

Evaluation of Strongly Acidic Ion-Exchange Catalysts and the Desulfonation Study in the Isobutylene Dimerization Reaction

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ABSTRACT: Three commercial ion-exchange resin based catalysts were compared under different temperature and liquid-volume hourly space velocity (LHSV) in the isobutene (IB, C₄) dimerization reaction using a plug flow reactor in the absence of any selectivity enhancing component. High IB conversion for all catalysts was obtained at or higher than 50°C. But, diisobutene (DIB, C₈) selectivity decreased with the increase of temperature. High C₈ selectivity was observed with LHSV higher than 1.5 at 50°C. The best catalytic performance of the three resins did not show obvious differences. The effect of the selectivity enhancers on the stability of the resins was also studied. Desulfonation was observed in the C₄ dimerization reaction when water or the commonly used enhancer *tert*-butyl alcohol (TBA) was added to the feed. The deactivation of catalyst resulted in decrease of both IB conversion and C₈ selectivity. Fourier Transform Infrared spectroscopy showed that desulfonation happened in both para and ortho positions of the sulfonated benzene rings. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

As macroporous polystyrene (PS) resin was developed in 1962,¹ cationic exchange resins as solid acid catalysts have been increasingly used in organic synthesis such as isopropyl alcohol (IPA), methyl isobutyl ketone (MIBK), and the well-known methyl tertiary-butyl ether (MTBE).² As a kind of gasoline blend, MTBE has been once the fastest growing chemical industry in the world during the past decades. However, due to its solubility in underground water, it has been causing increasingly environmental concern and a ban on MTBE took effect from January 2004 in California, leading to the current total phase out of MTBE in USA. As an alternative usage of isobutene (IB) in refineries, it would include the conversion of IB to isooctene first, followed by hydrogenation to isooctane, which can be directly blended into the gasoline pool. Isooctane has numerous advantages: high octane number (with research octane number (RON) and motor octane number (MON) of 100³), zero content of aromatics and sulfur, and low vapor pressure.

The oligomerization of IB over strongly acidic resin catalysts has been studied by Haag⁴ nearly 40 years ago, and it has also

been studied as a side reaction to the MTBE reaction.^{5–7} There are few articles issued on the subject until recent years. The effect of some parameters such as catalyst amount, temperature, and space velocity on the dimerization reaction has been studied in some articles.^{8–13} In general, high temperature resulted in a high conversion but low C₈ selectivity. However, the influence of catalyst amount and space velocity on the reaction is not the same in different testing systems. Another important issue affecting the reaction is the selectivity enhancer. *Tert*-butyl alcohol (TBA) is the most widely used enhancer because the selectivity will be increased without ether formation.³ The kinetics of IB dimerization with water and TBA as selectivity enhancers has also been investigated, and the results showed that diisobutenes (DIBs) formed using two active sites and triisobutenes (TRIBs) formed via DIBs and IBs using three active sites of the resins.^{9,12}

In one study,⁹ a small deactivation of the catalyst was found at the end of a 80°C–100°C–60°C–80°C cycle run with a TBA content of 0.8 mol %. Deactivation of catalysts is also very common in industry production. There are many mechanisms that

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can cause catalyst deactivation including pore blockage due to the formation of polymers and/or desulfonation caused by high temperature in the presence of water or other organic media.^{14–16} Of course, the presence of metal cations in feed will also cause catalyst deactivation.^{17,18}

In our early research, we found that trace water would cause the desulfonation of the resins at high temperature as well as in a plug flow reactor.^{19,20} More important, the desulfonation degree and deactivation performance were quite different for these testing samples. We also found lack of reports in literatures on desulfonation of strongly acidic catalyst in relation to the most-used selectivity enhancer TBA in the IB dimerization reaction, especially the study about the widely used commercial resins. The desulfonation caused by these selectivity enhancers is always ignored but shortens the catalyst life. It is important to show the effect of TBA on the desulfonation of the commercial resins in a plug flow reactor. So, we did this research in this work to give some advises to the plants. The IB dimerization catalyzed by some commercial macroporous, cationic exchange resin catalysts was first evaluated under different conditions without any selectivity enhancers added and then compared the results with the corresponding conditions, where the selectivity enhancer was online injected in a continual test to show its relationship to desulfonation. The temperature range was chosen as 30°C–100°C to get closer to practice.

EXPERIMENT

Materials

The synthetic C4 feed was made of IB (99.99%) and isopentane (IP, 99.3%) obtained from DaLian Airichem Specially Gases & Chemical Co, Dalian, China. The other chemicals were all of analytical grade. Cationic exchange resins were obtained from ion exchange vendors in China. The physical properties of these resins examined in this work are listed in Table I. All the resins used here were washed free from acid by deionized water and then dried at 60°C for 12 h and then at 105°C under vacuum over night before being loaded into the reactor.

Analysis

Feed and product stream analysis was performed by using gas chromatography (GC) techniques (Fuli 9750) fitted with a flame ionization detector (FID). The GC was equipped with an AT. SE64 capillary column of length 30 m, film thickness 0.33 μm , and diameter 0.32 mm. The column temperature was at 75°C. Nitrogen was used as the carrier gas at a flow rate of 20 mL min^{-1} . IP was used as a solvent and interior label here.

Procedure

The experimental setup for this study consisted of a tubular reactor with the length 210 mm and internal diameter 8 mm. Two temperature probes were placed on the skin of the reactor. During the experimental run, the position of the temperature probes was changed to obtain the temperature profile over the whole catalyst bed. The estimated uncertainty for temperature measurements is $\pm 2^\circ\text{C}$. The dry resins were not able to be swollen by IP. In other words, the volume of dry resins in the tubular reactor was constant, which made the liquid-volume

Table I. Physical Parameters of the Macroporous Resins Used in this Work

Resin	PL1	PL5	R6
Matrix	Styrene-divinylbenzene copolymer		
Functional group	–SO ₃ H		
Surface area (m ² /g)	26	24	33
Average pore diameter (Å)	284	540	240
Acid capacity (meq/g)	5.13	5.17	5.60

hourly space velocity (LHSV) to be calculated exactly. The volume of the resin in each experiment was 10 mL.

At the beginning of each experiment, the mixed flow containing IB and IP through a bypath pipe was analyzed by GC. When the flow rate and pressure were stabilized and the feed ratio has been accurately controlled, the flow was fed to the reactor and the side road was closed. The isothermal condition of the reactor temperature was maintained constant by a jacket through a constant temperature circuit. The reaction at each temperature studied was continued until a steady state was reached. The product composition was monitored with GC measurement in 1 h intervals (Figure 1).

For desulfonation study, the reactor was first running at 50°C for 12 h, then the temperature was elevated to 100°C. Twelve hours later, 1 mL water or TBA was injected into the reactor, and then the temperature of the reactor was decreased to 50°C slowly. The results at 50°C are compared before and after temperature ramping with 100°C. A control test was conducted on PL1 without the injection of water.

Calculations for Conversion and Selectivity

The equation used for the IB conversion and C8 selectivity:

$$\text{conversion}(\%) = (n_{\text{IB-in}} - n_{\text{IB-out}}) / n_{\text{IB-in}} \times 100\% \quad (1)$$

$$\text{C8 selectivity}(\%) = 2 \times n_{\text{C8}} / (n_{\text{IB-in}} - n_{\text{IB-out}}) \times 100\% \quad (2)$$

where $n_{\text{IB-in}}$, $n_{\text{IB-out}}$, and n_{C8} are the molar flow (mol min^{-1}) of the injected IB, IB in the products, and C8 in the products, respectively.

Dry Weight Acid Capacity Measurement

The resins taken out from the reactor after the C4 dimerization reaction and the original resins were first washed by ethanol and then washed by HCl (5%) and deionized water in turn. After dried at 105°C over night, the resins were cooled in a drier (Hangzhou Qianjiang Instrument Co., China). A total of 1.0 g dry resin was precisely weighed. The dry weight acid capacity of the resins was measured by conventional titrimetric technique. All the samples were washed by HCl (5%) and deionized water in turn. Then, the samples in acid form were immersed into NaCl solution (5%) overnight at room temperature. The protons (H^+) released in the solution were titrated with standardized 1M NaOH solution using phenolphthalein as the indicator. The acid capacity (meq g^{-1}) of the sample resins were calculated on the volume of NaOH consumed in the titration.

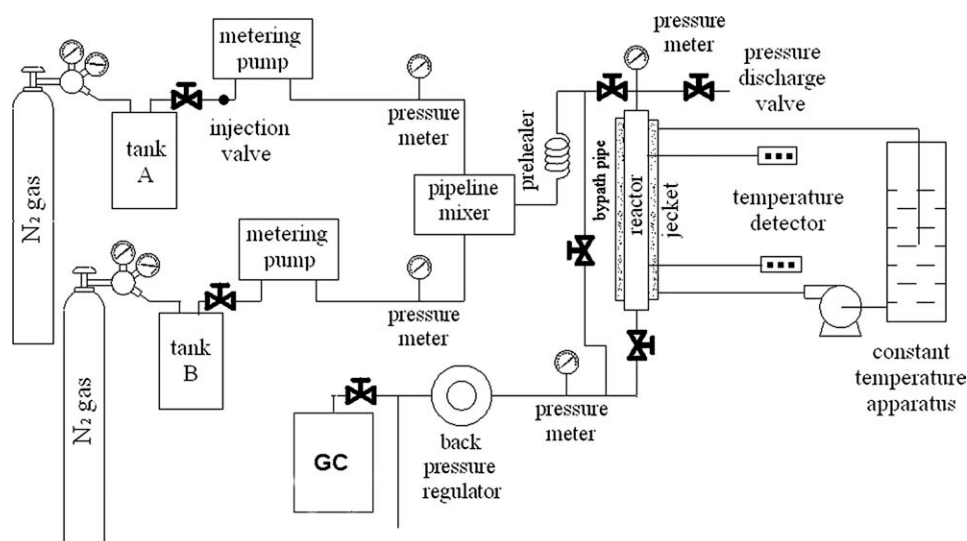


Figure 1. Scheme of the flow reactor.

Fourier Transform Infrared Spectroscopy

The spectroscopy of the resins was investigated by a Bruker Vector 22 Fourier Transform Infrared (FTIR) instrument. The resins were treated in the same way which was described in the previous section. A total of 2.00 mg samples were mixed with 100 mg of potassium bromide powder in liquid nitrogen and then pressed into pellets. The pellets were thoroughly dried under vacuum at 105°C overnight before the measurements. All the spectra represented an average of 32 scans taken in the wavenumber range of 4000–400 cm^{-1} .

RESULTS AND DISCUSSION

C4 Dimerization over PL1, PL5, and R6 in Plug Flow Reactor without Selectivity Enhancers

The catalyst testing for PL1, PL5, and R6 in a flow reactor was studied with IB content 17% and column pressure 1.2 MPa. The effects of LHSV and column temperature on both the conversion and C8 selectivity were investigated.

Effect of Temperature. Figure 2 presents the IB dimerization results over PL1, PL5, and R6 under different temperatures. In general, high bed temperature causes high conversion and low C8 selectivity, as reported in early research.¹⁰ Though IB dimerization is a highly exothermic reaction ($\Delta H_r = -82.9 \text{ kJ mol}^{-1}$ or $\Delta H_r = -107.2 \text{ kJ mol}^{-1}$ ¹³), some energy is needed to overcome the reaction activation barrier (activation energy was about 30 kJ mol^{-1} ⁹). The reaction becomes easier if temperature rises, which results in an increasing conversion. But, the temperature rise may make heat transfer of reactor difficult, which lowers the controllability of the dimerization reactor and forms some high molecular weight molecules like trimers and tetramers.¹² So for all the three resins, C8 selectivity decreases with the increase of temperature. It is also found that when the temperature is below 50°C, the performance of resins is directly related to their acid capacities: high acid capacity resulted in high conversion and low C8 selectivity. High acid capacity might lead a high dense of catalytic center, which resulted a high conversion. However, the dimerization of IB was thought

to be second order against acid capacity.¹⁰ As a result, C8 selectivity decreases with acid capacity at the same temperature.

Effect of LHSV. LHSV is another important factor for C4 dimerization in industry, but few works had been reported about the relationship between space velocity and C4 dimer or trimer in a flow reactor. One research showed that the conversion and trimers selectivity decreased with weight-hourly space velocity (WHSV), while the dimers selectivity increased slightly.¹¹ But, the situation was a little different in our works (Figure 3). When the LHSV is increased from 0.75 to 1.5, the conversion decreases obviously, while C8 selectivity increases for PL1 and PL5. Lower LHSV makes the heat of reaction easier to accumulate, which results in a higher conversion and lower C8 selectivity, as discussed above. When the LHSV is increased from 1.5 to 3.0, the conversion and C8 selectivity of PL1 and PL5 are almost the same. The heat transfer of reactor in this LHSV range may be quite good so a balance among the heat of C4 dimerization reaction, heat transfer, and reaction active

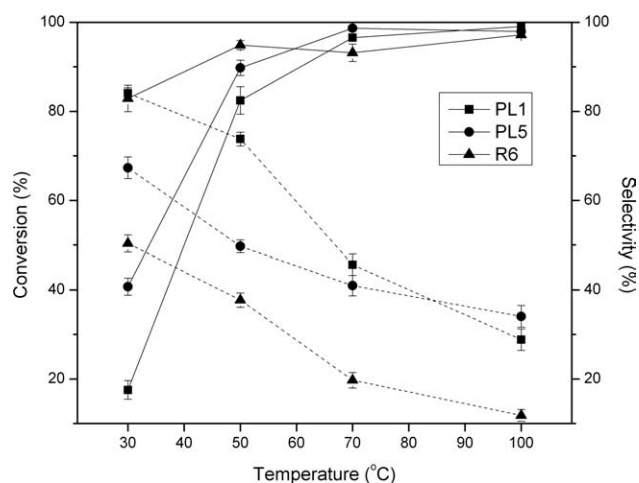


Figure 2. Conversion (solid) and C8 selectivity (dash) with the IB content of 17 wt %, LHSV of 1.5 at different bed temperatures.

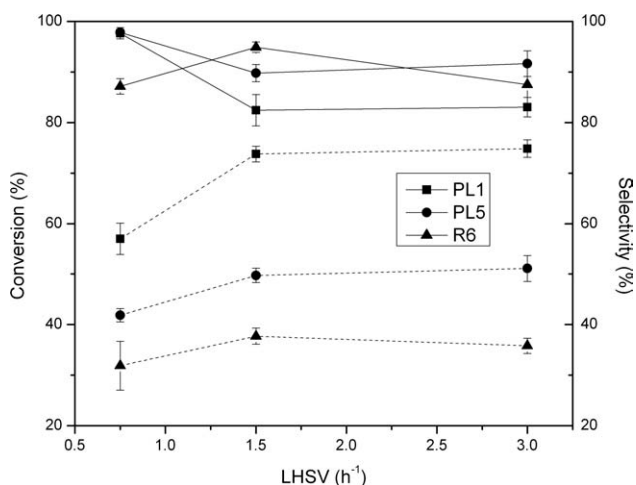


Figure 3. Conversion (solid) and C8 selectivity (dash) with the IB content of 17 wt % under different LHSV at 50°C.

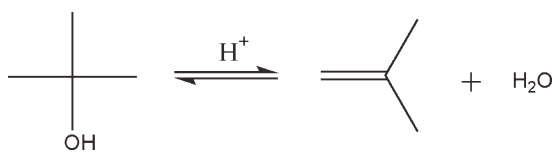
energy occurs. So, the conversion and C8 selectivity do not change with the LHSV. For R6, the situation is different. When LHSV is increased from 0.75 to 1.5, the conversion and C8 selectivity both increase. When LHSV is increased from 1.5 to 3.0, the conversion decreases, while the C8 selectivity changes little. The result may be also related to the balance among the reaction heat, heat transfer, and reaction activation energy. Only the proper LHSV will result in a high conversion and C8 selectivity.

The Evaluation of Desulfonation During C4 Dimerization with a Flow Reactor

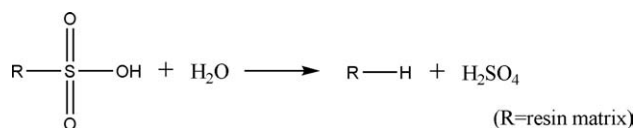
Different polar components such as methanol,^{21,22} MTBE,^{21,22} TBA,^{3,9} and water¹² have been studied as selectivity enhancers of C4 dimerization reaction. Basically, these enhancers contain commonly known as hydrophilic groups such as OH group and/or oxygen linkage so that they can interact with the functional group of sulfonic acid in the strongly acid cationic catalysts through solvation mechanism causing a lower activity of catalysts and a higher selectivity.

In practice, TBA is the commonly selected enhancer. It is known, at a given temperature, TBA is in equilibrium with water and isobutylene (Scheme 1). Water could be generated from the reverse reaction of TBA at high temperatures. It is also known that desulfonation reaction is a hydrolysis reaction (Scheme 2).¹⁶ Therefore, TBA can be a source of desulfonation in the C4 dimerization process.

To observe the desulfonation reaction in the C4 dimerization process in a reasonable timeframe and to be more close to actual production, in which lots of solvent and/or TBA would be added if the reactor temperature was too high, we have



Scheme 1. The reversible reaction of TBA and IB.



Scheme 2. The hydrolysis reaction of strong acid ion-exchange resins.

designed the experiments in one case where water was directly injected at the end of high temperature step (100°C), and then, the temperature was ramped to low (50°C). In another case, water was replaced with TBA. In both cases, desulfonation was observed. Water had a greater effect on desulfonation than TBA. This further provides evidence that water (injected or come from reversible reaction of TBA) is the source causing desulfonation, as shown in our early research.^{19,20} The desulfonation is proved not only by the measured loss of conversion but also by the loss of dry weight capacity.

Under the experiment condition (IB 17%, LHSV 1.5, pressure 1.2 MPa), all three tested resins (PL1, PL5, and R6) perform well (see Conclusion section, Figures 2 and 3). We chose this condition for the study. The temperature range was chosen as 50°C–100°C. The results are shown in Figure 4 and summarized in Table II.

In Figure 4, the results for PL1 are summarized including the performance of CT251 at 50°C and 100°C for the first 48 h in the absence of any enhancers and presence of enhancers shown at 50 h run. In the continuous run, it is clear, without the exist of enhancer, the conversion at 50°C was recorded at average 83% during the first 10 h as well as 25–35 h. When the temperature increased to 100°C at the 20 h and 40 h run, the conversion increased. During the entire cycle (50°C–100°C–50°C–100°C), the conversion and C8 selectivity were repeatable in a cycle at a given temperature (50°C or 100°C). The conversion and C8 selectivity were only a function of temperature. On the other hand, the acid capacity of PL1 was almost the same. The change of temperature will not cause the desulfonation when no enhancers are present.

However, when a small amount of water (1 mL) was injected at the moment when the temperature was reduced from 100°C to 50°C, significant loss of conversion at 50°C was observed (time period of 48–59 h). A temporary loss of catalyst activity by water quenching is observed at the first 3 h, and then, the catalyst activity recovered partly. Water in the reaction mixture cannot be detected by FID, so it was confirmed by the TBA peak in the GC spectra.¹² As shown in Figure 5, the peak of TBA almost disappeared after 3 h. The partial recovering of catalyst activity may be due to the water pushed out of the system. But, the conversion was still lower than before. At the end of the run, the dry weight capacity was analyzed. The dry weight acid capacity decreased by ~ 14%. For PL5 and R6, after injecting some water, the conversion and acid capacity also decreased. The loss of conversion must be due to desulfonation, which was caused by H₂O. Due to the sudden exchange of solvent, broken beads were found when the test was finished for all samples. For R6, the broken beads even blocked the reactor. So, there is no result on the conversion of R6 after injected water.

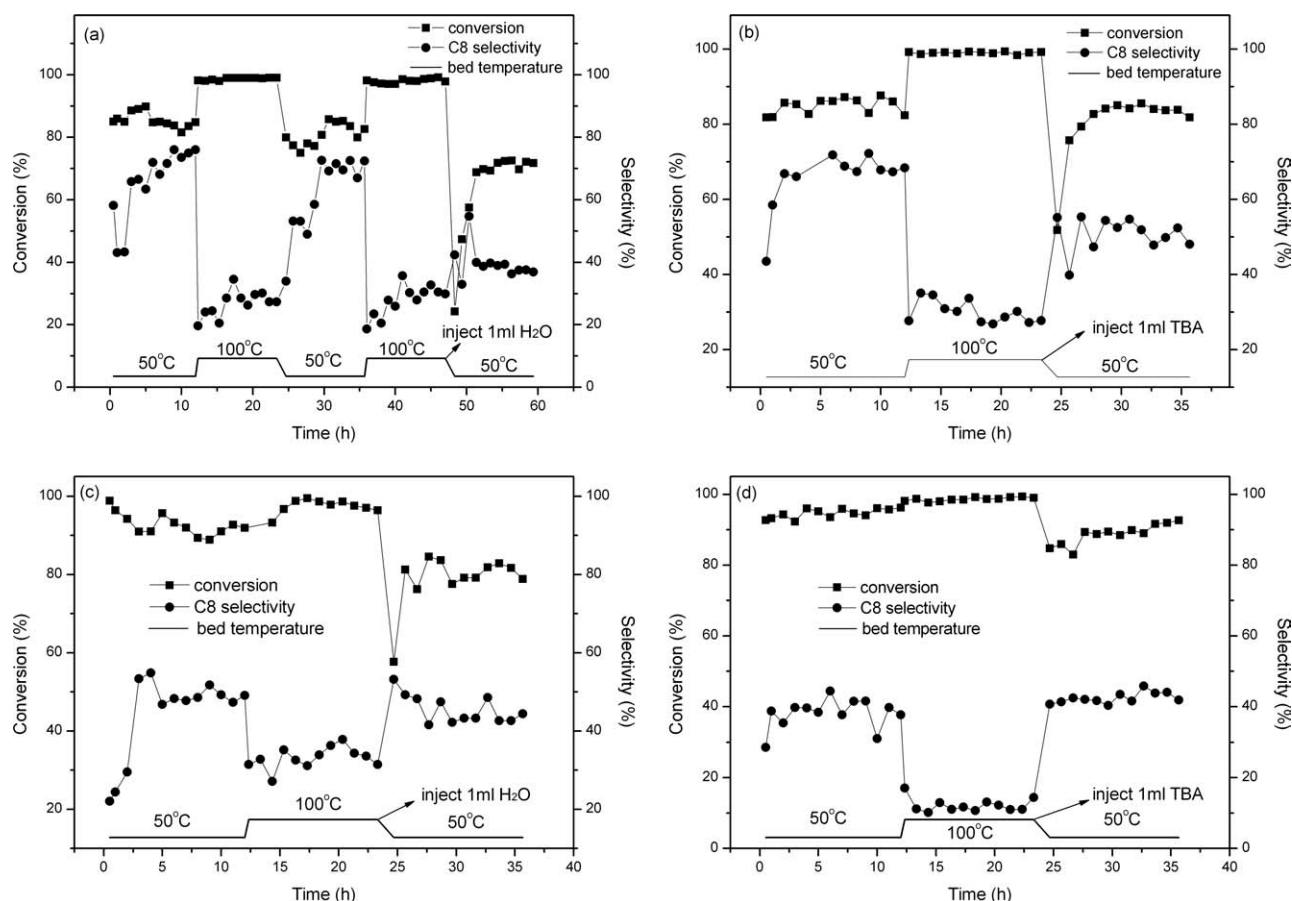


Figure 4. Conversion and C8 selectivity of the resins during the desulfonation test (IB content 17 wt %, LHSV 1.5): PL1 injected with water (a), TBA (b), PL5 injected with water (c), and R6 injected with TBA (d).

When TBA was injected instead of water, the average conversion and acid capacity of PL1 and R6 decreased in a less degree. When TBA was injected at high temperature, TBA could decompose to IB and water (Scheme 1). The water generated *in situ* is responsible for the desulfonation. The C8 selectivity also decreased when H₂O or TBA was injected except for R6. This may be caused by deactivation of the catalyst, like earlier results.¹⁰ For R6, even desulfonation occurred; its acid capacity

is still as high as 5.34 meq g⁻¹. The slight decrease of acid capacity is helpful to improve the controllability of the catalyst, as discussed above.

Detection of the Desulfonation of the Resins by FTIR

FTIR is used here to confirm the chemical structure changes of the resins under different isotherm treatments. The FTIR absorption spectra of PL1, PL5, and R6 are shown in Figure 6.

Table II. The Comparison on Conversion, C8 Selectivity, and Acid Capacity of PL1, PL5, and R6 at 50°C Before and After Injecting Water or TBA

Resins (injected)		PL1 (none)	PL1 (H ₂ O)	PL1 (TBA)	PL5 (H ₂ O)	R6 (H ₂ O)	R6 (TBA)
Average conversion (%) ^a	Before injected	83.99	83.24	85.58	91.27	94.20	95.20
	After injected	83.24 ^b	71.27	84.05	80.16	Null	90.40
	Changed (%)	0.89	14.38	1.79	12.17	Null	5.04
Average C8 selectivity (%)	Before injected	73.16	73.16	69.11	48.85	38.00	39.13
	After injected	70.70	38.05	51.04	43.83	Null	43.02
	Changed (%)	3.36	48.00	26.15	10.28	Null	-9.91
Acid capacity (meq/g)	Original resin	5.13	5.13	5.13	5.17	5.60	5.60
	After test	5.08	4.43	4.96	4.42	5.10	5.34
	Changed (%)	0.97	13.65	3.31	14.51	8.93	4.64

^aThe average of last 7 h for each step (temperature ramp was not included), ^bNo enhancer is injected, it is only the average of last 7 h the temperature decreased from 100°C to 50°C.

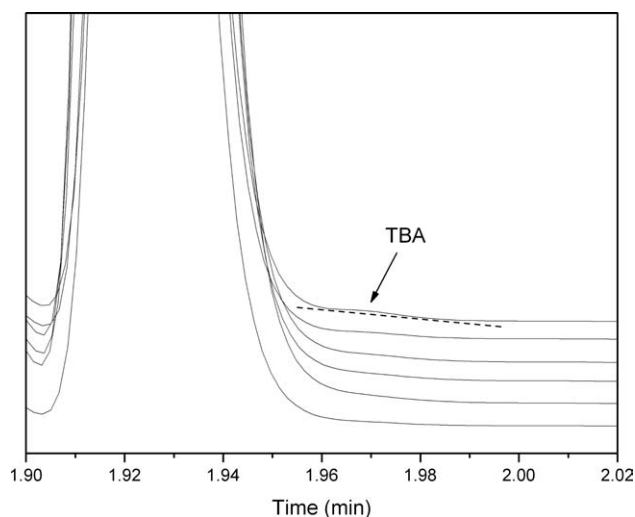


Figure 5. GC spectrum of PL1 after injecting H₂O when temperature was lowered to 50°C, from top to bottom: 0, 1, 2, 3, 6, and 11 h, respectively.

The antisymmetric and symmetric vibration adsorption peaks of the S=O group could be assigned to the peaks at around 1181 cm⁻¹ and 1037 cm⁻¹, respectively, which was used to measure the sulfonation degree.^{23–27} The peaks at 837 cm⁻¹ and 777 cm⁻¹ correspond to the C–H out-of-plane vibration for para-substitution and ortho-substitution of the benzene ring.^{27–29} The peak at 1600 cm⁻¹, which corresponds to the C–C in-plane stretching of the styrene ring, is insensitive to the chemical structure changes associated with the sulfonation along the chain.³⁰ So, the peak is used as an internal standard to normalize the spectra to eliminate the effect of variations in sample thicknesses.²² The result shows that relative intensities of the four peaks decrease in different degree. These give further evidence for the loss of S=O group of the resins after H₂O/TBA being injected. These also show that the desulfonation occurs at both para and ortho position of the benzene ring.

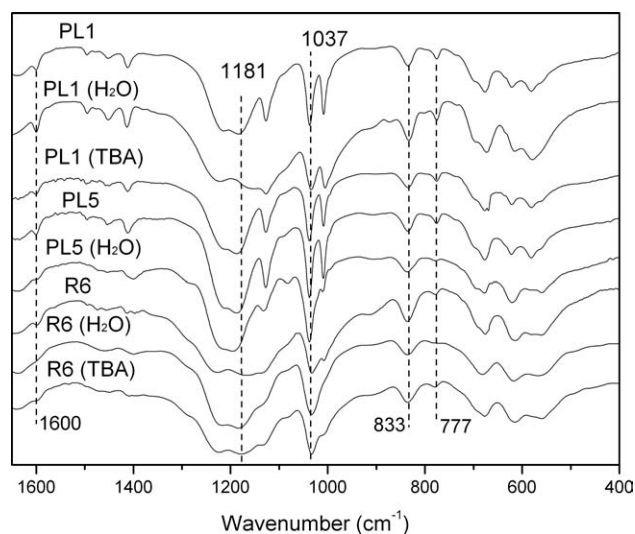


Figure 6. FTIR absorption spectra of PL1, PL5, and R6 before and after desulfonation test.

CONCLUSION

The influence of bed temperature and LHSV on the conversion and selectivity for commercial ion-exchange resin catalysis PL1, PL5, and R6 in plug flow reactor is investigated under different conditions. High bed temperature results in high conversion and low C8 selectivity. The increase of LHSV also improves the C8 selectivity. Under our laboratory condition, no significant performance difference was found among the three catalysts.

Water and TBA are the key factor for desulfonation during the C4 dimerization process. The average conversion and acid capacity decrease obviously after injecting some water. Obviously, for TBA, the average conversion and acid capacity also decrease to a less degree than water due to the water produced by reversible reaction between TBA and IB. Desulfonation also caused the deactivation of the catalyst, which resulted in the decrease of conversion and C8 selectivity both. By normalizing the intensities of the special peaks in FTIR spectra, desulfonation of the resins is confirmed, and it occurs in both para and ortho position of the sulfonated benzene ring.

For plants using TBA as selectivity enhancer, overheat must be avoided because more water would be generated at high temperature from decomposition reaction of TBA (Scheme 1), which may cause the desulfonation. Based on our results, we suggest the working temperature be better not higher than 50°C to avoid the desulfonation. Another way is to adjust the chemical structure of the resins. Strong electronegative group can be induced into the benzene ring to improve the thermostability. Our recent research also showed that the way was available to develop more thermostable resins.²⁰ Recent research also showed that cation-exchange composite materials like poly(styrene-codivinybenzene)/fiberglass exhibited excellent thermostability with a maximum decomposition rate temperature of 377.3°C,³¹ which is much higher than the sulfonated PS resins (about 310°C¹⁹). Its maximum acid capacity is 4 meq g⁻¹, which is higher than our chlorinated resin.^{20,31} This composite showed greatly potential as a thermostable catalyst.

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