LEWIS ACID SITES OF Mg²⁺-MODIFIED POLYSTYRENE SULFONIC ACID RESIN CATALYSYS FOR SYNTHESIS OF DIBUTYL SUCCINATE

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Artigo

The polystyrene sulfonic acid resin catalysts were fabricated, containing elements of Cl and Mg through oxidization and impregnation, and they were characterized by EDS, FT-IR spectra, Py-IR spectra, UV spectra, XPS and TGA to investigate their physiochemical properties. The catalytic performances of these catalysts were examined in the esterification reaction of succinic acid with n-butanol, and the catalytic results showed that modified resins exhibited the highest catalytic activity and achieved a high yield of dibutyl succinate (91.6%) in addition, the modified resin generated new Lewis acid sites and showed significantly higher thermal stability. The experimental results demonstrated that the Mg²⁺ coordinated with a sulfonic acid group to form stable active sites, which effectively decreased the deactivation caused by the thermal degradation of sulfonic acid. Moreover, the monomer structures of polystyrene sulfonic acid resin and modified polystyrene sulfonic acid resin have been modelled using B3LYP/6-311G(d,p) approximation.

Keywords: esterification reaction; polystyrene sulfonic acid resin; Lewis acid sites; thermal stability; dibutyl succinate.

INTRODUÇÃO

The importance of succinic acid in the bio-based chemical platform is due to its potential transformation to valuable derivatives and building blocks for chemical synthesis.[1] Succinate esters are considered to be precursors for many petrochemical products and can be used as a monomer for a wide range of polymers.[2] One facie way to produce esters is the direct esterification of carboxylic acids and alcohols in presence of homogeneous or heterogeneous catalysts.[3] Conventional homogeneous catalysts for esterification reaction include H_2SO_4, HF, H_3PO_4, $NaHSO_4$ and so on. However, these catalysts often posed drawbacks such as corrosion to reactor, acidic waste water, and difficulty in catalyst recovery.[4-6] Therefore, homogeneous acid catalysts were replaced by heterogeneous solid acids to avoid these problems. Heterogeneous solid acids such as ionic liquid,[7] zeolites,[8] heteropoly acids,[9] metal oxide,[10] and pillared clay[11] have been investigated as viable catalysts for esterification reactions. However, these catalysts had their own shortcomings such as the hybrid acid sites and deconcentrated acidity, leading to low selectivity toward target products.

Sulfonic acid bearing ion-exchange resins, such as sulfonated polystyrene-based Amberlyst and perfluorosulfonated resin Nafion have been widely employed as a solid catalyst for numerous acid-catalyzed esterification reactions under mild conditions.[12,13] Though progresses have been made, low acid strength still limits their catalytic performances. Some researchers attempted to solve this issue by introducing Lewis acids into the resins.[14,15] Ming and co-workers reported that Ce⁴⁺ modified cation-exchange resins were effective catalysts for the synthesis of methyl salicylate, and the conversion of salicylic acid reached 93.3%.[16] Bao and co-workers showed that $ZnCl_2$-modified ion exchange resin possessed excellent catalytic activity for the synthesis of bisphenol-A, and selectivity of products was 95.7%.[17] Ying and co-workers reported that $FeCl_3$-modified cation-exchange resin, which was tested in the esterification of ammonium lactate with butanol, achieved a yield of 96%.[18] It has been proved that the coordination of a Lewis acid with a Brønsted

acid can increase its original acidity,[19] but these metal-doped resins show poor thermal stability.[20] The additional of electron-withdrawing groups in sulfonated phenyl groups can increase the thermal stability.[21] Currently, few studies have foucused on cation-exchange resin chlorination and Mg impregnation for catalysis of succinate esters synthesis.

In this study, modified polystyrene sulfonic acid resin was developed and applied as a catalyst to produce dibutyl succinate from succinic acid and n-butanol. Important influential factors (catalyst loading, temperature, time and n-butanol to succinic acid molar ratio) were also optimized for a higher dibutyl succinate yield. Furthermore, theoretical calculations using the density functional theory (DFT) in B3LYP/6-311G(d,p) were conducted to show the optimum monomer structures.

PARTE EXPERIMENTAL

Materials

All chemicals were purchased from the Sinopharm Reagent Co. (Shanghai, China). The strong acid cation exchange resin (D002) was purchased from the Suqing Group in Jiangsu.

Modified catalysts preparation

Macroporous styrene type cation-exchange resin (D002) was firstly modified into hydrogen-form resin following the method in Chinese National Standard (GB/T 5476-1996).[22] 50 g of hydrogen type D002 resin, 100 mL of concentrated HCl, 30 mL of concentrated H_2SO_4 and 2 g of $FeCl_3·6H_2O$ were in sequence added in the reactor equipped with a stirrer, and 50 ml of H_2O_2 solution was slowly added using a dropping funnel. The reaction mix was let to reacte at 90 ºC for 6 hours. The solid products were washed with hydrochloric acid solution (4%wt) and water until the pH reached 7-9. The resulting solid was dried in a vacuum oven at 80ºC for 4 hours to obtain the chlorinated temperature resistant resin, designated as Cl-D002. Then the Cl-D002 was impregnated with $MgSO_4$ solution, mass fraction of solute was 5% of the Cl-D002 after 4 h of impregnation at room
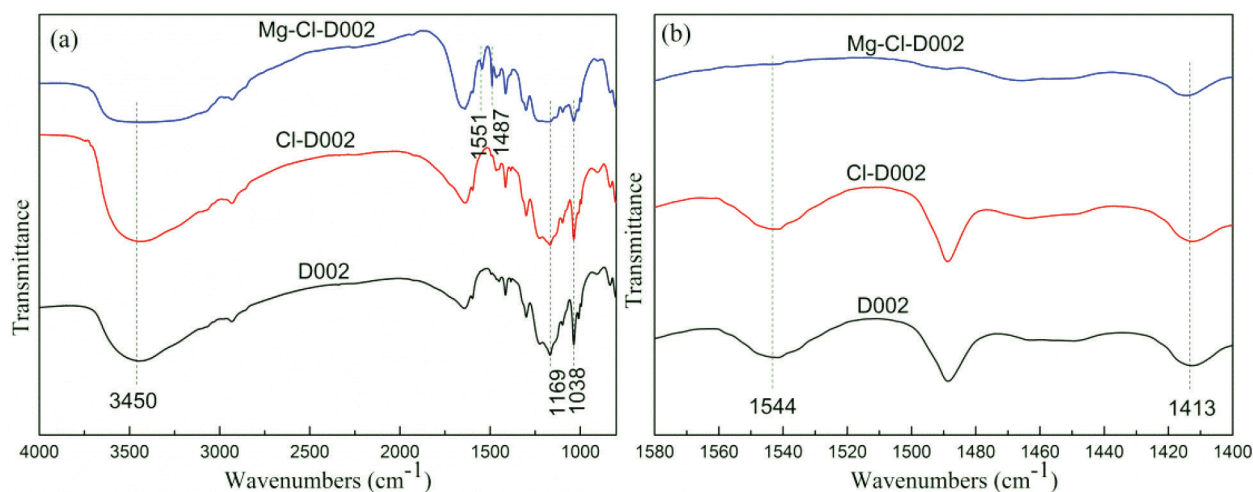
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Figure 1. (a) FT-IR spectra and (b) Py-IR spectra of resins

temperature, water was evaporated using a rotary evaporator. Finally, the products were dried at 80 °C under vacuum, and gave the modified cation-exchange resin designated as Mg-Cl-D002.

Catalyst characterization

X-ray photoelectron spectra were measured with a Kratos Axis HSi photoelectron spectrometer equipped with Al Kα radiation (hv = 1486.6 eV). A power of 250 W and a pass energy of 37.5 eV were used during the experiment. The base pressure of the chamber was higher than 3×10^{-9} Torr. FT-IR spectra were obtained using a Nexus 870 FT-IR spectrometer in the range of 4000 to 600 cm^{-1}. Py-IR spectra were recorded using a Perkin Elmer Spectrum One FT-IR spectrometer. The solid sample was pretreated under vacuum at 423 K for 24 h. About 20 mg of solid sample was pressed into a self-supporting wafer of 13 mm diameter and treated under vacuum at 423 K for 2 h. Then, pyridine was introduced to the sample for 5 min, and desorbed at 150 °C. UV-Vis spectra were obtained using a Lambda 950 UV-Vis spectrometer in the range of 500 to 200 nm.Thermogravimetric analysis curves were collected using a Perkin Elmer Diamond instrument with a heating rate of 10 °C min^{-1} from 30 to 500 °C, and the flow rate of N$_2$ is 10 mL min^{-1}. The chemical composition of the prepared nanostructures was measured by EDS (Energy Dispersive X-ray Spectroscopy).

Esterification of succinic acid with n-butyl alcohol by modified catalysts

In a typical experiment, 0.5 mol of succinic acid, 1.5 mol of n-butanol, a certain amount of cyclohexane for carrying water and 5.1 g of the catalyst were mixed in a three-necked flask. The reaction was carried out with reflux at 120 °C for a required time. The conversion of succinic acid was determined using gas chromatography (GC-2010) equipped with a SE-54 Gas Capillary Column. The PC yield was quantitatively analyzed through an external standard method.

RESULTS AND DISCUSSION

FT-IR and Py-IR analysis

The FT-IR spectra Figure 1(a) of D002, Cl-D002 and MgSO$_4$-Cl-D002 exhibited a broad band in the region 3450 cm^{-1}, which was a attributed to the -OH stretching vibration. The D002 and Cl-D002 catalysts exhibit two bands at 1038 cm^{-1} and

1169 cm^{-1} which were attributed to symmetric and asymmetric stretching vibration of SO$_3^-$, respectively.[23,24] The absorption peak of MgSO$_4$-Cl-D002 appeared at 1038 cm^{-1}, which were ascribed to the symmetric stretching vibration of SO$_3^-$. The absorption bands of MgSO$_4$-Cl-D002 appeared at 1487 cm^{-1} and 1551 cm^{-1}, which were ascribed to stretching modes of benzene ring.[25] Meanwhile, Figure 1(b) showed the Py-IR spectra of D002, Cl-D002, and MgSO$_4$-Cl-D002 catalysts. D002 and Cl-D002 catalysts exhibited bands at 1544 cm^{-1} and 1413 cm^{-1} that was assigned to pyridine bound to Brönsted and Lewis acidic sites, respectively.[26] The absorption peak of MgSO$_4$-Cl-D002 at 1413 cm^{-1} was assigned to Lewis acid site.

UV-Vis analysis

Figure 2 presented the UV spectra of the samples, showing that D002, Cl-D002 and Mg-Cl-D002 had characteristic absorption peaks of benzene ring ranging from 200 to 300 nm, which were attributed to the π-π* transition of conjugate backbone.[27] Compared with D002, the absorption peak of Cl-D002 and Mg-Cl-D002 shifted to 272 nm. This may be caused by the effect of electron withdrawing (Cl) and electron-donating group (Mg) in the -SO$_3$H, which impacted on the benzene ring absorption. The D002, Cl-D002 and Mg-Cl-D002 were characterized by EDS to determine the elemental composition (Figure 1S). In the EDS spectrum, Mg, and Cl peaks were observed. The result agreed well with the UV-Vis analysis.[28]
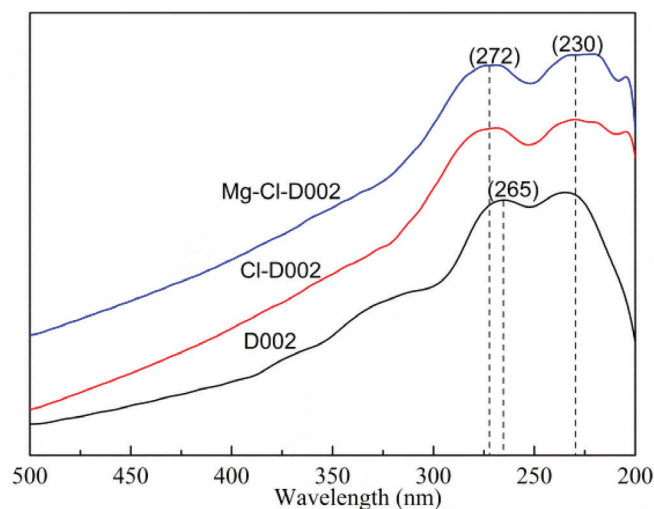

Figure 2. UV-Vis spectra of resins

XPS analysis

X-ray photoelectron spectroscopy (XPS) was utilized to identify the Mg and Cl states on the modified resin. Figure 3(a) presents XPS spectra for the D002, Cl-D002 and Mg-Cl-D002. Figure 3(b) showed the S 2p spectra of Cl-D002 at 168.16 eV and Mg-Cl-D002 at 169.58 eV, which suggested the presence of S^{6+}.[29] The Cl 2p XPS spectra (Figure 3c, 3d) of Cl-D002 and MgSO₄-Cl-D002 show the presence of characteristics peaks at around 200.5 eV and 201.4 eV. Figure 3(e) showed the Mg 2p spectra of Mg-Cl-D002 at 51.6 eV, indicating the Mg coordination to the polystyrene sulfonic acid ions.[30] The optimum monomer structures (Figure 2S) of D002, Cl-D002 and MgSO₄-Cl-D002 have been studied using density functional theory methods at the B3LYP/6-311G(d,p) computational level (Table 1S), which agreein general with the structure reported in literature.[31,32] The total energy of the Cl-D002 and MgSO₄-Cl-D002 were lower than observed for the D002, so the optimum monomer structuresof Cl-D002 and MgSO₄-Cl-D002 may exist.[28]

Thermal analysis

Figure 4 displayed the TGA curves of all samples. Two kinds of weight loss were observed (Figure 4a, 4b, 4c curves TG and DSC). The first peak (78 °C, 83 °C, and 85 °C) was due to the removal
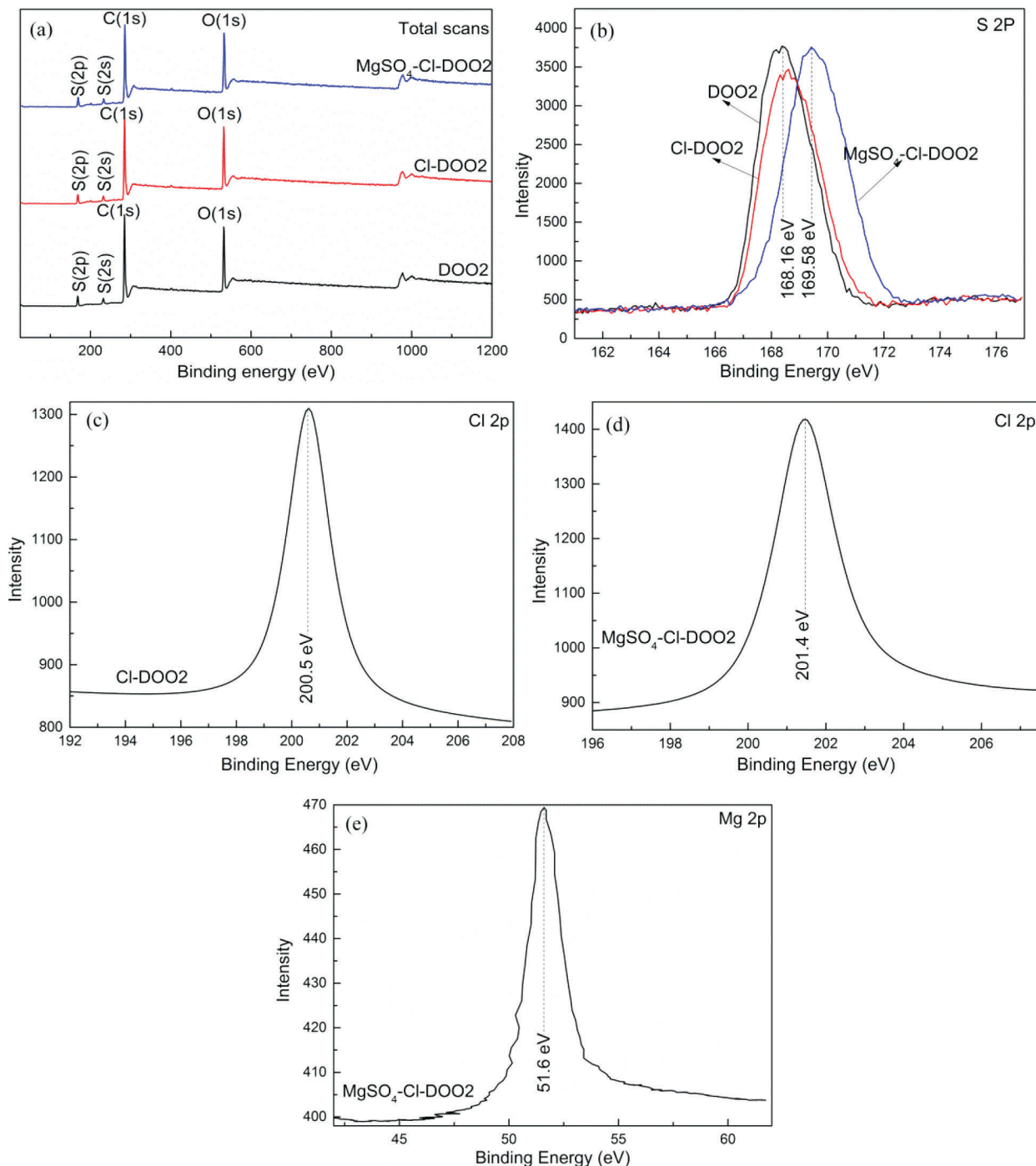

Figure 3. *(a) The survey scan of resins by XPS, (b) S 2p XPS spectra of resins, (c) Cl 2p XPS spectra of Cl-D002, (d) Cl 2p XPS spectra of Mg-Cl-D002, and (e) Mg 2p XPS spectra of Mg-Cl-D002*

of crystal water, and the second (293 °C, 298 °C, and 485 °C) corresponded to the removal of the SO_3^- group on the polystyrene,[33] which is protected by Mg coordination.[31] Accordingly, the thermal stability of the Mg-Cl-D002 catalyst was significantly improved.

Catalytic performance

The effects of the different catalyst of D002, Cl-D002 and Mg-Cl-D002 on the esterification reaction were investigated. The results are shown in Table 1. The reaction conditions were the following: $n_{n-butanol}$:$n_{succinic\ acid}$ was 3, the amount of resin catalyst was 3%, reaction temperature was 120 °C and the reaction time was 60 min. The yield of dibutyl succinate for $MgSO_4$-Cl-D002 reached to 91.6%, which increased by 42.8% compared with D002. The reason may be that introduction of Lewis acids enhanced the acid content of $MgSO_4$-Cl-D002.

The activities $MgSO_4$-Cl-D002 under different reaction conditions were investigated by varying the amount of $MgSO_4$-Cl-D002, PG/urea molar ratio, reaction time and temperature. The influence of the amount of $MgSO_4$-Cl-D002 was presented in Figure 5(a). The yield of dibutyl succinate increased as the function of the amount of $MgSO_4$-Cl-D002, and the optimal amount of $MgSO_4$-Cl-D002 was 3%, achieving the highest dibutyl succinate yield.

The effect of reaction temperature was investigated in the range from 90 to 130 °C (Figure 5(b)). The temperature increased from 90 to 120 °C resulted in the continuous increase in the activity, with the dibutyl succinate yield changing from 66.5% to 91.6%. However, the higher temperature of 130 °C did not increase the yield of dibutyl succinate significantly. Thus the optional reaction temperature was 120 °C.

The influence of reaction time was presented in Figure 5(c). The yield of dibutyl succinate increased with the reaction time, offering

the highest yield at 60 min. Further prolonging the reaction time did not improve the dibutyl succinate yield significantly, suggesting that the reaction reached to equilibrium at 60 min.

The optimal n-butanol/succinic acid molar ratio (Figure 5(d)) was 3 to generate the highest yield of dibutyl succinate.

The yield of dibutyl succinate from esterification using modified resin was higher than that of unmodified resin. The higher catalytic efficiency of the modified resin may be explained by the generation of a strong Lewis acid centre.[34] The proposed mechanism of catalysed esterification is shown in Scheme 1. Firstly, water molecule in the reaction system transformed the Lewis acid centres structure of modified resin into Bronsted acid centres. Secondly, the protonation of the carbonyl moiety in the succinic acid activates the carbonyl carbon atom for nucleophilic attack of n-butanol followed by the desorption of the succinic acid monobutyl ester.[19] After a new esterification process, the generated dibutyl succinate separated from the surface active sites of the catalyst.

Table 1. The effects of different resin catalysts on the esterification

Catalyst	The Yield of dibutyl succinate%
D002	48.8
Cl-D002	52.6
Mg-Cl-D002	91.6

Reaction conditions: $n_{n-butanol}$:$n_{succinic\ acid}$ = 3:1, the amount of resin catalyst was 3%, reaction temperature was 120 °C, reaction time was 60 min.

CONCLUSIONS

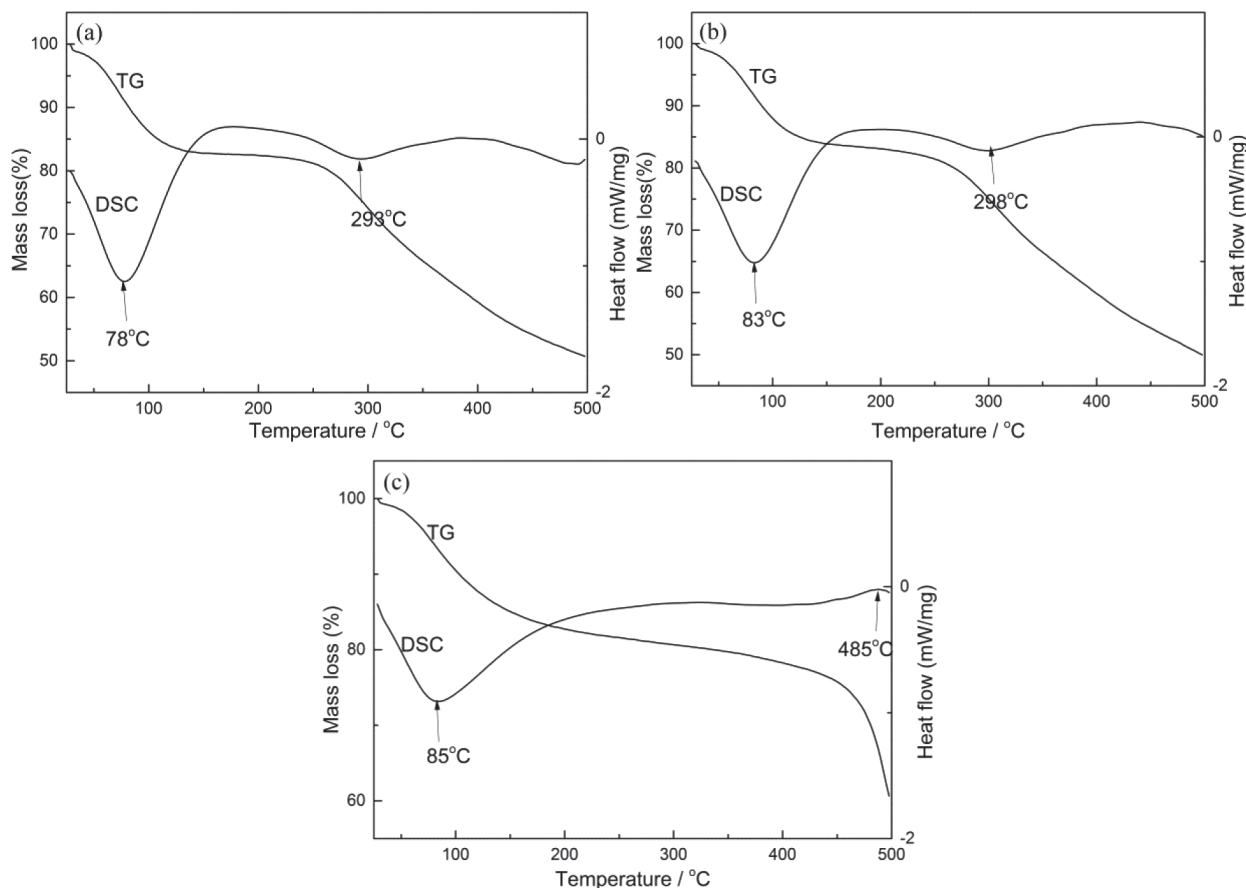Mg-Cl-D002 of the coordination polymers were formed by polystyrene sulfonic acid ions and metal moieties of Mg, which

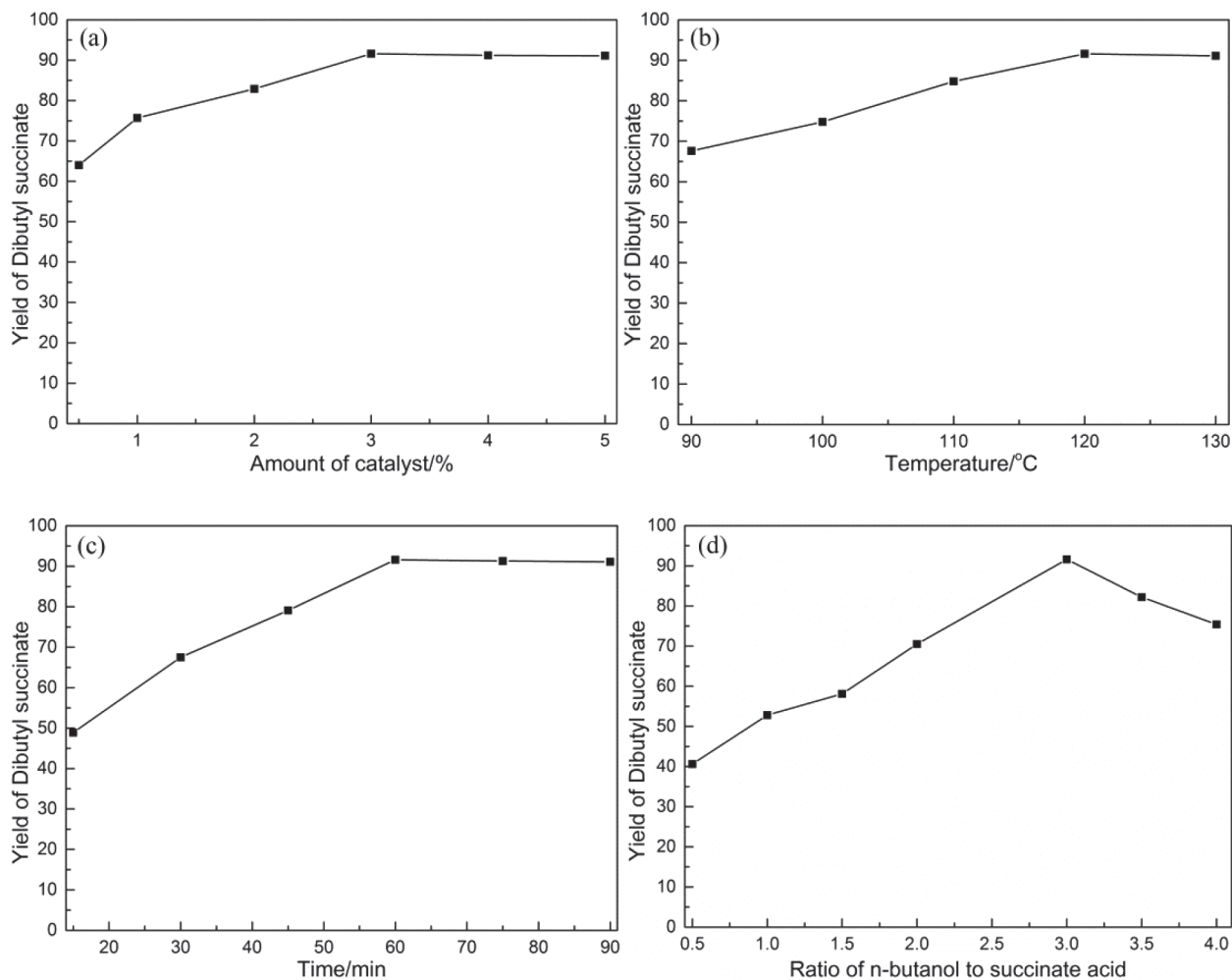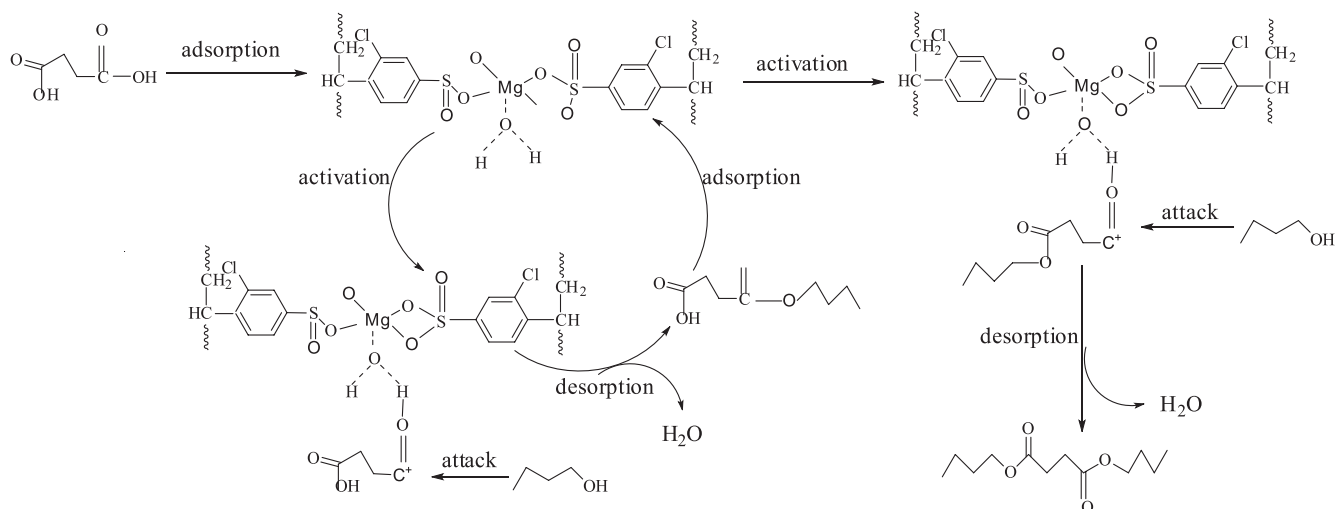**Figure 4.** *(a) thermal analyses of D002 resin, (b) Cl-D002, and (c) Mg-Cl-D002*

Figure 5. *(a) Influence of amount of MgSO₄-Cl-D002, (b) reaction temperature, (c) reaction time, and (d) $n_{n\text{-}butanol}$:$n_{succinic}$ acid ratio. Other associated reaction conditions were the optimized conditions when one parameter was changed*

Scheme 1. *Reaction mechanism*

showed significantly better thermal stability and formed stable active Lewis acid sites. Mg-Cl-D002 of modified resin was used as efficient catalysts for the esterification of succinic acid and n-butanol, compared to the unmodified resin. The yield of dibutyl succinate reached 91.6% under the optimized reaction conditions: the temperature of 120 °C, the time of 60 min, $n_{n\text{-}butanol}$/$n_{succinic\ acid}$ of 3, and the mass fraction of MgSO₄-Cl-D002 of 3%.

SUPPLEMENTARY MATERIAL

Supplementary information on the the elemental composition and optimum monomer structures can be found at http://quimicanova. sbq.org.br in PDF format, with free access.

ACKNOWLEDGMENTS

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