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COMMUNICATION

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The effect of citric acid on the catalytic activity of nano-sized MoS_2 toward sulfur-resistant CO methanation

Zhenhua Li | Zijia Yin | Weihan Wang | Ye Tian | Baowei Wang | Xinbin Ma

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin 300072, China

Correspondence
Li Zhenhua, School of Chemical Engineering and Technology, Tianjin University, 13820514923, China.
Email: lizhenhua001@gmail.com
Xinbin Ma, School of Chemical Engineering and Technology, Tianjin University Tianjin, China
Email: xbma@tju.edu.cn

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In this work, a facile hydrothermal route was used to prepare nano-sized MoS_2 catalyst. The effect of citric acid during the MoS_2 preparation process on the catalytic activity of sulfur-resistant CO methanation was investigated. It was found that citric acid played an adverse role on the catalytic activity of MoS_2 toward sulfur-resistant CO methanation. However, CO methanation performance turned out to be better when $NH_2OH{\cdot}HCl$ as a reductant was removed during the catalyst preparation process. The X-ray diffraction (XRD) and infrared spectroscopy (IR) were performed to discuss the possible mechanism for the effect of citric acid towards CO methanation performance.

KEYWORDS

citric acid, hydrothermal synthesis, molybdenum-citrate complex, MoS_2, sulfur-resistant methanation

1 | INTRODUCTION

Over the past few years, inorganic nanomaterials have drawn much attention because of their functional properties and potential applications, such as electrochemical hydrogen storage,[1] supercapacitor,[2] magnesium batteries[3] and industrial catalysts.[4] Nano-sized transition metal sulfide MoS_2, one of the famous inorganic nanomaterials, was commonly used as catalyst for CO methanation[5] and hydrodesulfurization.[6] In order to improve the activity of MoS_2 catalysts, different synthetic methods have been tried, such as calcination method,[7] thermal decomposing,[8] direct sulfurization,[9] hydrothermal synthesis[10] and so forth.

Among the preparation methods, hydrothermal synthesis was considered as an effective way to prepare nanosized MoS_2 due to its mild synthetic conditions and simple manipulation. In the hydrothermal process, additives were normally introduced in order to obtain MoS_2 particles with better properties. For example, it has been reported that MoS_2 nanomaterials could be obtained by adding silicontungstic acid as an additive.[11] Meanwhile, it was also reported that cetyl trimethyl ammonium bromide (CTAB) could assist hydrothermal process,[12] as well as sodium dodecyl benzene sulfonate.[13] Complexes of metal with citric acid have been reported for a long time.[14] Because of that, citric acid was widely used as an additive.[15] Landschoot,[16] for example, found that the citric acid complex method was an effective way to prepare submicron doped $LiCoVO_4$. Some researchers also reported that citric acid could facilitate the formation of ZnO nanostructure.[17]

In this paper, MoS_2 nanomaterial was synthesized by hydrothermal synthesis route. We chose citric acid as the additive and investigated the effect of citric acid on the catalytic activity of MoS_2 toward sulfur-resistant methanation of syngas. The effect of preparation process on the MoS_2 catalytic activity towards sulfur-resistant methanation of syngas was investigated to understand the structure-activity relationship.

2 | EXPERIMENT

2.1 | Catalyst Preparation

All chemical reagents used were analytic purity without further purification. In a typical synthesis, $Na_2MoO_4{\cdot}2H_2O$ (0.02 mol), $Na_2S{\cdot}9H_2O$ (0.08 mol) and $NH_2OH{\cdot}HCl$ (0.04 mol) were dissolved in distilled water (120 ml). And then citric acid (0.002 mol) was added into the above solution under vigorous stirring. The mixture solution was stirred for 30 min. Meanwhile the pH value was kept at 6 by adding 2 mol/L hydrochloric acid dropwise. The obtained solution was then transferred into a 250 ml Teflon-lined stainless steel autoclave and heated at 220 °C for 24 h. After the autoclave naturally cooling down to room temperature, black precipitates were collected by suction filtration then washed with distilled water and anhydrous ethanol for several times. Finally, the obtained product was dried under vacuum at 60 °C for 10 h. The catalysts can be denoted as Cat-X (X represented the mole ratio of citric acid and Mo element, corresponding to the value of 0, 0.1, 0.5 and 1). The Cat-1 catalyst was renamed as Cat-1-N when the reductant $NH_2OH{\cdot}HCl$ was removed in the catalyst preparation process.

2.2 | Catalyst Characterization

The X-ray diffraction (XRD) patterns were recorded in a RigakuD/max-2500 X-ray diffractometer, using a Ni-filtered Cu-Kα (λ=1.54056 Å) radiation. The scan speed was 8^{o}/min with a scanning angle ranged from 10 to 90^{o}.

IR spectra were obtained on Nicolet6700 FTIR spectrometer with a resolution of 4 cm^{-1} and KBr was used as the wafer. The scan range was from 4000 cm^{-1} to 400 cm^{-1}.

To investigate the morphology of the catalysts, SEM images were obtained by using a field emission scanning electron microscopy instrument (FE-SEM, Nanosem430, FEI).

The high-resolution transmission electron microscopy (HRTEM) was performed using a JEOL JEM-2010F transmission electron microscope. The catalyst powder was ultrasonically dispersed in ethanol, and the testing sample was prepared by dropping the suspension onto a carbon film supported by a Cu grid. Then the sample was transferred to a sample holder attached to the microscope in a stream of N_2.

2.3 | Catalytic evaluation

The catalytic methanation activity of the as-prepared MoS_2 (1 ml) was tested in a continuous flow fixed-bed reactor. Before reaction, the catalyst was sulfurized in situ by a 3% H_2S/H_2 flow at 400 °C for 4 h. The catalytic activity test was performed at 3.0 MPa and 500 °C with (3% H_2S/H_2)/CO ratio as 1, N_2 composition as 20 vol.% and space velocity as 6000 h^{-1}. After water was condensed by a cold trap, the outlet dry gases containing CO, CH_4 and CO_2 were analyzed qualitatively with an online SP3420 GC system equipped with a set of thermal conductive detector (TCD) and a set of flame ionized detector (FID).

The CO methanation performance was represented by the conversion of CO and the selectivity of CH_4, which were calculated according to the following formulas:

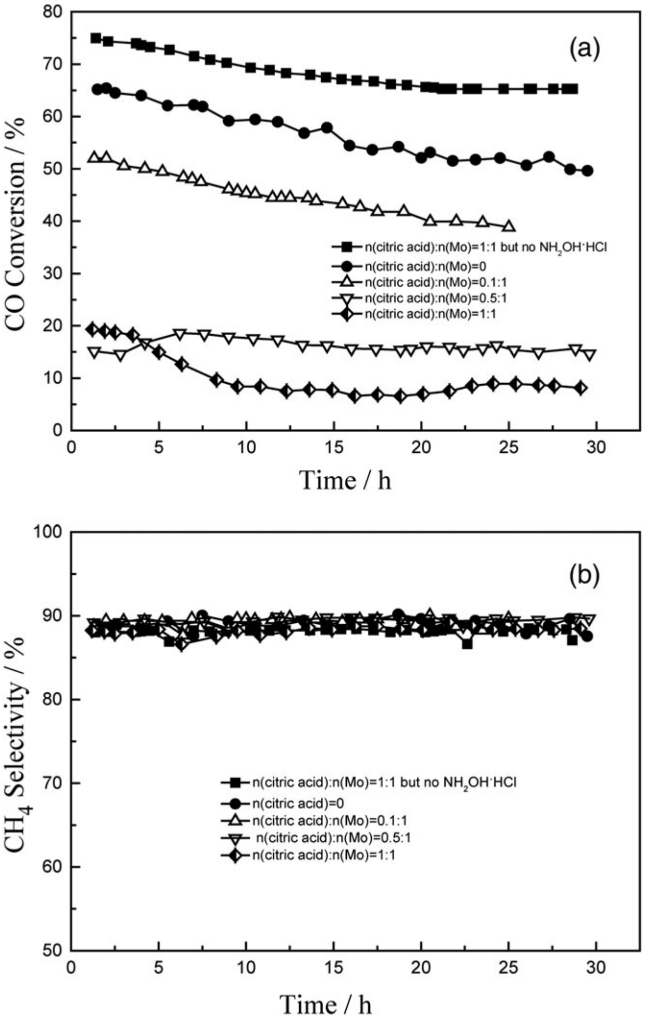

FIGURE 1 Methanation performance on different catalysts (a: CO conversion, b: CH_4selectivity)

$$X_{CO} = \frac{n_{COin} - n_{(CO,out)}}{n_{(CO,in)}} \times 100\%$$

$$S_{CH_4} = \frac{n_{(CH_4,out)}}{n_{(CH_4,out)} + n_{(C_2H_6,out)}} \times 100\%$$

$$S_{C_2H_6} = \frac{n_{(C_2H_6,out)}}{n_{(CH_4,out)} + n_{(C_2H_6,out)}} \times 100\%$$

$$C_B = \left[\frac{1 - n_{(CO_2,out)} + n_{(CO,out)} + n_{(CH_4,out)} + 2n_{(C_2H_6,out)}}{n_{(CO,in)}}\right] \times 100\%$$

Here C_B is the carbon balance after reaction, which is in the range of ±3% for all the tests, proving the credibility of the experimental results.

3 | RESULTS AND DISCUSSION

3.1 | CO methanation performance

The methanation performances of the as-prepared MoS_2 catalysts with different amounts of citric acid were shown in Figure 1. As showed in Figure 1, the effect of citric acid on the catalytic methanation activity was negative when reductant hydroxylamine hydrochloride acid was used. With the increase of citric acid amount, CO conversion of Cat-0.1, Cat-0.5, Cat-1 decreased more greatly. When the mole ratio of citric acid and Mo reached 1, CO conversion of Cat-1 was less than 10% after reaction for 8 h. However, when the reductant hydroxylamine hydrochloride acid was removed, CO conversion of Cat-1-N was higher than the Cat-1 and Cat-0. It suggested that citric acid displayed a positive effect when reductant $NH_2OH{\cdot}HCl$ was removed in catalyst preparation process. To understand this phenomenon, lots of characterizations were carried out to explain the effect of citric acid on the methanation activity in the following section.

3.2 | Characterization results and discussion

Figure 2(a) was the XRD pattern of the Cat-0 sample prepared at 220 °C for 24 h without citric acid added. It could be seen that all peaks were corresponding to the peaks of 2H-MoS_2, which were in good agreement with the standard card values (JCPDS No. 37-1492). No peaks related to other species were detected, indicating that Mo was mainly existed as MoS_2 state in the obtained Cat-0 sample without citric acid added. Meanwhile, the peak of (002) was very sharp and high, indicating that the layered structure of MoS_2 could be well formed with high crystallinity by hydrothermal method. When the citric acid was introduced during the catalyst preparation process, the peaks corresponding to MoO_3 began to appear. Just as shown in Figure 2(b) for Cat-0.5 product, the peaks corresponding to MoS_2 became weak while the peaks corresponding to MoO_3 became more intense. With the amount of

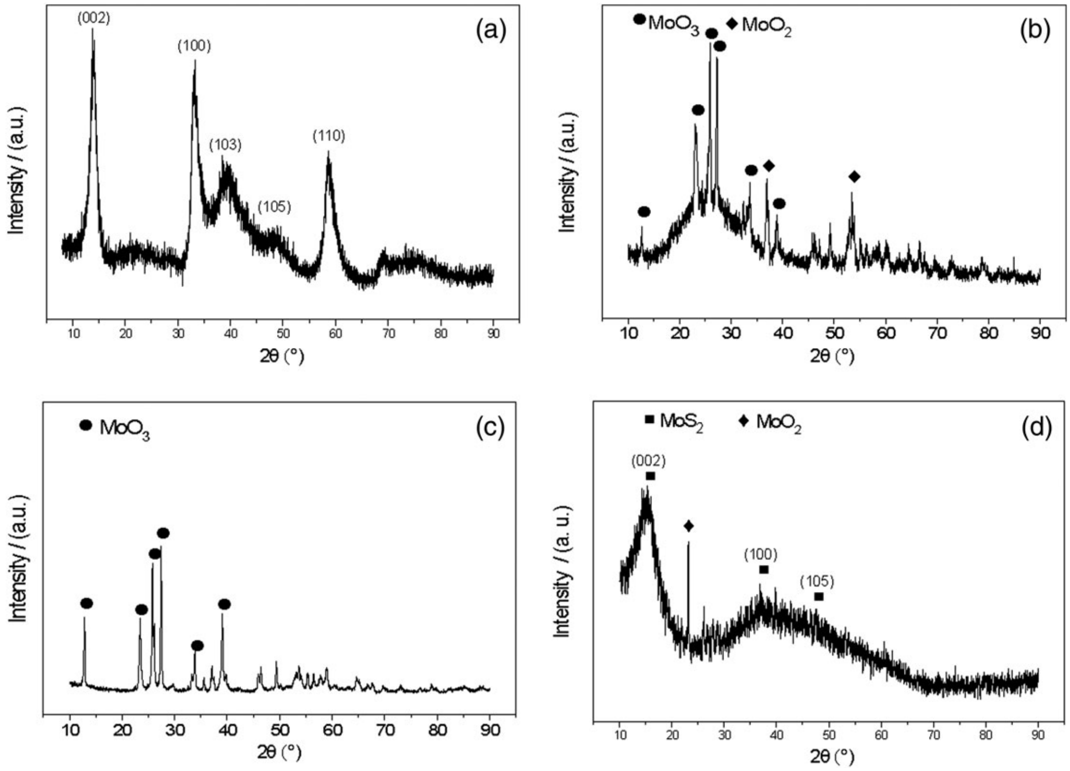

FIGURE 2 XRD patterns of the as-prepared catalysts with different amounts of citric acid added (a: Cat-0, b: Cat-0.5, c: Cat-1, d: Cat-1-N)

citric acid increased, it could be observed that when the mole ratio of citric acid and Mo reached 1, all of the peaks were corresponding to MoO_3. This illustrated that the formed molybdenum-citrate complex[14] did not react with sulfur ion to generate MoS_2 but decomposed into MoO_3 under this condition. The MoO_3 could not be fully sulfurized by H_2S under 400 °C. Since it is generally accepted that MoS_2 is the active site for sulfur-resistant CO methanation process, it is easy to understand why CO methanation activity became worse with the increasement of citric acid content.

In complementary with XRD, Figure 3 showed the FTIR spectra of different catalysts. Just as delivered in Figure 3(a), for Cat-1, the peaks at 988 cm^{-1}, 874 cm^{-1} and 601 cm^{-1} were assigned to Mo=O stretch vibration mode, asymmetric Mo-O bond and Mo-O-Mo bonding vibration mode of MoO_3, respectively.[18] Besides, the absorption at 1635 cm^{-1} was attributed to the asymmetric stretching vibrations of C=O in carboxyl groups ($-COO^-$).[19] No peak at 700-690 cm^{-1} was detected which was considered as anti-symmetric vibrations of the non-linear Mo-O-Mo bridge in dimers,[14] indicating that molybdenum-citrate complex had been decomposed under the hydrothermal condition. The FTIR spectra was in good consistent with the above XRD analysis results.

We speculated that hydroxylamine hydrochloride could inhibit molybdenum-citrate complex from reacting with sulfur ion to form MoS_2 species. Therefore, verification experiment without hydroxylamine hydrochloride added was conducted and the obtained product of Cat-1-N was analyzed by XRD and FTIR spectra. As observed in Figure 2(d), the main peaks were corresponding to the peaks of 2H-MoS_2, which indicated that molybdenum-citrate complex had reacted with sulfur ion under this condition. Sulfur ion substituted the oxygen in Mo=O bond of the molybdenum-citrate complex and the newly generated complex was transformed into MoS_2 under the hydrothermal condition. By comparing the XRD patterns of Cat-0 (Figure 2a) and Cat-1-N (Figure 2d), we found that Cat-0 was well crystallized, while the Cat-1-N had a poorly crystallized structure since peaks for Cat-1-N were weaker and more broadened. In addition, calculating the crystal particle size of MoS_2(002) plane by XRD spectra, we found that it was 5.6 nm and 2.2 nm for Cat-0 and Cat-1-N, respectively. It was widely recognized that a decrease in crystallite size of MoS_2 (002) plane means a deterioration in crystallinity of the catalyst and decreased MoS_2 stacking layers based on the same lattice spacing.[5] So, it could be concluded that Cat-1-N had a lower crystallinity and fewer MoS_2 stacking layers than the Cat-0. The poorly crystallized structure would generate more sulfur vacancies, which were generally considered as the active sites of MoS_2 catalyst.[5,20] Therefore, the Cat-1-N with rich sulfur vacancy structure displayed a better methanation performance. Another proof could be observed in FTIR spectra. As depicted in Figure 3 for Cat-1-N sample, there was no peak at 700-690 cm^{-1} which was assigned to the antisymmetric vibration of non-linear Mo-O-Mo bridge in dimers, indicating that the newly generated sulfur complex had been decomposed to MoS_2.

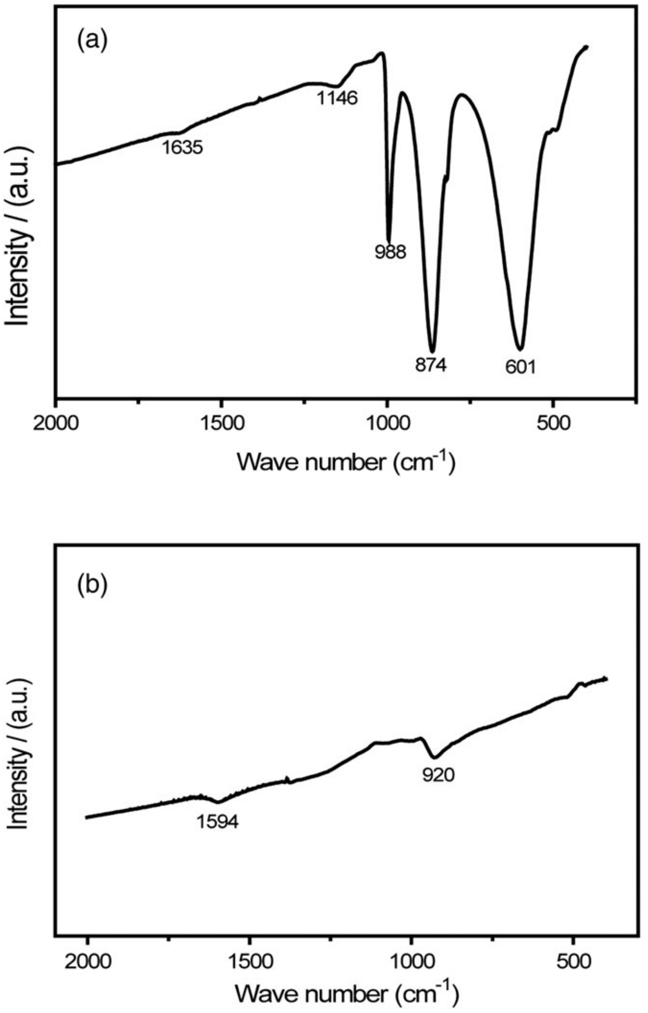

FIGURE 3 FTIR spectra of as-prepared products (a: Cat-1, b: Cat-1-N)

To further investigate the morphology and particle size of the obtained MoS_2 catalyst Cat-1-N, SEM image was also carried out. As shown in Figure 4, the obtained MoS_2 catalyst exhibited uniform MoS_2 cluster structure with the diameter of about 900 nm. The magnified image revealed that the cluster was consist of several nanosheets with the thickness around 20-30 nm.

To better understand the MoS_2 microstructure of Cat-1 and Cat-1-N, HRTEM characterization was also carried out. As shown in Figure 5(a), the as prepared Cat-1-N catalyst had typical multi-layered MoS_2 structure, while in

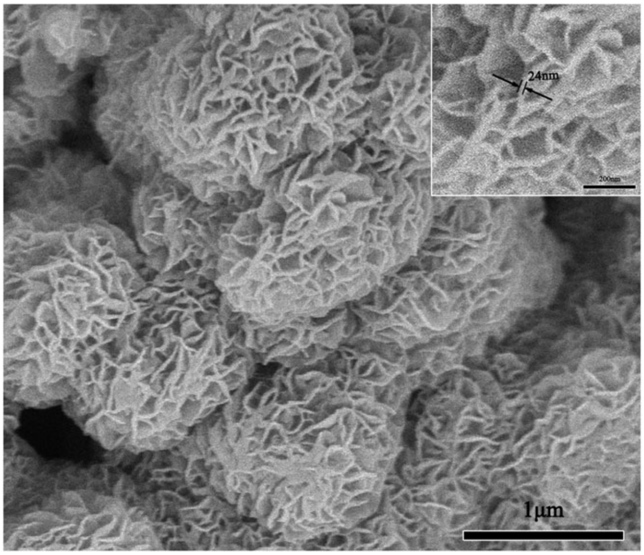

FIGURE 4 The SEM image of the catalyst Cat-1-N

Figure 5(b), the Cat-1 catalyst contained less MoS_2 phase. In addition, MoS_2 fringes of the Cat-1-N catalyst displayed clearly curvature with larger angles, compared to the Cat-1 catalyst with highly straight layered structure. It has been reported that curved nanostructure of MoS_2 catalyst would exhibit a better hydrogenation activity resulting from the formation of defect sites on the curved basal plane.[21] The result of the TEM images well explained why the Cat-1-N displayed best methanation activity, which was also consistent with the XRD and FTIR characterization results.

3.3 | Discussion

Based on the above results and discussions, a reaction network was proposed as described in Figure 6 to further illustrate the reaction process when the citric acid was introduced into the synthesis process. Just as shown in Figure 6, firstly, MoO_4^{2-} would react with citric acid to form molybdenum-citrate complex with the increasement of citric acid content while MoO_4^{2-} without citric acid would generate MoS_2 with good crystallinity to obtain Cat-0. After that, two pathways by adding $NH_2OH{\cdot}HCl$ or not were proposed, which could clearly show the intermediates formation pathways in these two situation. When $NH_2OH{\cdot}HCl$ was used, molybdenum-citrate complex would be prevented to further react with sulfur ion, which led to the decomposition of molybdenum-citrate complex into MoO_3 to obtain Cat-0.1, Cat-0.5, Cat-1 under hydrothermal synthesis. Under such conditions, the detailed synthetic reaction could be formulated as follows:

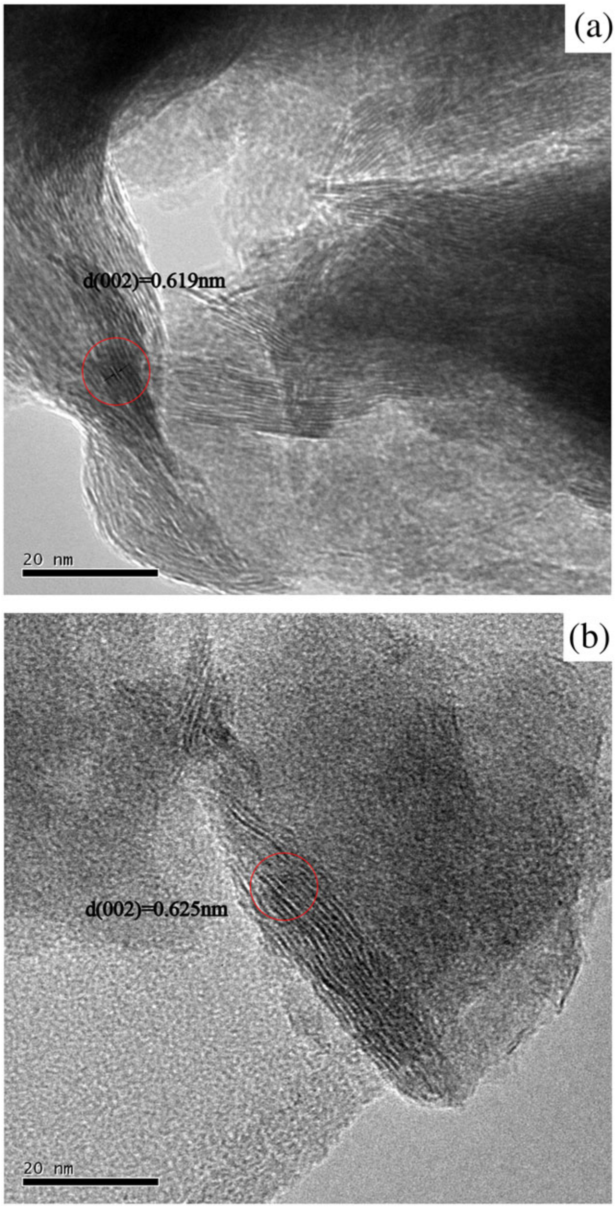

FIGURE 5 The HRTEM images of the catalysts (a: Cat-1-N, b: Cat-1)

$$Na_2MoO_4 + H_4Cit + 2HCl \longrightarrow MoO_2(Cit)OH_2{\cdot}4H + 2NaCl$$
$$MoO_2(Cit)OH_2{\cdot}4H \longrightarrow MoO_3 + H_2O + CO_2$$

When $NH_2OH{\cdot}HCl$ was removed in the preparation process, sulfur ion would more prone to substitute the oxygen in Mo=O bond of the molybdenum-citrate complex to form another new complex, which could be decomposed into MoS_2 with poorly crystallized structure to obtain Cat-1-N. So, in this condition, the reaction process was carried out by another pathway, which could be described as follows:

$$Na_2MoO_4 + 2Na_2S + H_4Cit + 6HCl \longrightarrow MoS_2(Cit)OH_2{\cdot}4H + 6NaCl + 3H_2O$$
$$MoS_2(Cit)OH_2{\cdot}4H \longrightarrow MoS_2 + CO_2 + H_2O$$

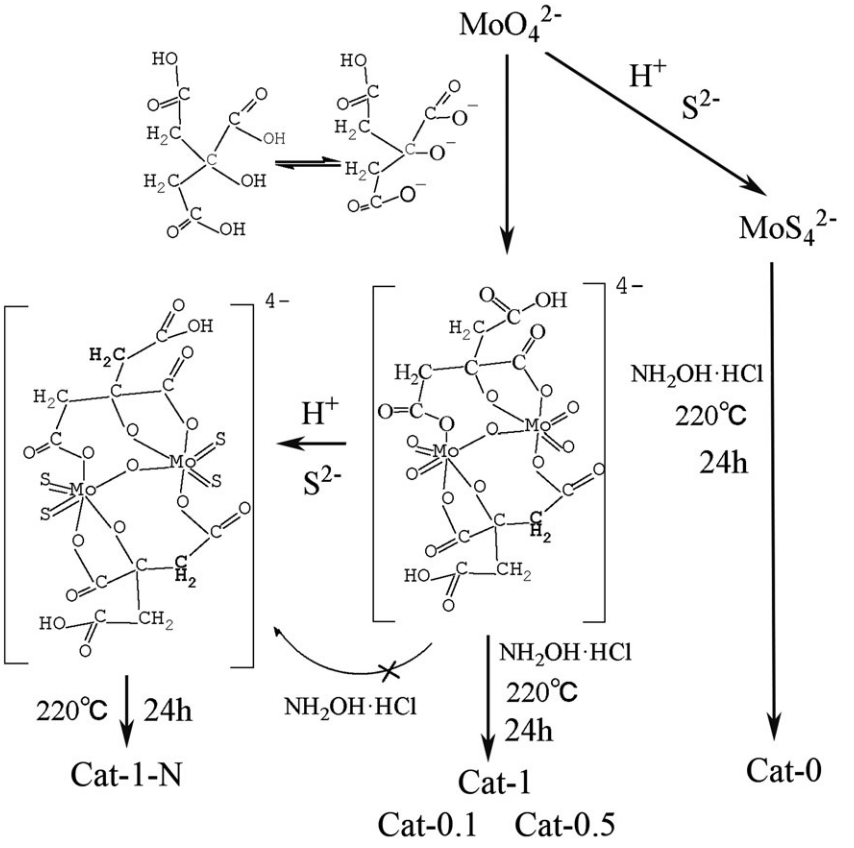

FIGURE 6 The reaction network on different catalysts with or without $NH_2OH·HCl$ added

4 | CONCLUSION

The MoS_2 nanomaterial had be synthesized by a facile hydrothermal route. When citric acid was introduced, the catalytic activity toward sulfur-resistant methanation became worse due to the decomposition of molybdenum-citrate complex into MoO_3. However, when $NH_2OH·HCl$ was removed, citric acid played a positive role on the catalytic activity of MoS_2 toward sulfur-resistant methanation. Characterization results proved that $NH_2OH·HCl$ could effectively inhibited molybdenum-citrate complex to react with sulfur ion to form MoS_2 active phase under hydrothermal synthesis. When there was no $NH_2OH·HCl$ in the preparation process, sulfur ion would substitute the oxygen in Mo=O bond of the molybdenum-citrate complex to form MoS_2 with poorly crystallized structure, which had more sulfur vacancies and exhibited better catalytic activity.

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CONFLICT OF INTEREST

No conflict of interest exits in the submission of this manuscript, and the manuscript is approved by all authors for publication.

ORCID

Zhenhua Li http://orcid.org/0000-0002-4101-2767
Zijia Yin http://orcid.org/0000-0002-7794-8786

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