Catalysis Communications 67 (2015) 103–107

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Effect of methanol addition on higher alcohol synthesis over modified molybdenum sulfide catalysts

Rodrigo Suárez París *, Magali Boutonnet, Sven Järås

KTH — Royal Institute of Technology, School of Chemical Science and Engineering, Department of Chemical Engineering and Technology, Stockholm, Sweden

ARTICLE INFO

Article history:
Received 5 February 2015
Received in revised form 10 April 2015
Accepted 14 April 2015
Available online 16 April 2015

Keywords:
Syngas
Higher alcohols
K/MoS_2
Nickel
Methanol cofeeding

ABSTRACT

One of the main problems in higher alcohol synthesis is the poor product distribution. Cofeeding of methanol, together with the synthesis gas, has been suggested in order to increase the yield of ethanol and higher alcohols. In this work, the effect of methanol addition on K–MoS_2 and K–Ni–MoS_2 catalysts was studied at 71 bar, 340 °C and GHSV = 6000 N mL/h · $g_{catalyst}$. Under these conditions methanol recycle is not a viable option for boosting higher alcohol production. The main result was an increase in methane yield, while the effect in higher alcohols was negative or not significant.

1. Introduction

Catalytic conversion of carbon monoxide and hydrogen (syngas) to ethanol and/or higher alcohols is an attractive alternative for producing fuels and fuel additives that can partially replace fossil fuels in the transportation sector. Syngas can be produced from coal, natural gas or biomass, which results in a great flexibility [1,2]. Modified molybdenum sulfide catalysts are among the most interesting catalytic systems for higher alcohol synthesis (HAS). In addition to their sulfur resistance, they present high activity for the water–gas shift reaction and the rate of coking is slow [1,3].

The carbon–carbon bond formation to transform C_1 to C_2 species is the rate-determining step in HAS. Therefore, homologation or cofeeding of lower alcohols has been proposed to increase the production of higher alcohols [3,4].

An increased yield of ethanol and higher alcohols upon methanol addition has been reported mainly on Cu/ZnO catalysts [4–6]. Isotope labeling experiments indicate that both methanol and CO are incorporated into the ethanol product [7,8]. However, there is still no full agreement about the effect of methanol addition. Calverley and Smith have shown a decrease in higher alcohol yield when methanol is cofed together with syngas over K_2CO_3/Cu/ZnO/Cr_2O_3 [9].

Regarding modified molybdenum sulfide catalysts, the information is even scarcer. Santiesteban et al. found improved ethanol yields upon injection of methanol, together with an increased production of methyl formate, methyl acetate and, specially, methane [10]. A similar behavior has been reported in a patent from The Dow Chemical Company [11]. However, in the latter case, no information regarding hydrocarbon production is shown.

The aim of this work is to study the effect of cofeeding methanol, in various concentrations, over K–MoS_2 and K–Ni–MoS_2 catalysts. To the authors' knowledge, there is no published information about this effect on nickel-modified alkali-doped molybdenum sulfide catalysts. The operating conditions in the study have been chosen in order to simulate the conditions of an industrial plant [12].

2. Experimental

2.1. Catalyst preparation and characterization

Two unsupported molybdenum-based catalysts were synthetized, containing either one or two promoters. The bipromoted catalyst (K–Ni–MoS_2) was obtained by coprecipitation of $Ni(CH_3COO)_2 \cdot 4H_2O$ and $(NH_4)_2MoS_4$ and further doping with K_2CO_3. The preparation procedure is described in detail in a previous paper by our group [13]. Briefly, the coprecipitation step produced a black precipitate that was aged, washed and recovered by centrifugation. This precursor was then dried, crushed, sieved to a pellet size of 45–250 μm and doped with K_2CO_3 (45–250 μm) through mechanical mixture. The final catalyst was obtained after thermal treatment at 450 °C (ramp: 20 °C/min) for 90 min, under H_2 flow (GHSV = 1200 N mL/h · $g_{catalyst}$). Thereafter, 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 tested.

---

* Corresponding author at: Teknikringen 42, SE-100 44, Stockholm, Sweden.
E-mail address: rosp@kth.se (R. Suárez París).

http://dx.doi.org/10.1016/j.catcom.2015.04.018
1566-7367/

The monopromoted catalyst (K–MoS_2) was synthetized using the same procedure, but excluding the coprecipitation step and thus the doping with nickel.

Detailed catalyst characterization is provided elsewhere, including TGA, ICP, XPS, N_2-adsorption, XRD, SEM–EDX and TEM analyses [13]. In this previous study by our group, it was shown that both materials have a low surface area and contain mainly macropores. A number of key features are presented in Table 1. As shown, the promoters have been successfully incorporated during catalyst preparation.

2.2. Catalytic testing

CO hydrogenation reactions were performed in a high-pressure fixed-bed tubular reactor operating in down-flow mode. Approximately 1.8 g catalyst, diluted with 7.5 g SiC (pellet size: 53–80 μm), was used in the tests. The reactor was heated by an electric furnace and the temperature was regulated by a cascade control, with a sliding thermocouple in the catalyst bed and a second thermocouple in the oven. This control architecture, together with the dilution with SiC and an external aluminum jacket, allowed for a temperature profile along the bed within ±0.5 °C of the set point.

A premixed syngas with H_2/CO ratio = 1 and 4 mol% N_2 as internal standard was used in the experiments. The reaction conditions were: P = 71 bar, T = 340 °C and GHSV = 6000 N mL/h · $g_{catalyst}$. The catalysts were first stabilized, under the aforementioned conditions, to ensure steady-state was reached. The stabilization period varied from about 20 h on stream (K–MoS_2) to 40 h on stream (K–Ni–MoS_2).

After the stabilization period, a He pocket (20 mol%) was introduced in order to keep the syngas partial pressure constant when methanol was cofed. Thereafter, different concentrations of methanol were added by means of a HPLC dosing pump (Gilson 307). The liquid was evaporated before being mixed with the gaseous stream, immediately prior to the reactor. The different conditions used in the study are summarized in Table 2. Note that in between each period of methanol addition a period without methanol cofeeding was run to check for deactivation.

Product analysis was carried out using an on-line GC, equipped with one TCD and two FID detectors. The carbon mass balance closures were typically higher than 98%. More details about the reaction and analysis setup can be found elsewhere [14].

3. Results

3.1. Methanol addition on K–MoS_2

The effect of methanol addition on CO conversion over the monopromoted catalyst is shown in Fig. 1. It should be noted that catalyst activity is fairly constant during the 6 days of operation: after introducing the He pocket, the conversion remains stable around 13% in the periods without methanol cofeeding. Addition of methanol slightly influences the conversion of CO, with values of around 10% for the different concentrations of added methanol.

The transient periods observed in Fig. 1 when changing the conditions (and also in the subsequent Figs. 2–4) might be explained by a combination of different factors: slow change in catalyst performance with time on stream; residence time in the reactor and the subsequent piping to the GC; time between each GC injection (approx. 90 min); and required time to get the desired flow of methanol through the reactor when the pump is started or stopped. All these factors may contribute to a greater or lesser extent to the fluctuations observed after a change in conditions. However, each period was kept for at least 8 h in order to be able to reach a pseudo-steady state.

Table 1
The main physicochemical properties of the tested catalysts.

Catalyst	ICP analysis (mol/mol)		EDX analysis (mol/mol)		XPS analysis (mol/mol)		BET surface area (m^2/g)
	Ni/Mo	K/Mo	Ni/Mo	K/Mo	Ni/Mo	K/Mo	
K–MoS_2	0	1.50	0	1.15	0	5.16	1
K–Ni–MoS_2	0.45	1.19	0.61	1.42	0.05	1.50	3

Table 2
Summary of experimental conditions used in the catalytic tests.

Period	P_{syngas} (bar)	P_{He} (bar)	P_{MeOH} (bar)	He added (mol%)	MeOH added (mol%)
Stabilization	68.2	0	0	0	0
1	54.5	14.2	0	20	0
2	54.5	10.6	3.6	15	5
3	54.5	14.2	0	20	0
4	54.5	7.1	7.1	10	10
5	54.5	14.2	0	20	0
6	54.5	12.4	1.8	17.5	2.5
7	54.5	14.2	0	20	0
8	54.5	13.1	1.1	18.5	1.5
9	54.5	14.2	0	20	0

The changes in alcohol and hydrocarbon space-time yields (STY) are presented in Fig. 2. Unexpectedly, the introduction of methanol in the reactor system does not result in improved yields of alcohols, but decreases the production of both ethanol and 1-propanol. On the other hand, methanol has the opposite effect on hydrocarbon STY. Methanol cofeeding increases their production, this effect being more pronounced with increasing methanol concentration.

A complete product distribution is shown in Table 3, together with CO and net methanol conversions. The presented data represents the average of at least three gas composition measurements at the same reaction conditions and with carbon mass balance closures higher than 98%. The net conversion of methanol is appreciably higher than CO conversion. The selectivity to the different products follows the same trend that was described above for ethanol, 1-propanol, methane and ethane yields. Methanol cofeeding clearly reduces the production of the different alcohols, while increasing hydrocarbon selectivity. Methane comprises up to 65% of the products (C%, CO_2-free basis) upon 10% methanol addition.

3.2. Methanol addition on K–Ni–MoS_2

The incorporation of a second promoter, nickel, on K–MoS_2 changes the previously shown trends, regarding both activity and selectivity. In this case, catalyst activity is also stable throughout the experiment, with values of about 2.5% in the periods without methanol cofeeding (Fig. 3). It has been previously reported that the incorporation of nickel on alkali-doped MoS_2 catalysts, despite increasing the selectivity to

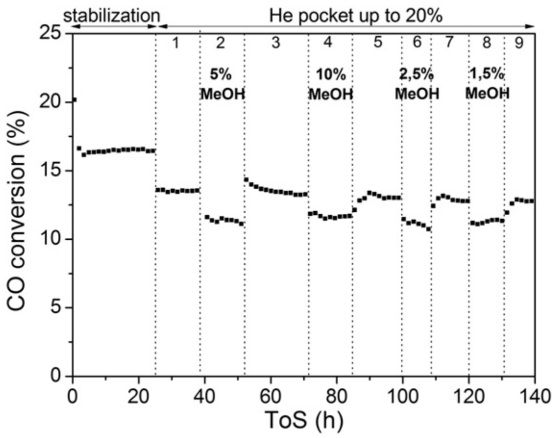

Fig. 1. Effect of methanol addition on CO conversion (K–MoS_2).