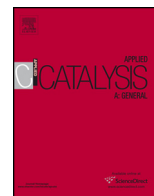




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Impact of potassium content on the structure of molybdenum nanophases in alumina supported catalysts and their performance in carbon monoxide hydrogenation

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ABSTRACT

The paper focuses on the effect of potassium content on the structure of alumina supported molybdenum sulphide catalysts and their performance in carbon monoxide hydrogenation at the conditions favouring olefin production. Molybdenum oxide is a major phase in the unpromoted calcined catalyst. The formation of mixed K–Mo, Mo–Al and K–Mo–Al oxides occurs in the calcined catalysts in the presence of relatively small amounts of potassium. The mixed potassium molybdenum oxides readily convert into mixed molybdenum sulphides after pre-treatment with H₂S. The presence of potassium results in a significant increase in the concentration of basic sites in the sulphided catalyst, while their strength is not much affected by the promotion.

The catalytic results suggest the presence of two types of sites associated to unpromoted molybdenum sulphide and K–Mo–S species. Higher olefin (and alcohol) production rates were observed on the mixed K–Mo sulphides, while carbon monoxide hydrogenation on unpromoted molybdenum sulphide leads to methane. Molybdenum oxysulphide seems not to be relevant to olefin synthesis.

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1. Introduction

The most common method for lignocellulosic biomass thermochemical conversion into liquid fuels involves gasification, which yields biosyngas (mixture of CO and H₂) [1,2]. The produced biosyngas is an important intermediate which can be converted depending on the catalyst and reaction conditions either into hydrocarbons (methane, olefins, long-chain paraffins) or into oxygenates (methanol, dimethyl ether, higher alcohols).

The presence of several impurities is a specificity of biosyngas produced from biomass gasification. Biosyngas usually contains several percents of CO₂ and methane, while tar, alkali, alkaline-earth metals, nitrogen-containing, and sulphur-containing compounds can be present in ppm concentrations. Among the biosyngas impurities sulphur is one of the most harmful elements for the catalysts which irreversibly contaminates active sites and dramatically reduces the catalyst activity [3]. Sulphur is generally present in biosyngas as H₂S with small amounts of COS, methylmercaptan and dimethyl sulphide [4,5]. Thus, there

is a general consensus in the literature that sulphur-containing compounds should be removed from biosyngas for stable process operation [3,6]. Deep desulfurization of biosyngas (to several ppb) is however a very expensive procedure. Design of sulphur-tolerant catalysts could be therefore a solution and is of major interest for converting biosyngas into valuable products.

For more than 50 years sulphides of transition metals have been used in the petroleum industry in hydrodesulfurization, hydrodenitrogenation, and hydrogenation reactions. Molybdenum disulphide (MoS₂) exhibits noticeable activity in carbon monoxide hydrogenation [7–9]. Because of its catalytic properties and excellent resistance to sulphur poisoning, molybdenum disulphide could be a potential candidate for valorisation of biosyngas. Moreover, the presence of sulphur in syngas is often even required for the stable catalyst operation [10]. Extremely low sulphur concentration in syngas could lead to sulphur loss in the catalysts and subsequent deactivation. On the non-promoted MoS₂ catalysts, syngas is mainly transformed to methane [7,10] which is a relatively inexpensive reaction product.

Carbon monoxide hydrogenation involves active sites which are located in the molybdenum sulphide phase. As was recently pointed out by Védérine [11], the structure and properties of the active sites in heterogeneous catalysts are strongly affected by

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electronic effects. Addition of different promoters may therefore lead to the modification of molybdenum sulphide structure, electronic properties and reactivity of active sites. The selectivity of molybdenum disulphide catalysts can be modified using promotion. Alkali metals are the most used promoters. Previous reports indicate higher selectivity of potassium-modified MoS_2 -based catalysts to mixed alcohols at high pressures [12]. Most of the publications describe bulk molybdenum sulphide catalysts, while very few reports have addressed the supported systems. The supported catalysts represent several advantages compared to bulk catalyst such as more efficient use of active phase and better chemical, mechanical and thermal stability. In addition, the support can affect chemical and electronic structures of the active sites and thus the catalytic performance of supported catalysts.

The potassium-promoted molybdenum sulphide catalysts also exhibit high activity for water–gas shift (WGS) reaction and show significant tolerance to coke deposition [13]. The function of K on one hand seems to reduce hydrogenation ability of alkyl species and hydrocarbon production, and on the other hand can favour alcohol formation [14]. Different potassium precursors have been used [15]. Use of potassium chloride [16] and sulphide may introduce acidity to the catalyst and thus, affect the selectivity. In addition to the catalyst composition, the selectivity of carbon monoxide hydrogenation on molybdenum sulphide catalysts is also affected by the reaction conditions (pressure, temperature, H_2/CO ratio). The linear alcohols are produced at 80–90 bar, while hydrocarbons are major products at lower pressures. The mechanism for the formation of higher alcohols (C_2+OH) is believed to be CO insertion [17].

Olefins serve as an important feedstock for the petrochemical industry because they can participate in a wide variety of reactions [18,19]. In the industry, olefins are typically obtained either by steam cracking of oil fractions or by methanol conversion to olefin (MTO) process. In the steam cracking, the olefins are by-side products and the selectivity to specific olefins is rather low. The MTO technology involves a number of technological steps which reduce the overall conversion efficiency. In addition, the catalyst undergoes noticeable deactivation. As a result, the produced olefins get rather costly.

High temperature Fischer–Tropsch (FT) synthesis represents a major interest for synthesis of light olefins [20,21]. In FT synthesis, light olefins are produced directly using carbon monoxide hydrogenation without any intermediate steps. Iron catalysts have shown so far the highest olefin productivity in direct FT synthesis; however they are sensitive to the presence of small amounts of sulphur in syngas. While a significant number of papers have described alcohol synthesis on molybdenum sulphide catalysts which usually occurs at higher reaction pressures (80–90 bar), very less information is available about potential use of the MoS_2 catalysts for selective olefin synthesis from syngas.

The present work addresses design of supported molybdenum sulphide catalysts for synthesis of olefins from syngas. This paper more particularly focuses on the effect of potassium content and catalyst activation on the structure of supported molybdenum sulphide catalysts and their performance in carbon monoxide hydrogenation. At different preparation stages, the catalysts were characterised by nitrogen adsorption, X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), temperature programmed reduction of hydrogen (H_2 -TPR) and temperature programmed desorption of CO_2 (CO_2 -TPD). The catalytic performance was evaluated in a fixed bed reactor at different CO conversion levels. To enhance olefin production, the catalytic experiments were conducted at relatively low total pressure (20 bar) compared to the conditions used for alcohol synthesis.

2. Experimental

2.1. Catalyst preparation

The $\gamma\text{-Al}_2\text{O}_3$ support (Puralox SCCA-5/17) was provided by SASOL (Germany). Molybdenum was deposited on the alumina support using incipient wetness impregnation with an aqueous solution of ammonium molybdate tetrahydrate (AMT, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, Sigma–Aldrich), which is a common precursor for MoS_2 -based catalysts [22]. The impregnated catalysts were dried at 60 °C for 12 h, and then milled mechanically with K_2CO_3 precursor (Prolabo). Previously it was found [23] that mechanical mixing of molybdenum sulphide with potassium resulted in better catalytic performance in carbon monoxide hydrogenation. The samples were calcined at 550 °C under air flow for 2 h. The calcined samples were then sulphided in a mixture of 10 mol% H_2S in H_2 at a flow rate of 100 ml/min at 400 °C for 2 h. After the sulphidation, the catalysts have been passivated in a flow of 1% O_2 in argon at room temperature. The molybdenum and potassium contents in the samples were between 6 and 15 wt.% and between 0 and 24 wt.% respectively. The K/Mo molar ratio varied from 0.5 to 4. The catalysts are labelled as $x\text{KyMo}/\text{Al}_2\text{O}_3$, where x designates potassium content (wt.%) in the catalysts and y stands for molybdenum loading (wt.%).

2.2. Characterisation

The BET surface area, pore volume, average pore diameter and pore size distribution of the catalysts were determined by N_2 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 BJH method [24]. The ex situ X-ray diffraction (XRD) patterns were recorded by a Siemens D5000 diffractometer using a Cu $\text{K}\alpha$ source. The catalysts were scanned from 2θ of 5° to 70° with a scanning rate of 0.02°s^{-1} . The diffraction patterns were analysed by Eva software (Bruker) and matched using the JCPDS database.

Temperature-programmed reduction (TPR) profiles of the sulphided samples were carried out in AutoChem II 2920 (Micromeritics) with 10 vol% H_2 diluted in argon stream. The total flow rate is $50 \text{ cm}^3/\text{min}$. The temperature was increased from room temperature to 1100 °C with the ramping rate at $10^\circ \text{C min}^{-1}$. Then the temperature was kept at 1100 °C for 1 h.

X-ray photoelectron spectroscopy (XPS) spectra were recorded with a VG ESCALAB 220 XL spectrometer equipped with a monochromatic Al $\text{K}\alpha$ ($E = 1486.6 \text{ eV}$) 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 $\pm 0.2 \text{ eV}$.

The Raman spectrometry is constituted by a multi-channel Raman spectrometer (Dilor XY800) with a Krypton ion laser (Spectra Physics model Beamlok) which allows varying the wavelength from the ultraviolet to the near infrared fields. The laser wavelength is 532 nm and a filter with $D = 0.6$ is employed. The spectrometer consists of three floors of 800 mm focal length equipped with a holographic grating plan 1800 lines/mm. The radiation is received by the CCD (charge coupled device) detector cooled with liquid nitrogen. The software allows LabSpec acquisition and data processing.

The temperature programmed desorption of carbon dioxide (CO_2 -TPD) was carried out in a quartz reactor connected to a mass spectrometer. The samples were first pre-treated in a flow of helium ($40 \text{ cm}^3/\text{min}$) at 400 °C for 1 h then the temperature was lowered to 30 °C. CO_2 was adsorbed on the sulphided samples using a pulse technique (0.49 cm^3 of CO_2) at 30 °C. The CO_2

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