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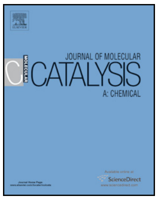

Passivation and reactivation of catalyst systems for the single step synthesis of dimethyl ether from CO-rich synthesis gas[☆]

Ruaa Ahmad[a], Ulrich Arnold[a,*], Diana Deutsch[a], Manfred Döring[b], Jörg Sauer[a]

[a] Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[b] Fraunhofer Institute for Structural Durability and System Reliability LBF, Schlossgartenstraße 6, 64289 Darmstadt, Germany

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ABSTRACT

A methanol catalyst based on $Cu/ZnO/Al_2O_3$ (CZA) was prepared and mixed with four different solid acids, a pure γ-Al_2O_3, a SiO_2-doped γ-Al_2O_3, an $AlPO_4$-doped γ-Al_2O_3 and the zeolite H-MFI 400, respectively. These admixed catalyst systems were tested in the direct synthesis of dimethyl ether from CO-rich synthesis gas ($CO:H_2 = 1$), which is typical for biomass-derived synthesis gas. Reactions were carried out in a laboratory plant at 250 °C and 51 bar for 120 h time-on-stream followed by catalyst passivation with O_2 and regeneration by hydrogenation. After catalyst regeneration, the reaction was run again for another 72 h. The catalyst system containing the zeolite exhibited highest CO-conversion. However, all catalysts showed a drop of activity after the passivation- and regeneration-process and the system with the SiO_2-doped γ-Al_2O_3 showed the lowest loss of activity. Investigation of the catalysts after reaction by N_2O-pulse chemisorption and XRD revealed that agglomeration of catalyst species took place leading to an increased Cu^0-particle size for all systems. This phenomenon was less pronounced in the case of the system containing the SiO_2-doped γ-Al_2O_3. Thus, the main cause of catalyst deactivation was found to be sintering of the catalytically active components.

1. Introduction

Dimethyl ether (DME) has gained enormous interest over the last years and is considered to be one of the most promising alternative fuels [1]. Applications of DME shifted from its use as propellant and chemical feedstock to various applications as an energy carrier [2]. The main use of DME today is as a LPG-substitute [3] and it can also be used as a diesel-substitute. In fact, Volvo announced the commercialization of their DME-trucks in North America in 2015 and DME will be produced by Oberon fuels [4]. The new possible applications of DME lead to an immense increase of the global production capacities from 0.03 MTPY in 2003 to 5 MTPY in 2009 and a further increase is ongoing [5].

The industrial production of DME proceeds via the dehydration of methanol using a solid acid, e.g. γ-Al_2O_3 or a zeolite, as catalyst. However, DME can also be produced directly from synthesis gas in a single step synthesis. In the latter case, a dual catalyst system is required and typically an admixed catalyst system containing a methanol catalyst ($Cu/ZnO/Al_2O_3$, CZA) and a solid acid is applied. Eqs. (1)–(3) express the main reaction pathways, i.e. methanol synthesis (1), methanol dehydration (2) and the water-gas shift reaction (3). The overall reaction is described by Eq. (4) [6].

$$2CO + 4H_2 \rightarrow 2CH_3OH \tag{1}$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{2}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{3}$$

Overall:

$$CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2 \tag{4}$$

The single step synthesis of DME has been tested only on pilot scale so far [7–9] and catalyst-deactivation, -passivation and -recovery phenomena have not been investigated sufficiently. One of the first studies in this field has been carried out by Peng et al. [10]. The deactivation of the admixed catalyst system in the single step synthesis was compared to the deactivation of each catalyst component in its respective reaction, i.e. methanol synthesis and methanol dehydration. The results showed that each catalyst component is rather stable in its respective process. However, if the catalysts are combined in an admixed system a strong deactivation

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[☆] Dedicated to Prof. Ulf Schuchardt on the occasion of his 70th birthday.
[*] Corresponding author. Fax: +49 721 608 22244.
E-mail address: ulrich.arnold@kit.edu (U. Arnold).

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was observed. It was concluded that the loss of activity is a result of close interactions between the catalyst components, which might lead to a migration of active Cu-species.

Studies of Luan et al. focused on catalyst regeneration [11], employing O_2, N_2O and CO_2 for the treatment of the spent catalyst system. Initial performance of the catalyst system in terms of CO-conversion and specific Cu-surface area could be re-established if O_2 was used in the regeneration procedure. The decrease of the Cu-surface area during the reaction indicated, that sintering of active Cu-species is the main cause of deactivation and that the solid acid has no significant influence on catalyst deactivation.

Barbosa et al. studied the influence of the synthesis gas composition (H_2/CO = 1 and 2) on catalyst stability [12]. After 300 min time-on-stream a strong deactivation was observed for a H_2/CO ratio of 1, whereas catalyst activity stayed constant for a H_2/CO ratio of 2. Investigation of the catalyst after reaction by FTIR and TGA revealed in both cases the presence of hydrocarbons on the surface of the solid acid H-ZSM-5. However, product selectivity was constant in the reaction with H_2/CO = 1, despite the strong deactivation. This suggests that the dehydration step in the DME synthesis process is not affected by the formation of hydrocarbons and coke. Therefore, they conclude that catalyst deactivation is mainly due to the formation of hydrocarbons on the dehydration component, which are subsequently transferred to the CZA-catalyst and the generation of hydrocarbons and coke is favored in case of H_2/CO = 1.

A comparison between a fixed-bed reactor and a bubble column reactor focusing on catalyst stability was carried out by Wang et al. [13]. After 180 h, catalyst deactivation was much stronger in the bubble column reactor. Therefore, a possible deactivation of the catalyst caused by reaction heat could be excluded, since heat removal is more efficient in bubble column reactors. Further experiments showed that water, which could not escape from the catalyst pores due to the high oil temperature in the bubble column reactor, lead to sintering of active Cu-species.

According to Zhang et al., the main cause for deactivation of the catalyst system is sintering of the CZA-component and coking is only a secondary phenomenon [14]. However, it is assumed that other effects, caused by the interaction between the CZA-component and the solid acid play an important role regarding long-term stability.

The influence of different solid acids (i.e. γ-Al_2O_3, NH_4-ZSM-5, H-ZSM-5) on catalyst stability was tested by Abu-Dahrieh et al. [15]. and the admixed catalyst system with H-ZSM-5 exhibited highest stability. TPO measurements showed that coke accumulated on the CZA-component, on the solid acid and also between both components. Thus, coking was identified as the main reason for catalyst deactivation in this study.

Various studies on catalyst-deactivation and -regeneration were carried out by Aguayo et al. In one of these studies the use of H_2/CO as feed for DME synthesis was compared to the use of H_2/CO_2 [16]. Employing H_2/CO_2, a higher long-term stability of the catalyst was observed than in the case of H_2/CO. The presence of CO_2 supports the reverse water-gas shift reaction, which produces water. Adsorption of thus produced water prevents pore blockage by coke and leads to higher stability. Moreover, if NaH-ZSM-5 was used as solid acid the initial activity could be re-established after regeneration, whereas the system with γ-Al_2O_3 could not be regenerated as well, due to its low thermal stability. The coking behavior of admixed catalysts was further investigated [17] and TPO-as well as NH_3-TPD-measurements proved that coking took place. However, the acidity was not influenced by the formation of byproducts. Moreover, the catalyst could be regenerated completely, so that deactivation by sintering could be excluded. Thus, it was concluded that the presence of coke on the CZA-component lead to catalyst deactivation. The influence of various reaction parameters on catalyst stability was also investigated [17,18]. It was reported that temperatures above 250 °C lead to a reduction of coking and the addition of water decreased the formation of coke. As long as the temperature stayed below 300 °C sintering of the Cu-species did not occur. Furthermore, high pressure supported coke formation and a pressure of 20 bar lead to the most stable CO-conversion.

Within this work, admixed catalyst systems containing different solid acids were tested focusing on their long-term stability in the single step synthesis of DME. CO-rich synthesis gas was employed with a H_2/CO-ratio of 1, which is typical for biomass-derived synthesis gas. The work concentrates not only on the long-term stability of the catalysts and their deactivation, but also on their passivation after reaction and regeneration by reductive treatment with H_2. Such investigations are mandatory regarding practical aspects such as safe removal of the catalyst system from the reactor, recovery and reuse of costly catalysts as well as catalyst storage. Furthermore, the influence of the solid acid on activity and stability and its interaction with the CZA-component are main topics, which are addressed within this work.

2. Experimental

2.1. Catalysts

The admixed catalyst system for the single step synthesis of DME comprised a methanol catalyst (CZA) and a solid acid. The CZA catalyst was synthesized by co-precipitation. A solution of 14.03 g $Cu(NO_3)_2{\cdot}3H_2O$, 10.75 g $Zn(NO_3)_2{\cdot}6H_2O$ and 3.50 g $Al(NO_3)_3{\cdot}9H_2O$ in 150 mL deionized H_2O was slowly dropped into 100 mL of deionized H_2O at 70 °C. A Na_2CO_3-solution (1 M) was used as precipitating agent and the pH was adjusted to 7–8 during the whole process. Afterwards, the obtained light-blue suspension was aged for 1 h. The precipitate was thoroughly washed, separated by centrifugation and finally filtrated. The filter cake was dried for 12 h at 80 °C and finally calcined (1 h at 175 °C and 4 h at 350 °C). The obtained CZA-catalyst was ground and mean sizes of the particles were between 80 and 355 μm.

Four different solid acids were used as dehydration components in the admixed catalyst systems: γ-Al_2O_3 (AA, from Alfa Aesar GmbH & Co., KG), SIRALOX 30 (SiAl, a SiO_2-doped γ-Al_2O_3 from SASOL, Germany GmbH), HS Alumina (AlPO, a $AlPO_4$-doped γ-Al_2O_3 from SASOL Germany GmbH) and zeolite H-MFI 400 (MFI400, from Süd-Chemie, AG). All solid acids were ground and mean particle sizes were between 80 and 355 μm. The admixed catalyst systems were prepared by mechanically mixing of the CZA-catalyst with the solid acid in a weight ratio of 1:1.

2.2. Catalyst characterization

Metal loadings were determined by SEM-EDX and XRF. The EDX analysis was carried out employing an INCAPentaFET-x3 unit from Oxford Instruments on several locations of the catalysts and SEM images were recorded with a FESEM DSM 982 Gemini microscope (ZEISS) equipped with a backscatter detector. A vario EL CUBE instrument from Elementar Analysensysteme GmbH was used for elemental analysis (CHNS-mode). XRF analyses were carried out employing a SIEMENS SRS 303 sequence-spectrometer and the obtained data were evaluated with the Siemens SemiQuant 3000 software 2.0. Rh was used as radiation-source with an accelerating voltage of 20–60 kV (at 5 mA) and a flow meter as well as a scintillation counter were used as detectors. Specific surface area (BET method, p/p_0 = 0.05-0.20), total pore volume (p/p_0 = 0.99) and micropore surface (V-t-method, $p/p_0 = 0.10 - 0.30$) were determined by N_2-physisorption using a Quantachrome Nova 2000e instrument. XRD diffractograms were recorded using a PANalytical X'PERT-PRO diffractometer. Cu-Kα-X-radiation (0.154 nm) was

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