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Supported molybdenum carbides for higher alcohols synthesis from syngas

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Introduction

The synthesis of higher alcohols (C₂₊ alcohols) has received a renewed attention lately for their application as alternative fuels and additives especially with syngas produced by biomass or coal gasification [1-4]. Previously, alkali modified bulk molybdenum carbide (β -Mo₂C) was shown to produce ethanol as the main alcohol product [5, 6]. However, the bulk β -Mo₂C suffers from a low specific surface area, which results in low activity for CO hydrogenation [6]. Therefore, it would be interesting to determine a suitable support material for molybdenum carbide. This work provides an investigation of the high pressure CO hydrogenation to higher alcohols on molybdenum carbide based catalysts supported on various materials, *i.e.* active carbon, carbon nanotubes and titanium dioxide. The investigation includes also a comprehensive characterization of the catalysts by BET, X-ray diffraction (XRD), *in-situ* transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAS) investigations.

Experimental

Molybdenum carbides supported on active carbon (AC), carbon nanotubes (CNTs), and titanium dioxide were prepared by temperature programmed reaction (TPR) of supported molybdenum oxide precursors in a flow of 20 vol% CH₄/H₂. These carbides were impregnated with an aqueous solution of K₂CO₃ with calculated amounts. The performance of catalysts for higher alcohols synthesis (HAS) from syngas has been evaluated in a fixed-bed continuous-flow reactor with a GC-FID/TCD detection system. Prior to the reaction, the supported carbides were treated *in-situ* with 20% H₂ in N₂ flow (35 ml/min) at 350 °C for 2 h to remove a possible passivation layer formed after exposure in air. Typical operating conditions were: P=100 bar; T=250-300 °C; GHSV=5000 h⁻¹; Feed: H₂/CO=1 (v/v). Particle sizes and phase compositions were investigated using XRD. The specific surface areas of both fresh and used catalysts were determined by N₂ adsorption at 77 K. *In-situ* TEM was used to study the catalyst morphology in H₂ gas flow from 25 to 600 °C. *In-situ* XAS, the Mo K-edge measurements were performed at the synchrotron of Hamburg HASYLAB-X beamline.

Results and Discussion

Table 1 shows the catalytic performance of K₂CO₃/Mo₂C/TiO₂ catalyst in CO hydrogenation at steady state. The CO conversion and selectivity to hydrocarbons were enhanced by increasing temperature, while the selectivity of methanol and higher alcohols decreased. The higher alcohols selectivity reached 34.3 mol% at 250 °C, however, the selectivity to both methanol and higher alcohols decreased dramatically when the temperature was increased. This may be caused by insufficient loading of the K₂CO₃ promoter. Indeed, it has been observed for bulk Mo₂C that the selectivity to alcohols increases with increasing the K₂CO₃ content up to 10 wt% and then stagnates [5]. Here 10 wt% K₂CO₃ based on active materials (Mo₂C) were

added for all catalysts and the dilution effect of support might be considered.

Table 1. Effect of temperature on the catalytic performance of K₂CO₃/Mo₂C/TiO₂ in CO hydrogenation at steady state.

Catalyst	T [°C]	CO conv. [mol%]	Carbon based, CO ₂ -free selectivity [mol%]		
			MeOH	C ₂₊ OH	HC
K ₂ CO ₃ /Mo ₂ C/TiO ₂	250	4.6	18.1	34.3	46.2
K ₂ CO ₃ /Mo ₂ C/TiO ₂	275	9.4	13.3	21.7	61.6
K ₂ CO ₃ /Mo ₂ C/TiO ₂	300	85.1	0.3	0.43	99.3

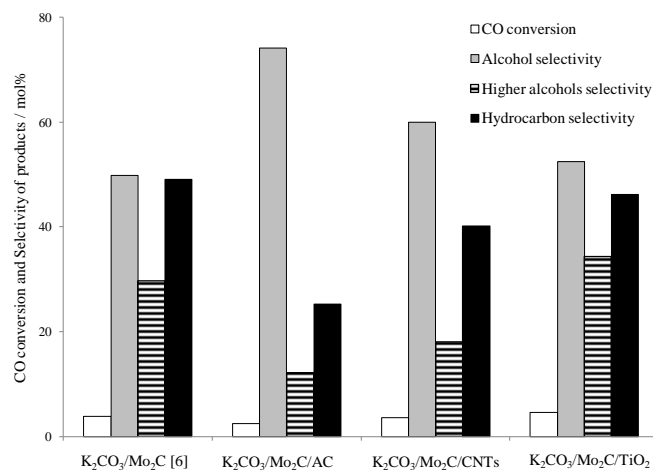


Figure 1. CO conversion and product selectivity (at 250 °C) at steady state over the investigated catalysts (5.3 wt% Mo₂C for all supported catalysts).

Figure 1 shows the CO conversion and the selectivity to different products at steady state. The active carbon supported catalyst exhibited the highest alcohols selectivity with methanol being the dominant alcohol. On the other hand, TiO₂ supported catalyst showed the highest selectivity to higher alcohols.

Conclusions

The catalytic activity of molybdenum carbides supported on different materials such as active carbon, carbon nanotubes, and titanium dioxide in higher alcohol synthesis from syngas is significantly affected by the support nature. In particular TiO₂ seems to be a promising support due to its better selectivity to higher alcohols. The future work is focused on improving both the selectivity of the catalysts towards higher alcohols by modifying the K₂CO₃ loading of the catalysts and the activity by increasing the loading of the Mo₂C.

Acknowledgement

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