



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

Robert Andersson*, Magali Boutonnet, Sven Järås

Royal Institute of Technology (KTH), Department of Chemical Engineering and Technology, Chemical Technology, Teknikringen 42, SE-10044 Stockholm, Sweden

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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–MoS₂ catalyst for mixed alcohol synthesis from syngas. All experiments were performed at 91 bar pressure and constant H₂/CO = 1 syngas feed ratio. For comparison, results from a non-promoted MoS₂ catalyst are presented. It was found that the CO conversion level for the K–Ni–MoS₂ 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–MoS₂) is also compared to a non-promoted (MoS₂) 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 C₂–C₆ 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 H₂ removed). This means that, e.g. methyl acetate selectivity (C₃) is correlated to the combination of methanol (C₁) and ethanol (C₂) selectivities.

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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 (H₂/CO) very attractive.

Syngas (H₂/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 MoS₂ 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].

* Corresponding author. Tel.: +46 87908281; fax: +46 8108579.

E-mail address: robean@ket.kth.se (R. Andersson).