



# Potassium promotion effects in carbon nanotube supported molybdenum sulfide catalysts for carbon monoxide hydrogenation



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## ABSTRACT

The paper focuses on the effect of potassium promotion on the structure and catalytic performance of carbon nanotube supported molybdenum sulfide catalysts for carbon monoxide hydrogenation. A combination of characterization techniques showed the presence of  $\text{MoO}_2$  and mixed K-Mo oxides in the calcined catalysts. The sulfidation of oxide phases leads to  $\text{MoS}_2$  and K-Mo sulfides.  $\text{MoS}_2$  showed somewhat lower extent of sulfidation compared to other molybdenum oxide species.  $\text{MoS}_2$  was principally responsible for  $\text{CH}_4$  production, while lighter olefins, paraffins, alcohols and higher hydrocarbons were produced on the mixed K-Mo sulfides. The catalyst basicity seems to be one of the important factors controlling the reaction selectivity; moderate basicity is essential for higher rates of olefin and alcohol synthesis.

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## 1. Introduction

The gasification of biomass and coal is considered as one of the most efficient ways to convert the energy embedded in fossil and renewable resources, which could be used as substitutes for oil-based fuels. The syngas produced in the gasification can be then converted to numerous value-added products (methane, olefins, long chain paraffins, methanol, dimethyl ether, higher alcohols, etc.).

Light olefins represent important feedstocks for the petrochemical industry [1,2]. In the industry, olefins are typically obtained by nafta and ethane hydrocracking or via methanol-to-olefins (MTO) synthesis. The hydrocracking suffers from low olefin selectivity, while the catalyst stability is a major challenge in MTO synthesis. Direct conversion of syngas into light olefins via Fischer–Tropsch to olefins (FTO) process is an interesting alternative compared to petroleum cracking [3].

Sulfur is one of the most harmful impurities in syngas which can irreversibly contaminate the catalyst active sites and dramatically reduce the catalyst activity [4]. The works of Professor Bartholomew and his group have provided major insights into the mechanisms of deactivation of metallic Fischer–Tropsch (FT)

catalysts and in particular in the presence of sulfur [5–11]. Design of sulfur resistant catalysts is therefore a major challenge for FT synthesis. In previous reports several sulfur tolerant catalysts have been used for this reaction, such as for example noble metals (Rh [12], Pd [13]) and transition metal sulfides ( $\text{MoS}_2$  [14],  $\text{WS}_2$  [15]).

Molybdenum disulfide ( $\text{MoS}_2$ ) exhibits noticeable activity in carbon monoxide hydrogenation [16–18]. Because of the catalytic properties and excellent resistance to sulfur poisoning, molybdenum disulfide could be a potential candidate for valorization of syngas containing small amounts of sulfur. During the reaction, molybdenum sulfide losses sulfur. Thus the smooth operation of molybdenum sulfide requires the continuous presence of small amounts of sulfur in syngas [19]. The major challenge of molybdenum sulfide catalysts is however, the efficient selectivity control. In fact, the non-promoted  $\text{MoS}_2$  catalysts principally yields methane, [16,19] which is a cheap and often useless reaction product.

Promotion is one of the methods to optimize the selectivity of carbon monoxide hydrogenation on molybdenum sulfide catalysts. Previous reports indicate higher selectivity of potassium-modified  $\text{MoS}_2$ -based catalysts to mixed alcohols at high pressures [20]. The potassium promoted molybdenum sulfide catalysts also exhibit high activity for water–gas shift (WGS) reaction and show significant tolerance to coke deposition [21]. The function of K seems to reduce on one hand, the catalyst hydrogenating ability and hydrocarbon production and on other hand, to favor alcohol formation [22]. In addition to the catalyst composition, the selectivity of

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carbon monoxide hydrogenation of molybdenum sulfide catalysts is also affected by the reaction conditions (pressure, temperature, H<sub>2</sub>/CO ratio). The linear alcohols are produced at 80–90 bar. Small amounts of olefins are also present during CO hydrogenation over molybdenum sulfide catalysts under higher pressure conditions [23]. While a significant number of papers have described alcohol synthesis on molybdenum sulfide catalysts which usually occurs at higher reaction pressures (80–90 bar), very few information is available about the catalytic performance at lower reaction pressures (20 bar) which could be more favorable for olefin synthesis.

The catalytic performance of molybdenum sulfide catalysts can be also affected by the support. The supported catalysts have several advantages compared to the bulk catalysts such as mechanical, thermal and chemical stability. Recently [24] two types of active sites associated to unpromoted molybdenum sulfide and K-Mo-S species were uncovered in alumina supported molybdenum sulfide catalysts. The concentration of these sites varied as a function of potassium content in the catalysts.

The use of carbon nanotubes (CNT) as supports for numerous catalysts has been recently drawing attention, due to their flexibility as support in tailoring the catalyst properties to specific needs [25]. Carbon nanotubes are resistant to acidic or basic media and stable at high temperatures. Moreover, they have several unique features, such as nanosized channels and sp<sup>2</sup>-C-constructed surfaces [26]. They also display exceptionally high mechanical strength, high thermal conductivity, and medium or high specific surface areas. A few previous reports [27–29] suggest that the CNT supported K-MoS<sub>2</sub> based catalysts exhibit a high C<sub>2+</sub> alcohol productivity in carbon monoxide hydrogenation at higher reaction pressures. It is not clear however how the reaction rate and selectivity could be affected by different potassium contents in the catalysts supported by carbon nanotubes.

The present work addresses the design of CNT supported molybdenum sulfide catalysts for synthesis of olefins from syngas. This paper more particularly focusses on the effect of promotion with K on the olefin selectivity over supported molybdenum sulfide catalysts. At different preparation stages, the catalysts were characterized by nitrogen adsorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction of hydrogen (H<sub>2</sub>-TPR) and temperature programmed desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD). The catalytic performance was evaluated in a fixed bed reactor as a function of K promotion. To enhance olefin production, the catalytic experiments were conducted at relatively low total pressure (20 bar) compared to the conditions typically used for alcohol synthesis.

## 2. Experimental

### 2.1. Catalyst preparation

The CNT support (Multi-wall carbon nanotubes, diameter: 20–40 nm, length: 5–15 μm) was provided by Io.Li.Tech (Ion Liquid Technologies, Germany). CNTs were treated with 63% nitric acid before the catalyst synthesis to eliminate impurities. Molybdenum was deposited on the CNT support using incipient wetness impregnation with an aqueous solution of ammonium molybdate tetrahydrate (AMT, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, Sigma-Aldrich), which is a common precursor for MoS<sub>2</sub> based catalysts [30]. The impregnated catalysts were dried at 60 °C for 12 h, then milled mechanically with K<sub>2</sub>CO<sub>3</sub> precursor (Prolabo). Previously, it was found [31] that mechanical mixing of molybdenum sulfide with potassium resulted in better catalytic performance in carbon monoxide hydrogenation. The samples were calcined at 550 °C under nitrogen flow for 2 h. The calcined samples were

then sulfided in a mixture 10 mol% H<sub>2</sub>S in H<sub>2</sub> at a flow rate of 100 ml/min at 400 °C for 2 h. After the sulfidation, the catalysts have been passivated in a flow of 1% O<sub>2</sub> in argon at room temperature. The molybdenum content in the samples was 15 wt.% and potassium content was between 0 and 15 wt.%, respectively. The K/Mo molar ratio varied from 0.25 to 2.5. The catalysts are labelled as xK<sub>y</sub>M/CNT, where x designates potassium content (wt.%) in the catalysts and y stands for molybdenum loading (wt.%).

### 2.2. Characterization

The BET surface area, pore volume, average pore diameter and pore size distribution of the catalysts were determined by N<sub>2</sub> physisorption at –196 °C using a Micromeritics ASAP 2010 apparatus. The pore size distribution curves were calculated from the desorption branches of the isotherms using the BJH method [32].

The ex-situ X-ray Diffraction (XRD) patterns were recorded by a Siemens D5000 diffractometer using a Cu Kα source. The catalysts were scanned from 2θ of 5° to 70° with a scanning rate of 0.02° s<sup>-1</sup>. The diffraction patterns were analyzed by Eva software (Bruker) and matched using the JCPDS database.

The Temperature-Programmed Reduction (TPR) profiles of the sulfated samples were measured using AutoChem II 2920 (Micromeritics) with 10 vol% H<sub>2</sub> diluted in argon stream. The total flow rate was 50 cm<sup>3</sup> min<sup>-1</sup>. The temperature was increased from room temperature to 1100 °C with the ramping rate was 10 °C min<sup>-1</sup>. Then the temperature was kept at 1100 °C for 1 h.

The X-ray Photoelectron spectroscopy (XPS) spectra were recorded with a VG ESCALAB 220 XL spectrometer equipped with a monochromatic Al Kα (E = 1486.6 eV) X-ray source. The binding energies (BE) of Mo 3d, Co 2p, C 1s and S 2p were determined by computer fitting of the measured spectra and referred to the Al 2p peak of the support at 74.6 eV, using Casa XPS software. The binding energies were estimated within ±0.2 eV.

The Temperature Programmed Desorption of carbon dioxide (CO<sub>2</sub>-TPD) was carried out in a quartz reactor connected with a mass spectrometer. The samples were first pre-treated in a flow of helium (40 cm<sup>3</sup>/min) at 400 °C for 1 h then the temperature was lowered to 30 °C. CO<sub>2</sub> was adsorbed on the sulfided samples using a pulse technique (0.49 cm<sup>3</sup> of CO<sub>2</sub>) at 30 °C. The CO<sub>2</sub> desorption was measured during continuous temperature increase (10 °C min<sup>-1</sup>) up to 800 °C.

TEM measurements were performed using a TECNAI microscope operating at a voltage of 200 kV. The sample powder was ultrasonically dispersed in ethanol and deposited on a copper grid prior to the measurements.

### 2.3. Catalytic measurements

The experimental catalytic tests were conducted using a high-pressure milli-fixed bed stainless steel reactor (id = 1.4 mm). The reactor and tubing were coated with Sulflnert® (Restek) to avoid sulfur loss and adsorption in the rig. The feed gas was composed of syngas with H<sub>2</sub>/CO ratio of 2 and contained 14 ppm of H<sub>2</sub>S. Carbon monoxide contained 5% of N<sub>2</sub> (internal standard). The reaction was conducted at 360 °C and 20 bar. The GHSV was 1050 cm<sup>3</sup>/g/h.

The gaseous reaction products were analyzed on-line using a GC-456 Bruker gas chromatograph equipped with a thermal conductivity and a flame ionization detectors. H<sub>2</sub>, N<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub> were separated with a Shincarbon (Resteck®) column and analysed by a TCD detector. C<sub>1</sub> to C<sub>5</sub> hydrocarbons and light alcohols were separated by a Q-Plot (Bruker®) column and measured by FID. The liquid products were collected in an off-line trap and analyzed by the same chromatograph. The selectivity of each product was calculated on carbon basis. The selectivity to hydrocarbons and alcohols takes into account CO<sub>2</sub> production in this reaction.

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