

Novel acid catalyst for the dehydration of methanol to dimethyl ether

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Introduction

Dimethyl ether (DME) is one of the most promising ultra clean, renewable and oxygenated alternative fuel for diesel engines. The reasons for this are numerous and include its lower auto-ignition temperature (cetane number, CN> 55), higher oxygen content (34.8% by mass) and C-O-C molecular structure. DME can be easily evaporated [1] is non-toxic, non-carcinogenic and non-corrosive. It is also considered as an environmentally friendly compound because of its low global warming potential over both short and long time horizons[2].

Alumina is one of the most important structural materials with several transition phases that have enormous technological and industrial significance [3]. It is thus the most common catalyst and catalyst support used in heterogeneous catalysis due to its low cost, good thermal stability, high specific surface area, surface acidity and interaction with deposited transitional metals [4].

Clearly the preparation method affects the activity of the catalysts as activity varies with both precursor type and the preparation procedure. For alumina there are a number of different preparation methods which can be used. In this work a comparative study was performed between the two cheapest and most readily available precursors which are aluminium nitrate and aluminium chloride. This was in order to identify which one was the best at producing an active catalyst with latter tests conducted to benchmark them against commercial materials.

Experimental

Catalysts were prepared from two precursors namely $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and AlCl_3 . After drying at 120 °C overnight, the precipitate was calcined at 300, 370, 550, 650 and 750 °C, respectively. All catalysts were characterized by TGA, XRD, BET, SEM and TPD-pyridine.

The activity testing was carried out in an isothermal fixed-bed reactor made of stainless steel (6 mm OD). The catalyst bed consisted of 200 mg (250–425 μm) of catalyst placed in between two plugs of quartz wool. Aera mass flow controllers were used to control the flow of He to the reactor. The liquid methanol was injected by patented Cheminert® M Series liquid handling pump.

Results and Discussion

From XRD patterns (not shown), $\gamma\text{-Al}_2\text{O}_3$ can be formed from aluminium chloride (AC) precursor and $\eta\text{-Al}_2\text{O}_3$ can be formed from aluminium nitrate (AN) precursor.

Figure 1 shows SEM images of $\eta\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$. It is clear that there is a difference in the morphology of the particles. Clearly the $\gamma\text{-Al}_2\text{O}_3$ produces a much smoother surface. It can thus be concluded from the SEM that the surface roughness is very different between both alumina phases.

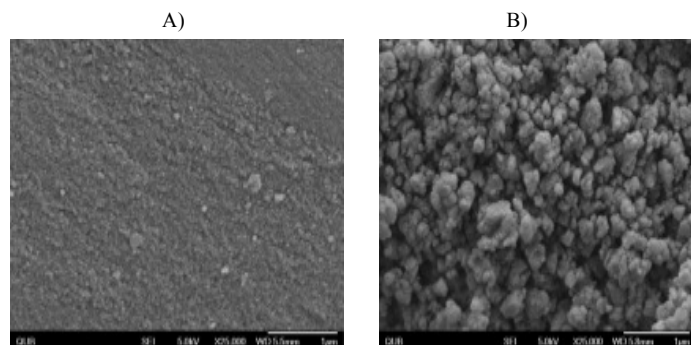


Figure 1. Representative SEM micrographs of (A) $\gamma\text{-Al}_2\text{O}_3$ and (B) $\eta\text{-Al}_2\text{O}_3$.

From the in situ DRIFTS spectra of pyridine desorption pyridine adsorbed on $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$ at 100 °C in the region 1800–1100 cm^{-1} (not shown), both alumina showed bands relative to Lewis acidic with strong sites at 1623 and about 1455 cm^{-1} , a small band related to weak Lewis acid sites (1575) and another small band related to Lewis and Brönsted (1488 cm^{-1}) sites. It is clear from DRIFTS spectra that the Lewis acidic sites are responsible for the acidity in both alumina and $\eta\text{-Al}_2\text{O}_3$ has higher acidity than $\gamma\text{-Al}_2\text{O}_3$.

Figure 2 shows the effect of calcination temperature of AN and AC catalysts for reactions carried out over the temperature range 180–300 °C. It is clear that for each reaction temperature, above a minimum of approximately 200 °C, that the methanol conversion increased until a maximum at calcination temperature of 650 °C, after which it decreases sharply for AC catalysts. The same for AN catalysts for each reaction temperature the methanol conversion increased until a maximum was found between 550 and 650 °C. This maximum is less clearly defined than in the case of the AC catalysts.

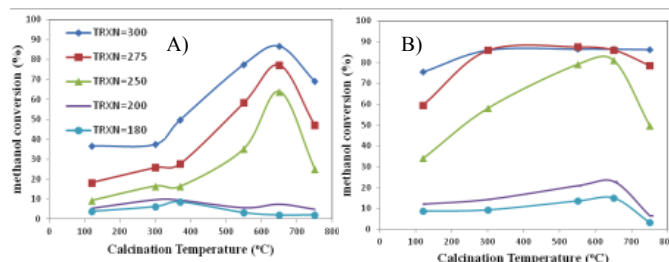


Figure 2. Effect of calcination temperature on methanol conversion over catalysts; A: (prepared from AC precursor); B: (prepared from AN precursor); at different reaction temperature. (T= 180–300 °C; catalyst weight= 200 mg; He flow rate = 80 ml/min; WHSV: 12.1 h^{-1}).

Conclusions

Herein different acid catalysts were prepared using two precursors with different calcination temperatures during the production of DME from methanol. From the X-ray diffraction (XRD) pattern, different transition states of alumina were detected based on this calcination temperature. The boehmite was changed to $\gamma\text{-Al}_2\text{O}_3$ at 550 °C, and the bayerite was completely changed to $\eta\text{-Al}_2\text{O}_3$ when calcined at 550 °C. Among these catalysts that produced using the alumina nitrate precursor and calcined at 550 °C showed the highest catalytic performance under the reaction conditions (T=180–300 °C, WHSV= 12.1 h^{-1}), compared it with $\gamma\text{-Al}_2\text{O}_3$ and commercial $\gamma\text{-Al}_2\text{O}_3$ and higher than commercial zeolite HZSM-5 (80) for temperatures above 275 °C. A comparison showed that this material had double the activity of the (commercial $\gamma\text{-Al}_2\text{O}_3$ and AC550) and 87% activity of commercial HZSM-5 (80) at 250°C. The acid site density over catalysts changed with the calcination temperature. In the methanol dehydration, the acid site density affected catalytic performance among the catalysts with alumina phase structure. It is thus recommended $\eta\text{-Al}_2\text{O}_3$ is a promising dehydration catalyst for using in the production of DME from methanol.

References

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