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Heteropolyacid based catalysts for the production of dimethyl ether from methanol. Effects of reaction pressure and nature of the support

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PURPOSE OF THE ABSTRACT

Intro

Dimethyl ether (DME) can be obtained from biomass derived syngas, so it is considered as a second-generation biofuel for several markets, e.g., power, diesel substitute, etc. [1]. DME is produced from methanol dehydration at 250-320 °C and 10-30 bar over acid solids such as γ -Al₂O₃ or zeolites [2, 3]. Heteropolyacids (HPA) with Keggin structure display excellent activity selectivity to DME at low temperature (180-200°C) and 1 bar, especially when supported on TiO₂ [4]. However, the effect of the nature of the support has not been determined so far. HPAs high activity has been ascribed to the contribution of surface activity and bulk-type or pseudo-liquid catalysis [5]. Moreover, little is known about the effect of temperature and pressure on their performance for DME production. Previous results in our group suggest that methanol production rate over HPAs decreases at temperatures above 200° C and 1 bar. In this work, we study the effects of T and P for DME production from methanol using different supported tungstosilicic acid (HSiW) catalysts. We show that the negative effect of increasing temperature on DME production can be compensated by increasing the pressure.

Experimental

The HSiW_X catalysts, where X denotes the support (TiO₂, BN, CeO₂, SiO₂, ZnO₂, Al₂O₃) were synthesized by the impregnation at incipient wetness method. The amount of HSiW added to each catalyst maintained the number of Keggin Units (KU) per surface area constant at 4.5 KU/nm², meaning that the masses of HSiW loaded to each support depended on its surface area. N₂ adsorption-desorption isotherms and XRD were performed on the supports. The resulting catalysts were characterized by in situ XRD and H-NMR spectra of the solids were also collected. Activity tests were carried out in a fixed-bed reactor loading 0.2 g of catalyst mixed SiC at 180-260 °C, 1-20 bar and feeding gaseous methanol at 2300 cm³ h⁻¹ g cat⁻¹ diluted in N₂.

Results and discussion

Table 1 shows that the catalysts have higher BET areas than bulk HSiW, but smaller than those of the supports. In situ XRD show that the Keggin structure of the HSiW remains unaltered after impregnation at all studied temperatures, except for HSiW_Al₂O₃. The collapse of the Keggin structure in the HSiW_Al₂O₃ might be related

to the strong interactions support-HSiW observed in the H-NMR spectra, which appeared to be weaker in the rest of the catalyst. Figure 1 shows the DME productivity per gram of HPA of the catalysts under study. The activity of the supported catalysts is higher than that of the bulk HPA, except for HSiW/CeO₂. DME productivities are not directly proportional to the HSiW content in the catalysts, suggesting that interactions between the HPA and the support were different for each catalyst and are determining in the catalytic performance. Stronger interactions might not let structural water of the HPA leave available the active sites for methanol to adsorb.

Although not shown in this abstract, increasing the reaction temperature (200 °C and above) at 1 bar, results in lower DME conversions. Thus, conversion decreases from 80% at 180°C and 1 bar, to ca 45 % at 200 °C and 1 bar (after 4 h on stream). This apparent deactivation can be overcome by increasing reaction pressure. Thus increasing P to 10 bar results in DME conversions to 80% at 200°C, remaining stable during at least 8 h. A similar trend is observed at higher temperatures, conversion decreases with temperature but increases again by increasing reaction pressure. This effect has been ascribed to lack of contribution of pseudo-liquid catalysis with the increasing temperature at low pressures.

Conclusions

This study reveals the importance of the interactions support-active phase of supported HSiW in the dehydration of methanol reaction. The apparent catalyst deactivation observed at temperatures above 200°C, due to the lack of contribution of pseudo-liquid catalysis, can be avoided by working at high pressure.

FIGURES

BET area ($\text{m}^2 \text{g}^{-1}$)		
	Support (X)	HSiW/X
TiO_2	53	44
SiO_2	129	42
Al_2O_3	147	49
ZrO_2	39	27
BN	19	15
CeO_2	76	57
bulk HSiW		8

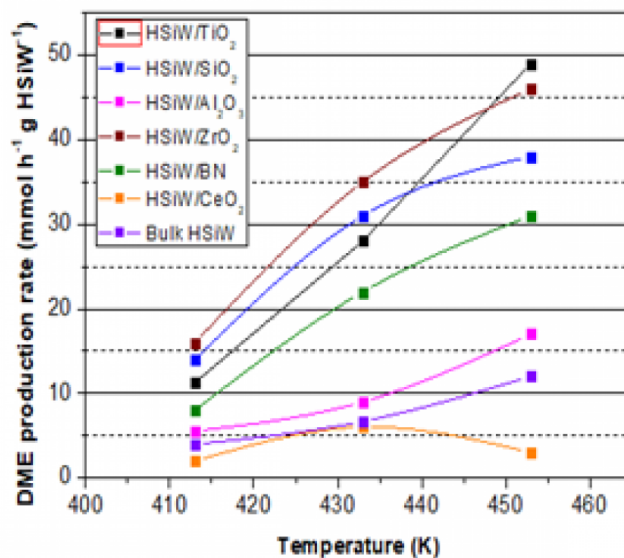


FIGURE 1

Table 1

BET areas of supports and catalysts

FIGURE 2

Figure 1

Catalytic activity of the supported and bulk HSiW at atmospheric pressure

KEYWORDS

Supported heteropolyacid | Dimethyl ether production | Methanol dehydration | Alternative fuel

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