Applied Catalysis A: General 417–418 (2012) 119–128

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Correlation patterns and effect of syngas conversion level for product selectivity to alcohols and hydrocarbons over molybdenum sulfide based catalysts

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ARTICLE INFO

Article history:
Received 21 July 2011
Received in revised form
16 December 2011
Accepted 19 December 2011
Available online 28 December 2011

Keywords:
Syngas
Higher alcohols
MoS_2
Synthetic fuels

ABSTRACT

The focus of the present study was to investigate the effect of the operation conditions, space velocity and temperature, on product distribution for a K–Ni–MoS_2 catalyst for mixed alcohol synthesis from syngas. All experiments were performed at 91 bar pressure and constant $H_2/CO = 1$ syngas feed ratio. For comparison, results from a non-promoted MoS_2 catalyst are presented. It was found that the CO conversion level for the K–Ni–MoS_2 catalyst very much decides the alcohol and hydrocarbon selectivities. Increased CO conversion by means of increased temperature (tested between 330 and 370 °C) or decreased space velocity (tested between 2400 and 18,000 ml/(g_{cat} h)), both have the same effect on the product distribution with decreased alcohol selectivity and increased hydrocarbon selectivity. Increased CO conversion also leads to a greater long-to-short alcohol chain ratio. This indicates that shorter alcohols are building blocks for longer alcohols and that those alcohols can be converted to hydrocarbons by secondary reactions. At high temperature (370 °C) and low space velocity (2400 ml/(g_{cat} h)) the selectivity to isobutanol is much greater than previously reported (9%C). The promoted catalyst (K–Ni–MoS_2) is also compared to a non-promoted (MoS_2) catalyst; the promoted catalyst has quite high alcohol selectivity, while almost only hydrocarbons are produced with the non-promoted catalyst. Another essential difference between the two catalysts is that the paraffin to olefin ratio within the hydrocarbon group is significantly different. For the non-promoted catalyst virtually no olefins are produced, only paraffins, while the promoted catalyst produces approximately equal amounts of C_2–C_6 olefins and paraffins. Indications of olefins being produced by dehydration of alcohols were found. The selectivity to other non-alcohol oxygenates (mostly short esters and aldehydes) is between 5 and 10%C and varies little with space velocity but decreases slightly with increased temperature. Very strong correlation patterns (identical chain growth probability) and identical deviations under certain reaction conditions between aldehyde and alcohol selectivities (for the same carbon chain length) indicate that they derive from the same intermediate. Also olefin selectivity is correlated to alcohol selectivity, but the correlation is not as strong as between aldehydes and alcohols. The selectivity to an ester is correlated to the selectivity to the two corresponding alcohols, in the same way as an ester can be thought of as built from two alcohol chains put together (with some H_2 removed). This means that, e.g. methyl acetate selectivity (C_3) is correlated to the combination of methanol (C_1) and ethanol (C_2) selectivities.

1. Introduction

The depletion of oil reserves and a rapidly increasing energy demand in the world, together with many countries being interested in reducing their dependence on foreign oil, makes mixed alcohols production of fuels and chemicals via the synthesis gas route (H_2/CO) very attractive.

Syngas (H_2/CO) can be produced by many different raw materials such as natural gas or coal. If biomass gasification (e.g. of wood or organic wastes) is used for the syngas production, it is also possible to produce greenhouse gas-neutral fuels and chemicals, at the same time as domestic energy security can be increased.

Fuel alcohols have many good characteristics, for example outstanding anti-knock properties and good miscibility with gasoline, which make them attractive as octane boosters in gasoline. Mixtures of higher alcohols and methanol are preferred over pure methanol because of their higher water tolerance, reduced fuel volatility and lower vapor lock tendency and also because of their volumetric heating values are higher than for pure methanol [1].

Alkali-free MoS_2 can be used as sulfur tolerant and coke resistant short hydrocarbon (methanation) catalyst in syngas conversion [2], however, when alkali (e.g. potassium) is added and pressure applied, the selectivity shifts greatly towards alcohols [3].

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doi:10.1016/j.apcata.2011.12.033

Promoters such as Co or Ni are often added to the alcohol catalyst to increase the higher alcohol-to-methanol ratio [3,4].

Alkali-promoted molybdenum sulfides have been shown to be among the most promising catalysts for this purpose due to their ability to catalyze the reaction with high selectivity to short alcohols (about C_1–C_5) as well as being sulfur tolerant. Deposition of coke is not a problem for this type of catalyst even when syngas with low H_2/CO ratio is used [2]. This, together with the water-gas-shift activity, makes it suitable for use with syngas derived from coal and biomass gasification, which generally generate a syngas with low H_2/CO ratio. Additional information about alkali promoted MoS_2 catalysts together with other types of “higher alcohol catalysts” are available in recent as well as classic review articles [5–8].

The alcohol product distribution from alkali-promoted MoS_2 catalysts as well as the hydrocarbon product distribution from alkali-free MoS_2 catalysts has often been deemed to approximately follow the so-called ASF (Anderson–Schulz–Flory) distribution [9]. Significant deviations from the ASF distribution are however often reported, especially for C_1 species when promoters like Ni or Co are added [2,10–12]. The ASF distribution is derived from polymerization kinetics with C_1 monomers and is valid when the probability of chain growth (α) is independent of chain length [13,14]. According to this model the product distribution can simply be described by a single parameter, the chain growth probability (α). This distribution can mathematically be represented in the following way:

$$S_n = n \cdot (1 - a)^2 a^{n-1} \tag{1}$$

where S_n is the carbon selectivity for chains with n carbon atoms and α is chain growth probability. A plot of $\ln(S_n/n)$ vs. n (ASF plot) gives a straight line when the chain growth probability (α) is independent of n:

$$\ln\left(\frac{S_n}{n}\right) = n \ln \alpha + \ln \frac{(1 - a)^2}{\alpha} \tag{2}$$

In the present paper, results obtained from a potassium and nickel-promoted MoS_2 catalyst for alcohol synthesis are evaluated. For comparison, results from a non-promoted MoS_2 catalyst are presented. The focus of this study was to investigate the effect of the operation conditions space velocity and temperature on product distribution, since, e.g. secondary reactions of previously produced reaction products seem to be of great importance for selectivity and activity in CO hydrogenation over MoS_2-based catalysts. To obtain clues about how these reactions occur and find correlations patterns between the various alcohols, olefins, paraffins, esters, aldehydes, etc., particular effort has been devoted to a well-developed online gas chromatograph system to ensure accurate separation, identification and quantification of as many reaction products as possible. Correlation patterns between different reaction products and how they are affected by the process parameters are discussed.

2. Experimental

2.1. Catalyst preparation

The unsupported alcohol synthesis catalyst (K–Ni–MoS_2) was prepared from two water solutions. The first one was prepared by dissolving 12.25 g (47 mmol) ammonium tetrathiomolybdate, $(NH_4)_2MoS_4$, in 450 ml of water and the second one by dissolving 11.7 g (47 mmol) nickel acetate in 250 ml of water. The nickel acetate solution was added dropwise under strong agitation to the $(NH_4)_2MoS_4$ solution. Nickel reacted immediately with the thiomolybdate and a black suspension was formed. The catalyst precursor was matured for 1 h under agitation and was then washed with ethanol and water, and centrifuged to remove excess liquid. The precursor was dried and thereafter crushed and sieved to a pellet size of 45–200 μm. Finely ground K_2CO_3 was then mechanically mixed with the “Ni–MoS_4” catalyst precursor and calcined/decomposed in a tube furnace at 450 °C for 90 min under flowing H_2 atmosphere. During this process a great amount of sulfur is removed from the catalyst both as elemental sulfur (seen as sulfur deposits when gas was cooled down) and as hydrogen sulfide (measured with a GC equipped with sulfur chemiluminesce detector).

For comparison a “pure” MoS_2 catalyst was prepared by decomposition of ammonium tetrathiomolybdate $(NH_4)_2MoS_4$ at 500 °C and 45 h under flowing H_2 atmosphere.

2.2. Catalyst characterization methods

Brunauer–Emmet–Teller (BET) surface area and porosity measurements were performed in a Micromeritics ASAP 2000 unit. The samples were evacuated and dried at 423 K overnight prior to analysis and the BET area and average pore diameter were measured by N_2 adsorption at liquid nitrogen temperature.

XRD measurements were performed on a Siemens D5000 over the 2θ range 5–100° with Cu Kα radiation with a step size of 0.02 and 10 s per step. The Scherrer equation was used to estimate the crystallite size.

2.3. CO hydrogenation

CO hydrogenation reactions were performed in a high-pressure down flow stainless-steel fixed-bed reactor (i.d. 9 mm) with 0.65 g catalyst (45–250 μm) diluted by 3 g SiC (average pellet size = 77 μm). The catalytic tests were carried out at a pressure of 91 bar, with temperatures ranging from 330 to 370 °C and gas hourly space velocities (GHSV) varying between 2400 and 18,000 ml/(g_{cat} h) (STP). The reactor tube was heated by means of a cascade temperature controlled oven with one sliding thermocouple in the catalyst bed and another one placed in the oven. This system together with an aluminum jacket placed outside the reactor, made an even temperature profile in the catalyst bed (set point ±0.5 °C) possible. In all measurements a premixed syngas with H_2/CO ratio 1:1 and 4% N_2 (internal standard) was used.

To prevent condensation of the products leaving the reactor, all parts after the reactor were heated to 185 °C, i.e. tubes and injection valves, etc. Product analysis was carried out on-line using an Agilent 7890 gas chromatograph equipped with a thermal conductivity detector (TCD) and two flame ionization detectors (FID). Light inorganic gases (H_2, CO, CO_2 and N_2) and methane were separated on packed columns and quantified with the TCD. A two-dimensional GC system with Deans switch was used for analysis of the organic products. As primary column a polar capillary column (HP-FFAP) which separates hydrocarbons (C_1–C_7) from oxygenates and also separates the individual oxygenates was used. The oxygenates (alcohols, esters etc.) then continue to the first FID detector while the light hydrocarbons (C_1–C_7) are sent to a second capillary column (HP-Al_2O_3) with a capillary flow device (Deans switch). There they are separated and quantified on a second FID. This makes it possible to achieve a very good separation and quantification of most compounds in about 60 min.

During the first 150 h on stream, the K–Ni–MoS_2 catalyst was run at 340 °C and 91 bar in syngas to create a stable catalyst, so the activity and selectivity would not change much with time on stream in the second, real, experimental part the study. After the stabilization period, experiments varying the process parameters temperature and space velocity were performed. Four different temperatures, from 330 to 370 °C and for each temperature four different space velocities (2400–18,000 ml/(g_{cat} h) (STP)) were tested. Every 90 min the process parameters were changed and at the end of every cycle the gas composition was measured using the GC