



Short communication

Halogenated macroporous sulfonic resins as efficient catalysts for the Biginelli reaction



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ABSTRACT

A series of halogenated macroporous sulfonic resins A-15-Cl, A-15-Br and A-15-I were synthesized from the precursor Amberlyst 15 by a typical halogenation reaction, and they were evaluated for the catalytic activities of the halogenated macroporous sulfonic resins via the Biginelli reaction in detail. These modified resins possessed a larger contact angle of water droplet than the precursor and a significantly improved thermal stability, which contributed to their higher catalytic activity. In particular, the resin A-15-Br containing 31.27% bromine exhibited the best catalytic activity and excellent recyclability.

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1. Introduction

Macroporous sulfonic resins are extensively used as catalysts in various chemical reactions because of their high catalytic activity, low toxicity, low cost and easy separation from the reaction system [1–4]. In general, they are sulfonated from the macroporous poly (styrene-co-divinylbenzene) using concentrated sulfuric acid as the sulfonating agent [5–8]. These resins can also be used as catalysts in aqueous or nonaqueous medium, where the catalytic mechanisms differ considerably [9,10]. In an aqueous medium, sulfonic groups of these resins are completely dissociated as sulfonate anions and protons, where the latter serve as active sites for the catalytic reaction. In a nonaqueous medium, several clusters are fabricated by intermolecular hydrogen bonds between the sulfonic groups on the polymer chains. Moreover, the clusters have a higher catalytic activity and better catalytic stability than the individual sulfonic groups because of the direct contact with the clusters due to the adsorption effect [11]. Of course, water is formed as the by-product for some special dehydration reactions such as condensation reaction, which not only affects chemical equilibrium of the reaction, but also causes damage to the sulfonic clusters in the polymer chains, thereby decreasing the catalytic performance of the sulfonic resins.

Recently, Stoerzinger et al. [12] have reported that intrinsic hydrophobicity of the catalysts should be considered in the design of highly active catalysts. They utilized the flexibility of the perovskite surface chemistry to show that the tendency of the perovskite surface toward hydroxylation was propitious to wetting and adverse to catalysis. Halogens are proved to be the feasible hydrophobic groups for

increasing the hydrophobicity of the sulfonic resins [13], and the hydrophobic interaction of the gel cavities in the sulfonic resins may be enhanced as some special halogenated groups are introduced in the polymer chains. In particular, the sulfonic clusters are more stable because of the inductive effect of halogenated groups, which enhances the catalytic performance of the sulfonic resins.

In this study, the precursor Amberlyst 15 was halogenated by different compounds (Cl_2 , Br_2 , and I_2), and a series of halogenated macroporous sulfonic resins A-15-X ($X = \text{Cl}$, Br , or I) was synthesized. The Biginelli reaction was then selected as a model reaction to evaluate the catalytic performance of the halogenated macroporous sulfonic resins. The Biginelli reaction is well known for the synthesis of dihydropyrimidinones (DHPMs) [14–16]. It generally involves one-pot condensation of an aldehyde, β -diketonate, urea, or thiourea using catalysts [17–22], and water is produced as the by-product in this reaction. It is found that the Biginelli reaction catalyzed by sulfonic resins produces a relatively low yield, and the catalyst exhibits poor recyclability [23–25].

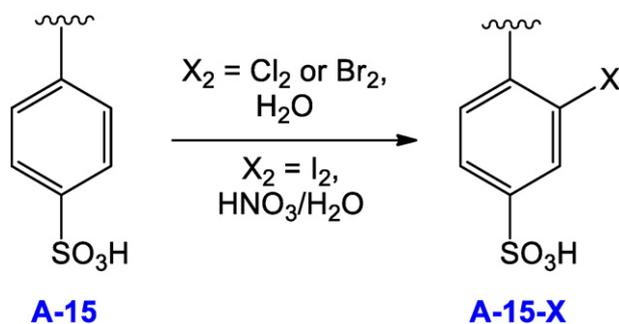
2. Experimental

2.1. Materials

Amberlyst 15 was supplied by Rohm and Haas Shanghai Chemical Industry Co., Ltd. and all other reagents were purchased from Aladdin Reagent Co., Ltd. (Shanghai), and used as received. Nitrogen adsorption experiments were conducted using a TriStar 3000 surface area and porosity analyzer. A TX 500 H spinning drop interfacial tensiometer was used to measure the contact angle of water in air on the surface of the sample.

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Scheme 1. Synthetic procedure for producing A-15-X.

2.2. Halogenation of Amberlyst 15

As shown in Scheme 1, the synthetic procedure for producing A-15-X was performed according to the method described in Refs. [26,27]. Amberlyst 15 (50 g) and water (80 mL) were placed in an agitated reaction vessel. Halogen (30 g) was mixed with the agitated suspension of the resins and the mixture was heated to 50 °C shielded from light and agitated at this temperature for different reaction times. The solid product was filtered and washed by a large amount of distilled water.

3. Results and discussion

3.1. Halogenation of Amberlyst 15

It is well known that halogenation of Amberlyst 15 follows the typical electrophilic substitution mechanism, which was similar to the halogenation of aromatic compounds such as benzene and toluene [28,29]. Furthermore, the halogen content of the modified resins (A-15-Cl and A-15-Br) was very low. It is interesting to observe that the synthesis of A-15-Cl and A-15-Br was successful in aqueous medium, and the electrophile X^+ can be easily formed and has a small ion radius. Furthermore, the sulfonic groups dissociate as sulfonate anions and protons, which have a smaller hindrance for X^+ . However, synthesis of A-15-I requires an acidic oxidizing reagent, such as nitric acid, because of the chemical inertness of iodine.

3.2. Performance analysis of the catalysts

The halogen content (W_X), mass exchange capacity (Q_m), volume exchange capacity (Q_v) of the resins were measured using procedures reported in Refs. [30,31], whose results are summarized in Table 1. It is found that the exchange capacity of the halogenated resins is decreased after introduction of halogens in the benzene ring of the

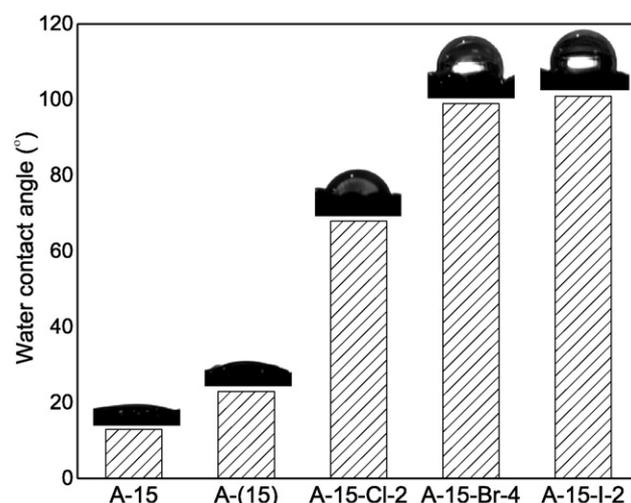


Fig. 1. Water droplet contact angle on Amberlyst 15, A-(15), and A-15-X.

polymer chains. This might be attributed to the following two reasons: (1) the mass increase of the modified resins after introduction of the halogenated groups and (2) the hydrolysis of the sulfonic groups in the acidic aqueous solution. In addition, it is observed that the BET surface area, pore volume, and average pore size of the modified resins are similar to those of the precursor, implying that halogenation reaction has almost no effect on pore structure. Although the BET surface area and pore volume decreased slightly, theoretically, they increased in the absence of the mass of halogen, which may be attributed to the hydrophilicity and hydrophobicity of the halogenated sulfonic resins.

After introduction of halogens on the surface of the sulfonic resins, a small amount of sulfonic groups will be removed during the halogenation reaction, and hence the hydrophilicity and hydrophobicity of the modified sulfonic resins would be slightly changed. Therefore, a sulfonic resin with a smaller cation exchange capacity, A-(15) ($Q_v = 1.02$ mmol/mL), was prepared by the desulfonation of Amberlyst 15. Moreover, the number of halogenated and sulfonic groups is shown to be the primary deciding factor of the hydrophilicity and hydrophobicity of sulfonic resins. Hence, halogenated resins having a similar molar ratio (~1.6: 1) of halogenated groups to sulfonic groups were chosen as the samples to measure the contact angle of water droplet. Fig. 1 shows the results of Amberlyst 15, A-(15), A-15-Cl-2, A-15-Br-4, and A-15-I-2 samples, respectively. It is evident from the figure that A-15-Cl-2, A-15-Br-4, and A-15-I-2 have higher contact angles, indicating their increased hydrophobic surface. As a result, hydrophobicity of the macroporous sulfonic resins was enhanced by the introduction of

Table 1
Characteristics of the sulfonic resins.

Sample	Time (h)	Cation exchange capacity		Halogen content (%)	$n_{(-X)}; n_{(-SO_3H)}^a$	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
		Q_m (mmol/g)	Q_v (mmol/mL)					
A-15	0	4.30	1.50	0	–	38.5	0.246	25.7
A-15-Br-1	2	3.58	1.39	10.03	0.35: 1	–	–	–
A-15-Br-2	8	3.13	1.35	16.20	0.65: 1	–	–	–
A-15-Br-3	24	2.72	1.12	26.79	1.23: 1	–	–	–
A-15-Br-4	36	2.45	1.08	31.27	1.60: 1	34.5	0.208	24.1
A-15-Br-5	48	2.32	0.98	34.94	1.88: 1	–	–	–
A-15-Br-6	72	1.97	0.64	38.98	2.47: 1	–	–	–
A-15-Cl-1	2	3.41	1.30	11.35	0.93: 1	–	–	–
A-15-Cl-2	6	3.10	0.95	17.90	1.63: 1	37.7	0.218	23.2
A-15-Cl-3	12	2.98	0.88	21.50	2.03: 1	–	–	–
A-15-I-1	48	2.35	1.20	30.58	1.02: 1	–	–	–
A-15-I-2	72	1.91	0.94	39.69	1.63: 1	29.4	0.183	24.8
A-15-I-3	96	1.73	0.72	42.36	1.93: 1	–	–	–

^a Molar ratio of halogenated groups to sulfonic groups.

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