ by the oxidation of K-Mo-S phase at air, XPS was applied to characterize the chemical bonding structures and the results were shown in Table S1 and Table S2. Moreover, the analysis results decomposed using an iterative least squares computer program, XPSPEAK version 4.1.¹ The MoS₂ and MoS₂-I samples without K additive treated at 330°C in the syngas were detected as reference to elucidate the existence of K-Mo-S phase and the formation of sulfate by the oxidation of K-Mo-S phase. MoS₂ sample exhibited only two characteristic peaks at 229.5 and 232.6 eV, representing the Mo 3d 5/2 and Mo 3d 3/2 binding energies for Mo⁴⁺.²

For K-MoS₂-E catalyst, the Mo 3d peak indicated the presence of more than one molybdenum states in the comparison to the MoS₂ sample.³ The decomposition of Mo 3d exhibited six characteristic, the binding energies of Mo 3d doublet peak at 229.3 eV was assigned to disulfide MoS₂ (Mo⁴⁺), Molybdenum can exist as a Mo oxide phase (Mo⁶⁺), which is located at 232.9 eV (Mo 3d5/2) and 236.0 eV (Mo 3d3/2),^{1,4} suggesting that the existence K active phase (K-Mo-S) compared to MoS₂ sample without K, and it was more easily oxidized forming Mo oxide phase by exposing air after reaction. Previous researchers also reported K-Mo-S phase existed on the K-MoS₂ catalyst and the exposure of catalyst to the atmosphere caused the oxidation of its surface.^{5,6} Moreover, a partially oxidized Mo oxysulfide (MoOxSy, Mo⁵⁺) was also observed, which appears at approximately 230.4 eV (Mo 3d5/2).^{1,2} The presence of the peak at 162.1 and 163.2eV was associated to S²⁻, whereas the observation of S 2p 1/2 and 2p 3/2 energies at 170.2 and 169.1 eV was attributed to the formation of sulphate species originated from the oxidation of K-Mo-S phase in air because the S 2p spectra of non-promoted MoS₂ sample showed only the S 2p 1/2 and 2p 3/2 orbitals of divalent sulfide ions (S²⁻).^{1,7}

Similar results were also observed on the K-MoS₂-I catalyst, Mo oxide phase peaks and the sulphate species appearing at 233.0 and 169.4 eV have been seen in Table S2. However, these peaks were not detected on the MoS₂-I sample, demonstrating that K promoter caused the appearance of oxide phase peaks. Moreover, K₂SO₄ phase was a hydrocarbon chain-growth phase and an inactive phase for alcohol,^{7,8} the catalytic activity of K-MoS₂-E and K-MoS₂-I have no obviously decline during reaction, indicating that K₂SO₄ phase was not formed during reaction. Thus, the oxidation of K-Mo-S phase led to the formation of K₂SO₄ phase after reaction at air.

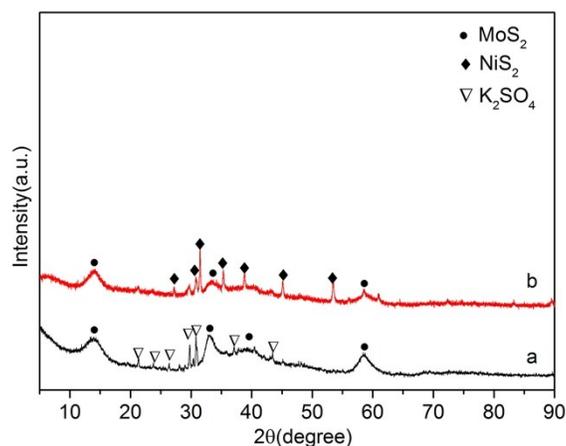
Table S1. XPS parameters of the different contributions of Mo3d obtained for the molybdenum sulfide catalysts.

catalyst	Mo ^{IV} (ev)		Mo ^V (ev)		Mo ^{VI} (ev)	
	Mo 3d5/2	Mo 3d3/2	Mo 3d5/2	Mo 3d3/2	Mo 3d5/2	Mo 3d3/2
MoS ₂	229.5	232.6				
MoS ₂ -I	229.3	232.4				
K-MoS ₂ -E	229.3	232.4	230.4	233.5	232.9	236.0
K-MoS ₂ -I	229.2	232.3	230.8	233.9	233.0	236.1

Table S2. XPS parameters of the different contributions of S 2p obtained for the molybdenum sulfide catalysts.

catalyst	S ²⁻		S ₂ ²⁻		sulfate	
	S 2p 3/2	S 2p 1/2	S 2p 3/2	S 2p 1/2	S 2p 3/2	S 2p 1/2
MoS ₂	162.4	163.5				
MoS ₂ -I	162.3	163.4				
K-MoS ₂ -E	162.1	163.2	163.4	164.5	169.1	170.2
K-MoS ₂ -I	161.9	163.0	163.1	164.2	169.4	170.5

4. PXRD analysis

**Fig. S1** PXRD patterns of the spent catalysts: (a) K-MoS₂-E(330); (b) K-Ni-MoS₂-E(330)

Comparing the PXRD patterns of catalysts prepared by *in situ* method and *ex situ* method calcined at 500°C, we found *in situ* method can produce a lower stacking layers and a much smaller size of (002) basal planes of MoS₂. In fact, calcination temperature influences morphology, crystallite size, surface properties, which are related to the catalytic activity. Thus, in order to eliminate the influence of high temperature calcination procedure on the morphology of K-MoS₂-E and K-Ni-MoS₂-E, which were prepared by *ex situ* method calcined at 330 °C. The PXRD patterns of K-MoS₂-E(330) and K-Ni-MoS₂-E (330) after reaction showed the typical peaks of MoS₂ crystallites in Fig. S1. The reflection peak at 2θ≈14° corresponds to the (0 0 2) basal planes of MoS₂.^{9,10} Obviously, the characteristic reflection peak of the (0 0 2) planes of MoS₂ domains appeared on K-MoS₂-E(330) and K-Ni-MoS₂-E (330) prepared by

ex situ method calcined at 330 °C compared to the catalysts prepared by *in situ* method, indicating that forms relatively larger MoS₂ particle size and better MoS₂ crystallinity.^{11,12} Thus, *ex situ* method was unfavorable for the exposure of active sites.

5. Catalytic performance

Table S3 Catalytic performance of the catalysts for higher alcohols synthesis.

Samples	CO	Selectivity ^a (%)		Alc.STY (mg/g/h)	Product selectivity (%)		
	Conv.%	CH _x	ROH		CH ₃ OH	C ₂ H ₅ OH	C ₂₊ OH
K-MoS ₂ -E(330)	37.1	40.7	59.3	227	24.9	12.3	34.3
K-Ni-MoS ₂ -E(330)	39.3	25.3	74.7	386	23.0	33.2	51.7

To elucidate catalysts prepared by *in situ* decomposition method resulting in increasing the formation of higher alcohols and eliminate the influence factors of high temperature calcination at 500°C on catalytic activity of catalysts. K-MoS₂-E(330) and K-Ni-MoS₂-E(330) were prepared by *ex situ* method, and then the catalytic performance of the K-MoS₂-E(330) and K-Ni-MoS₂-E(330) for higher alcohols synthesis was tested under the conditions of 330°C, 10MPa, WHSV = 3000 h⁻¹ and H₂ to CO molar ratio of 1. The CO conversion, alcohols selectivity and the STY of the total alcohols data were calculated after a stability period of 70h and are shown in Table S3. Through the comparison of the catalytic performance of catalysts prepared by *ex situ* method at 330°C and the catalysts prepared by *in situ* method (K-MoS₂-I, K-Ni-MoS₂-I), it was found that the activities of K-MoS₂-E(330) and K-Ni-MoS₂-E(330) catalysts were slightly higher than that of the catalysts prepared by *ex situ* method calcined at 500 °C, but still far lower than that of the catalysts prepared by *in situ* method. The results indicated that the catalytic activity was not only referred to calcination temperature, but also related to other factors. A possible reason is that promoter could be fast to migrate and redistribute on coordinated unsaturated sites produced under *in situ* condition, thereby decorating the edge sites of MoS₂ domains and forming active phases to increase the catalytic activity.

For K-MoS₂-I, *in situ* method is favourable for producing huge amount of smaller MoS₂ slabs, leading to the exposure of more active sites on the surface of catalysts, thus enhancing the catalytic activity. When Ni promoter was added by *in situ* method, it was found that both catalysts have similar STY, the selectivity of total alcohols and higher alcohols for K-Ni-MoS₂-I catalyst increased respectively by 8% and 18.1%, indicating that *in situ* method played the same role in STY of total alcohols for K-Ni-MoS₂-I, while Ni further improved the selectivity of total alcohols and higher alcohols on the basis of *in situ* method. The main reason was that nickel had an excellent ability for CO insertion and promotion of carbon chain growth.^{13,14} Moreover, previously reported results by several researchers indicated Ni promoter produced smaller crystalized MoS₂ and increase the number of active sites in MoS₂ domains. It was due to that Ni promoter broke MoS₂ slabs and inhibited the growth of MoS₂ slabs along the c-axis direction by the structural modification of Ni promoter.^{13,15,16} Thus, Ni promoter has two aspect functions. First, Ni had an excellent ability for CO insertion and promotion of carbon chain growth. Second, Ni increased the number of active sites in MoS₂ domains by breaking MoS₂ slabs. Based on the above discussion, it is therefore reasonable to consider that *in situ* method played the same role in producing huge amount of smaller MoS₂ slabs and exposing more active sites as Ni promoter by breaking MoS₂ slabs. For K-Ni-MoS₂-E, Ni promoter was added by *ex situ* method, the STY increase more than twice compared with that of K-MoS₂-E without Ni modification due to two major of functions of Ni promoter. However, when Ni promoter was introduced to K-MoS₂-I by *in situ* method, *in situ* method played a prominent role in forming smaller particles and exposing more active sites for the formation of alcohols than Ni promoter, while Ni promoter played a primary role in the ability for CO insertion on the basis of *in situ* method. Therefore, the STY of K-Ni-MoS₂-I has no obvious change compared to K-MoS₂-I.

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