

# Effect of different metal sulfate precursors on structural and catalytic performance of zirconia in dehydration of methanol to dimethyl ether

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**Abstract:**  $ZrO_2$  was treated with 10%  $SO_4^{2-}$  from different metal sulfate precursors for methanol dehydration to dimethyl ether. All the samples exhibited tetragonal phase and no diffraction peaks corresponding to metal sulfates or metal oxides were observed. The FT-IR results revealed that there were different interactions between sulfate and  $ZrO_2$ , and this had a great effect on the surface area of the samples. The catalytic activity was measured over the catalysts in the temperature range of 100–300°C. The results revealed that sulfated zirconia with  $CuSO_4 \cdot 5H_2O$  and  $Al_2(SO_4)_3 \cdot 16H_2O$  showed the best catalytic activity. The maximum yield of DME  $\approx$  87% was obtained over CuSZ at a reaction temperature of 275°C. Moreover, the catalytic activity of the catalysts was correlated well with their surface acidity that measured by dehydration of isopropanol.

**Key words:**  $MSO_4/ZrO_2$ ; methanol; dehydration; DME

Nowadays, sustainable and environmentally friendly fuel production and consumption are becoming key challenges in this century<sup>[1]</sup>. Accordingly, dimethyl ether (DME) has been considered as an alternative fuel because it can be produced from non-petroleum feedstocks<sup>[2]</sup>. Also, DME combustion results in exhaust gas containing lower amounts of  $NO_x$ ,  $SO_x$  and CO emissions than conventional fuels<sup>[3]</sup>. DME is also used as an aerosol propellant in the cosmetics industry, coolant, key intermediate for the production of many important chemicals, source of hydrogen for fuel cells and fuel in gas turbines for power generation<sup>[4]</sup>. Another advantage of DME is that it can be used as an additive for diesel fuel due to its high cetane number, high oxygen content and lack of C–C bond<sup>[5,6]</sup>.

DME can be produced by two methods; the first method is considered the indirect method, in which it is produced by dehydration of methanol over solid-acid catalysts<sup>[7]</sup>. The second method is the direct, since DME can be synthesized from synthesis gas over a hybrid catalyst<sup>[8]</sup>.

Various solid acid catalysts such as  $\gamma-Al_2O_3$ , niobia-modified alumina,  $TiO_2-ZrO_2$ , sulfated zirconia, mesoporous silicates, zeolites and zeotypes have been studied for methanol dehydration<sup>[2]</sup>. As mentioned previously<sup>[9]</sup>, zeolite materials tend to deactivate rapidly and  $\gamma-Al_2O_3$  exhibits lower methanol rates. So, it is important to develop

new catalysts to replace the acids commonly used in this reaction and to overcome the problems take place by using other solid acid catalysts.

Sulfated zirconia (SZ) has recently attracted wide attention due to its acid characteristics and its consequent potential as solid “superacid” catalyst for many industrially important reactions. It has been widely used to catalyze reactions such as hydrocarbon isomerization, methanol conversion, alkylation, acylation, esterification, etherification, condensation, nitration and cyclization<sup>[10]</sup>. The acidity as well as the catalytic performance of SZ significantly depends upon its method of preparation, surface area, source of zirconia, precipitating agent, source of sulfate, processing pH value, temperature, aging time and finally the calcination temperature and environment of storage<sup>[11]</sup>. The typical procedure for a SZ catalyst synthesis includes impregnation of amorphous  $ZrO_2 \cdot xH_2O$ , crystalline  $ZrO_2$  or  $Zr(OH)_2$  with sulfate-containing compounds (e.g.,  $H_2SO_4$ ,  $(NH_4)_2SO_4$ ,  $(NH_4)_2S_2O_8$ ,  $H_2S$ ,  $SO_2$  or  $CS_2$ )<sup>[10,12]</sup>.

Recently, we have reported the use of  $(NH_4)_2SO_4$  as a sulfating agent for the synthesis of SZ catalyst for methanol dehydration to DME<sup>[9]</sup>. The results indicated that the sample with 10%  $SO_4^{2-}$  showed the higher catalytic activity with 83% conversion and 100% selectivity toward DME at 230°C

reaction temperature. However, SZ catalyst exhibits high initial activity, but deactivation of activity occurs very quickly<sup>[13]</sup>. In addition, the leaching of active  $\text{SO}_4^{2-}$  groups from the surface of SZ catalyst and the formation of  $\text{H}_2\text{SO}_4/\text{HSO}_4^-/\text{SO}_4^{2-}$  ions were also observed in the presence of alcohol and water<sup>[14,15]</sup>. In fact, incorporation of metal leads to a SZ catalyst that retains its activity for a much longer period of operation than the metal free SZ<sup>[16,17]</sup>. However, the effect of different metal sulfate precursors on the catalytic activity of zirconia in dehydration of methanol to DME to our best knowledge has not been reported.

Therefore, the aim of this study was to compare the effects of different metal sulfate precursors (sulfating agent) on the structural and catalytic performance of SZ in dehydration of methanol to DME. The catalytic activity of SZ has been correlated with their structure and surface properties.

## 1 Experimental

### 1.1 Materials

$\text{Zr}(\text{OH})_4$  (Aldrich),  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Ag}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  (Pure Lab. Chemicals provided by El Nasr Pharmaceutical Chemicals Co., Egypt), methyl alcohol (obtained as pure reagents and used without further purification).

### 1.2 Catalyst preparation

A series of 10%  $\text{SO}_4^{2-}/\text{ZrO}_2$  (10% SZ) catalysts were prepared by incipient wetness impregnation of appropriate amount of sulfate precursor solutions corresponding to 10%  $\text{SO}_4^{2-}$  in the final catalyst with zirconium hydroxide. Samples were designated as MSZ, where *M* indicates the metal type. The typical synthesis procedure was indicated by 10% CuSZ. A 0.26 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was dissolved in small amounts of de-ionized water, and then added 1.16 g of  $\text{Zr}(\text{OH})_4$  powder and the mixture was admixed carefully to obtain a homogeneous paste. After the impregnation, the SZ catalysts were dried overnight at 100°C and calcined at 450°C for 3 h in a static air atmosphere. The percent of metal loaded in all the samples were calculated theoretically and cited in Table 1.

### 1.3 Catalyst characterization

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded in the 1800–500  $\text{cm}^{-1}$  range with a Nicolet 6700 spectrometer. The samples were pelletized with KBr.

The crystal structures of the catalysts were determined by a powder X-ray diffraction (XRD) on Philips (Netherlands) diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ), at accelerating voltage and current of 40 kV and current of 20 mA, respectively. The catalysts were scanned in the range of  $2\theta$  from 4° to 80° with a step interval of 0.06°.

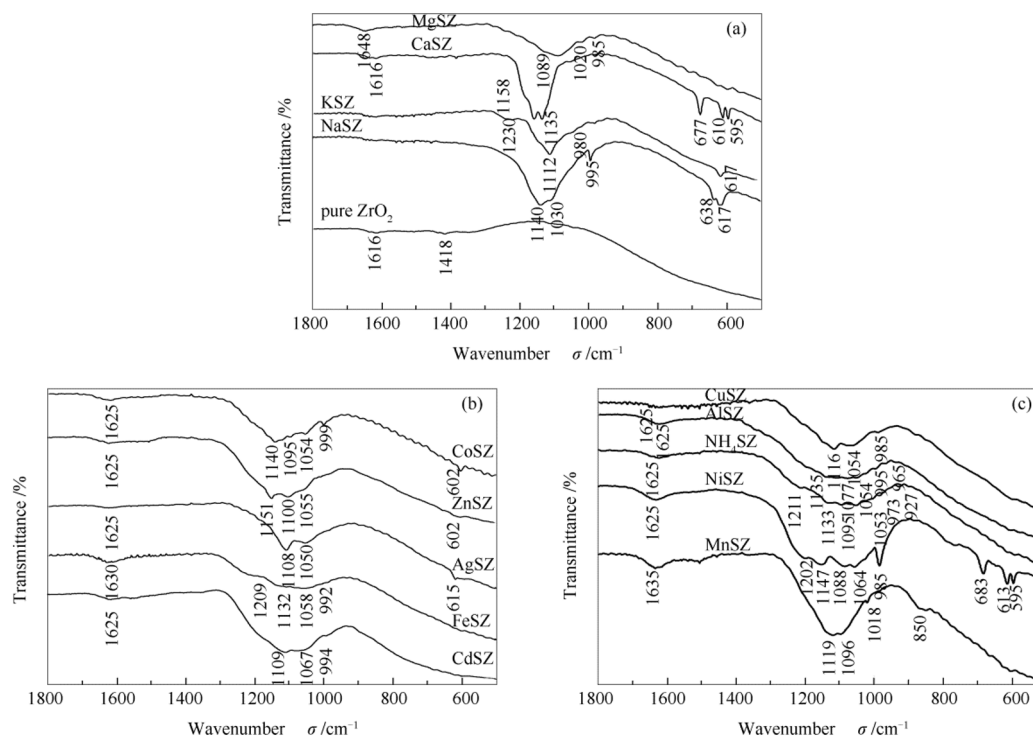


Fig. 1 FT-IR spectra of pure  $\text{ZrO}_2$  and the different sulfated samples

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