Higher alcohol synthesis over nickel-modified alkali-doped molybdenum sulfide catalysts prepared by conventional coprecipitation and coprecipitation in microemulsions

Rodrigo Suárez París [a,*], Vicente Montes [b], Magali Boutonnet [a], Sven Järås [a]

[a] KTH—Royal Institute of Technology, School of Chemical Science and Engineering, Department of Chemical Engineering and Technology, Stockholm, Sweden
[b] University of Córdoba, Organic Chemistry Department, Córdoba, Spain

ABSTRACT

Ethanol and higher alcohols are one of the most interesting alternatives to replace fossil fuels in the transportation sector. Nickel-modified alkali-doped molybdenum sulfide is a potential catalyst for the conversion of syngas to mixed alcohols. In this work, K-Ni-MoS$_2$ catalysts were synthetized by coprecipitation in aqueous solution or in microemulsions, followed by alkali doping. The influence of the preparation route in CO hydrogenation was investigated at 91 bar, 340/370 °C and GHSV = 2000–14,000 NmL/h g$_{catalyst}$. The catalysts were also characterized by TGA, ICP, XPS, nitrogen adsorption, XRD, SEM-EDX and TEM. The novel microemulsion catalyst outperformed the conventional one, resulting in higher yields of ethanol and higher alcohols. The higher activity and selectivity was attributed to a higher concentration of promoters on the microemulsion catalyst surface, together with a lower degree of crystallinity.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Environmental concerns and the shortage of fossil fuels have recently increased the search for new energy sources. Second-generation biofuels, including ethanol, are becoming a promising alternative to conventional fuels, while avoiding problems related to food and feed production [1]. Second-generation ethanol can be produced by means of either a biochemical or a thermochemical route. The thermochemical route has a higher flexibility, since a wide variety of feedstocks (e.g. lignocelullosic biomass, waste streams) can be used as raw materials to produce syngas [2]. Syngas is then catalytically converted to ethanol and higher alcohols in the so-called higher alcohol synthesis (HAS). Ethanol can be used not only as a neat fuel or fuel additive, but also as a hydrogen carrier in fuel cells [3]. Higher alcohols also have a great potential as fuel additives [4,5].

No commercial plants applying the aforementioned technology have been implemented yet, since the catalytic systems developed so far suffer from low catalytic activity, poor product distribution or severe reaction conditions [6]. Therefore, the search for a more efficient and cheaper catalyst has become essential to make this process commercially attractive.

Although noble metal catalysts (mainly Rh-based) exhibit high ethanol selectivities, they are unattractive for commercial purposes due to the reduced availability and high cost of the metals [6]. On the other hand, non-noble catalytic systems have been widely studied and they are usually classified into three categories [3,6]: modified methanol catalysts, modified Fischer-Tropsch catalysts and modified molybdenum-based catalysts.

Molybdenum sulfide catalysts are one of the most promising options for HAS due to their sulfur resistance, high water–gas shift activity and slow deactivation by coke deposition [6,7], thus avoiding the need for ultra-desulfurization or water separation units. In addition, they are suitable for processing syngas with low H$_2$/CO ratios, typically obtained when gasifying biomass [8]. Modification with promoters is however essential to enhance the yield of the desired products, one of the main challenges in HAS [3,6,9].

Alkali metals (Li, Na, K, Cs) have proven to shift selectivity from hydrocarbons to alcohols [6]. According to Santiesteban [10], the reaction scheme over alkali-doped molybdenum sulfide catalysts is based on a CO-insertion mechanism. The function of the alkali is to decrease the rate of hydrogenation of alkyl species and increase the rate of CO insertion [11]. Further addition of 3d transition metals (Co, Ni) increases the selectivity to ethanol and higher alcohols [3].

The microemulsion technique appears to be a suitable method to manufacture the catalyst. A microemulsion (ME) is an optically transparent and thermodynamically stable solution which consists of spherical aqueous nanodroplets stabilized by a layer of surfactant molecules [12]. Metal salts can be solubilized inside the aqueous core of the nanodroplets and then precipitated to form particles in nano-sized range and with narrow size distribution [12]. Catalysts prepared using MEs have shown enhanced properties in many applications when compared with conventional catalysts [13].

There are several studies regarding the conversion of syngas over unsupported Ni-modified K-doped molybdenum sulfide catalysts [14–18], but none of them applies the ME technique in the catalyst synthesis. The aim of this work is to develop and study the performance of a novel Ni-modified K-doped molybdenum sulfide catalyst prepared through coprecipitation in MEs and compare it with an analogous catalyst prepared by conventional coprecipitation. Two additional conventional catalysts, promoted only with nickel or potassium, have also been synthetized, characterized and tested, in order to get a better understanding of the individual effect of each promoter and be able to explain the differences between the ME catalyst and the conventional one.

2. Methods

2.1. Catalyst preparation

The bipromoted catalysts, containing both nickel and potassium, were synthetized by coprecipitation and subsequent alkali doping. The conventional catalyst was obtained through coprecipitation in aqueous solution, while the ME catalyst was obtained by mixing two water-in-oil MEs. Detailed information about the catalyst preparation procedures is shown below. The monopromoted catalysts were synthetized using the same procedure as for the conventional catalyst, but excluding the doping step with nickel (K-MoS$_2$) or potassium (Ni-MoS$_2$).

2.1.1. Conventional catalyst

The conventional catalyst (K-Ni-MoS$_2$) was prepared by adding dropwise, under continuous stirring, an aqueous solution of Ni(CH$_3$COO)$_2$·4H$_2$O to an aqueous solution of (NH$_4$)$_2$MoS$_4$. The resulting black precipitate was aged for 24 h and then recovered by centrifugation. The recovered precipitate was first washed with deionized water (*miliQ*) and, subsequently, with a mixture of ethanol and deionized water (mass ratio 1:1). After each wash, the powder was recovered by centrifugation. The washed powder was dried at 50 °C and then crushed and sieved to a pellet size of 45–250 μm. Alkali doping was achieved by mechanically mixing the dried catalyst precursor with K$_2$CO$_3$ (45–250 μm). The final catalyst was obtained after a thermal treatment at 450 °C (ramp: 20 °C/min) for 90 min, under H$_2$ flow. A second sieving was performed to discard particles with a pellet size above 250 μm that could be formed during the heat treatment. The final sample was kept in a tightly closed container before being characterized and tested.

2.1.2. Microemulsion catalyst

Two analogous water-in-oil ME systems were prepared: the first ME (ME1) contained the nickel salt and acetic acid; the second ME (ME2) contained the molybdenum salt. The detailed composition of the systems is shown in Table 1. MEs with similar composition were previously used for catalyst preparation [19–21].

The ME catalyst (ME K-Ni-MoS$_2$) was prepared by adding dropwise, under continuous stirring, ME1 to ME2. The coprecipitation step is illustrated in Fig. 1. The black precipitate was aged for 24 h and then recovered by centrifugation. In order to remove surfactant and hydrocarbon residues, the washing procedure was modified:

Table 1
Composition of the ME systems.

Phase	Compound (s)	Composition (wt%)
Oil	Iso-octane	53
Surfactant	CTAB	15
Co-surfactant	1-Butanol	12
Water	ME1: water, Ni(CH$_3$COO)$_2$·4H$_2$O, acetic acid; ME2: water, (NH$_4$)$_2$MoS$_4$	20

the precipitate was first washed with a mixture of chloroform and methanol (mass ratio 1:1) and, then, twice with methanol. The rest of the preparation procedure is analogous to that used for the conventional catalyst: drying, crushing and sieving, alkali doping and, finally, thermal decomposition under H$_2$ flow. The temperature ramp during the H$_2$ treatment was set to 0.5 °C/min in this case, so as to ensure complete elimination of the catalyst precursor residues not removed during the washing steps.

2.2. Catalyst characterization

A thermogravimetric analysis (TGA) of the non-calcined ME catalyst was performed on a Netzsch STA 449 F3 Jupiter instrument. The sample was subjected to the same temperature program as in the thermal decomposition (0.5 °C/min to 450 °C, held 90 min), under H$_2$ flow. An equivalent test was also carried out on the bipromoted conventional catalyst.

The contents of nickel, potassium and molybdenum in the catalysts were determined using inductively coupled plasma-mass spectroscopy (ICP-MS), following EPA methods 200.7 and 200.8 [22,23].

X-ray photoelectron spectroscopy (XPS) data were recorded on 4 mm × 4 mm pellets, 0.5-mm thick, obtained by gently pressing the powdered materials. Prior to analysis, the pellets were outgassed in the instrument pre-chamber at 150 °C to a pressure below 2 × 10^{-8} Torr, in order to remove chemisorbed volatile species. XPS spectra were recorded on a Leibold-Heraeus LHS10 spectrometer, equipped with an EA-200MCD hemispherical electron analyzer with a dual X-ray source, using Mg Kα (1253.6 eV) at 120 W and 30 mA, with C(1s) as energy reference (284.6 eV).

Nitrogen adsorption measurements were performed in a Micromeritics ASAP2000 unit. The samples were outgassed by evacuation at 250 °C for a minimum of 4 h before being analyzed.
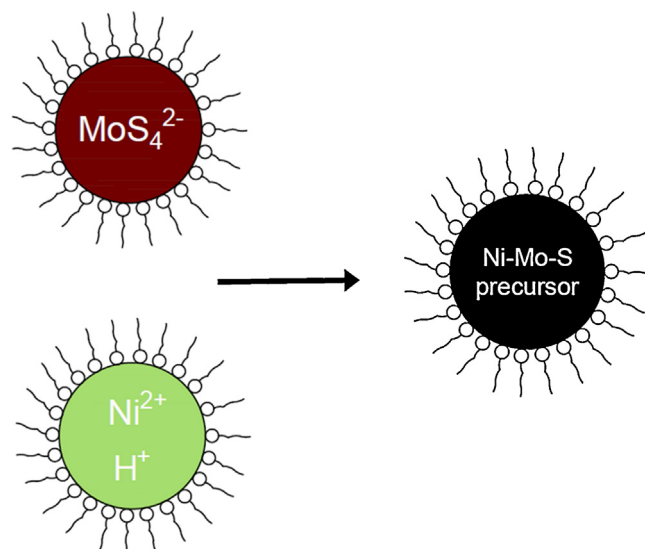

Fig. 1. Coprecipitation in MEs.