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Original article

$ZnCl_2$-modified ion exchange resin as an efficient catalyst for the bisphenol-A production

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ABSTRACT

A $ZnCl_2$-modified ion exchange resin as the catalyst for bisphenol-A synthesis was prepared by the ion exchange method. Scanning electron microscope (SEM), Fourier transform infrared spectrophotometer (FT-IR), thermo gravimetric analyzer (TGA) and pyridine adsorbed IR were employed to characterize the catalyst. As a result, the modified catalyst showed high acidity and good thermal stability. Zn^{2+} coordinated with a sulfonic acid group to form a stable active site, which effectively decreased the deactivation caused by the degradation of sulfonic acid. Thus the prepared catalyst exhibited excellent catalytic activity, selectivity and stability compared to the unmodified counterpart.

1. Introduction

Bisphenol-A [2,2-bis(4-hydroxyphenyl)propane; BPA] is mainly used for the production of polycarbonate and epoxy resins. It is commonly prepared by the condensation of phenol and acetone and the catalyst plays a very important role in this reaction. Till now, some novel catalysts have increasingly drawn attention, such as layered silicate [1], mesoporous MCM silica [2–4], heteropoly acids [5–7], and zeolites [8]. These catalysts, although promising, still require considerable R&D efforts prior to the commercial scale applications. Since 1960 when U.C. Corporation [9] first brought the cation exchange resins into industrialized application for the BPA production, ion exchange resins have been widely used in industry due to their high selectivity, easy separation and minimal equipment corrosion. However, poor thermal stability and low acidity are their intrinsic drawbacks. At the same time, partial exchange of H^+ between cationic impurities from reactants and the resin accelerates the deactivation of the catalyst.

To overcome the shortcomings of ion exchange resins, numerous efforts have been made, including loading thiol groups and/or amine groups by means of reduction [10], esterification [11], neutralization [12] or ion exchange method [13]. Takahim and Toshitaka [14] successfully synthesized a modified catalyst with mercapto alkyl amine, which showed a great improvement in the condensation of phenol and acetone. Carvill *et al.* [15] discovered that 4-(2-mercaptoethyl)-pyridine was a good modified reagent. Terajima *et al.* [16] invented a novel thiol-modified resin catalyst with a phosphate structure, and it proved to possess very high activity. These methods have obviously achieved great improvements, but they are also greatly limited by the complexity in synthesis and easy deactivation.

Ion exchange resins have been used in other reactions, such as esterification [17], transesterification [18], oligomerization [19]. Low acid strength is also one of their main drawbacks affecting the reaction efficiency. Some researchers attempted to solve this issue by introducing Lewis acids into the resins [20–23]. Magnotta and Gates [20] reported that the acidic property of the complex formed by $AlCl_3$–sulfonic acid can be similar to that of the superacid solution of $SbF_5 + FSO_3H$. Shi *et al.* [23] showed that the efficiency of acid-catalyzed transesterification and esterification reactions depend on the subtle balance between Lewis and Brønsted acidities. It has been proved that the coordination of a Lewis acid with a Brønsted acid can increase its original acidity [24]. Therefore, the design of dual acid catalysts based on resins can be advantageous in the BPA production. In this study, $ZnCl_2$ acting as a Lewis acid was added into cationic ion exchange resins to fabricate a more efficient catalyst. To the best of our knowledge, this is the first resin catalyst for producing BPA that contains both a Brønsted acid and a Lewis acid.

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2. Experimental

2.1. Catalyst preparation

Phenol (99.8%), acetone (≥99.9%) and ethanol (≥99.5%) were purchased from Tianjin Reagent Company (China). $AlCl_3$ (≥97.0%), $FeCl_3$ (≥99.0%), $SnCl_2$ (≥98.0%), $ZnCl_2$ (≥98.0%) were purchased from Tianjin Guangfu Company (China).

A strong acidic ion-exchange resin (Amberlyst-15, Rohm and Haas Company) was washed by ethanol and deionized water with the speed of 15 cm/min until the effluent was colorless, and was subsequently dried in an oven for 24 h at 70 °C. Certain amount of $ZnCl_2$ was dissolved in ethanol to produce different concentrations (w/w); then 5 g of treated ion exchange resin was added into the $ZnCl_2$ solution (100 mL) and kept for 6 h at room temperature. Finally the modified catalyst was washed with deionized water until no Cl^- exists in the solution, and then was dried in a vacuum oven for 48 h at 70 °C.

The preparation of $AlCl_3$, $FeCl_3$ and $SnCl_2$ modified catalysts employed the same procedure as that of $ZnCl_2$ modified one mentioned above.

2.2. Catalyst characterization

The crystal morphology was observed on a Hitachi S-4800 SEM at 5.0 kV. FT-IR spectra were recorded in a Nicolet NEXUS spectrophotometer using KBr pellets in the 4000–400 cm^{-1} region. IR spectrum of pyridine adsorption was also used to obtain the type of acid sites ranging from 1700 cm^{-1} to 1300 cm^{-1}; the samples were pre-treated under vacuum at 70 °C for 2 h prior to the adsorption of pyridine at room temperature for 48 h and subsequently desorbed at 100 °C for 1 h to physically remove adsorbed pyridine. Thermo gravimetric analysis curves were collected using a Perkin Elmer Diamond instrument with a heating rate of 10 °C/min from 30 to 800 °C, and the flow rate of N_2 is 40 mL/min.

The acid strength of the catalysts was determined by the Hammett indicator method.

$$\text{For } AH^+ \rightleftharpoons A + H^+$$

$$Ka = \frac{a_A \cdot a_{H^+}}{a_{AH^+}} \qquad H_0 = pKa$$

where A is the indicator; H^+ is the acidic site; Ka is the equilibrium constant; a_A, a_{H^+} and a_{AH^+} are the activity of A, H^+ and AH^+, respectively; H_0 is the function of acid strength.

2.3. Catalytic reaction

The synthesis of BPA was carried out in the liquid phase under atmospheric pressure in a 250 mL three-neck round-bottom flask equipped with a condenser, a magnetic stirrer and a thermometer. Phenol (13.6 g) and catalyst (2.0 g) were added into the reactor, and the reactants were heated at 70 °C for 5 h with a stirring rate of 800 revolutions per minute (rpm), then acetone (1.7 g) was added. After 150 min, the reaction mixture was cooled to 30 °C, then the catalyst was separated from the reaction solution. Reaction products were analyzed by an HPLC (Agilent 810) and methanol/water (60:40, v/v) was used as the mobile phase with the flow rate of 1.0 mL/min.

Catalytic results were recorded as conversion (C_{Acetone}, wt%, based on acetone) and selectivity (S_{BPA}, wt%), which were calculated by HPLC analysis. These parameters are defined as

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

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

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

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

3. Results and discussion

Fig. 1 illustrates the catalytic activity affected by the concentration of $ZnCl_2$ (Fig. 1a) and exchange time (Fig. 1b), respectively. Catalytic activity was enhanced greatly with increased $ZnCl_2$ concentration before 2.0% (Fig. 1a). The coordination of Zn^{2+} with a sulfonic acid group formed a stable Brønsted–Lewis

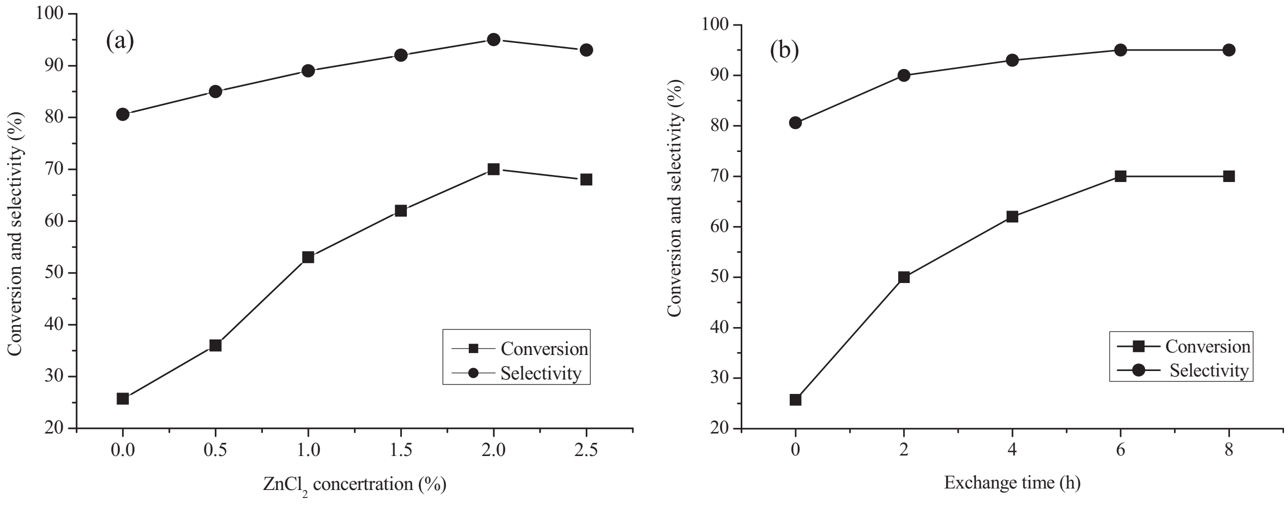

Fig. 1. Effects of preparation conditions on catalytic activity of $ZnCl_2$-modified ion exchange resin catalyst for phenol and acetone condensation. (a) $ZnCl_2$ concentration; (b) exchange time. Reaction conditions: phenol 13.6 g, acetone 1.7 g, catalyst 2.0 g, 70 °C, 150 min, stirring rate 800 rpm.

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acid site. But we should note that an excessive amount of loaded $ZnCl_2$ could occupy active sites and decrease effective catalytic surface area. Consequently, the optimal concentration of $ZnCl_2$ is 2.0%. The same tendency was observed for the exchange time (Fig. 1b). When the exchange time exceeded 6 h the conversion and selectivity changed little, for Amberlyst-15 ion exchange resin has a fixed exchange volume of 4.7 mmol/g [25].

The SEM images were obtained to show surface morphologies of the catalysts before (Fig. 2a and c) and after modification (Fig. 2b and d). Fig. 2a shows that there are many cracks on the surface of the unmodified catalyst due to the introduction of the sulfonic acid groups during the sulfonation process [26]. After being modified, it had fewer or no cracks (Fig. 2b). The pore diameter became much smaller than the unmodified ones (Fig. 2c and d). This can be attributed to the fact that $ZnCl_2$ and sulfonic acid groups can form a new network structure.

The IR spectra of pyridine adsorbed on the samples are shown in Fig. 3a. The intense peak at 1550 cm^{-1} was attributed to the

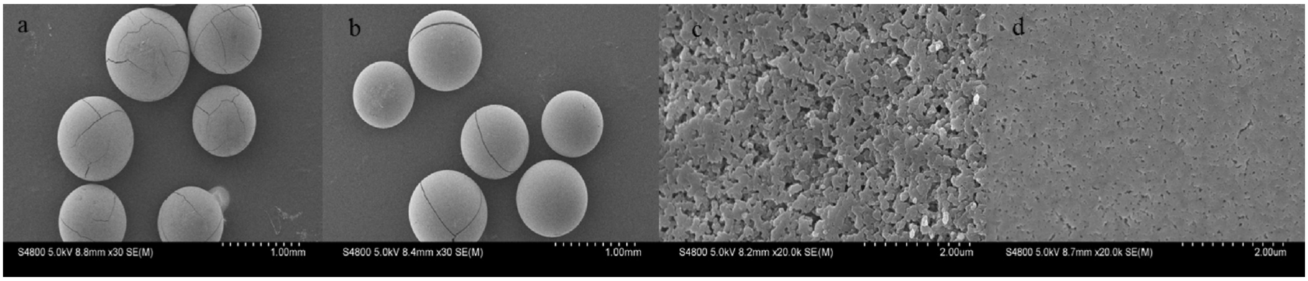

Fig. 2. SEM images of (a, c) unmodified and (b, d) $ZnCl_2$-modified catalysts.

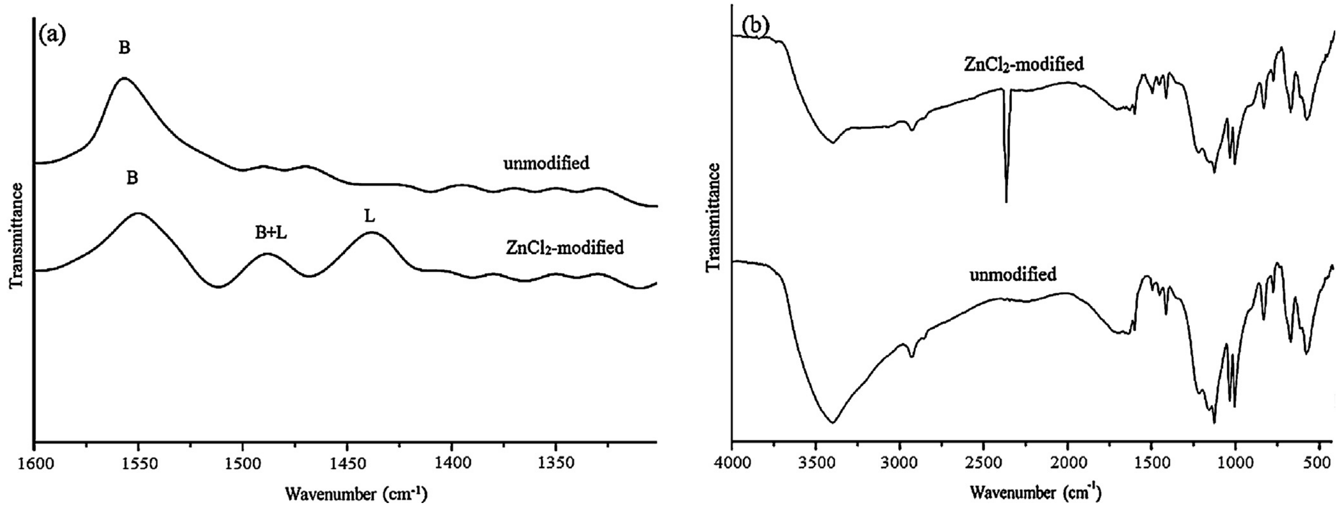

Fig. 3. (a) IR spectra of pyridine adsorbed on unmodified and $ZnCl_2$-modified catalysts. B: Brønsted acid site, L: Lewis acid site. (b) FT-IR spectra of unmodified and $ZnCl_2$-modified catalysts.

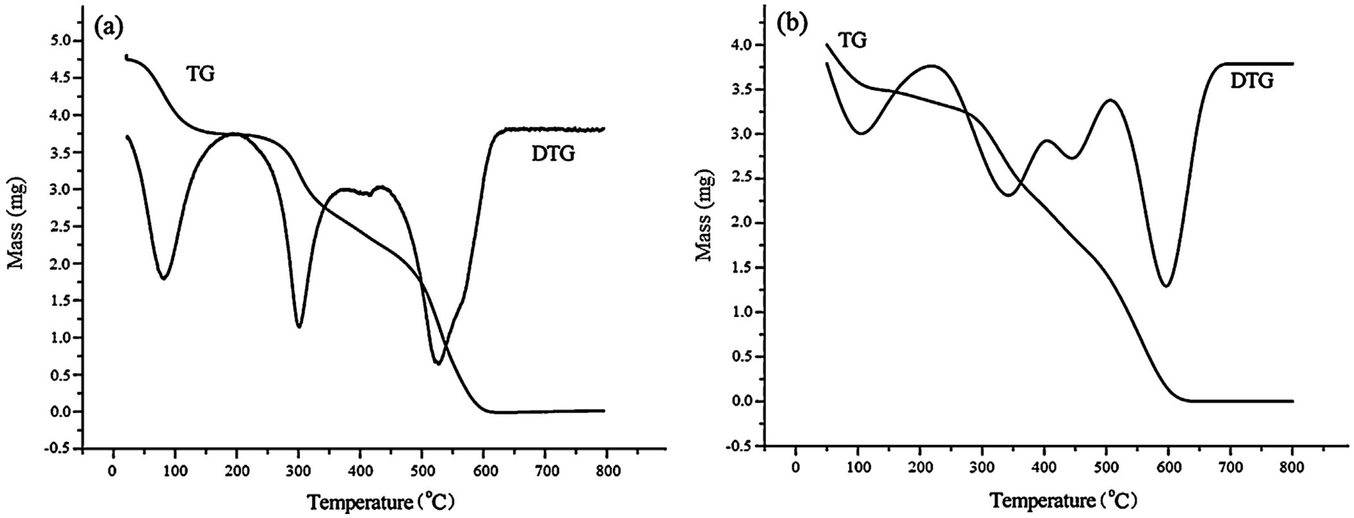

Fig. 4. TGA patterns of (a) unmodified and (b) $ZnCl_2$-modified catalysts.

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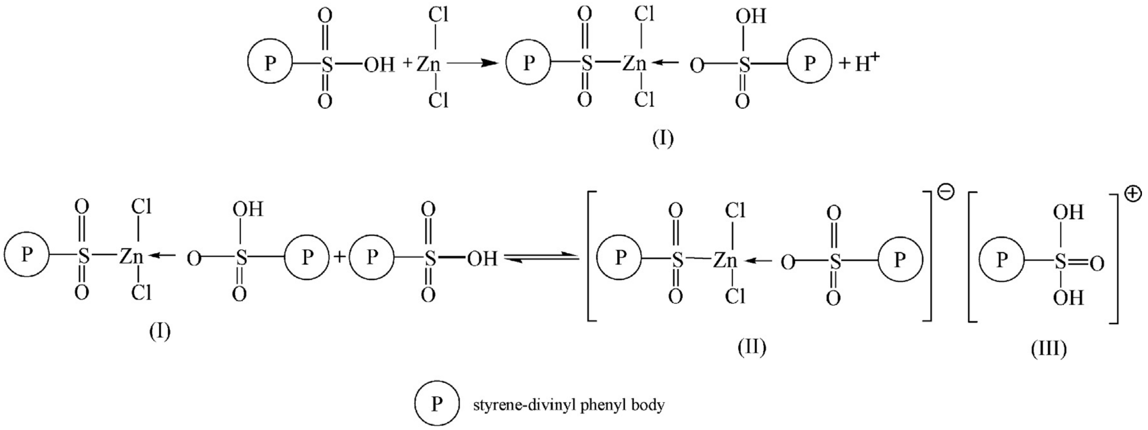


Scheme 1. Coordination reaction between sulfonic acid group and $ZnCl_2$.

Brønsted acid site. After modification two new peaks appeared at 1486 cm^{-1} and 1435 cm^{-1}, which corresponded to the Brønsted–Lewis site and the Lewis acid site, respectively [27]. The measurement result indicates that the Lewis acid was successfully introduced to the resin catalyst by partially exchanging H^+ with Zn^{2+}.

The FT-IR spectrum indicates that the basic skeleton of the resin did not changed except the modified one contained a new absorption peak at 2358 cm^{-1} shown in Fig. 4b, which could be due to the asymmetric stretching vibration of S═O in $-SO_3H$ [28]. After the resin modified with $ZnCl_2$, Zn^{2+} interacted with the lone pair electron of the O to form a π–d coordinate bond, which could make the two S═O asymmetric. This bond can exist either in one molecule or between two molecules, thus forming a peripheral shielding that stabilizes the sulfonic acid groups. Moreover, the π electron on the S can be transferred to the empty orbitals of Zn^{2+}. The positive charge can be delocalized in the sulfonic acid group [27] thereby greatly improved the stability of the ion exchange resin.

As shown in Scheme 1, $ZnCl_2$ can coordinate with the sulfonic acid group to form structure (I), which is unstable and can reversibly form structure (II) and structure (III) [28]. It can be seen that structure (III) is a strong proton-donor that possesses a high acid strength. The Hammett indicator method was used to measure the acid strength of the catalysts. The $ZnCl_2$ modified catalyst ($-8.2 < H_0 < -5.6$) exhibited higher acid strength than the unmodified one ($-5.6 < H_0 < -3.0$). Therefore, we believe that the coordination of the Lewis acid with Brønsted acid led to high acidity and good catalytic activity.

Fig. 4 shows the TGA patterns of unmodified catalyst and 2.0% $ZnCl_2$ modified one. Three kinds of weight loss exist in this process for the unmodified catalyst (Fig. 4a, curve DTG), and it is generally considered that the first peak (80 °C) is produced by the removal of solvent, the second (300 °C) corresponds to the removal of the sulfonic acid group and the last (520 °C) is responsible for the resolving of the styrene–divinyl phenyl body [29].

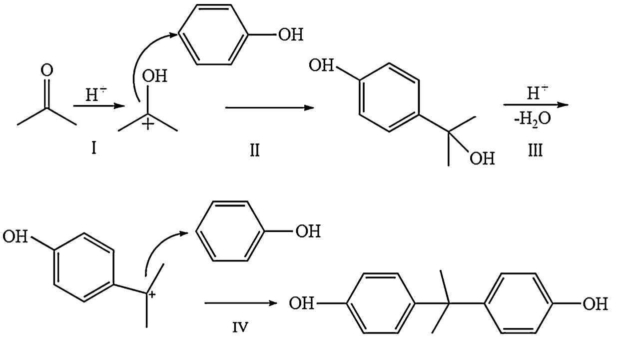
After being modified the second peak split into two peaks (Fig. 4b, curve DTG). According to the analysis of the FT-IR spectra above, the coordination of Zn^{2+} with the sulfonic acid group changed the structure of the catalyst, leading to a two-step process for the sulfonation removal (the removal of single sulfonic acid groups and the removal of sulfonic acid groups coordinating with metal ions). Thus the sulfonic acid group was protected by coordination and still functioned well at a relatively high temperature. Accordingly, the thermal stability of the catalyst has been significantly improved.

$AlCl_3$, $FeCl_3$ and $SnCl_2$ modified catalysts were also prepared as references, and the preparation conditions were the same as that of $ZnCl_2$ modified one. The electronegativities of Al^{3+}, Fe^{3+}, Zn^{2+} and Sn^{2+} are 26.72, 15.38, 10.38 and 8.12, respectively [30], and the electron acceptability of these cations is in parallel to the electronegativity. So the sequence of these Lewis acids' strength is $AlCl_3 > FeCl_3 > ZnCl_2 > SnCl_2$. Table 1 demonstrates the catalytic activity of different Lewis acid modified catalysts. Moderate strength Lewis acid modified catalyst was found to produce the best catalytic activity. A certain strength of Lewis acid is obviously needed to form stable Brønsted–Lewis active sites to increase the proton-donating ability, thus making acetone more easily protonated to form a stable carbenium ion to initiate the reaction (Scheme 2, step I). However, it is important to note here that a stronger Lewis acid do not necessarily results in a better catalytic activity. If a metal cation is an overly strong Lewis acid, it is speculated to be prone to coordinate with acetone, which prohibits

Table 1
Catalytic activity of different Lewis acid modified catalysts.[a]

Modified reagent[b]	Electronegativity	Conversion (%)	Selectivity (%)
None	–	25.7	80.6
$AlCl_3$	26.72 (Al^{3+})	37.2	86.3
$FeCl_3$	15.38 (Fe^{3+})	44.1	89.9
$ZnCl_2$	10.38 (Zn^{2+})	69.5	95.2
$SnCl_2$	8.12 (Sn^{2+})	58.4	93.2

[a] Reaction conditions: phenol 13.6 g, acetone 1.7 g, catalyst 2.0 g, 70 °C, 150 min, stirring rate 800 rpm.
[b] Preparation methods are the same as $ZnCl_2$ modified one.



Scheme 2. Reaction mechanism of bisphenol-A synthesis on acidic catalyst.

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acetone to undergo further reaction. Therefore, metal cations with intermediate Lewis acidity provide the highest catalytic activity.

4. Conclusion

We have successfully fabricated a $ZnCl_2$-modified ion exchange resin that possesses excellent catalytic activity for the synthesis of bisphenol-A. The final conversion of acetone and selectivity of BPA are 69.5% and 95.7%, respectively. The increased activity and stability after adding Lewis acid have been preliminarily explained by analyzing the IR spectra and the rein structure coordinating with $ZnCl_2$. The TGA patterns also indicated that the thermal stability of the resin catalyst was dramatically increased after modification. Compared with the widely used thiol-modified ion exchange resin, the $ZnCl_2$-modified catalyst is easier to prepare and less susceptible to oxidation. The synergistic effect of Brønsted and Lewis acids not only extends the use of resin catalysts in industry, but also provides a guideline for the design of new catalysts.

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