Bis (2-mercapto-ethyl) Amine Modification of Macroporous Sulfonic Resin Catalyst in Bisphenol-A Synthesis

Baohe Wang, Hao Sun, Jing Zhu, Lili Wang, and Shuang Chen
Key Laboratory for Green Chemical Technology of Ministry of Education, Research and Development Center of Petrochemical Technology, Tianjin University, Tianjin 300072, People's Republic of China

DOI 10.1002/aic.14129

A novel catalyst for bisphenol-A synthesis was prepared by bis (2-mercapto-ethyl) amine adsorbed on macroporous sulfonic resin through neutralization reaction. The physicochemical properties of two resin catalysts before and after bis (2-mercapto-ethyl) amine absorption were compared by scanning electron microscope and nitrogen adsorption. The kinetic of the new catalyst preparation process was studied and it was found that this is a chemical adsorption and endothermic process. The adsorption rate is mainly controlled by the intraparticle diffusion, affected by boundary layer diffusion and chemical reaction as well. The thermodynamic activation parameters were calculated. Compared with unmodified catalyst, the modified resin catalyst showed higher selectivity and acetone conversion in the continuous bisphenol-A synthesis process. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 3816–3823, 2013
Keywords: sulfonic resin, bis (2-mercapto-ethyl) amine, absorption kinetics, thermodynamic parameters, bisphenol-A

Introduction

2,2-Bis(4-hydroxyphenyl)propane, more commonly known as bisphenol-A (BPA), is a valuable raw material for the production of many polymers, such as epoxy resins and polycarbonates. The end-products are widely used in adhesives, potting compounds, and lenses. In the past few years, there is a rapidly growing demand for BPA in industry of high-tech production, such as compact discs and digital video discs.[1]

BPA is customarily manufactured by an acid-catalyzed condensation reaction of acetone and phenol. Traditional production methods mainly use sulfuric acid and hydrogen chloride as catalysts. In 1960, U.C.Corporation[2] first brought the cation exchange resin into industrialized application. Currently, the industry standard is the use of a cation exchange resin. In recent years, new catalysts, such as acid functionalized mesoporous[3–5] heteropoly acids,[6–9] ion liquids,[10] and zeolites,[11,12] have also attracted researchers' great attention. However, most of the new catalysts are still under research. Sulfonated cation exchange resin, due to less pollution, no equipment corrosion, high selectivity and simpler refining process, is always the preferred catalyst for synthesis BPA in industry. The disadvantage of the sulfonated cation exchange resin, however, is the relative low acid content that results in low reaction rates.[13] Efforts have been made to improve the quality of the BPA product and the efficiency of BPA process by modifying the catalyst with modifier.[14–20]

Wagner RB[17] transformed part of sulfonic groups into mercapto groups by reduction reaction, showed a great improvement in the condensation of phenol and acetone. Apel et al.[18] obtained a novel resin by esterifying part of the cationic exchanging groups with mercapto alcohols. Pressman and Willey[13] successfully formed ionic bond between mercaptoalkylamine and sulfonic groups through neutralization reaction. It has been discovered that the partial neutralization reaction may be a better method for the preparation of improved catalyst, as it not only increases the efficiency of the strong-acid resin as catalyst but also can minimize byproduct formation.[16] Although substantial performance improvement is achieved in the reaction with mercapto compounds, the final results exhibited a great difference among different mercapto compounds. Therefore, to choose appropriate mercapto compound is essential to the reaction.

Among the different mercapto compounds, bis (2-mercapto-ethyl) amine (BMEA) may be an ideal modifier due to the moderate spatial diffuse resistance and chain length. Such structure not only can prevent the effect of water which decreases the catalytic activity, but also ensure the access of reactants. At present, although many research on mercapto-modified catalysts have been studied, little on the reaction kinetics and thermodynamics has been reported during the catalyst preparation process. In this article, BMEA-modified macroporous sulfonic resin (SSDB) catalyst for BPA synthesis was prepared by neutralization reaction. The kinetics and thermodynamics of the resin-modified process were also studied to optimize the preparation conditions of catalyst. Thirty-five days of continuous BPA synthesis processes were carried out to evaluate the catalytic activity and stability of the BMEA-modified SSDB.

Materials and Methods

Chemicals

Styrene (GR) and divinylbenzene (65% divinylbenzene isomers and 33% ethylvinylbenzene measured by GC), were

---

Correspondence concerning this article should be addressed to. B. Wang at wangbh2012@yeah.net.

washed with 10% aqueous sodium hydroxide solution and water to remove the residual inhibitors, benzoyl peroxide (BPO, AR) was used as initiator, refined paraffin wax and NY-200$^{\#}$ petroleum(>75%, Daqing Petrochemical Company) were used as pore forming agents. BMEA was laboratory-prepared.[15] H_2SO_4 (98%), phenol (AR), and acetone (AR) were from Tianjin Reagent Company (China).

Catalyst preparation and characterization

The suspension polymerization was carried out in a flask fitted with a mechanical stirrer, N_2 inlet condenser, and an Hg seal. The basic macroporous resin beads were prepared by polymerizing divinylbenzene in styrene. The solution containing the monomers (the weight ratio of divinylbenzene to styrene is ~1:9), the diluent (refined paraffin wax and NY-200$^{\#}$ petroleum, 30 wt % of the monomer), and initiator (BPO, 1 wt % of the monomer) were poured into the reactor, which already contained the aqueous phase at room temperature. Under stirring, the synthetic solution was heated to 351–353 K, the time of the polymerization was about 2 h, and then the temperature rose to 358–363 K for another 6 h. The final copolymers were washed and dried to obtain white beads.

The small resin beads were extracted by benzene at room temperature. The copolymer beads were kept in contact with 1,2-dichloroethane for 24 h (10 ml of solvent for 1 g of copolymer). The swollen polymer beads were sulfonated with concentrated sulfuric acid for 10 h under slow stirring at 373 K. Then the sulfonic resin was filtered, washed with water until neutralization, and finally dried to obtain white spheres which were named SSDB.[19,20] The exchange capacity of SSDB is ~4.5 meq/g dry resin.

154.0 g SSDB and deionized water were added into a tubular glass reactor equipped with a magnetic stirrer. The stirring should be quick enough to suspend the resin in deionized water. When the temperature was up to 363 K, an aqueous solution containing 26.26 g BMEA was added in 40 min. The final solution volume was 0.5 L and adjusted pH = 3 with hydrochloride. Resin samples were taken every 30 min. After 7 h of sampling, these samples were handled with absolute ethyl alcohol, laid aside overnight, then washed several times with deionized water and dried under vacuum for 24 h at 343 K to measure exchange capacity.

The pore size and surface area of copolymer samples (specific surface area, S_{BET} in m^2/g) were determined by Brunauer–Emmett–Teller (BET) methods from low-temperature nitrogen adsorption isotherms at 77 K using a Micromeritics TriStar 3000 (American Micromeritics) automated system.

The shape and surface texture of the particles had been monitored with a scanning electron microscope (SEM, Hitachi S-4800) at 10 kV accelerating rate.

Determination of BMEA content and catalytic properties

To determinate the content of BMEA, about 1 g SSDB or BMEA-modified SSDB was poured in 250 ml conical beaker, and 50 ml 1N NaCl aqueous solution was added in. Then, the beaker was slightly swayed. Phenolphthalein solution or pH test paper was used as an indicator to titrate with calibrated 0.1N NaOH aqueous solution.

Evaluation of BMEA-modified SSDB as catalysts was carried out in a continuously packed bed isothermal glass reactor (440 mm × 15 mm) at 353 K. Catalyst loading is about 40 g, the reaction mixture of phenol and acetone in molar ratio $R = 11.5{:}1$ for 1 h of residence time. All the experimental data (selectivity and conversion) were based on acetone.

The solution samples were analyzed by HPLC (Waters 810) with a column of Nova-Pak Silica, 4 μm, 8 × 100 nm and chloroform/petroleum ether (1:1, V/V), and isopropanol used as the mobile phase with a flow rate of 2.0 mL/min.

Catalytic results were recorded as conversion (C, wt %) and selectivity (S, wt %), which were determined by HPLC. Those parameters are defined as

$$C_{\mathrm{Acetone}} = \frac{C_{\mathrm{BPA}}\left(M_{\mathrm{Phenol}}R + M_{\mathrm{Acetone}}\right)}{M_{\mathrm{BPA}}} \times 100\%$$

where C_{BPA} is the content of BPA in the product, M_{Phenol} is the molecular weight of phenol, R is the mole ratio of the starting phenol to acetone, M_{Acetone} is the molecular weight of acetone and M_{BPA} is the molecular weight of BPA

$$S_{\mathrm{BPA}} = \frac{C_{\mathrm{BPA}}}{C_{\mathrm{BPA}} + C_2 + C_3 + C_4 + C_5} \times 100\%$$

where C_{BPA}, C_2, C_3, C_4, and C_5 are the contents of BPA, 2,4-bisphenol-A, triphenol, chroman, and other impurities in the reaction product, respectively.

Results and Discussion

Copolymer characterization

In order to obtain a more direct insight into the structure of the resins, SEM was carried out. Figure 1a shows that the surface of the SSDB particles appears to be irregular and porous. It also indicates that the adsorbent has an adequate morphology for BMEA adsorption. Figure 1b depicts the surfaces of particles after BMEA adsorption on the SSDB, it is clear to see that the apertures become small but not blocked completely. Nitrogen adsorption isotherms for the synthesized resins before and after BMEA adsorption were measured, and the physical properties of the obtained resins are listed in Table 1. After BMEA modification, BET surface area, average pore diameter, and pore volume of SSDB decreased, which showed that BMEA had doped into the inner side of the resin.

Effect of the preparation conditions

In liquid phase, the adsorption is essentially a "competition" between solvent and adsorbate for the adsorbent. The effect of solvent adsorption can be ignored when the BMEA solution is dilute, and the adsorption system can be seen as single-component adsorption. Figure 2 shows the SSDB preparation and modification process. The modification process is a chemical adsorption process, and BMEA is fixed in resin through neutralization reaction. The adsorption mechanism for the adsorption process may be assumed to involve the following four steps: external diffusion of BMEA, boundary layer diffusion, intraparticle diffusion, and BEMA adsorption on the adsorbent surface.

Figure 3 shows the effect of time and temperature on the BMEA-modified SSDB preparation process. In order to ensure the effectiveness of the test results, each experiment had been repeated three times in the process of data collection to minimize the error, the data in Figure 3 are average values. In the adsorption process, the amount of BMEA adsorption on SSDB increased greatly at initial stage, but after 4 h, it remained unchanged with time which means the

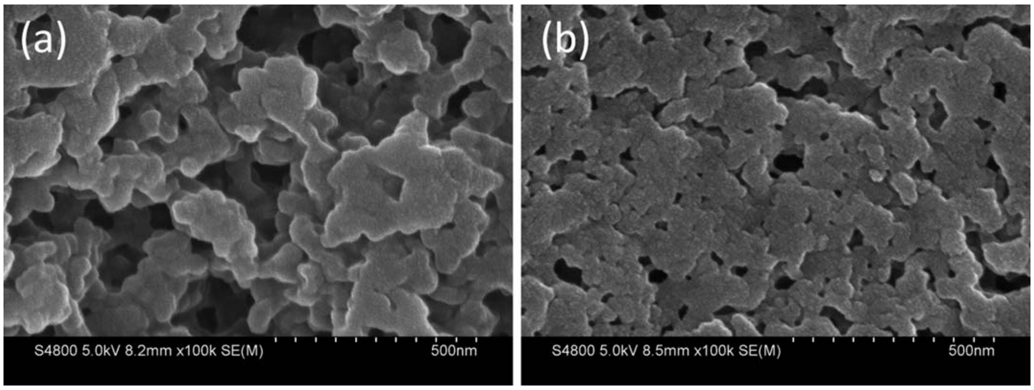

Figure 1. SSDB before (a) and after (b) the BMEA adsorption.

adsorbed amount of BMEA reached equilibrium. Moreover, the adsorption rates increased as temperature rises from 343 to 363 K, which demonstrates that high temperature is favorable to the adsorption process.

Adsorption kinetics

In the industrial production of BPA, modified resin preparation is very important. For the sake of understanding the controlling factors and optimum conditions, it is necessary to explore the adsorption kinetics.

A simple kinetic analysis of adsorption is the Lagergren first-order rate equation. In this equation, the average value of the rate constant, k_1, for BMEA adsorption on SSDB can be calculated in the form

$$\frac{dq_t}{dt}=k_1(q_e-q_t) \tag{1}$$

where k_1 is the rate constant of the first-order model (h^{-1}), q_e and q_t are the amounts of BMEA per unit mass of the adsorbent (mol/g) at equilibrium and time t, respectively.

The kinetic data obtained were also fitted to the pseudo-second-order rate equation which can be written as follows

$$\frac{dq_t}{dt}=k_2(q_e-q_t)^2 \tag{2}$$

where k_2 is the rate constant of the pseudo-second-order model (g/mol min). After definite integration by applying the initial conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, Eqs. 1 and 2 become[21,22]

$$\ln(q_e-q_t)=\ln q_e-k_1t$$

$$\frac{t}{q_t}=\frac{1}{k_2{q_e}^2}+\frac{t}{q_e}$$

Figure 4 shows the straight line plots of first-order and pseudo-second-order models for BMEA adsorption on SSDB. As seen in Table 2, the correlation coefficients for the line plots of t/q_t against t are greater than 0.996. However, a lack of fit is demonstrated by the first-order model, the deviation of the points from the line is distinct, especially at 353 K and 363 K. This suggests that the adsorption process does not fit the first-order model, but corresponds to pseudo-second-order model. Based on this assumption, it confirms that the adsorption of BMEA onto SSDB surface may be mainly chemical sorption because the pseudo-second-order model involves valency forces through sharing or exchange of electrons between adsorbent and adsorbate. The adsorption rate constants increase with temperature indicating the endothermic nature of adsorption,[23] and high temperature is conducive to the adsorption process.

Table 1. The Physical Properties and Characteristics of Polymeric Materials

Structure	Average particle size (mm)	BET surface area (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3/g)
SSDB	0.5	530.0	8.4	0.67
BMEA-SSDB	0.5	370.2	3.9	0.43

Half-adsorption time, $t_{1/2}$ is defined as the time required for half-adsorption of BMEA. This $t_{1/2}$ is used as a measure of the diffusion coefficient[24]

$$t_{1/2}=\frac{1}{k_2q_e} \tag{3}$$

The values of $t_{1/2}$ determined for the tested parameters are given in Table 2.

Intraparticle diffusion

In the BEMA-modified process, understanding and eliminating the adverse factors can shorten the time to adsorption equilibrium. The adsorption process in the batch reactor with severe stir is often particle diffusion controlled. The possibility of intraparticle diffusion was explored by the Kannan and Sundaram intraparticle diffusion model[24,25]

$$q_t=k_pt^{1/2}+C \tag{4}$$

where k_p is the intraparticle diffusion rate constant (mol/h$^{1/2}$ g), and q_t is the amount of BMEA per unit mass of the adsorbent (mol/g) at time t.

If intraparticle diffusion is rate-limited, then plots of adsorbate uptake, q_t, versus the square root of time ($t^{1/2}$) would result in a linear relationship. k_p and C values can be obtained from these plots (Figure 5) and are presented in Table 2.

The regression coefficient values suggest that this functional relationship maybe corresponds to the characteristic of intraparticle diffusion. However, it also can be seen from Figure 5 that the plots do not pass through the origin of coordinates, indicating that particle diffusion of BMEA determines the adsorption rate, but not exclusively. Values of intercept C give an idea about the thickness of boundary layer, the larger the intercept, the greater boundary layer

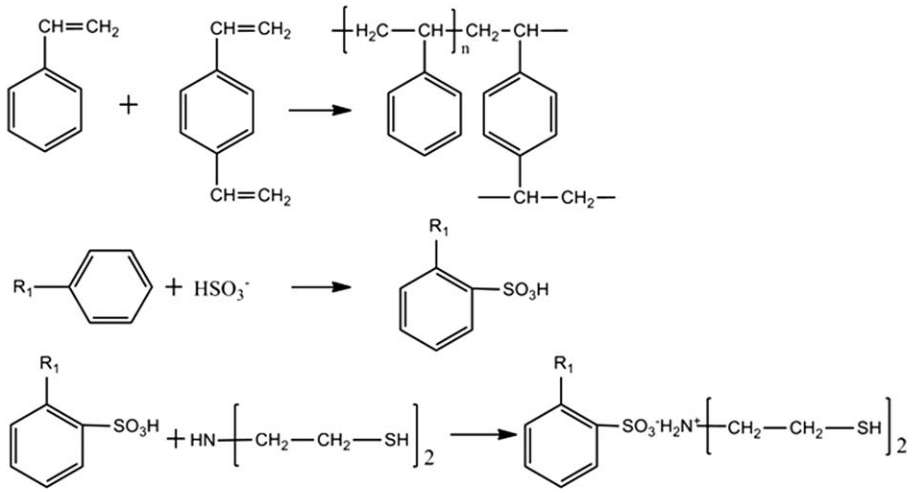

Figure 2. Preparation routes of thiol-based resin, *n* is the degree of polymerization, *R*$_1$ is the resin skeleton.

effect.[26] The values of intercept C are lower than 1, indicating that the effect of boundary layer diffusion is small. The value of $E_a < 40.0$ kJ/mol generally indicates that diffusion-controlled processes and higher values represent chemical reaction processes.[27] In our study, $E_a = 44.6$ kJ/mol, indicating that chemical reaction may have a certain influence on the adsorption rate. Based on these results, it seems that the adsorption rate is mainly controlled by the intraparticle diffusion, but boundary layer diffusion and chemical reaction also have an effect on the adsorption process. As adsorption process is mainly affected by the intraparticle diffusion, the stirring rate maintained at 200 rpm can suspend the resin to meet the preparation requirement.

Diffusion coefficient

The values of diffusion coefficient, which also reveal the adsorption speed, largely depend on the surface properties of adsorbents. The diffusion coefficients for the intraparticle transport of BMEA within the pores of SSDB particles had been calculated under various conditions by employing Eq. 5[28–31]

$$t_{1/2} = \frac{0.03 r_0^2}{D} \tag{5}$$

where D is the diffusion coefficient with the unit cm^2/s, $t_{1/2}$ is the time (s) for half-adsorption of BMEA, and r_0 is the radius of the adsorbent particle in cm. The value of r_0 is

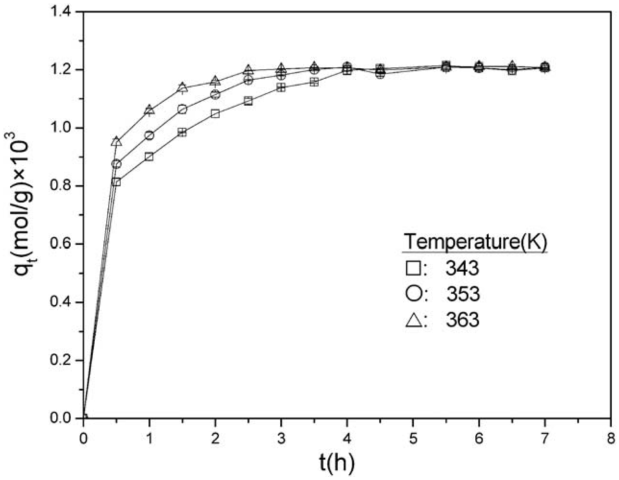

Figure 3. The effect of contact time on amount of BMEA adsorption on SSDB at different temperatures, pH = 3 (error bars represent the standard deviation).

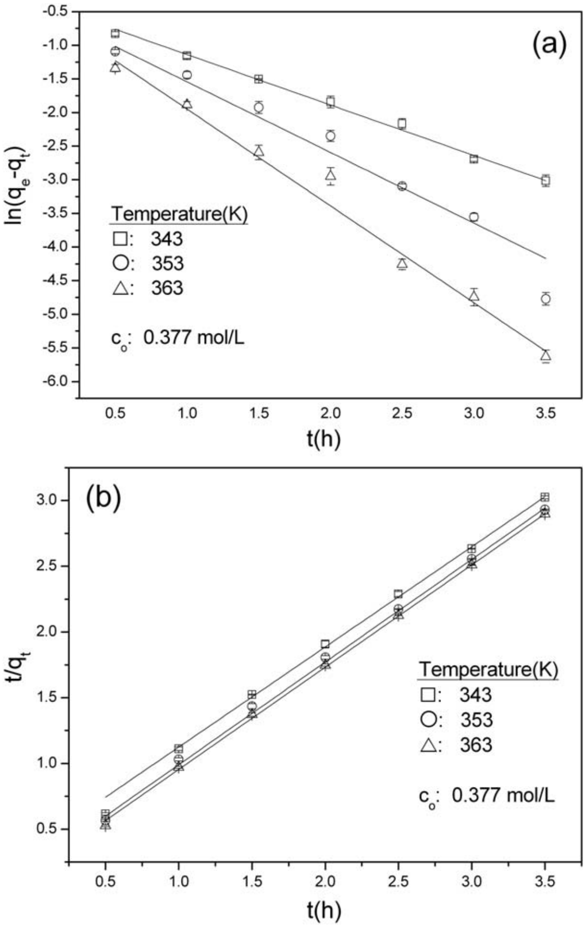

Figure 4. (a) First-order model and (b) Pseudo-second model for BMEA adsorption on SSDB at different temperatures (error bars represent the standard deviation).

Table 2. Kinetics and Intraparticle Diffusion Data Calculated for the Adsorption of BMEA on SSDB

	Kinetic Models						Intraparticle Diffusion			
	Lagergren-First-Order		Pseudo-Second-Order							
T (K)	K_1(h^{-1})	R^2	q_e(cal.)[a] ($\times 10^3$ mol/g)	q_e(exp.)[b] ($\times 10^3$ mol/g)	K_2 ($\times 10^{-3}$ g/mol·h)	R^2	K_p ($\times 10^3$ mol/$h^{1/2}$·g)	R^2	$t_{1/2}$ (h)	D ($\times 10^8$ cm^2/s)
343	0.734 ± 0.023	0.990	1.284 ± 0.030	1.207 ± 0.005	1.677 ± 0.056	0.996	0.298 ± 0.010	0.993	0.464	1.122
353	1.062 ± 0.075	0.970	1.290 ± 0.014	1.209 ± 0.010	2.490 ± 0.043	0.999	0.299 ± 0.017	0.984	0.311	1.675
363	1.440 ± 0.062	0.984	1.276 ± 0.007	1.211 ± 0.008	3.954 ± 0.073	0.999	0.277 ± 0.014	0.989	0.198	2.630

[a] Theoretical adsorption capacity.
[b] Experimental adsorption capacity.

0.025 cm for resin sample. As seen from Table 2, the values of diffusion coefficients increase from 1.122 × 10^{-8} to 2.630 × 10^{-8} cm^2/s with change in temperature from 343 to 363 K. This phenomenon also indicates that high temperature is conducive to the adsorption process. However, thermal stability of resin catalysts is very limited and the modified process cannot be used at higher temperatures. In this article, satisfactory results can be obtained at the adsorption temperature of 363 K with the equilibration time of 3.5 h.

Adsorption isotherms

The equilibrium adsorption data are correlated to the following two isotherm equations: Freundlich and Langmuir.[32,33] The Langmuir model assumes monolayer surface coverage on equivalent sites. The Freundlich model, on the other hand, assumes a heterogeneous adsorption surface with sites that have different adsorption energies. The well-known Langmuir isotherm has the following form

$$C_e/q_e = C_e/q_0 + 1/(q_0 \cdot b) \tag{6}$$

where q_0 (mol/g) is related to maximum sorption capacity and b is the Langmuir constant, q_e is the observed equilibrium adsorption capacity (mol/g) and C_e is the equilibrium concentration (mol/L). Figure 6a shows a plot of the linearized form of the Langmuir isotherm model of the sorption process.

The data were further analyzed using the Freundlich equation

$$q_e = K_f C_e^{\,1/n} \tag{7}$$

A linear form of this equation can be obtained as follows

$$\lg q_e = (1/n)\lg C_e + \lg K_f \tag{8}$$

K_f and n are the Freundlich constants indicating adsorption capacity and adsorption intensity, respectively. A plot of lgq_e vs. lgC_e gives n and K_f from the slope and intercept. The adsorption isotherm parameters of Freundlich and Langmuir along with the correlation coefficients are presented in Table 3. The values of R^2 are all larger than 0.987, indicating that the linear correlations between the values of (1) lgq_e and

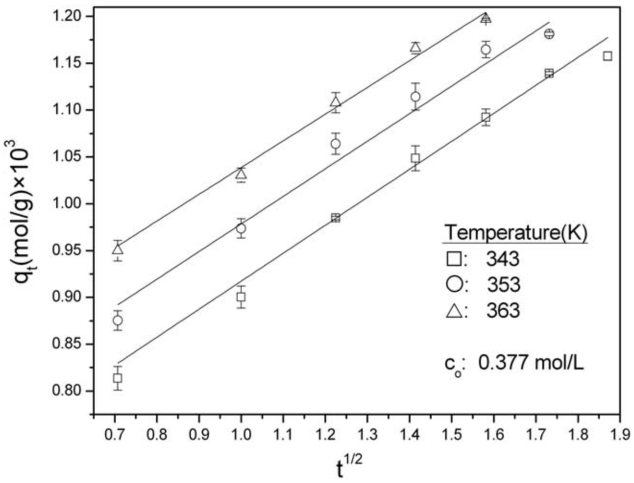

Figure 5. Intraparticle diffusion plots for BMEA adsorption on SSDB at different temperatures (error bars represent the standard deviation).

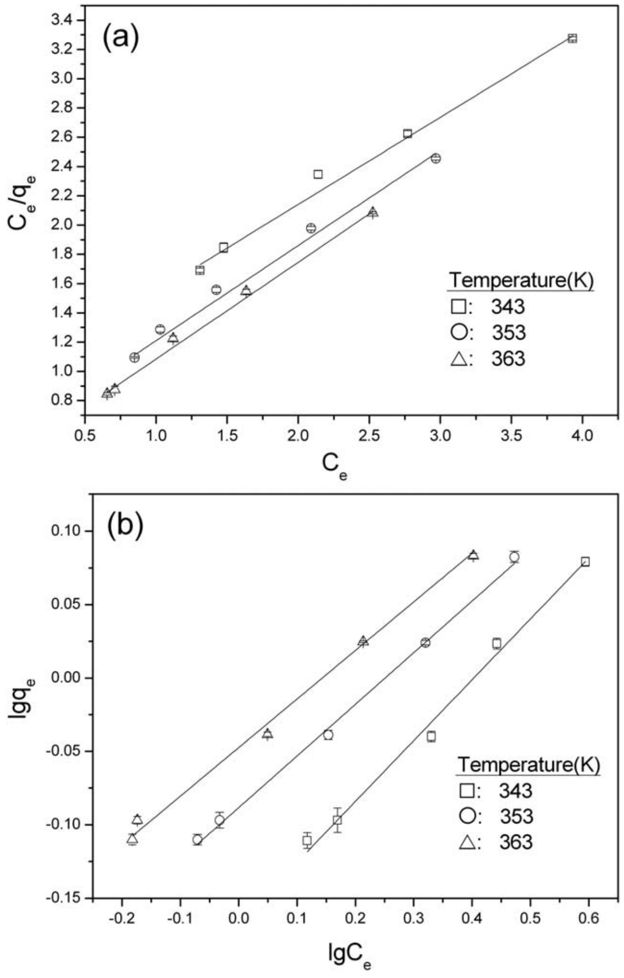

Figure 6. (a) Langmuir isotherm and (b) Freundlich isotherm plots for BMEA adsorbed on SSDB at different temperatures (error bars represent the standard deviation).

Table 3. Adsorption Isotherm Parameters of BMEA Adsorption on SSDB

	Langmuir Isotherm			Freundlich Isotherm		
T (K)	q_0 ($\times 10^3$ mol/g)	b ($\times 10^{-3}$ L/mol)	R^2	n	k_f	R^2
343	1.679 ± 0.064	0.608 ± 0.024	0.993	3.022 ± 0.136	0.897 ± 0.007	0.991
353	1.583 ± 0.061	1.016 ± 0.089	0.994	2.842 ± 0.074	0.816 ± 0.005	0.997
363	1.513 ± 0.035	1.560 ± 0.092	0.997	2.413 ± 0.130	0.681 ± 0.017	0.987

lgC_e, and (2) (C_e/q_e) and C_e are good. However, the values of n, which are in the range 2.413–3.022, not only indicate that the BEMA adsorption process is a favorable adsorption,[34] but also correspond to a monolayer adsorption with a more homogeneous active surface.[35] Meanwhile, $1/n < 1$ also corresponds to a normal L-type Langmuir isotherm.[32,36] Moreover, the presence of solvent water also can decrease the heterogeneity of SSDB surface.[37] Based on these views, the Langmuir isotherm may be a better model which indicates the adsorbent surface is described by homogeneous adsorption sites.

Activation parameters

Activation energy determines the difficulty of the reaction. The temperature dependence of virtually all reactions can be fit successfully to the Arrhenius equation[28]

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{9}$$

where E_a is the Arrhenius activation energy, A is the Arrhenius factor, k_2 is rate constant (g/mol s), R is gas constant, and T is temperature.

To extract A and E_a from kinetic data, as shown in Figure 7, we plotted the series of rate constants measured at different temperatures in a graph of lnk_2 vs. $1/T$. The obtained value of E_a is 44.6 kJ/mol for adsorption of BMEA on SSDB, indicating that the adsorption process corresponds to a chemisorption.[23] As the chemisorption is a monolayer adsorption, reasonably controlling the amount of BMEA can improve the utilization of mercapto compound. As will be shown later, when the equilibrium adsorption capacity q_e was 1.21 × 10^{-3} mol/g, the BMEA-modified catalyst showed a high conversion and selectivity in the BPA continuous production.

Thermodynamic properties of adsorption

Adsorption enthalpy is closely related to adsorption capacity. When adsorption is constant, the derived enthalpy change is the isosteric enthalpy. Van't Hoff equation was used to calculate the thermodynamic parameters involved in the adsorption processes[38]

$$\ln(1/C_e) = \ln K_0 + (-\Delta H/RT) \tag{10}$$

where C_e is the equilibrium concentration of BEMA at temperature T for specific equilibrium adsorption q_e (mol/g), K_0 is equilibrium constant. A graph of ln($1/C_e$) versus $1/T$ is shown in Figure 8, and isosteric enthalpy, ΔH (kJ/mo1), was calculated from the slope of the plot.

Adsorption free energy, ΔG, by Gibbs was derived from isotherm equation

$$\Delta G = -RT \int_0^{C_e} (q_e/C_e) dC_e \tag{11}$$

where q_e can be replaced by the Langmuir equation.

Gibbs–Helmholtz equation $\Delta S = (\Delta H - \Delta G)/T$ is used to calculate the adsorption entropy in the adsorption processes.[39]

As shown in Table 4, the positive values of ΔH indicate the endothermic nature of BMEA adsorption on SSDB. However, these values are relatively small, which indicates a diffusion-controlled process.[40] The positive values of E_a and ΔH suggest the presence of an energy barrier in the adsorption process and endothermic process.[41] The negative values of ΔG indicate the spontaneity of adsorption. The smaller the value of ΔG, the more spontaneous is the process. The decrease of ΔG with temperature also shows that the adsorption process is endothermic and more favorable at high temperature. The positive values of ΔS suggest the increased randomness at the solid/solution interface during the adsorption of BMEA on SSDB.[41] As solute and solvent coexist in

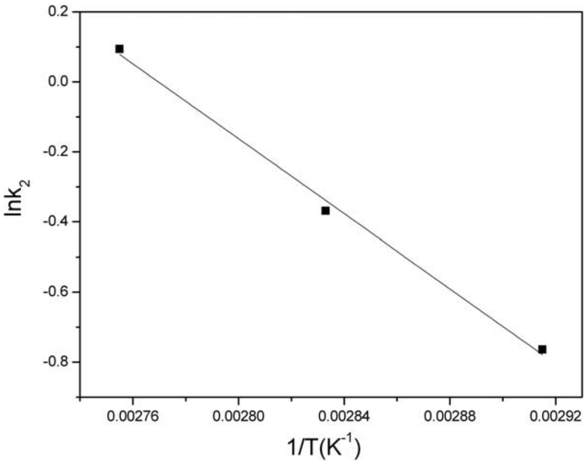

Figure 7. Arrhenius plot for the adsorption of BMEA on SSDB.

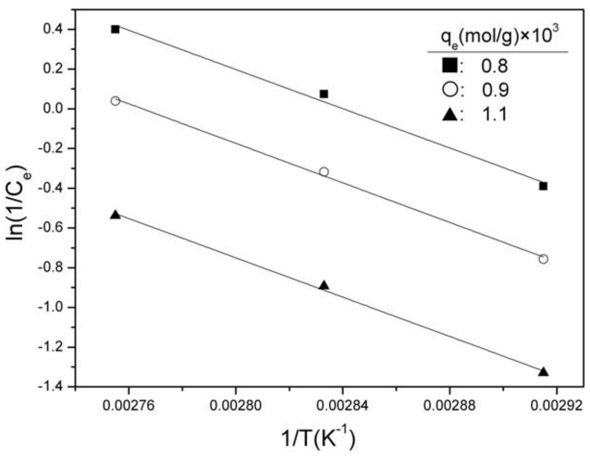

Figure 8. Determination of isosteric enthalpy for BMEA adsorption on SSDB at different q_e.

Table 4. Thermodynamic Parameters for the Adsorption of BMEA on SSDB

		ΔG (kJ/mol)			ΔS (kJ/mol K)		
q_e ($\times 10^3$mol/g)	ΔH (kJ/mol)	343K	353K	363K	343K	353K	363K
0.8	41.07	−3.067	−3.085	−3.269	0.129	0.125	0.122
0.9	41.40	−3.978	−4.058	−4.183	0.132	0.129	0.126
1.1	41.17	−5.713	−5.797	−5.939	0.137	0.133	0.130

solution, solute adsorption must be accompanied by solvent desorption. As the molar volume of water is less than the adsorbate, there will be larger number of water molecules that return to the solution for free movement, resulting in a higher degree of randomness in the entire system.[42] Fundamentally, the adsorption thermodynamics are influenced by the adsorption properties, the data can be used to improve the parameters in catalyst production process.

Continuously catalytic reactivity

Continuous BPA synthesis was carried out in order to test catalytic performance of the catalyst before and after BMEA modification. With 40 g catalyst, reactions were done at 353 K in a continuous packed bed reactor for a continuous run of 35 days. Phenol and acetone (molar ratio 11.5: 1) were laid in the catalyst bed for a residence time of 1 h.

Figure 9a shows that after 35 days of continuous production over SSDB, the selectivity of BPA remained at 80%. Although the SSDB showed good stability, the acetone conversion was just maintained at 24%, which is low for industrial production need. As shown in Figure 9b, the BMEA-modified SSDB under continuous reaction conditions exhibited superior performance. The BPA selectivity and acetone conversion are about 96.5% and 92%, respectively.

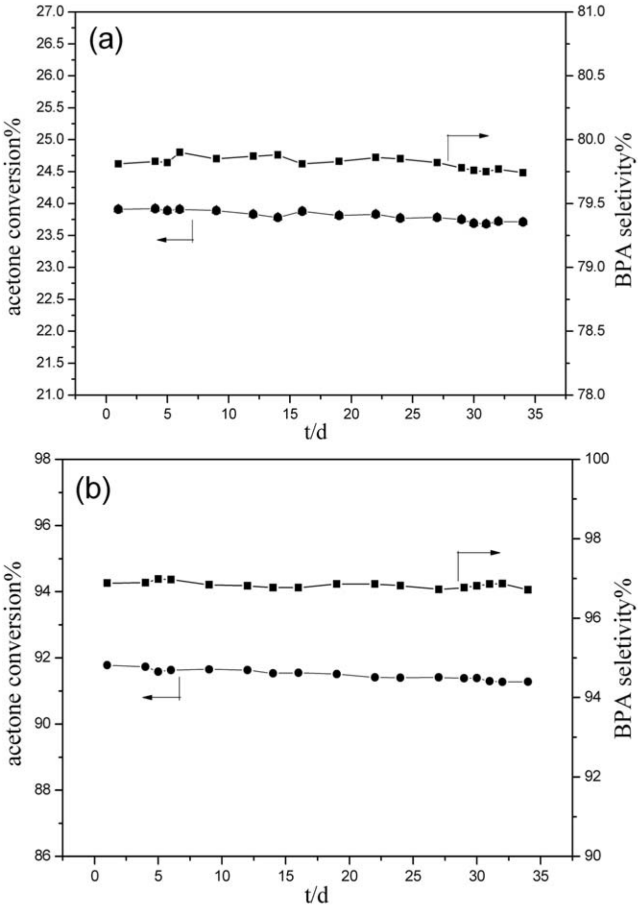

Figure 9. The yield of BPA and acetone selective for 35 days of continuous production by (a) SSDB and (b) BEMA-modified SSDB.

The introduction of BMEA makes the acid content of BMEA-modified SSDB close to or slightly lower than the SSDB (as acid environment is necessary for the reaction[8]), but the acetone conversion and BPA selectivity both became higher. This can be explained from the fact that acid quantity is not the only factor that influences reaction. Water can easily bind to the sulfonic acid groups instead of reactant and inhibit the catalyst activity.[22] The structure of BMEA-modified SSDB could prevent water and sulfonic acid groups from forming hydrogen bonds. At the same time, S-atoms, with lone pair electrons, could combine or dissociate hydrogen ion to form concerted catalyst with sulfonic acid group, which enhances the catalytic activity.

In the condensation reaction of acetone and phenol, several byproducts such as 2,4-bisphenol-A, 4-hydroxyphenyl-2,2,4-trimethyl-chroman, and 4-hydroxy-phenyl-2,4,4-trimethyl-chroman were also obtained by the reactions of phenol with mesityl oxide or 2,4-bisphenol-A with acetone. The introduction of thiol can not only improve the catalytic activity, but can also inhibit the occurrence of side reactions. On the one hand, with the anchoring of BMEA in the resin channels, the average pore diameter of SSDB decreases. When the reaction occurs inside the pores, the bulky byproducts are hard to be formed by the geometric limitation.[7] On the other hand, this pore size is just suitable for synthesis of BPA, so that the selectivity of BPA is high. Besides, the BMEA-modified SSDB maintained high catalytic activity in the 35 days continuous production.

To the best of our knowledge, the catalyst exhibited high activity and selectivity at moderate reaction conditions, which may also be due to the help of the high surface area and the accessibility of the inner acid sites in resin by the reactants. The reaction results suggest that BMEA-modified SSDB as catalyst is suitable for pilot amplification and provide a possibility for BPA industrial production.

Conclusions

Our research provides a reference for the mercapto-modified resin preparation. From a theoretical point, the main influence factors of the resin modification process were analyzed. The adsorption of BMEA on SSDB is a chemical adsorption process. The adsorption rate is mainly controlled by the intraparticle diffusion; meanwhile, it is also affected by boundary layer diffusion and chemical reaction. The kinetics of the adsorption fits pseudo-second-order model and shows the endothermic nature of adsorption. The adsorption is in conformity with Langmuir isotherm, which indicates the adsorbent surface is better described by homogeneous adsorption sites. The values of ΔH, ΔS, and

ΔG are calculated to predict the kinetic aspects of BMEA adsorption. After 35 days of continuous BPA synthesis process, the BMEA-modified SSDB exhibited good performance in terms of acetone conversion, BPA selectivity, and stability. Therefore, the BMEA-modified SSDB may be a potential catalyst for the BPA industrial production.

Acknowledgments

The authors gratefully acknowledge Research and Development Center of Petrochemical Technology. The authors also thank the management of their college for providing research facilities and constant encouragement.

Literature Cited

1. Chen CC, Cheng S, Jang LY. Dual-functionalized large pore mesoporous silica as an efficient catalyst for bisphenol-A synthesis. *Microporous Mesoporous Mater.* 2008;109:258–270.
2. Zheng BS. Present station of BPA at home and abroad and suggestions on development of Chinas BPA. *Fine Spec Chem* 2001;12: 7–10.
3. Das D, Lee JF, Cheng S. Sulfonic acid functionalized mesoporous MCM-41 silica as a convenient catalyst for bisphenol-A synthesis. *Chem Commun.* 2001;21:2178–2179.
4. Das D, Lee JF, Cheng S. Selective synthesis of bisphenol-A over mesoporous MCM silica catalysts functionalized with sulfonic acid groups. *J Catal* 2004;223:152–160.
5. Kaleta W, Nowińska K. Immobilisation of heteropoly anions in Si-MCM-41 channels by means of chemical bonding to aminosilane groups. *Chem Commun.* 2001;6:535–536.
6. Shimizu K, Kontani S, Yamada S, Takahashi G, Nihisyama T, Satsum A. Synthesis of bisphenol-A from phenol and acetone using organic–inorganic modified heteropoly acid catalyst, In: 18th Saudi Arabia–Japan Joint Symposium, Dhahran, Saudi Arabia, November 16–17, 2008.
7. Nowińska K, Kaleta W. Synthesis of bisphenol-A over heteropoly compounds encapsulated into mesoporous molecular sieves. *Appl Catal A: General.* 2000;203:91–100.
8. Shimizua K, Kontani S, Yamada S, Takahashi G, Nishiyama T, Satsuma A. Design of active centers for bisphenol-A synthesis by organic–inorganic dual modification of heteropolyacid. *Appl Catal A: General.* 2010;380:33–39.
9. Yadav GD, Kirthivasan N. Synthesis of bisphenol-A: comparison of efficacy of ion exchange resin catalysts vis-a-vis heteropolyacid supported on clay and kinetic modeling. *Appl Catal A: General.* 1997;154:29–53.
10. Jia LJ, Hua CY, Dai LY, Shan YK. Synthesis of bisphenol A catalyzed by Et_3NHCl-$AlCl_3$ ionic liquids. *React Kinet Catal Lett.* 2004;81:235–240.
11. Hou LJ, Cai QH, Lu B. A novel solid acid for synthesis of bisphenol A. *Catal Lett.* 2006;111:153–157.
12. Singh AP. Preparation of bisphenol-A over zeolite catalysts. *Catal Lett.* 1992;16:431–435.
13. Pressman EJ, Willey PR. Method and catalyst for making bisphenol (G. E. Company). US Patent 3394089, 1986.
14. Li SM. Isomerization of by-products of bis-phenol synthesis (S.O. Company). US Patent 4822923, 1987.
15. Li SM. Process and catalyst for production of bisphenol-A (S.O. Company). US Patent 4820740, 1989.
16. Mcnutt BW, Gammill BB, Jackson L. Ion exchange catalyst for the preparation of bisphenols (D.C. Company). US Patent 3394089, 1968.
17. Wagner RB. A-preparation using ion exchange resin containing mercapto and sulfonic acid groups (H.P. Company). US Patent 3172916, 1965.
18. Apel FN, Conte LB, Bender HL. Cationic exchanging polymeric resin (U.C. Corporation). US Patent 3153001, 1964.
19. Coutinho FMB, Souza RR, Gomes AS. Synthesis, characterization and evaluation of sulfonic resins as catalyst. *Eur Polym J.* 2004;40:1525–1532.
20. Tan Q, Jin ZQ, Jiang HS, Liu ZZ, He BJ. Ion exchange resin catalyst for the synthesis of bisphenols and the process for preparing the same. US Patent 5759942, 1998.
21. Esparza P, Borges ME, Díaz L, Alvarez-Galván MC, Fierro JLG. Equilibrium and kinetics of adsorption of methylene blue on Ti-modified volcanic ashes. *AIChE J.* 2011;57:819–825.
22. Ho YS, McKay G. Pseudo-second order model for sorption processes. *Process Biochem.* 1999;34:451–465.
23. Anirudhan TS, Radhakrishnan PG. Thermodynamics and kinetics of adsorption of Cu(II) from aqueous solutions onto a new cation exchanger derived from tamarind fruit shell. *J Chem Thermodyn.* 2008;40:702–709.
24. Doğan M, Özdemir Y, Alkan M. Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. *Dyes Pigments.* 2007;75:701–713.
25. Ho YS, McKay G. Sorption of dye from aqueous solution by peat. *Chem Eng J.* 1998;70:115–124.
26. Kannan N, Sundaram MM. Kinetics and mechanism of removal of methylene blue by adsorption on various carbons – a comparative study. *Dyes Pigments.* 2001;51:25–40.
27. Bartlett RJ, James BR. Redox chemistry of soils. In: Sparks DL, editor. Environmental Soil Chemistry. San Diego: Academic Press, 1995:187–202.
28. Doğan M, Alkan M. Adsorption kinetics of methyl violet onto perlite. *Chemosphere.* 2003;50:517–528.
29. Singh BK, Rawat NS. Comparative sorption kinetic studies of phenolic compounds on fly ash and impregnated fly ash. *J Chem Technol Biotechnol.* 1994;61:51–65.
30. Bhattacharya AK, Venkobachar C. Removal of cadmium(II) by low cost adsorbents. *J Environ Eng.* 1984;110:110–122.
31. Helfferich F. Ion Exchange. New York: McGraw Hill Book Company, 1962.
32. Monazam ER, Shadle LJ, Miller DC. Equilibrium and kinetics analysis of carbon dioxide capture using immobilized amine on a mesoporous silica. *AIChE J.* 2013;59:923–935.
33. Deshpande PA, Polisetti S, Madras G. Dispersed ZrO_2 nanoparticles in MCM-48 with high adsorption activity. *AIChE J.* 2012;58: 2987–2996.
34. Alkan M, Karada M, Doğan M, Özdemir Y. Adsorption of CTAB onto perlite samples from aqueous solutions. *J Colloid Interface Sci.* 2005;291:309–318.
35. Onyango MS, Kojima Y, Aoyi O, Bernardo EC, Matsuda H. Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9. *J Colloid Interface Sci.* 2004;279:341–350.
36. Munir K, Yusuf M, Noreen Z, Hameed A, Hafeez FY, Faryal R. Isothermal studies for determination of removal of bi-metal (Ni and Cr) ions by Aspergillus niger. *Pak J Bot.* 2010;42:593–604.
37. Dai XY, Cheng JD, Wang HS. Adsorption properties influenced by the moisture of adsorbent. *Ion Exch Sorption.* 1993;9:134–137.
38. Pan BC, Xiong Y, Li AM, Chen JL, Zhang QX, Jin XY. Adsorption of aromatic acids on an aminated hypercrosslinked macroporous polymer. *React Funct Polym.* 2002;53:63–72.
39. Srivastava VC, Mall ID, Mishra IM. Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA). *Chem Eng J.* 2007;132:267–27.
40. Khraisheh MAM, Al-Degs YS, Allen SJ, Ahmad MN. Elucidation of controlling steps of reactive dye adsorption on activated carbon. *Ind Eng Chem Res.* 2002;41:1651–1657.
41. Hameed BH, Ahmad AA, Aziz N. Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash. *Chem Eng J.* 2007;133:195–203.
42. Vasu AE. Studies on the removal of rhodamine B and malachite green from aqueous solutions by activated carbon. *E-Journal Chem.* 2008;5:844–852.

Manuscript received Oct. 30, 2012, and revision received Mar. 12, 2013.