

Preparation and Characterization of Macroporous Phenol-Furfural Sulfonic Acid Resin Catalyst

ZHIXING SU, YUNTAO LI, YUANZHAO MIAO, TIEJUN WANG, QIAOSHENG PU

Department of Chemistry, Lanzhou University, Lanzhou 730000, China

Received 25 October 1999; accepted 14 July 2000

ABSTRACT: The macroporous phenol-furfural sulfonic acid resin catalyst (PFuSR) was prepared. The resin was characterized by chemical analysis, thermal analysis, scanning electron microscopy, Fourier transform infrared spectroscopy, and reactions of esterification. There exist in PFuSR different kinds of acidic groups such as —OH, —COOH, and —SO₃H. The catalytic relative activity of PFuSR in the reaction of acetic acid and *n*-butanol is 104 times that of macroporous polystyrene sulfonic acid resin D72. Thermal analysis showed that PFuSR did not begin to desulfonate until temperatures of 220°C were reached. The resin is suitable for use continually up to 200°C, verified by successfully performing the reaction of maleic anhydride with 2-ethyl-1-hexanol to form di-2-ethylhexyl maleate. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1764–1769, 2001

Key words: phenol-furfural sulfonic acid; cation exchange resin; polymer catalyst; esterification; catalysis

INTRODUCTION

Since the idea that ion exchangers can be used as a substitute for mineral acids and base was given in 1911, cationic ion exchange resins have been developed significantly as catalysts because of their distinct advantages both from the standpoint of catalysis as well as engineering of reactions for commercial purposes. The most important resins of this type are macroporous polystyrene sulfonic acid resins. They have been used as catalysts for many years in a large number of applications. Chakrabarti and Sharma¹ have published a comprehensive review on this subject. However, a key limitation of such resins is their relatively low thermal stability. For conventional

cation exchange resins like Amberlyst-15, operation at 150°C for a long time may cause desulfonation, leading to a release of sulfonic acid as well as a drop in the activity. Perfluorinated resins (Nafion) can go up to about 200°C, but unfortunately, such materials are relatively very expensive.

In this work, an attempt has been made to synthesize a low-cost, high-heat resistance cationic ion exchange resin catalyst. Furan resin is widely used as molding powder because of its resistance to heat and acid.² The catalyst phenol-furfural sulfonic resin (PFuSR) was prepared by using chlorosulfonic acid to sulfonate the macroporous phenol-furfural resin (PFuR), which was synthesized by condensation polymerization of phenol and furfural. The catalyst was characterized by chemical analysis, thermal analysis, scanning electron microscopy, and infrared (IR). The applicability of this catalyst for use in esterification has been investigated.

Correspondence to: Z. Su (suzx@lzu.edu.cn).

Contract grant sponsor: Science Foundation of Gansu Province; contract grant number: ZS981-A25-005-Z.

Journal of Applied Polymer Science, Vol. 80, 1764–1769 (2001)
© 2001 John Wiley & Sons, Inc.

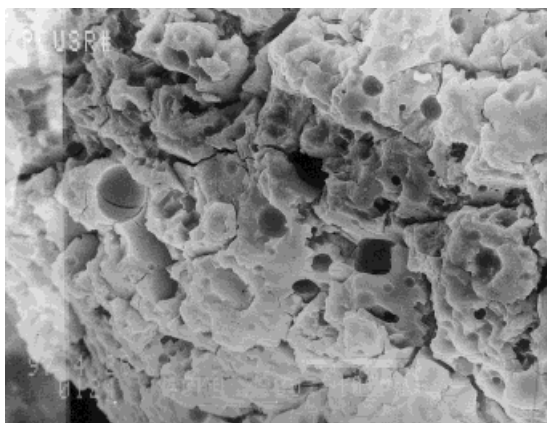


Figure 1 Scanning electron microscopy photo of PFuSR. Original magnification $\times 200$.

EXPERIMENTAL

Catalyst Preparation

Macroporous PFuR was prepared according to the method in the literature,³ modified by using 15% calcium carbonate and liquid paraffin as the porogenes. The latter was abstracted by xylene overnight in a Soxhlet abstractor, and the former was decomposed with excessive 10% hydrochloride until no carbon dioxide bubbles evolved. PFuSR was obtained by sulfonation of 15 g of the predried PFuR (120°C under vacuum for 2 days) with 30 mL of chlorosulfonic acid at 50°C for 5 h. The excessive chlorosulfonic acid was removed gradually until the elution liquid became neutral. PFuSR was then washed with methanol, and dried at 130°C under vacuum for 2 days. Particle size of PFuSR is $0.3 \sim 0.4$ mm.

Characterization of the Catalyst

The catalyst was characterized as follows:

- Sulfur content: the S content of PFuSR was determined by decomposing beads in oxygen-

flask combustion followed by titration against BaCl_2 .

- Exchange capacity: Exchange capacity of the strong-acid groups (C_s) and total exchange capacity (C_t) of PFuSR was determined by the method of pH titration, according to the literature.⁴
- Surface area: the surface area of PFuSR was analyzed by the Research Institute of Lanzhou Chemical Industrial Company, Lanzhou, PRC.
- Degree of swelling: a centrifuge method according to the literature⁵ was used to determine the swelling of PFuSR in water, ethanol, acetone, acetic acid, benzene, and petroleum ether, respectively.
- Surface morphology: the surface morphology of PFuSR was observed on a JEM-1200EX/S system (Joel, Japan) with the accelerating voltage of 40 keV and 200 times amplification.
- IR: IR spectra of PFuSR were recorded using a Nicolet FT-IR 170SX (Wisconsin, USA) spectrometer with potassium bromide compressing tablets.
- Thermal analysis: Thermal property of PFuSR was examined under air and N_2 atmosphere, respectively, by methods of thermogravimetry (TG) and differential thermal analysis using a Dupont (USA) 1090 thermal analysis instrument. The heating rate was $10^{\circ}\text{C}/\text{min}$.

Catalytic Esterification Reaction

Esterification of Acetic Acid

The esterification of acetic acid and *n*-butanol is taken as the model reaction to test the acidic catalytic properties of PFuSR, macroporous polystyrene sulfonic acid resin D72 and $\text{TiCl}_4/\text{D72}$ under the same reaction condition.⁶ The experiment was performed in a glass-jacketed reactor

Table I Characterization of PFuSR

Sulfur Content (wt %)	Exchange Capacity of Strong-Acid Groups (mmol/g)	Total Exchange Capacity (mmol/g)	Surface Area (m^2/g)
8.4	2.04	2.90	1.45

Table II Swelling of PFuSR in Nonaqueous Solvents

% Swelling in					
Water	Ethanol	Acetone	Acetic Acid	Benzene	Petroleum Ether
36	42	9	5	0	0

kept in a constant temperature bath with circular water maintained at $80 \pm 0.1^\circ\text{C}$. The reactor was equipped with a constant-rate agitator. In the reactor, 1.0 mL of acetic acid and 0.2 g of catalyst were first heated to 80°C , and then 20.8 mL of preheated *n*-butanol was added. The speed of the agitator was 300 rpm. The concentration of acetic acid in the reaction system was determined by titration against NaOH.

Esterification of acetic acid was conducted with 1.5 equivalents of alcohol in the presence of PFuSR under refluxing. The amount of catalyst was 10 wt % of acetic acid in all reactions. Anhydrous magnesium sodium was added to remove water formed in the reaction. The percentage conversation was determined by determining the acid value of unreacted acetic acid.

Synthesis of di-2-Ethylhexyl Maleate (DOM)

Maleic anhydride reacts with 2-ethyl-1-hexanol in the presence of PFuSR to form DOM. 2-Ethyl-1-hexanol was used to remove water formed in the reaction. The reactor was kept in an oil bath at 210°C and the reaction was performed under reflux. The amount of catalyst was 5 wt % of maleic anhydride. The esterification product DOM was analyzed on a Shimadzu (Japan) GC-9A gas chro-

matogram and a Nicolet FT-IR 170SX spectrometer.

The reusability of PFuSR was investigated by recycling the same reaction at 210°C . The mol ratio of maleic anhydride to 2-ethyl-1-hexanol used was 1:2.6. The reaction was performed for 0.5 h. The amount of catalyst was 5 wt % of maleic anhydride and the catalyst was reused simply after being filtered from the last recycling experiment.

RESULTS

Catalyst Structure

The scanning electron micrograph of PFuSR (Fig. 1) demonstrates its macroporous structure. The details of the resin structure depend on the conditions of synthesis from the monomers. The average diameter of macropores is 100 nm so that the surface area of the resin is relatively small.

Table I gives some properties of the catalyst. Comparing the values of *S* content and exchange capacity of strong-acid groups, we infer that 1.86 wt % sulfur present as sulfone bridge which can improve thermal stability of the resin.

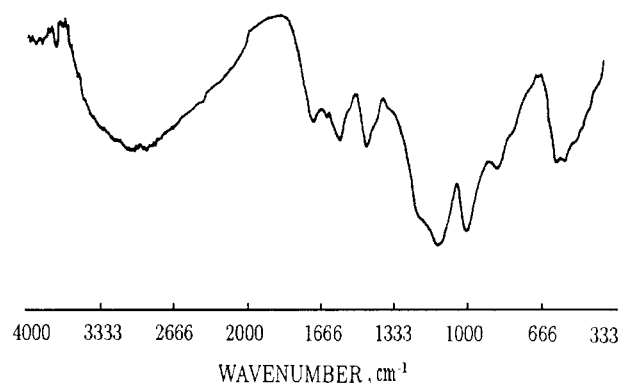
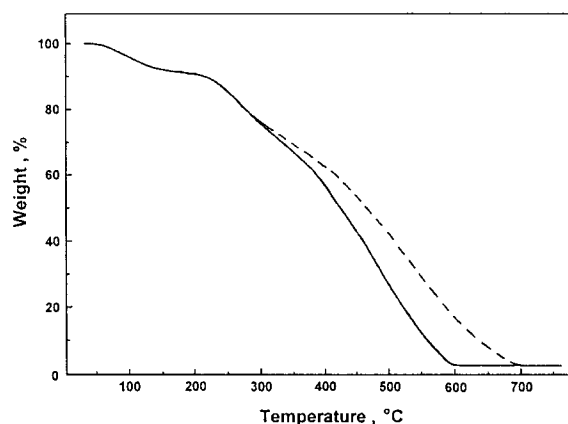
**Figure 2** IR spectrum of PFuSR.**Figure 3** TG curves of PFuSR in air (—) and in N_2 (- - -).

Table III Weight Loss at Different Temperatures for PFuSR Calculated from the TG

Atmosphere	Weight Loss (%) at Temperature (°C) up to						
	100	200	250	300	400	450	500
Air	4.0	9.0	14.0	25.0	46.0	58.0	75.0
N ₂	4.0	9.0	14.0	22.5	39.0	48.0	59.0

Degrees of swelling of PFuSR in nonaqueous solvents are given in Table II. PFuSR swells to only a limited degree because of its relatively high degree of crosslinking so that the resin can maintain stable catalytic activity and high thermal stability in organic reactions.

The FTIR spectrum of PFuSR is shown in Figure 2. It was observed that the O—H vibrations cover a broad region from 2600 to 3400 cm⁻¹. The C=C vibrations of phenyl ring appeared at 1597 and 1468 cm⁻¹, respectively. The absorption signal at 1714 cm⁻¹ is characteristic of the C=O stretching of carboxylic groups. The characteristic asymmetric and symmetric O=S=O stretching vibrations of sulfonic acid groups are seen at 1151 and 1023 cm⁻¹, respectively. The appearance of sulfonic acid groups at lower frequency are due to hydration of sulfonic acid groups with moisture in the air.

Thermal Analysis

TG curves of PFuSR in air and in an atmosphere of N₂ both indicate three major stages of decomposition (Fig. 3). Weight loss at difference temper-

atures for PFuSR calculated from the TG is shown in Table III.

The derivative thermogram of PFuSR shows three peaks at 98, 263, and 466°C in air and 98, 265, and 512°C in N₂, respectively. The weight loss up to 200°C is due to the elimination of resin-bound water and decarboxylation. The second stage of decomposition is started at 217°C both in air and N₂ due to desulfonation. PFuSR lose aromatic fragments and decompose extensively in the third stage whereas 50% weight loss of the sample is observed at 423°C in air and 465°C in N₂, respectively. The decrease of thermal stability of PFuSR in air is attributed to the oxidation degradation.

Catalyst Performance

*Kinetics of Esterification of Acetic Acid and *n*-Butanol*

The second order reaction of esterification can be designed as pseudo-first order if we use a large excess of a reactant to keep a concentration constant. Esterification of acetic acid and *n*-butanol was conducted with 13 times equivalents of *n*-butanol in the presence of PFuSR at 80°C. Plotting $-\ln C_{\text{HAc}}$ versus the reaction time gives a straight line (Fig. 4). The slope is the pseudo-first order rate constant k' .

We use the pseudo-first order rate constant k' of this reaction as parameter value to test the

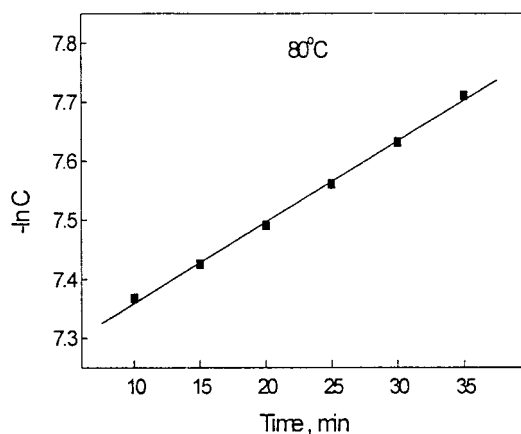
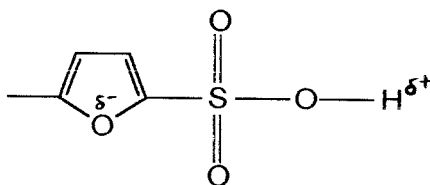


Figure 4 $-\ln C$ versus time in the esterification of acetic acid with *n*-butanol catalyzed by PFuSR at 80°C.

Table IV Comparison of Catalytic Activity

Catalyst	Rate Constant k' (10 ⁻⁶ s ⁻¹)	Relative Catalyst Activity
D72*	2.20	1
TiCl ₄ /D72*	68.0	31
PFuSR	229	104

* Corresponding to ⁵.



Scheme 1

acidic catalytic properties of PFuSR, macroporous polystyrene sulfonic acid resin D72, and $\text{TiCl}_4/\text{D72}$. The results are given in Table IV. PFuSR showed much higher activity in the reaction because there exist in PFuSR different kinds of acidic groups such as $-\text{OH}$, $-\text{COOH}$, and $-\text{SO}_3\text{H}$ so that the catalyst can provide more acid sites to catalyze the esterification.

The induction effect of oxygen atom on furan ring can also strengthen the acidity of sulfonic groups of PFuSR (Scheme 1). In addition, resins based on furan ring show greater polarity than those on polystyrene so that PFuSR can catalyze the reaction more effectively.

Esterification of Acetic Acid

The results for esterification of acetic acid are listed in Table V.

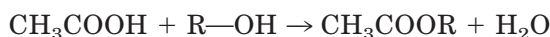


Table V The Results for Esterification of Acetic Acid Catalyzed by PFuSR

Alcohol	Conversion of Acetic Acid (%)			
	1 h	2 h	3 h	4 h
Ethanol	70.8	73.6	75.0	74.8
1-Propanol	77.4	80.1	83.0	83.1
2-Propanol	19.3	39.8	54.7	60.6
1-Butanol	75.3	84.0	85.5	85.8
2-Butanol	57.2	79.6	84.0	84.3
1-Pentanol	82.1	87.3	88.1	87.3
Cyclohexanol	62.0	75.5	76.9	82.2
1-Propen-3-ol	57.0	57.3	58.9	58.5
Benzyl alcohol	55.7	76.1	81.0	85.0
2-Ethyl-1-hexanol	92.6	96.8	96.8	96.8
Dodecanol*	69.9	85.8	88.6	88.7
Cetanol*	76.8	86.5	88.8	89.0

* Reaction temperature was 100°C.

Table VI The Results of the Esterification of Maleic Anhydride with 2-Ethyl-1-hexanol

Catalyst	Molar Feed Ratio Anhydride/Alcohol	Reaction Time (min)	Yield (%)
PFuSR	1:2.6	10	89.2
No catalyst	1:2.6	10	38.3
PFuSR	1:2.6	20	94.0
PFuSR	1:2.6	30	98.4
No catalyst	1:2.6	30	69.8
PFuSR	1:2.6	60	98.9
PFuSR	1:2.0	60	94.6

After refluxing a mixture of acetic acid and primary or secondary alcohols in the presence of PFuSR for 4 h, high conversions (60 ~ 90%) were obtained. However, tertiary alcohols did not react under these conditions.

Synthesis of DOM

The results of the esterification of maleic anhydride with 2-ethyl-1-hexanol are shown in Table VI. It can be seen from Table VI that high yields (about 90%) of DOM were obtained only in 10 min in the presence of PFuSR.

The reusability of PFuSR was tested out by performing the same esterification reaction. The graph of yield versus run number is shown in Figure 5. It can be seen that there has been only a marginal decrease in the yield of DOM between 10 runs, indicating that the catalytic activity of PFuSR is not affected by repeated usage up to 200°C.

CONCLUSIONS

PFuSR can be effectively used as catalyst. The catalyst shows greater activity in esterification reac-

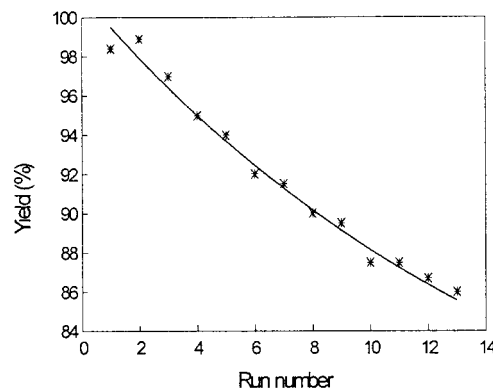


Figure 5 Yield of DOM versus run numbers of PFuSR.

tion because of furan rings and more acidic sites in its structure. PFuSR also has excellent thermal stability and solvent resistance. The resin is suitable for use continually up to 200°C, verified by successfully performing the reaction of maleic anhydride with 2-ethyl-1-hexanol to form DOM.

REFERENCES

1. Chakrabarti, A.; Sharma, M. M. *React Polym* 1993, 20, 1–45.
2. Emel'yanov, Y. V.; Zaitseva, Z. M.; Eremina, R. E. *Issled Zashch Met Khim Prom-Sti* (Russian) 1976, 4, 77.
3. Su, Z.; Wang, T. *React Funct Polym* 1995, 28, 97–102.
4. Dorfner, K. *Ion Exchangers: Properties and Applications*; Ann Arbor Science Publishers: Ann Arbor, MI, 1972; Chapter 2.
5. Zhang, D.; Zhang, Y. *Yuanzineng Kexue yu Jishu* (Chinese) 1962, 9, 693.
6. Liu, F.; Zhao, J.; Huang, H. *Cuihua Xuebao* (Chinese) 1991, 5, 394.