

## Preparation of Amine Functionalized Porous Silica by Ultrasonic Technique for the Methylation Reaction of Phenol with Dimethyl Carbonate

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**Summary:** Amine functionalized silica catalysts, including (3-aminopropyltrimethoxysilane (APTMS)) NH<sub>2</sub>/SiO<sub>2</sub>, (Diazabicycloundecene/SiO<sub>2</sub>) DBU/SiO<sub>2</sub> and (1, 5, 7-triazabicyclo [4, 4, 0] dec-5-ene/SiO<sub>2</sub>) TBD/SiO<sub>2</sub>, which were characterized by <sup>29</sup>Si NMR, elemental analysis and indicator dye adsorption, were prepared by ultrasonic technique under mild conditions. Such hybrid solid bases showed high catalytic activity and well reusability towards the methylation reaction of phenol with dimethyl carbonate (DMC).

**Keywords:** Amine functionalized porous silica; Ultrasonic technique; Methylation reaction.

### Introduction

The attempt to heterogenize homogeneous catalyst as alternatives to more traditional reagents and catalysts has been one area of research that has seen increasing interest [1-3]. Much recent work was focused on the preparation of organically modified solid bases to heterogenize homogeneous amine catalyst. The modification process was generally operated by stirring, heating, refluxing, etc [4-6]. Recently, the interest in synthetic sonochemistry reactions has grown [7]. The ultrasonic technique has been widely applied in two-phase systems due to its advantages, such as high accuracy and rapidity. Most of these reactions have involved a heterogeneous chemical interaction [8]. In the area of porous materials functionalized by organic groups, however, only limited applications of ultrasound have been explored [9, 10]. In the present work, an alternative synthetic route for the formation of amine functionalized porous silica was developed by using ultrasonic energy, which can produce chemical modifications on solids by cavitation phenomenon [11]. The synthetic amine functionalized porous silica were promising catalysts for a variety of reactions [12-14].

Aryl methyl ethers, which are widely applied to antioxidants, stabilizers for polymers, dyes, agricultural chemicals, etc., are important intermediates in fine chemicals. Aryl methyl ethers are usually synthesized by O-methylation of hydroxyarene with methyl halides (or dimethyl sulfate), which can cause serious security and environmental problems. DMC is a new kind of green chemical material and possesses such merits as security, high efficiency and environmental protection. Therefore, recently there is a large body of investigations into DMC and its application to O-

methylation reaction. At the present time, the main catalysis systems are gas-liquid phase transfer catalysis [15, 16], tetrabutylammonium bromide homogeneous catalysis [17] and NaX zeolite [18] heterogeneous catalysis. Few studies have reported the use of amine functionalized porous silica as catalysts for the methylation reaction of phenol with dimethyl carbonate. The amine functionalized porous silica has great potential in this kind of reaction.

In the present work, amine functionalized silica catalysts, including NH<sub>2</sub>/SiO<sub>2</sub>, DBU/SiO<sub>2</sub> and TBD/SiO<sub>2</sub>, were prepared with APTMS and 3-chloropropyltrimethoxysilane (CPTMS) as the coupling agents by ultrasonic technique under mild experimental conditions. In addition, the catalytic activity of the organic solid base catalysts was evaluated by the synthesis of aryl methyl ether from phenol and DMC.

### Results and Discussion

#### Modification of Porous Silica with Amine Groups

The <sup>29</sup>Si NMR spectra in solid state indicated that the covalent bond formed between silylant agents and silanol groups on the silica surface (Fig.1). Two resonances at -109 and -99 ppm could be attributed to <sup>29</sup>Si nuclei having four Si-O-Si linkages and <sup>29</sup>Si nuclei having three Si-O-Si linkages and one -OH, respectively. The resonances at -58 and -67 ppm were assigned to RSi(OSi)(OH)<sub>2</sub> and RSi(OSi)<sub>3</sub>, respectively [19, 20], which illustrated the amine groups were grafted onto the porous silica by covalent bonds. C/N value (molar ratio) could also reflect the degree of grafting reaction between silanol groups and organosilanes [21]. NH<sub>2</sub>/SiO<sub>2</sub>, DBU/SiO<sub>2</sub> and TBD/SiO<sub>2</sub> showed the C/N=3-3.5, 6-7 and 3.3-4,

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respectively (Table-1). The results also suggested the anchorage of  $-(\text{CH}_2)_3\text{NH}_2$ ,  $-(\text{CH}_2)_3\text{TBD}$  and  $-(\text{CH}_2)_3\text{DBU}$  by Si-O-Si bonds. This agreed with the result of the  $^{29}\text{Si}$  NMR spectra. Furthermore, the elemental analysis results also showed that there were no carbon and nitrogen in the amine-free porous silica, i.e. the carbon, nitrogen in amine-free porous silica were from the grafting reaction between amine groups and silanol groups on the porous silica surface. According to the  $N_{\text{org}}\%$  of the grafted organic groups, the quantity of the grafted organic groups was different. The  $N_{\text{org}}\%$  was decreased as  $-(\text{CH}_2)_3\text{NH}_2 > -(\text{CH}_2)_3\text{TBD} \sim -(\text{CH}_2)_3\text{DBU}$ . For the sample modified with  $-(\text{CH}_2)_3\text{TBD}$  and  $-(\text{CH}_2)_3\text{DBU}$ , it should be attributed to the big framework of  $-(\text{CH}_2)_3\text{TBD}$  and  $-(\text{CH}_2)_3\text{DBU}$  groups. The big framework took up more space than  $-(\text{CH}_2)_3\text{NH}_2$ . Consequently, the  $-(\text{CH}_2)_3\text{TBD}$  and  $-(\text{CH}_2)_3\text{DBU}$  groups could not contact fully with the surface free  $-\text{OH}$ .

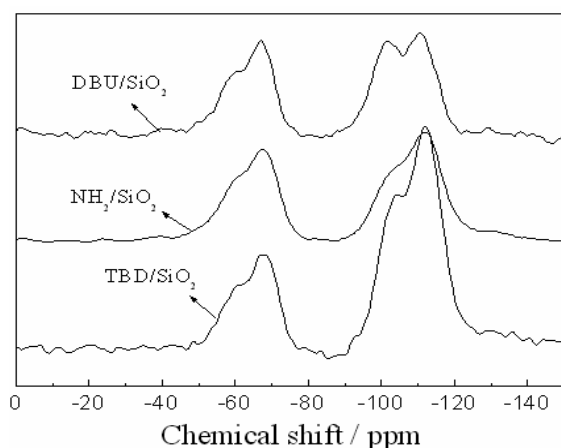


Fig. 1:  $^{29}\text{Si}$  NMR solid state spectra of amine functionalized silica.

Table-1: Results for elemental analysis.

Sample	N%	C%	H%	Wt.org. (%)	$N_{\text{org}}\%$ (mmol/g)	C/N (Number ratio)	
						Actual data	theoretical data
Porous silica	0	0	0.73	0	0	0	0
$\text{NH}_2/\text{SiO}_2$	2.80	7.68	2.02	11.55	2.00	3.2	3.0
$\text{TBD}/\text{SiO}_2$	4.20	12.78	1.69	18.11	1.00	3.5	3.3
$\text{DBU}/\text{SiO}_2$	2.86	14.75	1.63	19.18	1.02	6.1	6.0

#### Basicity of Samples

The base strength  $H_-$  ( $H_- = \text{pKa} (= \text{pK}_{\text{BH}}) + \log [B^-]/[BH]$ ) of a solid surface is defined as the ability of the surface to convert an adsorbed electrically neutral acid into its conjugate base. Thus, it was generally possible to determine the basic strength by observing the color changes of acid indicators over a range of  $\text{pKa} = H_-$  values (When the indicators show

intermediate color, the base strength of solid base nearly equal to  $\text{pK}_{\text{BH}}(\text{pKa})$  of the indicator.) [22]. A solid with a large positive  $H_-$  has strong basic sites. Grafting with different functional groups could result in different base strengths. As shown in Table-2,  $\text{TBD}/\text{SiO}_2$  had the highest base strength of  $H_- \approx 15.0$ , while  $\text{NH}_2/\text{SiO}_2$  and  $\text{DBU}/\text{SiO}_2$  had the basicity of  $H_- \approx 9.3$  and  $H_- = 12$ , respectively. Thus, the basic strength of the samples was in the order of  $\text{TBD}/\text{SiO}_2 > \text{DBU}/\text{SiO}_2 > \text{NH}_2/\text{SiO}_2$ .

Table-2: Basic strengths of the samples and results for the synthesis of aryl methyl ether.

Catalysts	pKa value of indicators			Reaction results	
	7.2	9.3	15.0	Conversion (%)	Isomer selectivity (%)
None				27.3	72.3
Porous silica				35.7	68.3
$\text{NH}_2/\text{SiO}_2$	+	±	-	99.6	100.0
$\text{DBU}/\text{SiO}_2$	+	+	±	99.9	100.0
$\text{TBD}/\text{SiO}_2$	+	+	±	99.8	100.0

(+) color changes clearly; (-) color does not change; (±) color changes unclearly.

Reaction conditions: 473K, amount of catalyst was 0.1g, reaction time= 12h

#### Catalytic Performance

The catalytic activity was tested in the methylation reaction of phenol and DMC (Table-2). As shown in Table-3, among the catalysts, the amine-free porous silica is completely inert, and hence, anchored amine groups were the catalytic species (Table-3). After 12 h of reaction,  $\text{NH}_2/\text{SiO}_2$ ,  $\text{TBD}/\text{SiO}_2$  and  $\text{DBU}/\text{SiO}_2$  catalysts all showed high phenol conversion (>99%) and selectivities towards anisole (100%), which suggested that it should be indeed the grafted amine groups that catalyzed the reaction. And it was also shown that the samples containing different types of amine groups made little differences for the conversions and selectivities, indicating that the methylation reaction of phenol and DMC could be successfully catalyzed by the three types modified samples. The  $\text{NH}_2/\text{SiO}_2$ ,  $\text{TBD}/\text{SiO}_2$  and  $\text{DBU}/\text{SiO}_2$  catalysts were easily recovered by filtration, and subjected to utilization for 5 recycles with conversion of phenol 13.8%, 51.0% and 55.2%, respectively, i.e. the higher basic strength, the better reusability of the catalyst (Table-3). And for all the catalysts, the utilization for 5 recycles hardly changed the selectivities to anisole.

Table-3: The reusability of the samples for the methylation reaction of phenol and DMC.

Conversion of phenol (%)	$\text{NH}_2/\text{SiO}_2$	$\text{DBU}/\text{SiO}_2$	$\text{TBD}/\text{SiO}_2$
1 time	99.6	99.9	99.8
2 times	99.4	99.5	99.5
3 times	60.1	85.6	88.7
4 times	37.5	76.8	79.0
5 times	13.8	51.0	55.2

Reaction conditions: 473K, amount of catalyst was 0.1g, reaction time= 12h

## Experimental

### Synthesis of Amine Functionalized Porous Silica

NH<sub>2</sub>/SiO<sub>2</sub> was prepared as follows: 10.0 g of SiO<sub>2</sub> material was heated for 12 h at 473 K in vacuum to remove all adsorbed moisture but not surface OH groups. The material was left to cool in vacuo, and then transferred into a 250 mL conical flask. It was mixed with 40.0 mL of cyclohexane, and 0.05 mol of APTMS was then added. The mixture in conical flask was put into the ultrasonic bath at ambient temperature (300 K). After 2 hours, the mixture was filtered. The catalyst was extracted with toluene in a Soxhlet extractor over a period of 24 h and dried at 333 K in vacuo.

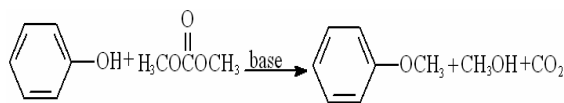
TBD/SiO<sub>2</sub> was prepared by two steps: silica was firstly modified by CPTMS via the same method as that of NH<sub>2</sub>/SiO<sub>2</sub>, and chloropropylsilyl-functionalized SiO<sub>2</sub> was then reacted with 0.05 mol TBD in cyclohexane (40.0 mL). The resultant was treated by ultrasonic vibration for 1 h. Afterwards, the catalyst was obtained by extracting with toluene in a Soxhlet extractor over a period of 24 h and drying at 333 K in vacuum. The same method was used for the preparation of DBU/SiO<sub>2</sub>.

### Characterization

<sup>29</sup>Si MAS NMR spectra were recorded on a Bruker MSL-400 spectrometer at 59 MHz using zirconium oxide rotors and a rotation frequency of 4000 Hz, respectively. The content of carbon, nitrogen, and hydrogen in all the modified samples was determined using a Vario EL analyzer. For each sample three measurements were performed with the relative error of less than 0.1%. The base strength of samples was detected by hammett indicators. The samples were degassed at 373 K for 6 h before transferring into cyclohexane under N<sub>2</sub> for the measurement.

### Catalytic Test

All modified catalysts were tested in the methylation reaction of phenol with DMC (see Scheme-1). The reaction was carried out in a sealed stainless steel kettle (100 mL). In a typical procedure, mixture of 9.41 g of phenol and 18.00 g of DMC (molar ratio=1:2) was added to each catalyst (0.10 g) respectively. The mixture was stirred for 12 h at 473 K. After completion of the reaction, the product was cooled to room temperature, then filtered and analyzed by gas chromatography.



Scheme-1: Reaction scheme for organic solid-base catalyzed methylation reaction from phenol and DMC

## Conclusion

The efficient ultrasonic technique was used for the preparation of amine functionalized porous catalysts for the synthesis of anisole from phenol and DMC. The characterization indicated that the amine groups were grafted onto the silica surface by covalent bond. The anchored amine groups are the main catalytic species in the methylation reaction. Such hybrid solid bases showed high conversion (>99%) with 100% selectivity towards anisole. The catalysts could be recovered by filtration and were subjected to utilization for several recycles. Catalyst basicity was found to have influence on their reusabilities. The higher basic strength, the better reusability of the catalyst.

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