



## A new facile method to synthesize mesoporous $\gamma$ -Al<sub>2</sub>O<sub>3</sub> of high surface area and catalytic activity

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### ABSTRACT

The present investigation describes a new method to prepare a high surface area mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by controlled calcination of Al (III) nitrate with urea. The alumina catalyst thus obtained is characterized by XRD, adsorption–desorption isotherms and acidity measurements. The catalytic activity is evaluated for dehydration of methanol to form dimethyl ether. It showed high conversion and 100% selectivity to DME as compared to the other mesoporous aluminas, as well as zeolite catalysts. The results are discussed in relation to the surface area and the strength of the acid sites.

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### 1. Introduction

The advances in nanotechnology have led to an increasing demand for multifunctional materials. Highly ordered mesoporous materials function as excellent catalysts due to high surface areas and surface functionalities. They also function as electrode material in solid oxide fuel cells. Thus, synthesis of ordered mesoporous materials has attracted great deal of research in the recent years. The novel approach of using structure directing agents for synthesis, has added a new dimension to the synthesis of porous materials. However, synthesis of ordered mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is found to be much more difficult and hence considered as a challenging task [1].

Pinnavaia and coworkers [2] first synthesized mesoporous alumina using aluminium alkoxide via a hydrothermal method. Vaudry et al. [3] made use of caproic and lauric acid and synthesized mesoporous alumina having surface area 710 m<sup>2</sup>/g but the pore size was in the microporous range (19 Å).

Recent research in this area includes the sol gel method of synthesis using surfactants such as CTAB and non ionic templates such as Triton X-114 as structure directing agents [4]. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> obtained is reported to have high surface area but the use of costly surfactants as template make such a method uneconomical.

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Zhang et al. [5] reported the synthesis of high surface area mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> using Al(NO<sub>3</sub>)<sub>3</sub>/NH<sub>3</sub>/urea/CTAB system. This mixture was subjected to hydrothermal treatment at 100 °C for 48 h. They observed that with only Al(NO<sub>3</sub>)<sub>3</sub>/urea mixture, very low surface area of 158 m<sup>2</sup>/g with a pore volume of 0.14 cm<sup>3</sup>/g was obtained. The surface area then increased to 276 m<sup>2</sup>/g and the pore volume to 0.21 cm<sup>3</sup>/g with the addition of CTAB.

The two above samples were further characterized by XRD. They report that only one broad peak at 1–2° was observed for the sample prepared with CTAB, indicating a disordered wormlike mesostructure and however, no peak appeared in the low-angle XRD pattern of the sample prepared without CTAB, manifesting the vital role of CTAB in production of wormlike mesopores.

Ordered mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in particular, with high surface area and tunable pore structure has attracted much attention due to its potential application as catalyst support in automotive and petrochemical industries [6].

Dimethyl ether (DME) is an important alternative diesel fuel due to its low NO<sub>x</sub> emission, near zero smoke and less engine noise compared with those of traditional diesel fuels [7,8]. Hence catalytic dehydration of methanol to DME is one among the many important researches of the recent years.

In spite of all the research work done till date, more simpler methodologies are required to synthesize ordered mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> via a cost effective route.

In this paper, we present a simple urea calcination method to obtain mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> having a high surface area and high catalytic activity.

## 2. Experimental

### 2.1. Materials

Aluminium nitrate, DL-malic acid, urea were purchased from Loba Chemicals, India and used without any further purification.

### 2.2. Synthesis of mesoporous $\gamma$ - $\text{Al}_2\text{O}_3$

#### 2.2.1. By sol gel method

About 75.03 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in 100 mL of deionised water. A 2.5% ammonia was added drop wise until the  $\text{pH} > 3.8$ . About 350 mL of 2.5% ammonia was then directly added and then the precipitate formed was washed several times and then dispersed in 200 mL of deionised water. It was then peptized with 1 M  $\text{HNO}_3$  at 80 °C under vigorous stirring conditions for 4 h to obtain stable boehmite sol of 1 mol/L [9].

Desired amount of DL-malic acid was then added to boehmite sol in 2:1 ratio. The mixture was stirred vigorously at 80 °C for 1 h and aged on water bath at 90 °C for 3 h. The gel was then dried at 120 °C for 6 h to obtain the dry gel followed by calcination at 500 °C for 4 h to form stable mesoporous  $\gamma$ - $\text{Al}_2\text{O}_3$  [10]. The sample was labeled as AM = ( $\gamma$ - $\text{Al}_2\text{O}_3$  prepared using malic acid).

#### 2.2.2. By calcination with urea

About 75.03 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in 100 mL of deionised water. Desired amount of urea was then added maintaining  $\text{Al}^{3+}$  to urea ratio of 1:2. The mixture was then vigorously stirred for 1 h and then dried at 120 °C.

The dry solid mixture was heated very slowly at 250 °C for about 3 h till the gas evolution due to decomposition of the nitrates is complete. The nitrate free sample was ground to a fine powder and then calcined at 500 °C for 3 h to form mesoporous  $\gamma$ - $\text{Al}_2\text{O}_3$ . This sample was labeled as AU = ( $\gamma$ - $\text{Al}_2\text{O}_3$  prepared using urea).

### 2.3. Catalyst characterization

The catalysts were characterized by X-ray diffraction (Rigaku Miniflex,  $\text{Cu K}\alpha$  radiation, 30 kV and 15 mA), BET surface area and adsorption–desorption isotherms (NOVA 1200 Quanta chrome).

Acidity measurement was carried out using Temperature Programmed Desorption technique (TPD) using ammonia as a probe molecule in the temperature range of 40–440 °C. A 0.5 g of the catalyst was activated in air at 300 °C for 1 h in a catalytic reactor. The catalyst was then cooled to room temperature in nitrogen atmosphere. Anhydrous ammonia was passed over the catalyst for 30 min followed by flushing of the catalytic reactor with nitrogen to remove the unadsorbed ammonia. The sample was then heated at a rate of 5 °C/min and the amount of ammonia desorbed was measured as a function of temperature.

Pyridine desorption studies were carried out on the synthesized samples in the temperature range of 50–400 °C. About 0.5 g of the sample was activated in air at 300 °C and then gradually cooled in nitrogen atmosphere to avoid any physisorption of atmospheric water. A pyridine gas was then passed through the catalyst for 1 h followed by degassing in inert atmosphere to remove any unadsorbed pyridine. The FTIR spectra of these samples were recorded on IR Prestige 21 Shimadzu spectrometer.

### 2.4. Catalytic dehydration of methanol to dimethyl ether (DME)

The activity of the synthesized mesoporous  $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst for dehydration of methanol to DME was assessed in a fixed-bed stain-

less steel reactor. Methanol was introduced to the reaction zone by bubbling ultra-pure helium gas through a glass saturator (2 L capacity) filled with ultra-high pure methanol and maintained at 20 °C. In each run 0.05 g of the catalyst was tested at 260 °C at GHSV of 4000  $\text{mL g}_{\text{cat}}^{-1} \text{h}^{-1}$ . The tail gas out of the reactor was analyzed by an on-line GC (Agilent 7890 A) equipped with a thermal conductivity detector and HP-Plot Q capillary column.

## 3. Results and discussion

### 3.1. XRD studies

The wide angle XRD pattern of the alumina showed that they are crystalline and belong to the  $\gamma$  phase [5] (JCPDS card 10-0425).

The low-angle XRD pattern (Fig. 1) of AM showed a half peak centering at 0.6° between 0.5° and 2° which indicates the presence of randomly distributed pores (interparticle voids) with a wide pore size distribution [4]. However,  $\gamma$ - $\text{Al}_2\text{O}_3$  prepared using urea,

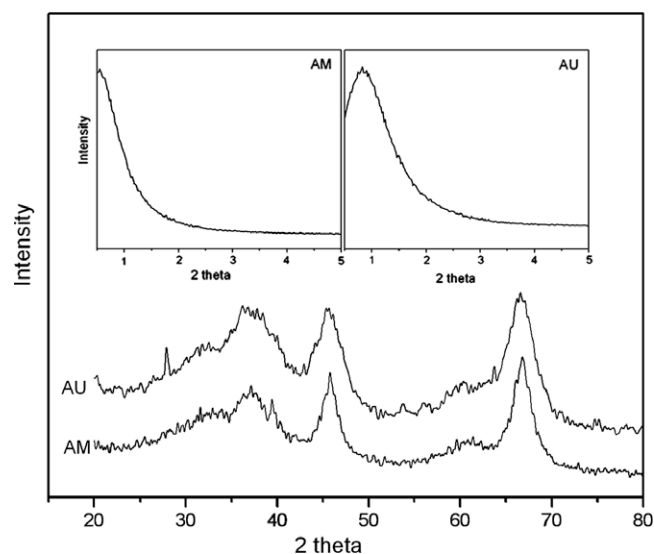


Fig. 1. The low-angle and wide angle XRD pattern of (1) AM (alumina prepared using malic acid) and (2) AU (alumina prepared using urea).

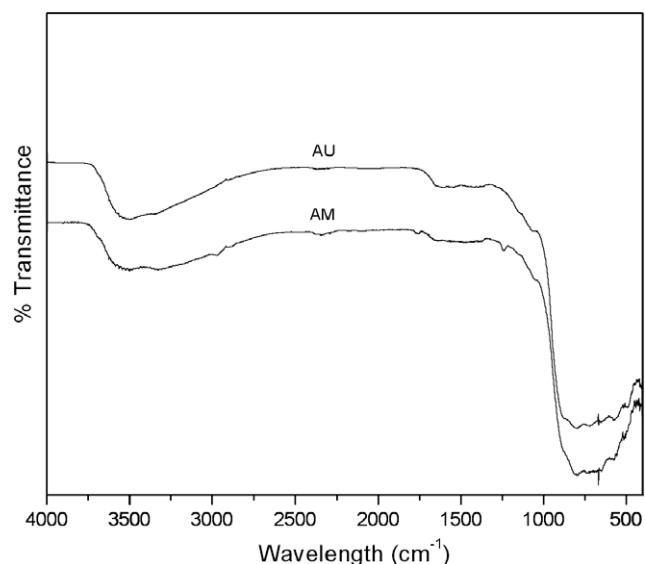


Fig. 2. FTIR spectra of (1) AM (alumina prepared using malic acid) and (2) AU (alumina prepared using urea).

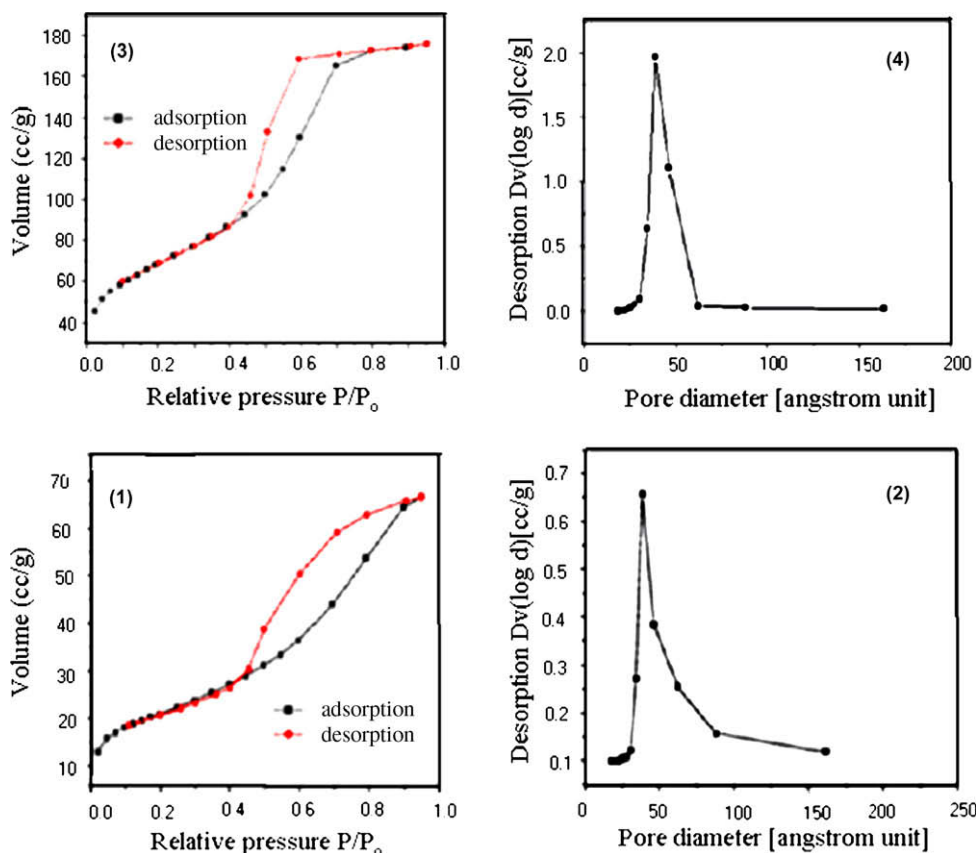


Fig. 3. Nitrogen adsorption–desorption isotherms (1, 3) and corresponding pore size distribution (2, 4) of mesoporous  $\gamma$ - $\text{Al}_2\text{O}_3$  prepared using malic acid (1, 2) and urea (3, 4).

displayed the characteristic peak of mesoporous aluminas as evident at  $2\theta$  between  $0.5^\circ$  and  $2^\circ$  [11].

### 3.2. FTIR studies

The samples were initially activated to  $300^\circ\text{C}$  to remove the physisorbed water followed by cooling in nitrogen atmosphere and then the FTIR spectra were recorded (Fig. 2). All the  $\gamma$ -alumina samples displayed a broad absorption peak at around  $3500$ – $3700\text{ cm}^{-1}$ . These are typical absorptions due to O–H stretching vibrations of chemisorbed water molecules. Water is known to undergo physisorption followed by chemisorption onto the  $\gamma$ -alumina surface and forms M–H and M–OH bonds. The presence of these M–OH bonds is the possible reason for Bronsted acidity.

Absence of peaks corresponding to the organic compounds confirms the complete removal of the structure directing agent on calcination at  $500^\circ\text{C}$ . Absorption bands at  $473$  and  $620\text{ cm}^{-1}$  were due to the vibrations of Al–O–Al, while the peak at  $742$  and  $1070\text{ cm}^{-1}$  can be assigned respectively to the bending vibrations of Al–O and O–H.

### 3.3. Nitrogen sorption studies

Mesoporous aluminas prepared by both the methods, displayed typical type IV isotherms [12] as evident from Fig. 3. The sample

AM displayed a wide pore size distribution with average pore diameter of  $3.83\text{ nm}$  and a pore volume of  $0.1\text{ cm}^3\text{ g}^{-1}$ .

In contrast, sample AU displayed a narrow pore size distribution. The nitrogen adsorption isotherms recorded on organized mesoporous aluminas are characterized by a relatively steep increase in the adsorbed amount starting at  $P/P_0 = 0.4$ – $0.8$ . The hysteresis loop of the type H1 in this region is due to the capillary condensation within the uniform mesopores.

The sample AU has an average pore diameter of  $3.9\text{ nm}$  and a pore volume of  $0.25\text{ cm}^3\text{ g}^{-1}$  which is more than twice as compared to AM (Table 1). The sample also showed much higher surface area of  $246\text{ m}^2\text{ g}^{-1}$ , as a result of uniform mesopores. The absence of the large pores is evident from the fact that the isotherm ends with a nearly horizontal plateau [9].

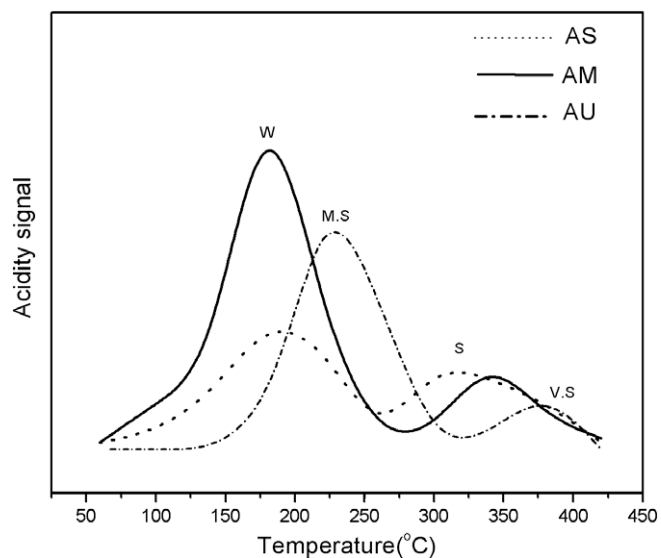
### 3.4. Catalytic activity studies

Catalytic dehydration of methanol to DME was used to study and compare the catalytic activities of mesoporous  $\gamma$ - $\text{Al}_2\text{O}_3$ . The results of the catalytic dehydration reaction are as shown in Table 1.

From Table 1 it is evident that the percentage conversion of methanol increases in the following order  $\text{AS} < \text{AM} < \text{AU}$  with 100% product selectivity. However, BET surface area follows the order  $\text{AM} < \text{AS} < \text{AU}$ . Although the highest conversion of 64% was achieved in case of catalyst AU having surface area of  $246\text{ m}^2/\text{g}$ , there was no

Table 1  
Catalytic dehydration of methanol over synthesized mesoporous  $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst.

Catalyst	Description	BET surface area ( $\text{m}^2/\text{g}$ )	Pore diameter (nm)	Pore volume ( $\text{cm}^3/\text{g}$ )	% Conversion of methanol	Selectivity to DME (%)
AM	$\gamma$ - $\text{Al}_2\text{O}_3$ prepared using malic acid	75	3.83	0.10	26	100
AS	$\gamma$ - $\text{Al}_2\text{O}_3$ prepared using salicylic acid	106	3.83	0.15	20	100
AU	$\gamma$ - $\text{Al}_2\text{O}_3$ prepared using urea	246	3.90	0.25	64	100



**Fig. 4.**  $\text{NH}_3$ -TPD profiles of (1) AS (alumina prepared using salicylic acid), (2) AM (alumina prepared using malic acid), (3) AU (alumina prepared using urea), W = weak, S = strong, MS = moderately strong, VS = very strong acid sites.

clear correlation between the surface area and the catalytic activity. Hence it was necessary to investigate the nature of the acid sites.

As reported in the literature [13], both Bronsted and Lewis acid sites play a key role in catalytic dehydration of methanol as in case of zeolites. Hence the type and the strength of the acid sites must

have an important contribution to the observed catalytic conversion in case of  $\gamma\text{-Al}_2\text{O}_3$  as well. Hence acidity measurements were carried out on the synthesized catalysts.

### 3.5. Acidity measurements

#### 3.5.1. $\text{NH}_3$ -TPD profiles

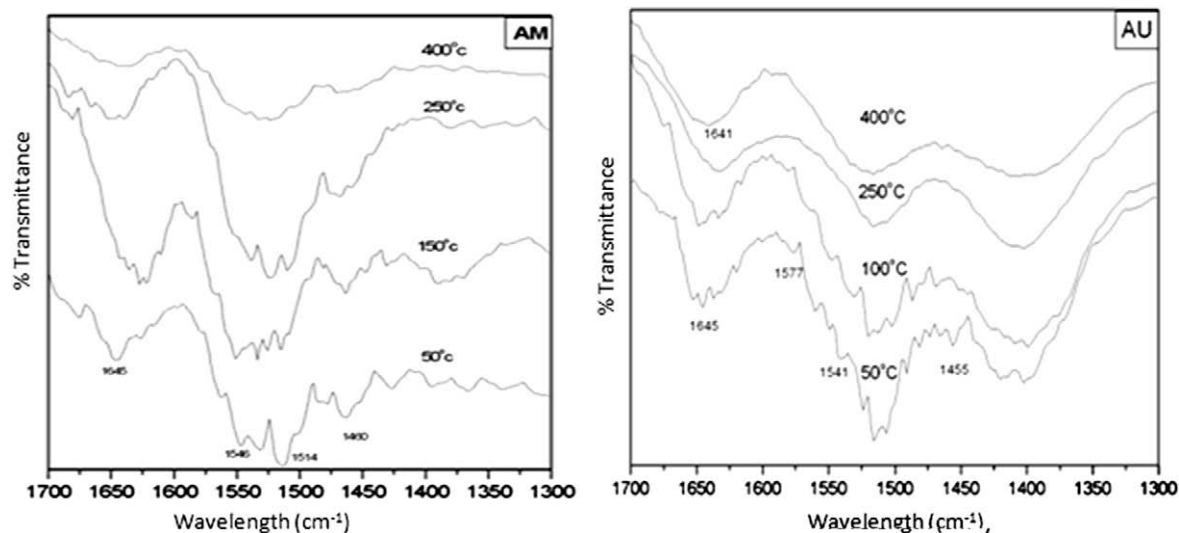
It is evident from the  $\text{NH}_3$ -TPD profiles (Fig. 4) that both AS and AM showed a broad peak in the temperature range of 120–250 °C. However, the number of acid sites in AM is almost twice as compared to those present in AS. This could be one of the reasons for the higher conversion of AM in spite of having a lower surface area than AS. Further, sample AU has high surface area and stronger acid sites than AM and AS as indicated by the broad peak in the temperature range of 200–300 °C which are labeled as MS (moderately strong acid sites). Both these factors add to the observed high conversion. It is also clear from the data on HZSM-5 zeolites  $Z_1$  and  $Z_2$  (Table 2) that % conversion is dependent on these moderately strong acid sites. Thus  $Z_1$  having a high Si/Al ratio (225) and hence lower Bronsted acidity showed lower conversion as compared to  $Z_2$  (HZSM-5, Si/Al = 40) which has a high conversion but mixed selectivity. In Ref. [13] it is reported that Na-H-ZSM-5(30) obtained from H-ZSM-5(30) by performing ion exchange with aqueous  $\text{NaNO}_3$  was found to have much reduced number of acid sites and, especially, eliminated the very strong acid sites. Therefore, subsequent reactions of DME over strong acid sites to form light olefins were reduced by sodium ion exchange. Thus, Na-H-ZSM-5(30) gave a higher selectivity for DME than H-ZSM-5. Our results are in good agreement with the above findings and the presence of moderately strong Bronsted acid sites in AU explains its higher selectivity as

**Table 2**

Total acidity of the synthesized  $\gamma\text{-Al}_2\text{O}_3$  in relation to the surface area, catalytic activity and selectivity.

S. no.	Catalyst	Description	Total acidity (mmol/g)	BET surface area ( $\text{m}^2/\text{g}$ )	% Conversion of methanol	Selectivity to DME (%)	Others*
1	AM	$\gamma\text{-Al}_2\text{O}_3$ prepared using malic acid	0.074	75	26	100	–
2	AS	$\gamma\text{-Al}_2\text{O}_3$ prepared using salicylic acid	0.040	106	20	100	–
3	AU	$\gamma\text{-Al}_2\text{O}_3$ prepared using urea	0.061	246	64	100	–
4	$Z_1$	Zeolite HZSM-5 (225)	0.069	305	53	97	3
5	$Z_2$	Zeolite HZSM-5 (40)	0.240	358	75	80	20

\* Others include ethene, propene, CO/ $\text{CO}_2$ .



**Fig. 5.** FTIR spectra of pyridine desorption on AM (alumina prepared using malic acid) and AU (alumina prepared using urea).

compared to the zeolite samples. Clearly, catalyst AU showed a relatively good % conversion as well as excellent selectivity to DME as compared to rest of the catalysts investigated here.

### 3.5.2. Pyridine FTIR studies

Fig. 5 shows temperature dependent FTIR spectra of adsorbed pyridine. Both AM and AU showed absorptions in the range of 1500–1570  $\text{cm}^{-1}$  as well as around 1640  $\text{cm}^{-1}$  due to Bronsted acid sites. The absorptions at  $\sim 1460 \text{ cm}^{-1}$  due to pyridine coordinated to the Lewis acid sites are less intense and more significant in AM than AU. A clear indication of the presence of strong Bronsted sites on AU sample is the presence of an intense signal at ca. 1640  $\text{cm}^{-1}$  after desorption at 400 °C. In addition to this, the shape of the TPD profile in Fig. 4 (high temperature signal) is a clear indication that this sample features the strongest Bronsted acid sites of the series.

Therefore it is concluded that high conversion shown by catalyst AU is due to the large presence of relatively strong Bronsted acid sites dispersed over large surface area.

## 4. Conclusion

A new facile method was developed to obtain mesoporous  $\gamma\text{-Al}_2\text{O}_3$  having a large surface area and relatively uniform pore sizes.

The mesoporous  $\gamma\text{-Al}_2\text{O}_3$  prepared using urea showed a high catalytic activity of  $\sim 64\%$  as well as 100% selectivity to DME.

The high catalytic activity is attributed to a combination of some favorable factors such as high surface area, uniform pore size and large presence of relatively strong Bronsted acid sites.

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