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Styrene from toluene by side chain alkylation over a novel solid acid-base catalyst

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ABSTRACT

A novel solid acid-base catalyst with aluminum and nitrogen were prepared from aluminum and amine by using triblock copolymer Pluronic F127 as a template and resol as framework via evaporation induced organic–organic assembly method. The catalyst was characterized by UV–vis absorption spectra (UV–vis), fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), the acid-base properties of the catalyst were determined by temperature programmed desorption (TPD) using CO_2 and NH_3 as probe molecules, and the side chain alkylation of toluene with methanol over the catalyst has been investigated. The results show that Cat–$NH(C_2H_5)_2$ demonstrates the higher activity and selectivity, styrene yield reaches 44.9% and selectivity 97.6%. It is considered that the strength of base and distance of the specific surface acid-base pairs over the catalysts are favored to bimolecular side-chain alkylation reaction.

1. Introduction

Styrene is an industrially important chemical that is used for production of plastics and rubbers. It is industrially produced by two subsequent reactions: the alkylation of benzene with ethylene to produce ethylbenzene and its dehydrogenation to styrene. There is a potentially interesting alternative route for production of styrene, which involves the direct side-chain alkylation of toluene with methanol. The side-chain alkylation of toluene with methanol over a base catalyst has been known for several decades [1]. Initially, the base catalysts such as MgO and CaO were used for side-chain alkylation [2], but activities and selectivities over these base catalysts were low. When these alkali compounds were supported on zeolites, they demonstrated the yield (ethylbenzene + styrene) of about 20% and styrene selectivity of about 10% [3–6]. Some other studies found that the selectivity to styrene could be improved by adding B, P, Cu or Ag to these basic zeolite [7–9]. Also, small quantities of alkali-hydroxide particles entrapped within the alfa cavities of faujasite, strongly increase the alkylation in the side-chain of alkylaromatics [10–12].

For the side-chain alkylation of toluene with methanol, acid sites catalyze preferentially ring alkylation reactions, but surface acidity is also necessary to catalyze side-chain alkylation via combined acid–base pathways. A base site activates the methyl group of toluene, whereas the acid site interacts with the aromatic ring. Thus, it has been suggested that the side-chain alkylation of toluene with methanol requires a cooperative action of acid/base pairs for efficiently promoting the rate-limiting step in the reaction mechanism [13–15].

In an attempt to improve activities and selectivities of catalyst for the alkylation of toluene with methanol, a novel solid acid-base catalyst with aluminum and nitrogen is prepared from aluminum and amine by using triblock copolymer Pluronic F127 as a template and resol as framework via evaporation induced organic–organic assembly method.

2. Experiment

2.1. Catalysts preparation

2.1.1. Synthesis of resol

Resol was prepared from phenol and formaldehyde in a base-catalyzed process. Phenol of 9.4 g was melted in a flask and mixed with 10 ml ethanol under stirring at 313 K. After 10 min, 16.0 ml of formalin (37 wt% formaldehyde) was added dropwise below 323 K. Upon further stirring at 358 K for 2 h, the mixture was cooled to room temperature. The pH was adjusted with 0.6 M HCl solution until it reached a value of 7.0.

2.1.2. Synthesis of solid acid-base catalyst

The solid acid-base catalyst was prepared from aluminum and amine by using triblock copolymer Pluronic F127 as a template and resol as framework via evaporation induced organic–organic assembly method. 13.5 ml 28% ammonia (NH_3), 17.3 ml ethylenediamine ($NH_2C_2H_4NH_2$) or 21.0 ml diethylamine ($NH(C_2H_5)_2$) was added to the resol precursor solution and stirred at 358 K for 2 h.

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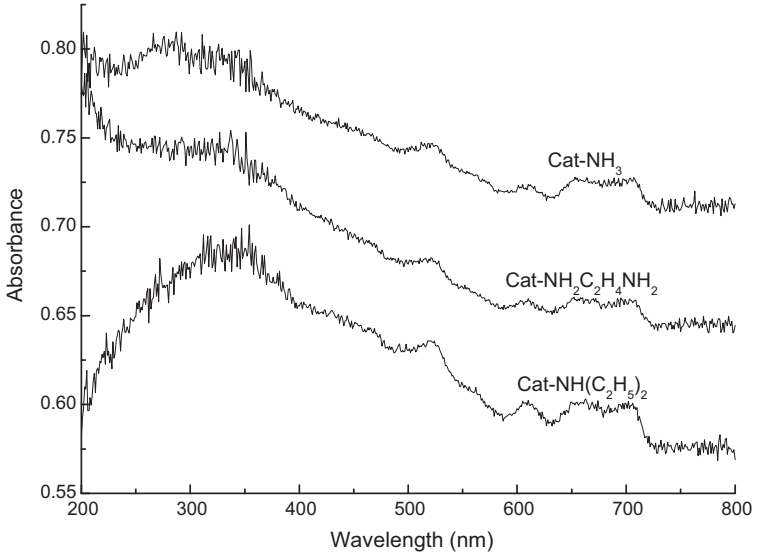


Fig. 1. UV–vis absorption spectroscopy of the catalysts.

Then 100 ml of polydimethylsiloxane and 0.6 g aluminum were added. The mixture was stirred at 453 K for 3 h. After filtering, the obtained solid was crushed into powders. The solid powder was added into the solution, in which F127 of 5.0 g was dissolved in 10.0 ml methanol. After stirring for 2 h, the mixture was poured into a dish and placed for 5–8 h, and then kept in an oven at 403 K for 5 h. The obtained sample was calcined in a tubular furnace under a nitrogen with a flow rate of 30 cm^3/min at 873 K for 10–12 h. The heating rate was 1 °C/min. The final products were designated as Cat-NH_3, Cat-$NH_2C_2H_4NH_2$ and Cat-$NH(C_2H_5)_2$.

2.2. Catalyst characterization

UV–vis absorption spectra were recorded on a Cary 300 Bio spectrophotometer, and waters 996 PDA detector was used to analyze components under 200–800 nm wavelength with a resolution of 1.2 nm. The FTIR spectra are obtained on a Bio-Rad FTS-60A spectrometer with KBr dispersion method. XRD patterns were recorded on a Rigaku D/max 2500 X-ray diffractometer using Ni-filtered Cu Kα radiation (1.5406 Å). X-ray photoelectron spectra were acquired on an ESCALAB 250 spectrometer (VG Scientific Ltd., UK) equippedwithan Al Kα ($h\upsilon$ = 1486.6 eV). NH_3-TPD or CO_2-TPD experiment was performed on a TP-5000 instrument with a thermal conductivity detector (TCD). The catalyst adsorbed NH_3 or CO_2 at 323 K until saturation and purged with helium for 30 min to remove the physisorbed NH_3 or CO_2. The TPD data were collected in flow helium from 323 to 1073 K at a heating rate of 10 K/min. Density functional theory (DFT) method of quantum chemistry calculation was adopted to calculate space distances in molecules and the calculations were performed using the D mol^3 program mounted on Materials Studio Modeling 4.0 package.

2.3. Catalytic test

The alkylation of toluene with methanol was carried out in a fixed-bed tubular reactor at normal atmosphere. The catalysts were sieved to retain particles with 0.35–0.42 mm diameter for catalytic measurements and treated under nitrogen at 723 K for 2 h before reaction in order to remove H_2O, hydrocarbons, and CO_2. A liquid mixture of toluene and methanol with a molar ratio 5:1 was pumped at a rate of 1.0–2.0 ml h^{-1} and vaporized into a flowing nitrogen stream. The reaction was carried out at 673 K, employing a space velocity (WHSV) of 2 h^{-1}. The reaction products were analyzed by on-line gas chromatography with a 0.53 mm × 50 m, HP-FFAP capillary column connected to a flame ionization detector (FID). A Porapak Q (80/100 mesh) mesh, 10 ft, stainless steel packed column connected to a thermal conductivity detector (TCD) was used to analyze for carbon monoxide and carbon dioxide. Reaction was maintained for 8 h.

Conversion, selectivity and yields are defined as follows (quantities are molar flow rates):

$$\text{MET conversion} = \frac{1 - \text{MET}_{\text{exit}}}{\text{MET}_{\text{feed}}}$$

$$\text{X selectivity} = \frac{\text{X}}{\text{MET}_{\text{feed}} - \text{MET}_{\text{exit}}}$$

$$(\text{EB} + \text{STY}) \quad \text{yield} = (\text{EB} \quad \text{selectivity} + \text{STY} \quad \text{selectivity}) \times \text{MET} \quad \text{conversion}$$

where MET, TOL, EB, STY, XYL, DME and X represent methanol; toluene; ethyl benzene; styrene; xylene; dimethylether; and EB, STY, XYL, CO_x or 2 × DME, respectively.

3. Results and discussion

3.1. UV–vis absorption spectroscopy

The UV–vis absorption spectra of Cat-NH_3, Cat-$NH_2C_2H_4NH_2$ and Cat-$NH(C_2H_5)_2$ are shown in Fig. 1. All samples show B band and weak R band absorption from 250 to 350 nm, which indicates the existence of the simple-ring aromatic compound with heteroatomic substitution compounds [16].

The K band absorption appears only on Cat-$NH(C_2H_5)_2$, expressing unsaturated conjugated double bonds [16]. In Cat-$NH(C_2H_5)_2$, K band exhibited bathochromic shift and connected to a broad absorption peak with the B band, showing that the degree of conjugation increased. Compared with Cat-NH_3 and Cat-$NH_2C_2H_4NH_2$, the molecule structure of Cat-$NH(C_2H_5)_2$ is the aromatic compounds with other conjugated side chains (Ar–N).

3.2. FTIR spectra

The IR spectra of Cat-NH_3, Cat-$NH_2C_2H_4NH_2$ and Cat-$NH(C_2H_5)_2$ are shown in Fig. 2. The aromatic ring stretching absorptions

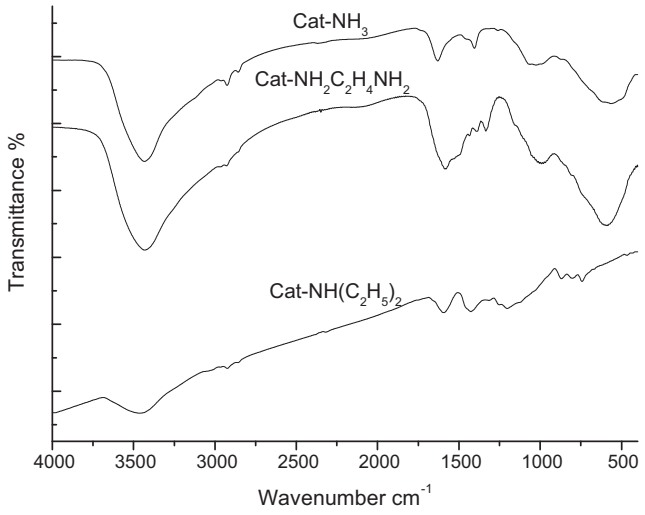


Fig. 2. Infrared spectra of the catalysts.

(C=C) can be seen in the range 1404–1593 cm^{-1}. The asymmetric and symmetric C–H stretches of the catalysts are observed in the ranges 2915–3930 cm^{-1} and 2845–2955 cm^{-1} respectively. The C–O (phenol) stretch is observed at 990–1030 cm^{-1}. The Al–O stretch due to aromatic ring appears at 740–870 cm^{-1}. The absorptions at 3433–3435 cm^{-1} in Cat-NH_3 and Cat-$NH_2C_2H_4NH_2$ show aliphatic secondary N–H stretch. The peak at 1335 cm^{-1} in Cat-$NH_2C_2H_4NH_2$ and 1204 cm^{-1} in Cat-$NH(C_2H_5)_2$ correspond to aliphatic and aromatic tertiary C–N stretch respectively. The absorption of Al–N stretch is observed at 550–600 cm^{-1} in Cat-NH_3 and Cat-$NH_2C_2H_4NH_2$.

3.3. XRD diffraction

XRD patterns of Cat-NH_3, Cat-$NH_2C_2H_4NH_2$ and Cat-$NH(C_2H_5)_2$ are shown in Fig. 3. Broad diffraction halos are the main features in the XRD, indicating that the metal aluminum change to Al associated with phenol (Al–O–Ar). Compared with Cat-NH_3 and Cat-$NH_2C_2H_4NH_2$, the peak intensity of Cat-$NH(C_2H_5)_2$ increases, and shifts to lower angles. This indicates that the molecule structure of Cat-$NH(C_2H_5)_2$ is larger than Cat-NH_3 and Cat-$NH_2C_2H_4NH_2$.

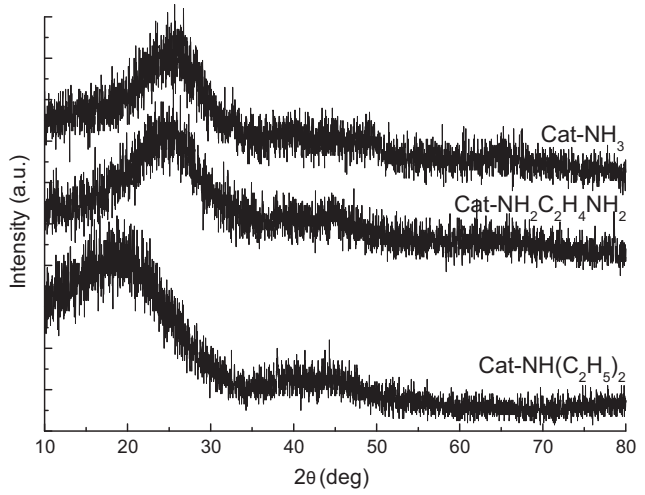


Fig. 3. XRD diffraction patterns of the catalysts.

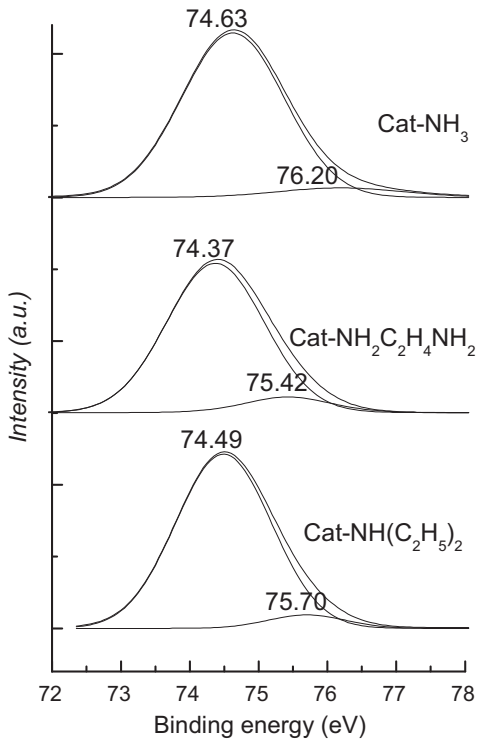


Fig. 4. XPS spectra of Al 2p of the catalysts.

3.4. XPS spectra

The binding energies of Al 2p and N 1s in Cat-NH_3, Cat-$NH_2C_2H_4NH_2$ and Cat-$NH(C_2H_5)_2$ are shown in Figs. 4 and 5, respectively. From Fig. 4, The major peak component at the Al binding energy of Cat-NH_3 about 74.63 eV has been assigned to the formation of N–AlO_z complex [17], as well as the Al–O–C complex [18,19]. The Al binding energy of Cat-$NH_2C_2H_4NH_2$ is 74.37 eV,

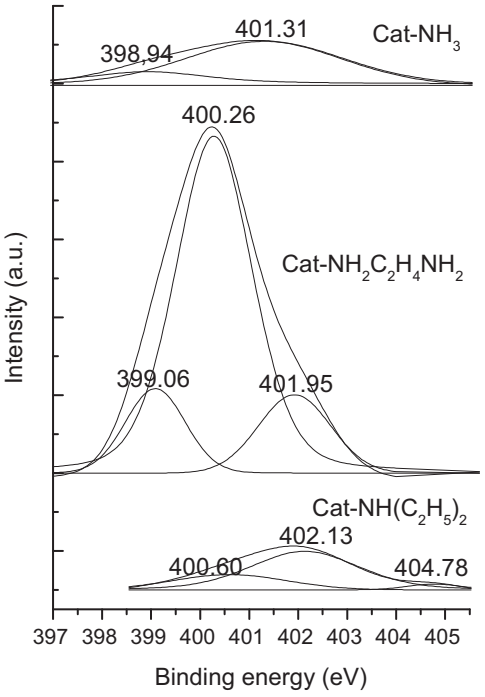


Fig. 5. XPS spectra of N 1s of the catalysts.

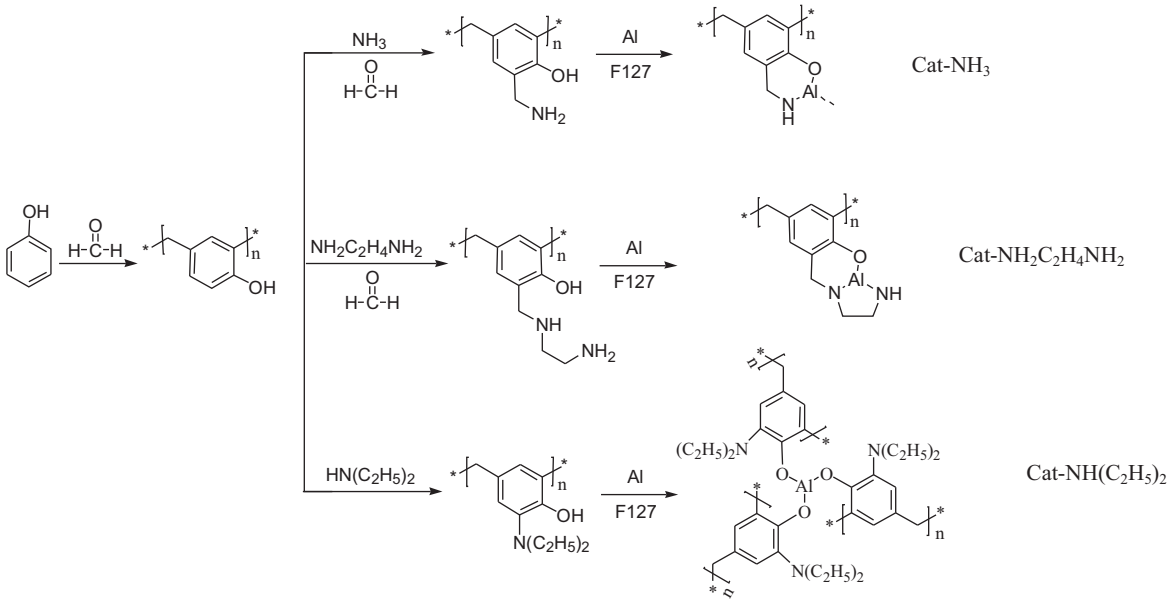


Fig. 6. Scheme for the preparation of the catalyst.

indicating the combination of Al with two N atoms. However the Al binding energy of Cat-$NH(C_2H_5)_2$ at 74.49 eV is attributed to the stronger electron donating ability of amidophenolic groups compared with nitrogen in molecule of Cat-$NH(C_2H_5)_2$. That is, the combining forms of aluminum in Cat-NH_3, Cat-$NH_2C_2H_4NH_2$ and Cat-$NH(C_2H_5)_2$ molecules are N–Al–$(O–)_2$, O–Al–$(N–)_2$ and Al–$(O–Ar–N–)_3$ respectively.

Fig. 5 shows the XPS peaks corresponding to different nitrogen species of Cat-NH_3, Cat-$NH_2C_2H_4NH_2$ and Cat-$NH(C_2H_5)_2$. The peaks at about 398.94 and 399.06 eV most likely correspond to the formation of N–Al–O complex [20]. The peaks at about 400.26 and 400.60 eV are distributed to aliphatic and aromatic tertiary nitrogen [21]. The peaks at 401.31 and 401.95 eV are considered N–H bonds, whose binding energy is generally 401.2 eV [22–26]. The slight increase in the binding energy is due to amine nitrogen associated with aluminum (NH–Al) where electrons shift to aluminum. The peak at about 402.13 eV could attribute to nitrogen atoms associated with benzene ring.

From UV–vis, FTIR, XRD and XPS results, the confirmed molecule structure of Cat-NH_3, Cat-$NH_2C_2H_4NH_2$ and Cat-$NH(C_2H_5)_2$ is shown in Fig. 6

3.5. Thermal stability

The catalytic material thermal stability experiment was performed on a TP-5000 instrument, and a mass spectrometry detector was used to analyze the pyrolysis products. The data were collected in flow helium from 50 to 900 °C at a heating rate of 10 °C/min. The results (see Fig. 7.) show that the catalysts decomposed above 650 °C, and thermal decomposition H_2 is only product detected by mass.

3.6. Catalytic reaction

Table 1 summarizes the reactivity data at the reaction of 1 h for Cat-NH_3, Cat-NH2C2H4NH2 Cat-$NH(C_2H_5)_2$ and the reference zeolite-based catalyst in the literature[3]. Figs. 8 and 9 show (ethylbenzene + styrene) selectivities and yields as a function of reaction time over catalysts (Cat-$NH(C_2H_5)_2$, Cat-$NH_2C_2H_4NH_2$ and Cat-NH_3). It is obvious that the selectivities and yields decreased with increasing reaction time in initial reaction of 1–3 h. After that,

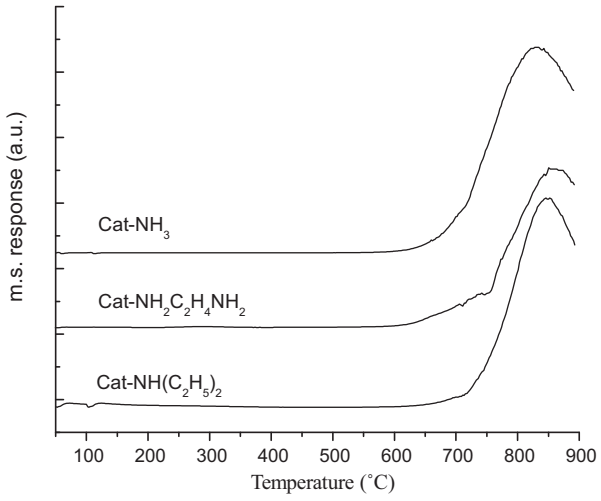


Fig. 7. Thermal decomposition of catalysts.

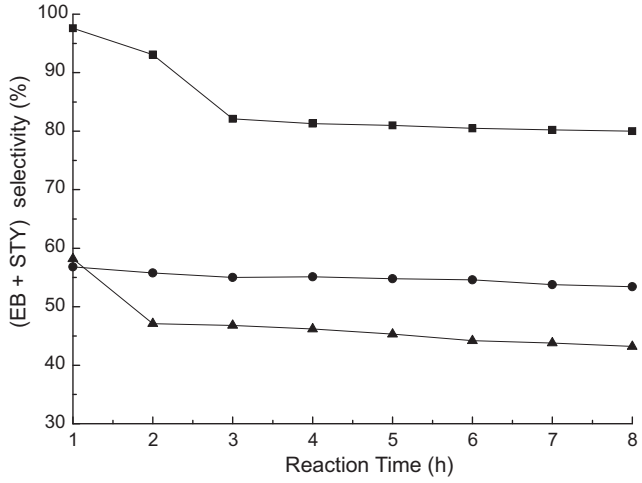


Fig. 8. (ethylbenzene + styrene) selectivities over catalysts. $T = 673$, WHSV = 2 h^{-1}, toluene: methanol = 5. (■) Cat-$NH(C_2H_5)_2$; (●) Cat-$NH_2C_2H_4NH_2$; (▲) Cat-NH_3.

Table 1
Catalytic performance comparing the reference zeolite-based catalyst and the catalysts.

Catalytic performances	Reference (%)	Cat-NH_3 (%)	Cat-$NHC_2H_4NH_2$ (%)	Cat-$NH(C_2H_5)_2$ (%)
MET conversion	70.8	28.0	30.9	45.9
EB selectivity	80.2	17.5	18.7	0
STY selectivity	8.8	58.2	56.8	97.6
XYL selectivity		9.0	4.9	0
CO_x selectivity		0.9	1.6	0
DME selectivity		14.4	17.9	2.4
(EB + STY) yield	20.6	21.2	23.4	44.9

MET: methanol; TOL: toluene; EB: ethylbenzene; STY: styrene; XYL: xylene; DME: dimethylether.

they became even. Table 1 also shows clearly that the activity and styrene selectivity of the catalysts with aluminum and nitrogen, especially Cat-$NH(C_2H_5)_2$ are higher than the reference zeolite-based catalyst. In order to discover the reason of high activity and styrene selectivity of the catalysts with aluminum and nitrogen, acid–base properties and distances between acid and base sites on the catalysts are also investigated in this work.

For the acidity of the catalysts, which is shown by the NH_3–TPD profiles in Fig. 10, the strength and density of weak (about 100 °C) and middle (about 300 °C) acid sites on the catalysts are similar among the three catalysts, but the density of strong acid sites (about 650 °C) on the Cat-$NH(C_2H_5)_2$ becomes weaker than Cat-NH_3 and Cat-$NH_2C_2H_4NH_2$.

Fig. 11 shows the CO_2-TPD of Cat-NH_3, Cat-$NH_2C_2H_4NH_2$ and Cat-$NH(C_2H_5)_2$. There is only one peak (about 350 °C) on the profiles of Cat-$NH(C_2H_5)_2$, while there are several peaks on the spectra of Cat-NH_3 and Cat-$NH_2C_2H_4NH_2$. The peaks of Cat-NH_3 are about 290 °C and 650 °C, and the peaks of Cat-$NH_2C_2H_4NH_2$ are about 330 °C and 650 °C. Thus, Cat-NH_3 and Cat-$NH_2C_2H_4NH_2$ has both middle and strong (main) base sites. Relating the reactivity and the results of NH_3 and CO_2-TPD measurement, it is concluded that weak and middle acid and base sites on the catalyst are adequate to the side chain alkylation of toluene.

The adsorption and activation of toluene (together with the formation of formaldehyde) are the critical factors to initiate the side chain alkylation of the toluene [14]. It is generally believed that the center of benzene ring of toluene is fixed on acid sites of catalyst, and the effective polarization of the methyl group of toluene occurs on base sites of catalyst. In this work, the distance between acid site and base site has been calculated.

Table 2 gives the distances between acid (Al) and base (N) sites on the catalysts calculated by DFT method. Because of considering the benzene is adsorbed on an acid site, which is produced from Al, the distance between center of benzene ring of toluene and the nitrogen atom adsorbed a methyl in toluene (c) (see Fig. 12). The calculation is based on the distances between center of benzene ring and hydrogen of toluene (a), and that between nitrogen atom of amine and hydrogen atom of the methyl in toluene (b). The nitrogen atom of the amine, the center of benzene ring and the hydrogen atom of the methyl in toluene forms a triangle, so the range of c is about at 3.547 ± 1.000 Å ($a - b < c < a + b$).

Compared the distances (c) between acid and base sites on the catalysts, it is found that the distance between acid and base sites of Cat-$NH(C_2H_5)_2$ is only in the range of 3.547 ± 1.000 Å. So the most

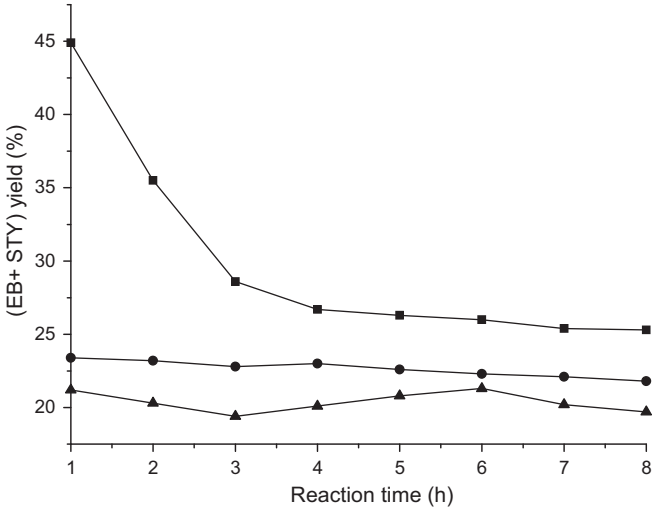


Fig. 9. (ethylbenzene + styrene) yields over catalysts. $T = 673$, WHSV = 2 h^{-1}, toluene: methanol = 5. (■) Cat-$NH(C_2H_5)_2$; (●) Cat-$NH_2C_2H_4NH_2$; (▲) Cat-NH_3.

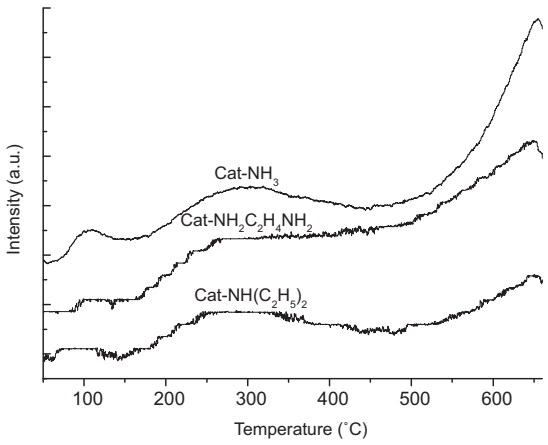


Fig. 10. NH_3-TPD profiles of the catalysts.

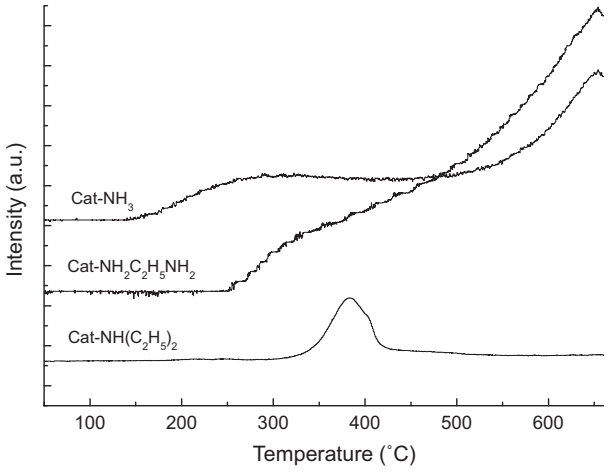
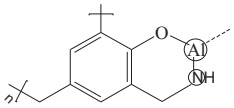
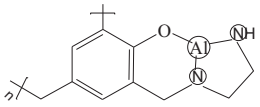
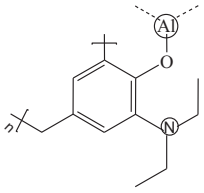
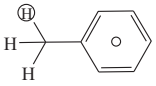
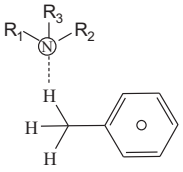


Fig. 11. CO_2-TPD profiles of the catalysts.

Table 2
Calculated space distances in molecules.

Catalysts	Calculated results	
	Molecular structures	Distances (Å)
Cat-NH_3		1.767[a]
Cat-$NH_2C_2H_4NH_2$		1.766[a], 1.772(H)[a]
Cat-$NH(C_2H_5)_2$		4.314[a]
Toluene		3.547[b]
Amine		1.000[c]
Amine adsorbed toluene		3.547 ± 1.000[d]

Distances: *a* between acid (Al) and base (N) sites, *b* between center of benzene ring and hydrogen, *c* between nitrogen and hydrogen, *d* between center of benzene ring and nitrogen.

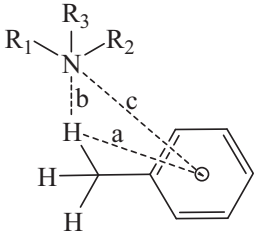


Fig. 12. Model of the calculated distances.

effective polarization of the methyl group of toluene can occur on base sites of Cat-$NH(C_2H_5)_2$.

4. Conclusions

A novel solid acid-base catalyst containing N and Al atoms has been synthesized successfully and characterized by UV–vis, FTIR, XRD, XPS. It is concluded for side chain alkylation, three parameters of catalyst are crucial, i.e., the weak and (or) middle acid sites, middle base sites and the befitting distance between acid and base sites (3.547 ± 1.000 Å). When all these requirements are met on one catalyst, high activity and selectivity for side chain alkylation of toluene with methanol can be achieved.

Acknowledgements

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