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BRIEF
COMMUNICATIONS

Synthesis of Novel Polymer as Solid Acid-Base Catalyst for Styrene from Toluene*

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Abstract—A novel solid acid-base catalyst Cat-$NH_2C_2H_4NH_2$ with aluminum and nitrogen was prepared from phenol and formaldehyde by using triblock copolymer Pluronic F127 as a template and resol as a catalyst precursor via evaporation induced organic–organic assembly method. The catalyst was characterized by Fourier transform infrared spectroscopy (FTIR) and 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. The side chain alkylation of toluene with methanol over the catalysts had been studied. The results showed that Cat-$NH_2C_2H_4NH_2$ has demonstrated the higher activity and selectivity than the conventional alkali exchanged zeolites. This may be because that the weak or middle acid-base pairs on the catalyst are favored to bimolecular side-chain alkylation reaction.

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A novel solid acid-base catalyst Cat-$NH_2C_2H_4NH_2$ with aluminum and nitrogen was prepared from phenol and formaldehyde by using triblock copolymer Pluronic F127 as a template and resol as a catalyst precursor via evaporation induced organic–organic assembly method. The catalyst was characterized by Fourier transform infrared spectroscopy (FTIR) and 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. The side chain alkylation of toluene with methanol over the catalysts had been studied. The results showed that Cat-$NH_2C_2H_4NH_2$ has demonstrated the higher activity and selectivity than the conventional alkali exchanged zeolites. This may be because that the weak or middle acid-base pairs on the catalyst are favored to bimolecular side-chain alkylation reaction.

INTRODUCTION

Styrene is an industrially important chemical that is used for production of plastics and rubbers. This molecule 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 base catalysts has been known for several decades [1]. Although base catalysts such as MgO and CaO were successfully used for side-chain alkylation [2], alkali-exchanged zeolites have demonstrated the highest activities [(ethylbenzene + styrene) yield is about 20%] and selectivities (styrene selectivity is about 10%) for side-chain alkylation of toluene with methanol [3–5]. More specifically, basic zeolites such as Cs–X, Rb–X and Cs–Y give side-chain alkylation [1], and the selectivity to styrene can be improved by adding B, P, Cu or Ag to the basic zeolite [6–8]. Also, small quantities of alkali-hydroxide particles entrapped within the alfa cavities of faujasite, strongly increase the alkylation in the side-chain of alkyl aromatics [9–11].

The side-chain alkylation of toluene with methanol over base catalysts has been known for several decades [12]. Acid sites catalyze preferentially ring alkylation

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* The text was submitted by the authors in English.

reactions, but surface acidity is also necessary to catalyze side-chain alkylation via combined acid–base pathways. Abase 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 phenol and formaldehyde by using triblock copolymer Pluronic F127 as a template and resol as a carbon precursor via evaporation induced organic–organic assembly method.

EXPERIMENTAL

Catalysts Preparation

Synthesis of resol. Resol was prepared from phenol and formaldehyde in a base-catalyzed process. 6.1 g of phenol was melted at 40°C in a flask and mixed with 20 mL of ethanol under stirring. After 10 min, 10.5 mL of formalin (37 wt % formaldehyde) was added dropwise below 50°C. Upon further stirring for 2 h at 75°C, 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.

Synthesis of Aluminum Phenolic Resinate. Aluminum phenolic resinate was prepared from aluminum and resol. 6.1 g of phenol was melted at 40°C in a three necked flask and mixed with 250 mL of polydimethylsiloxane under stirring. Then 5.8 g of aluminum and 44 g of prepared resol were added. The mixture was heated with stirring at 180°C for 3 h. After the mixture was cooled and filtered, the filter cake was collected.

Organic–organic assembly. After filtering the solids obtained were crushed into powders. 1.0 g of F127 was dissolved in 20.0 mL methanol. The solid powders prepared were added. After stirring for 2 h, the mixture was poured into dishes to evaporate methanol at room temperature for 10 h, followed by heating in an oven at 100°C for 5 h.

Calcination. Calcination was carried out in a tubular furnace under a nitrogen with a flow rate of 30 cm^3 min^{-1} at 600°C. The heating rate was 1°C min^{-1}.

Chloromethylation reaction. The chloromethylation reaction was carried out in a fournecked flask of 250 mL of equipped with a mechanical stirrer, a reflux condenser, a dropping funnel and a thermometer. 10 mL of formalin (37 wt % formaldehyde) and 8 mL of concentrated hydrochloric acid were added, following the addition of 6.8 g of the powders calcined under stirring condition. The temperature was risen to 65°C. After the reaction run for 9 h, the reaction was ended and finally dried under vacuum at 100°C for 5 h.

Amination reaction. The chloromethylated powders were mixed with 30 mL of ethanol under stirring, then 5 mL of 1,2-diaminoethane was added dropwise below 25°C. The mixture was heated with stirring at 45°C for 8 h, followed by heating in an oven at 100°C for 3 h.The final product was designated as Cat-$NH_2C_2H_4NH_2$ and shown in Fig. 1.

Catalyst Characterization

The FTIR spectra are obtained on a Bio-Rad FTS-60A spectrometer with KBr dispersion method. X-ray photoelectron spectra were acquired on an ESCALAB 250 spectrometer (VG ScientificLtd.,UK) equippedwithan AlK_α ($h\nu$ =1486.6 eV). NH_3-TPD and CO_2-TPD experiment were performed on a TP-5000 instrument. The catalysts 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^{-1}.

Catalytic Test

The gas phase alkylation of toluene with methanol was carried out in a fixed-bed tubular reactor at 1 atm. Catalysts were sieved to retain particles with 0.35–0.42 mm diameter for catalytic measurements and treated under nitrogen at 450°C for 2 h before reaction in order to remove H_2O, hydrocarbons, and CO_2. A liquid mixture of toluene and methanol having a 5 : 1 molar ratio was pumped at a rate of 1.0–2.0 mL h^{-1} and vaporized into a flowing nitrogen stream that bypassed the reactor. After flow rates and temperatures were stabilized, the reactant stream of nitrogen and organics (5 : 1 molar ratio of N_2 to organics) was fed to the reactor. The reaction was carried out at 400°C, employing a space velocity (WHSV) of 2 h^{-1}. The reaction products (toluene, methanol, styrene, and ethylbenzene) were analyzed by on-line gas chromatography using a 0.53 mm × 50 m capillary column HP-FFAP connected to a flame ionization detector (FID).

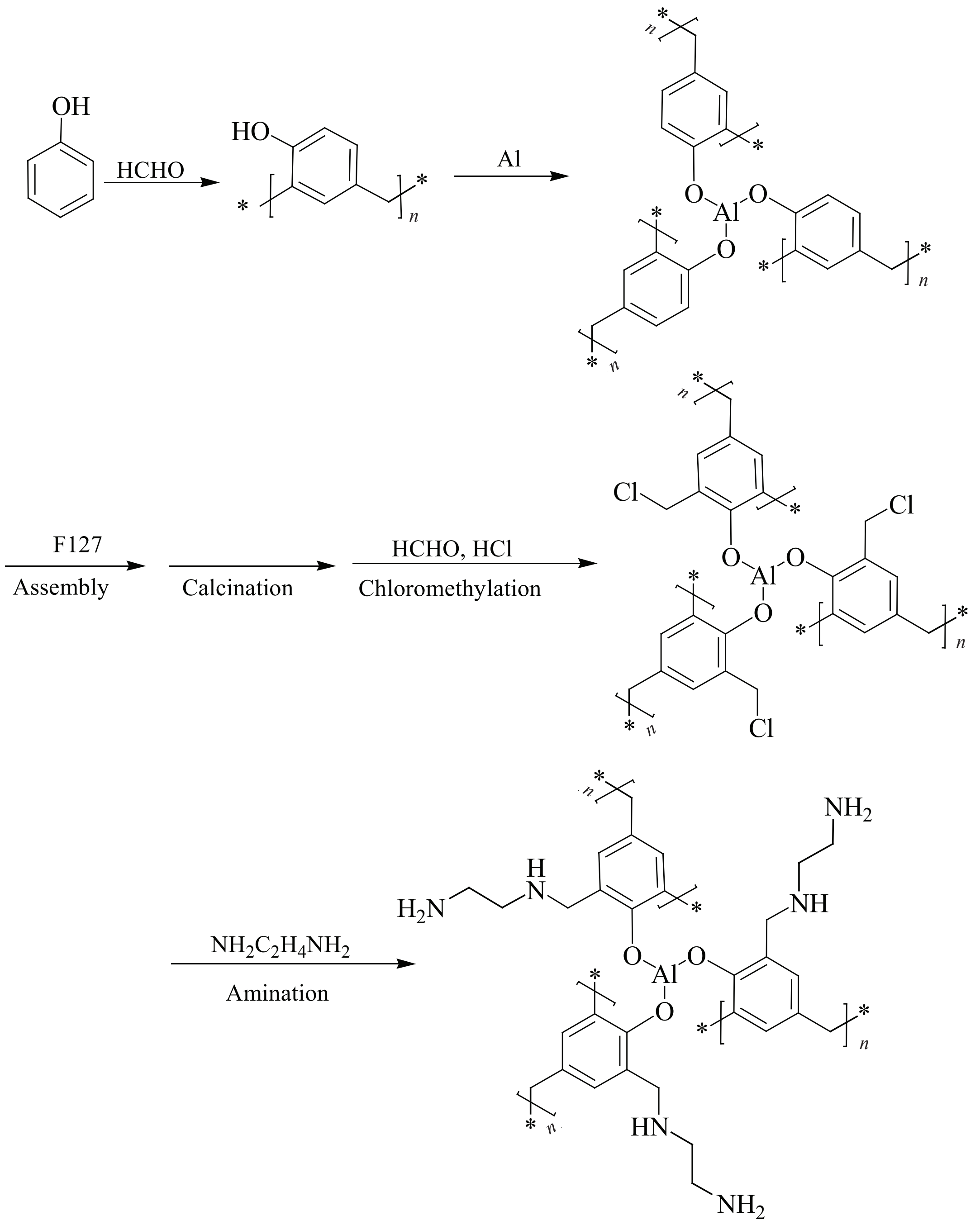

Fig. 1. Scheme for the preparation of Cat-$NH_2C_2H_4NH_2$.

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 during 8 h (time on stream). Catalytic results are calculated with the products analysis obtained after reaching catalyst stabilization.

RESULTS AND DISCUSSION

Catalyst Characterization

IR. The IR spectra of resol, aluminum phenolic resinate, calcination, chloromethylation and amination (Cat-$NH_2C_2H_4NH_2$) are shown in Fig. 2. The aromatic ring

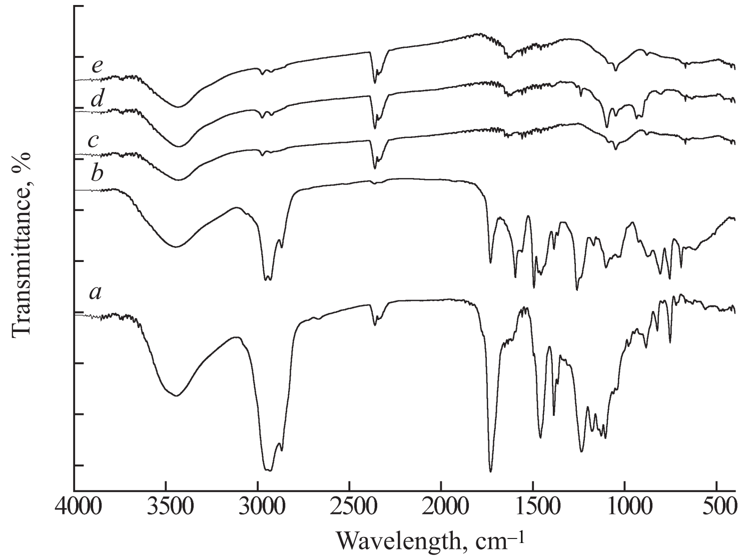

Fig. 2. Infrared spectra of samples. (*a*) resol; (*b*) aluminum phenolic resinate; (*c*) calcination; (*d*) chloromethylation; (*e*) amination.

stretching absorptions (C=C) can be seen at 1388, 1464 and 1620 cm^{-1}. The asymmetric and symmetric stretches in these curves are observed at about 2872 and 2959 cm^{-1}, respectively. The C–O (phenol) stretch is observed at about 1035 cm^{-1}. The Al–O stretch due to aromatic ring appears at about 670 and 1050 cm^{-1}. The absorptions at 1120~1185 cm^{-1} show O–H stretch. The peak at 935~905 cm^{-1} correspond to C–Cl (benzyl) stretch.

XPS. The binding energies of Al 2p and N 1s in Cat-$NH_2C_2H_4NH_2$ are shown in Figs. 3 and 4, respectively. The major peak (Fig. 3) component at the binding energy of Cat-$NH_2C_2H_4NH_2$ 74.63 eV has been assigned to the formation of the Al–O–C complex [16, 17]. The binding energy of Cat-$NH_2C_2H_4NH_2$ depressed from 74.63 to 74.43 eV, which indicates the complexation between phenolic groups and Al. That is, the forms of aluminum in Cat-$NH_2C_2H_4NH_2$ molecules are Al–(O–Ph)$_3$.

The peaks located at 398.50 and 400.51 eV corresponding to different nitrogen species are observed from XPS spectra of Cat-$NH_2C_2H_4NH_2$ (Fig. 4). The peaks at 398.50 eV most likely correspond to the formation of primary amine (–NH_2) [18]. The peaks at about 400.51 eV is distributed to attributed to secondary amine (–NH–) nitrogen [19–23].

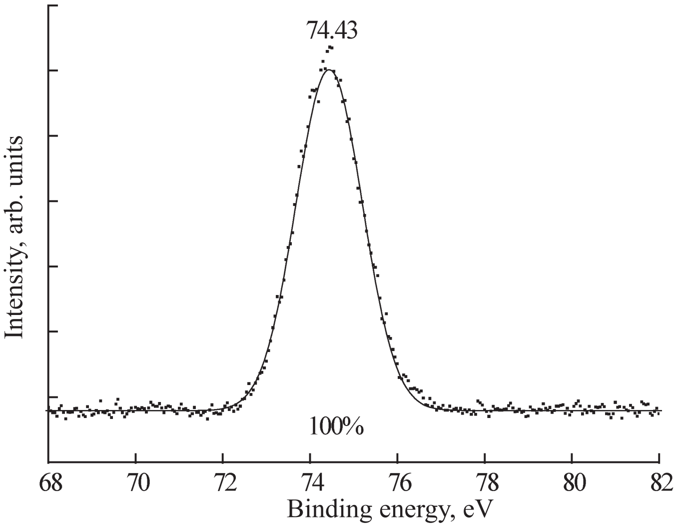

Fig. 3. XPS of Al 2p of Cat-$NH_2C_2H_4NH_2$.

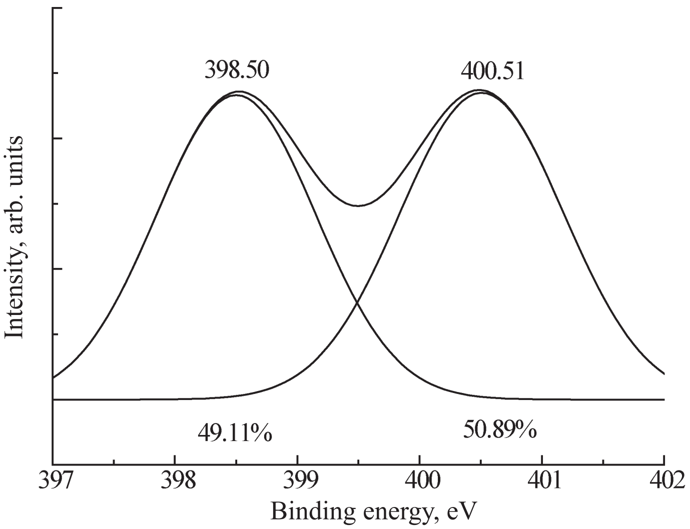

Fig. 4. XPS of N 1s of Cat-$NH_2C_2H_4NH_2$.

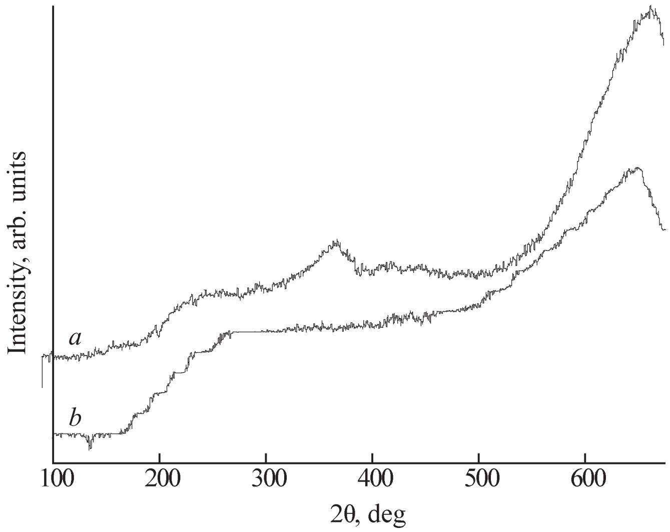

Fig. 5. NH_3-TPD of Cat-$NH_2C_2H_4NH_2$. (*a*) after reaction; (*b*) before reaction.

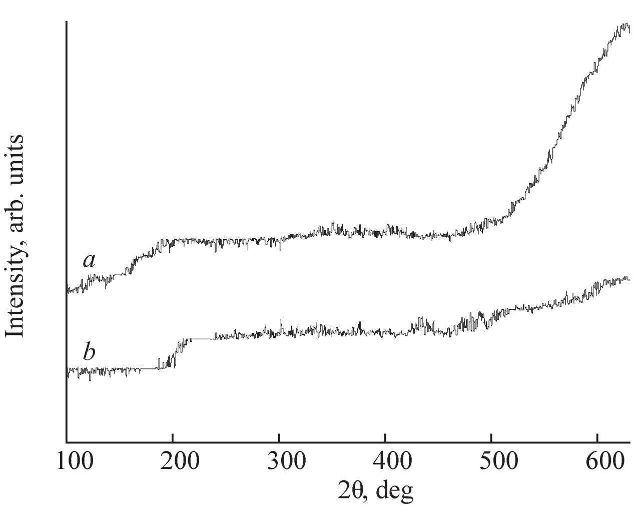

Fig. 6. CO_2-TPD of Cat-$NH_2C_2H_4NH_2$. (*a*) after reaction; (*b*) before reaction.

Catalytic Reaction

The table summarizes the reactivity results for the reference zeolite-based catalyst in [3] and Cat-$NH_2C_2H_4NH_2$. The results show clearly that the styrene selectivity of Cat-$NH_2C_2H_4NH_2$ is much higher than the reference zeolite-based catalyst.

The acidities of the catalystsbe before and after reactions are shown in Fig. 5 by the NH_3-TPD profiles. The density of weak and middle (< 500°C) acid sites on the catalysts decreases and that of strong acid sites (about 650°C) increases, which leading to the decrease of the reactivity and styrene selectivity of Cat-$NH_2C_2H_4NH_2$. That is the weak or middle (< 500°C) acid sites are beneficial to side-chain alkylation of toluene with methanol.

Catalytic performance comparing the reference zeolite-based catalyst and the catalysts[a]

Catalytic performances	Reference, %	Cat-$NHC_2H_4NH_2$, %	
Reaction time, h		1	8
MET conversion	70.8	73.4	71.2
TOL conversion	23.2	21.3	19.1
EB selectivity	80.2	8.9	9.1
STY selectivity	8.8	81.2	80.9
(EB+ STY) yield	20.6	26.4	23.8

[a] MET: methanol; TOL: toluene; EB: ethylbenzene; STY: styrene.

Figure 6 shows the CO_2-TPD of Cat-$NH_2C_2H_4NH_2$ before and after reactions. It is very similar to the NH_3-TPD, so it can be concluded that the weak or middle (< 500°C) acid and base sites are required for side-chain alkylation of toluene with methanol.

CONCLUSIONS

The novel solid acid-base catalyst Cat-$NH_2C_2H_4NH_2$ could be synthesized successfully, and characterized by FTIR and XPS. The styrene selectivity of Cat-$NH_2C_2H_4NH_2$ is much higher than the conventional zeolite-based catalyst. From the activity and selectivity of Cat-$NH_2C_2H_4NH_2$, CO_2, and NH_3-TPD, it can be concluded the weak or middle (< 500°C) acid and base sites are required for side-chain alkylation of toluene with methanol.

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