

From Synthesis Gas to a Clean Transportation Fuel Dimethyl Ether: New Nanocomposite Bifunctional Catalyst Pairs

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ABSTRACT

Dimethyl ether (DME) is a promising diesel fuel alternative due to its high cetane number and clean burning properties. Direct synthesis of DME from syngas has major thermodynamic advantages over the conventional process. In this work, new catalysts were synthesized for both methanol synthesis and dehydration steps and performances of different pairs of these catalysts were tested in DME synthesis at 50 bar. For methanol synthesis, a Cu-Zn-Zirconia was synthesized and its performance was compared with Cu-Zn-Alumina. For methanol dehydration, a silicotungstic acid incorporated SBA-15 type nanocomposite material (STA@SBA-15) was synthesized and its performance was compared with γ -Alumina. Quite high DME yield was obtained with (STA@SBA-15)+(Cu-Zn-Alumina). Highest DME selectivity values were obtained in the temperature range of 220-260°C. Catalyst mixture, which was composed of zirconia based methanol synthesis catalyst and γ -Alumina also showed high DME selectivity in the temperature range of 200-225°C. Addition of CO₂ to the feed mixture was shown to hinder WGS and increase DME selectivity.

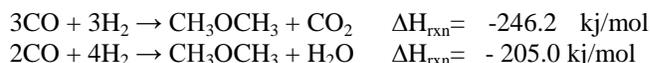
Keywords: dimethyl ether, clean fuel, silicotungstic acid, SBA-15

1 INTRODUCTION

Due to fast depletion of petroleum and combustion related environmental concerns, development of green transportation fuel alternatives have attracted major attention of researchers and fuel producers in recent decades. Dimethyl ether (DME) is a highly promising diesel fuel alternative due to its high cetane number (55-60) and clean burning properties, resulting very low particulate matter and NO_x emissions during its combustion [1-2]. Having similar physical properties, it has also been considered as a good alternative or additive to LPG. DME can be synthesized starting from natural gas, coal, biomass and agricultural residues.

Conventional method of production of DME involves gasification/reforming of these resources to produce synthesis gas, which may then be converted to methanol. Then, DME can be produced by dehydration of methanol over solid acid catalysts in a second reactor. Direct synthesis of DME from synthesis gas has major

thermodynamic advantages over the conventional two step process involving consecutive reactors for methanol synthesis and dehydration [3-4]. In-situ conversion of produced methanol to DME in the reactor was shown to cause significant improvement in DME yield [5]. The overall stoichiometry of DME synthesis from synthesis gas can be written as follows:



The reaction scheme of direct DME synthesis involves methanol synthesis, methanol dehydration and water gas shift reactions. Due to thermodynamic limitations, high pressures are needed to increase conversion of CO, and temperature range is generally selected as between 225-300°C. At higher temperatures equilibrium limitations of methanol synthesis and occurrence of side reactions cause significant reduction in DME yield.

Technological development of the direct synthesis route of DME requires development of new bi-functional catalytic systems, involving both methanol synthesis and dehydration sites. Conventional methanol synthesis catalysts are Cu-Zn-alumina based materials. However, for the dehydration function of methanol, catalysts with high Brønsted acidity are needed. Conventionally γ -alumina or zeolites were tested for the dehydration reactions of alcohols. Coke deposition was reported to be an important factor in such microporous materials. In our recent studies a new series of TRC type mesoporous solid acid catalysts were synthesized by incorporation of heteropolyacids into the mesoporous silicate structured materials with ordered pore structures [6-8].

2 EXPERIMENTAL

Catalyst synthesis and characterization:

In the present study different catalysts were synthesized for both methanol synthesis and dehydration. For the methanol synthesis, performances of Cu-Zn-Zirconia and Cu-Zn-Alumina were compared. As for the solid acid dehydration catalyst, a new silicotungstic acid impregnated SBA-15 type mesoporous material with ordered pore structure was synthesized and its performance was compared with the performance of γ -alumina.

Synthesis of Cu-Zn-Zirconia type catalytic materials was performed by a co-precipitation procedure [9].

Effects of promoter type, aging time, washing procedure, calcination temperature and reduction temperature on the catalytic performances of these materials were investigated by Celik [9]. A commercial Cu-Zn-Alumina catalyst was also used in some experiments.

SBA-15 type silicate structured mesoporous material with ordered pore structure was synthesized following a hydrothermal route using P-123 as the structure directing template following the procedures reported in the literature [10]. This material had a surface area of 808 m²/g with an average pore diameter of 7.8 nm. In order to increase the Brønsted acidity of this material, silicotungstic acid (STA) was impregnated into SBA-15, to obtain catalysts with W/Si ratios in the range of 0.4-1.0. These materials are denoted as STA@SBA. The surface area of the material with the W/Si ratio of 0.4 was 187 m²/g (Table 1) and XRD analysis indicated ordered mesoporous structure. Nitrogen adsorption/desorption isotherms correspond to an ordered mesoporous structure and pore size distribution is quite narrow with an average pore diameter (evaluated from BJH using desorption data) of about 7.8 nm (Fig. 1 & 2). XRD and SEM-EDX results indicated well dispersion of STA within the SBA-15 pores.

	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Av. Pore Diameter (nm)
SBA-15	808	1.32	7.8
STA@SBA-15 (W/Si=1)	73	0.13	7.7
STA@SBA-15 (W/Si=0.4)	187	0.37	7.8

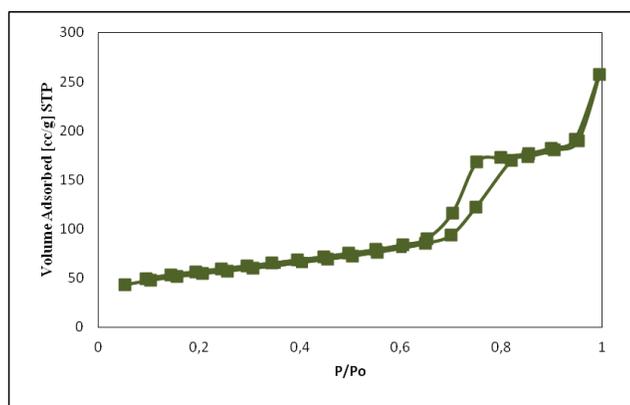


Fig. 1. N₂ adsorption/desorption isotherm of STA@SBA-15 (W/Si=0.4)

Activity test experiments:

Performances of different pairs of methanol synthesis and dehydration catalysts were tested in a differential flow reactor using physical mixtures of these catalysts at equal weight fractions (each being 0.1 g). Experiments were performed at 50 bar in a temperature range of 200-300°C.

The feed stream to the reactor contains equimolar amounts of CO and H₂ in most experiments, while keeping the the flow rate as 50 ml/min, measured at atmospheric pressure and room temperature. Composition of the reactor exit stream was analyzed by a gas chromatograph. Results showed that 30 min was sufficient to reach steady state and data points obtained within a reaction point of about two hours showed no significant variation in product distributions.

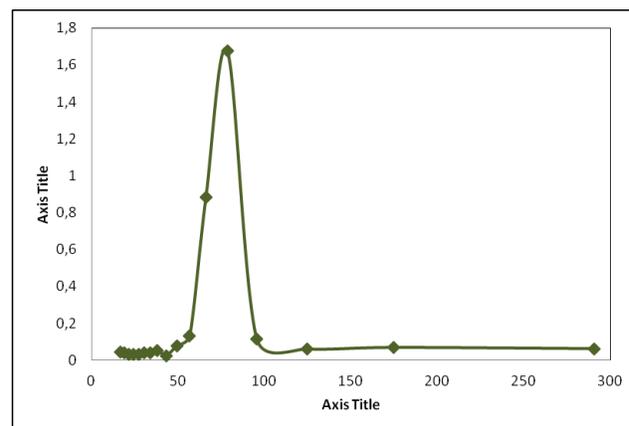


Fig. 2. Pore size distribution of STA@SBA-15 (W/Si=0.4)

3 ACTIVITY RESULTS AND DISCUSSIONS

Experiments performed with different pairs of methanol synthesis and STA based dehydration catalysts showed that CO conversion values were the highest with the STA@SBA-15 (W/Si=0.4) (Fig.3). Apparently, impregnation of STA at higher amounts into SBA-15 caused significant reduction in surface area of the catalyst due to plugging of significant fraction of the pores, which caused reduction in activity of the catalyst. As for the comparison of Cu-Zn-Alumina and Cu-Zn-Zirconia type methanol synthesis catalysts were concerned, performance of Cu-Zn-Alumina was better. Product selectivity values obtained with the Cu-Zn-alumina + STA@SBA-15 (W/Si=0.4) catalyst mixture showed the highest DME selectivities in the temperature range of 220-260°C (Fig. 4). CO conversion approaching to 20% was obtained at a space time of 0.24 s.g.cm⁻³ at 275°C with this catalyst mixture.

On the other hand, the catalyst mixture, which was composed of zirconia based methanol synthesis catalyst and γ -Alumina showed quite high DME selectivity values (of about 70%) in the temperature range of 200-225°C (Fig. 5). However, CO conversion values were much lower with this catalyst mixture at these temperatures. Direct DME synthesis involves methanol synthesis, methanol dehydration and water gas shift reactions (WGS) at the same proximity of the reactor. Apparently, in-situ conversion of produced methanol to DME causes enhancement in CO conversion. In fact this fact was

illustrated in our recent publication by comparing conversions and product distributions obtained in experiments performed with the the mixed and consecutive arrangement of the methanol synthesis and the dehydration catalysts [5].

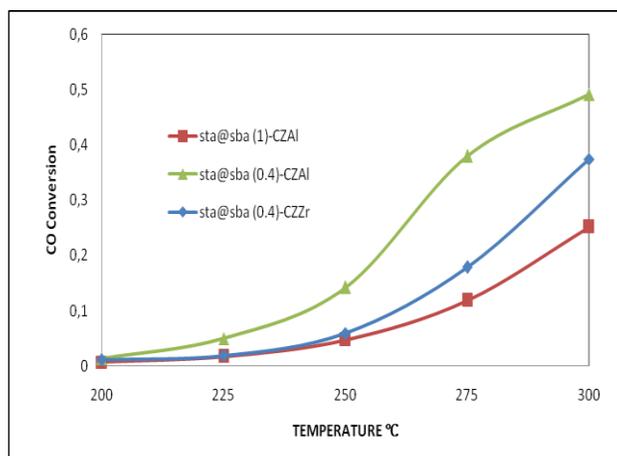


Fig.3. CO conversions obtained with Cu-Zn-alumina and STA@SBA-15 mixtures. (STA@SBA(1) contains W/Si=1; STA@SBA(0.4)contains W/Si=0.4)

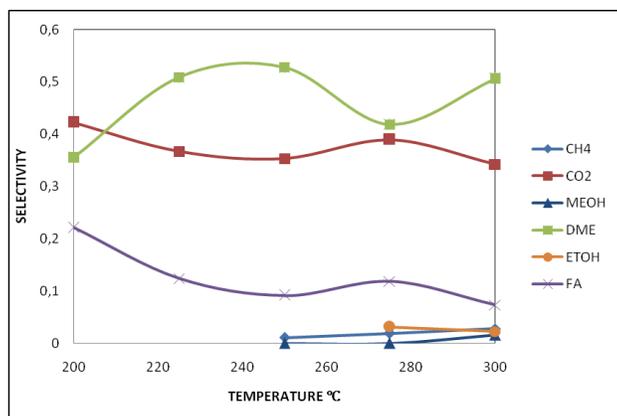


Fig.4. Product selectivities with STA@SBA-15 (W/Si=0.4) + Cu-Zn-alumina catalyst mixture.

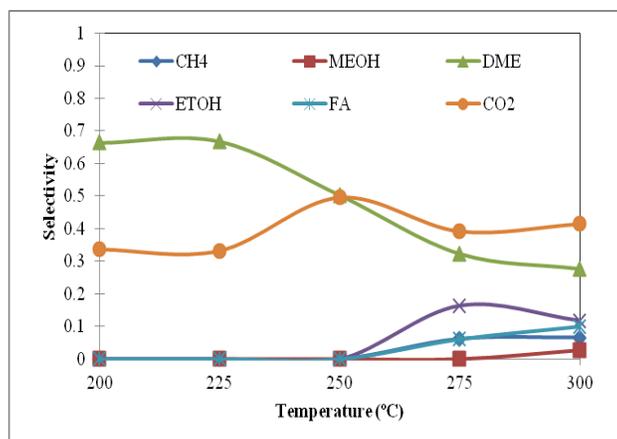


Fig.5. Product selectivities with the γ -Alumina + Cu-Zn-Zirconia catalyst mixture.

4 CONCLUDING REMARKS

Silicotugstic acid impregnated SBA-15 type mesoporous catalyst containing a W/Si ratio of 0.4 showed excellent performance in in-situ dehydration of produced methanol to DME during its synthesis directly from synthesis gas. Lower activity of STA@SBA-15 containing a W/Si ratio of 1.0 was due to significant reduction of surface area as a result of pore plugging. Although the activity of Cu-Zn-Zirconia was low in methanol synthesis, very high DME selectivity values obtained with the mixture of this material with a conventional solid acid catalyst (γ -alumina) was highly promising.

5 ACKNOWLEDGEMENTS

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