



## Preparation and Catalytic Performance of Ionic Liquid Catalyst Immobilized by ZrO<sub>2</sub>

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A novel Brønsted acidic ionic liquid catalyst [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> loaded by ZrO<sub>2</sub> was prepared under impregnation method and characterized by means of X-ray diffraction, FT-IR spectroscopy, thermogravimetric analysis-derivative thermogravimetry, scanning electron microscope and element analysis. The results showed that the capacity of ionic liquid [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> was 21.01 %. The catalyst can be used in the esterification of maleic anhydride and iso-octanol and the conversion rate of maleic anhydride was 99.8 % under the following conditions: 140 °C, maleic anhydride 0.05 mol, iso-octanol 0.2 mol, toluol 6 g, catalyst 0.8 g and reaction time 100 min. The esterification could still reach to 94.9 % after the catalyst was reused for 9 times. The catalyst has exhibited good thermal stability and repeatability performance.

**Key Words:** ZrO<sub>2</sub>, Ionic liquid, Supported catalyst, Esterification.

### INTRODUCTION

Ionic liquid, which is acidic adjustable and have good stability and solubility in chemical reactions is a new-type efficient environmental-friendly catalyst<sup>1,2</sup>. However, this kind of catalytic reactions belongs to homogeneous catalysis. Products and reactants can't separate instantly though most of ionic liquid can subside after the reaction (when the reaction system to room temperature). Therefore, the catalyst can't be industrialized, which enormously limits its industrial application.

Loaded ionic liquid can immobilize ionic liquid, in response to the separation of the catalytic after the reaction, which speed up the industrial application of ionic liquid and make the research of its properties a hot spot<sup>3-5</sup>. However, the researches at present are mainly focus on loading ionic liquids on SiO<sub>2</sub><sup>6,7</sup>, molecular sieve<sup>8</sup> and nanoparticles<sup>9-11</sup> through chemical bonding and grafting. Zhang *et al.*<sup>12</sup> used SiO<sub>2</sub> as the carrier to load ionic liquid [(TESP) MIM]HSO<sub>4</sub>. When use this catalyst in the esterification reaction of acetic acid and butanol, the esterification rate of 99.4 % and after reused for 6 times the esterification rate still can up to 74.7 %. Shen *et al.*<sup>13</sup> prepared ionic liquid-Pro/SBA-15 catalyst with ionic liquid and SBA-15 mesoporous molecular sieves, which showed excellent catalytic performance in Knoevenagel condensation reaction. However, the preparation is complicated and the cost

is high, so that it can't play the significant role to the industrialization of ionic liquid.

In this paper, an ionic liquid loaded catalyst is prepared, in which ZrO<sub>2</sub> is used as a supporter to load ionic liquid [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> under impregnation method. The preparation is simple and the catalysis in esterification reactions is good. Meanwhile, the catalyst has some other advantages, such as the long service life and hard to be poisoned, which has important meaning in the industrialization of the use of ionic liquid.

### EXPERIMENTAL

Maleic anhydride (A.P.), isooctanol (A.P.), toluene (A.P.), cyclohexane (A.P.), zirconium oxychloride (A.P.), hexadecyltrimethyl ammonium bromide (CTAMBr, A.P.), ammonia (A.P.), concentrated H<sub>2</sub>SO<sub>4</sub> (A.P.), 1,4-sulfonylurea lactone, 1-methyl imidazole.

D<sub>8</sub>FOCUS XRD (BRUKER, Germany), S-3400 scanning electron microscopy (Toshiba, Japan), STA 409 thermogravimetric analyzer, (Netzsch, Germany), Magna-IR550 FT-IR (Nicolet, USA), Elementar Vario ELIII Element analyzer; BS110S electronic balance (Beijing Saiduoli Inc., China), SHZ-C vacuum pump (Yingyu electronic instrument factory, China), temperature control system, JJ-1 electric mixer (Guohua Inc., China), HH-4 digital electronic constant temperature water-bath (Aorui equipment factory, China).

### Preparation of catalyst

**[HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>:** Ionic liquid [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> is prepared through the method refers to literature<sup>14</sup>. Dissolve 1 mol of 1,4-butane sulfonylurea lactone into toluene and dropwise add 1 mol 1-methyl imidazole under magnetic stirring. Then heat it up to 80 °C for 2 h, after which the reaction liquid is filtered. Wash the white precipitate with ethyl acetate three times and vacuum dry 5 h at 100 °C, then the intermediate 1-methyl imidazole inside sulfonate is got. Dissolve the intermediate into deionized water, dropwise add 1 mol 98 % H<sub>2</sub>SO<sub>4</sub> under room temperature, then heat it up to 90 °C for 2 h, dehydrate in vacuum and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> ionic liquid which is light yellow viscous liquid is obtained.

**Preparation of ZrO<sub>2</sub><sup>15</sup>:** Add 2.0 g CTAMBr into 24 mL deionized water, stir well to get mixture A. Soluble 25.8 g oxygen chlorinated zirconium in 24 mL deionized water to get mixture B. Dropwise add B into A under intense stirring and adjust pH to 8-9 with ammonia, then keep stirring for 1 h and static cool down till the foam disappears. Pour the mixture into the reaction kettle with PTFE, take crystallization for 24 h under 105 °C, then get the white powder. After wash it with absolute ethyl alcohol to neutral, roast 3 h in the muffle furnace under 500 °C and ZrO<sub>2</sub> is obtained.

**[HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub><sup>16</sup>:** Dropwise add [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> (4.5 g) on the roasting ZrO<sub>2</sub> (5.0 g), then add 2 mL anhydrous alcohol. After stirring to uniformity with the magnetic stirring apparatus, ultrasonic clean it for 2 h, then seal and stir under room temperature for 24 h. Excessive ionic liquid is extracted by dichloromethane in the Soxhlet extractor (40 °C, 24 h). At last, vacuum dry 12 h under 110 °C and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> is obtained.

**Esterification:** Connect the 250 mL round bottom flasks with thermometer, water segregator and condenser, add 0.05 mol maleic anhydride, 0.2 mol *iso*octanol, catalyst and toluene, then start the backflow reaction under magnetic mixing. Take samples timely to determine the conversion rate. After the complete of the reaction, pour out the upper reaction liquid and the catalyst left can be used to evaluate the reutilization property.

**Determination of conversion rate:** According to GB1668-2008, sampling analysis the acid value of reaction system, then determine the conversion (*y*) of maleic anhydride in the esterification reaction on the basis of the change of acid value. Formula (1).

$$y = [1 - (w_2 / w_1)] \times 100 \% \quad (1)$$

In the formula: *w*<sub>1</sub>-the system acid value before reaction; *w*<sub>2</sub>-the system acid value after reaction.

## RESULTS AND DISCUSSION

**Architectural feature of ZrO<sub>2</sub> and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub>:** In Fig. 1, A and B are wide angle XRD of ZrO<sub>2</sub> and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub>. The lattice plane value showed in A is the eigenvalue of tetragonal system, while the lattice plane value showed in B is the eigenvalue of monoclinic system. The figure indicates that a mixed crystal carrier ZrO<sub>2</sub> is obtained after being roasted and the tetragonal phase has not only high crystallinity, but high content through the

calculation and analysis of the diffraction intensity. The contrast of A and B shows that the peak form does not change significantly, which indicates ionic liquid doesn't obviously influence the crystal of ZrO<sub>2</sub>.

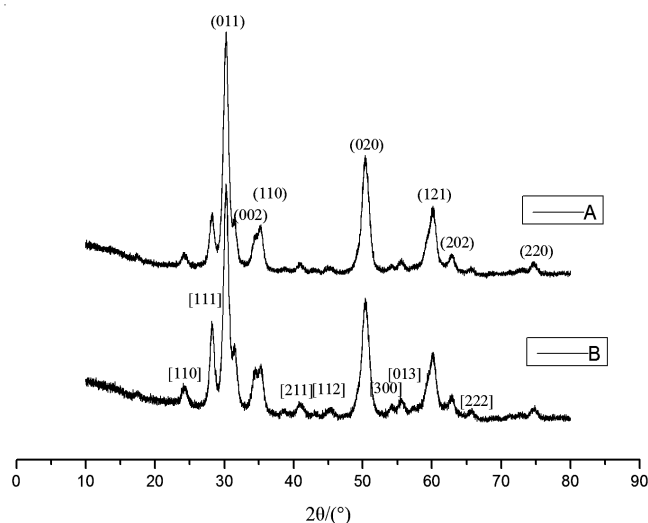


Fig. 1. XRD patterns of ZrO<sub>2</sub>(A) and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub>(B)

In Fig. 2, curves A, B and C are FT-IR spectrograms of ZrO<sub>2</sub>, [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> and ionic liquid. In spectrograms B and C, absorption peaks at 3156 cm<sup>-1</sup> and 3115 cm<sup>-1</sup> represent stretching vibration of aromatic C-H on imidazole ring; absorption peak at 2953 cm<sup>-1</sup> represents stretching vibration of methyl C-H on imidazole ring; absorption peaks at 1709, 1572 and 1461 cm<sup>-1</sup> represent coupled vibration of C=C in imidazole ring; 1233, 1167, 1031 and 876 cm<sup>-1</sup> represent characteristic absorption peak of [HSO<sub>4</sub>]<sup>-</sup>. The contrast of B and C shows that absorption peaks at 1233 cm<sup>-1</sup> and 876 cm<sup>-1</sup> in Fig. B have a redshift and become weak; absorption peaks at 1167 cm<sup>-1</sup> and 1031 cm<sup>-1</sup> narrows down, which indicates [HSO<sub>4</sub>]<sup>-</sup> in [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> reacts with ZrO<sub>2</sub> that causes the change of absorption peak of [HSO<sub>4</sub>]<sup>-</sup>. One possibility is that [HSO<sub>4</sub>]<sup>-</sup> combines with the alkali centre of ZrO<sub>2</sub>. Other absorption peaks don't change, indicates that the imidazole ring doesn't react with ZrO<sub>2</sub>.

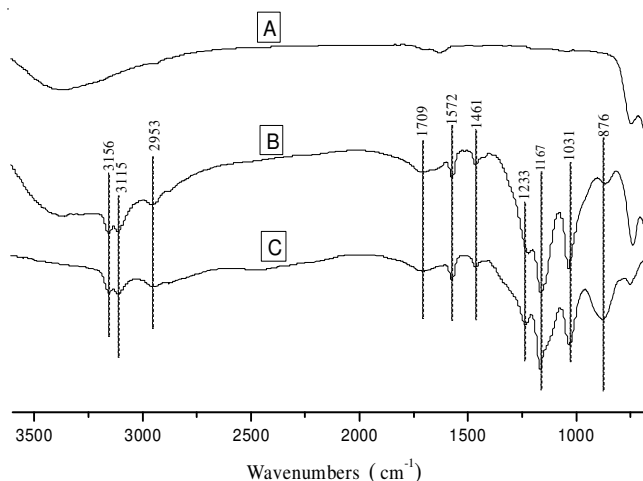


Fig. 2. FT-IR spectra of ZrO<sub>2</sub>(A), [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> (B) and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>(C) samples

**Thermostability of ZrO<sub>2</sub> and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub>:** Fig. 3 are the TG curves of ZrO<sub>2</sub> and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub>. It shows that ZrO<sub>2</sub> losses weight smoothly in testing range which may be due to the thermal decomposition of some substances in prepared ZrO<sub>2</sub> or the impurities adsorbed through the process of sample reserve. For [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub>, there is an obvious weight loss area between 300-550 °C. The value of weight loss reaches maximum between 350-450 °C and the total value is about 20 % weight, which indicates the load of ionic liquid [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> on ZrO<sub>2</sub> is 20 % and catalyst [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> can't be used when temperature is over 300 °C.

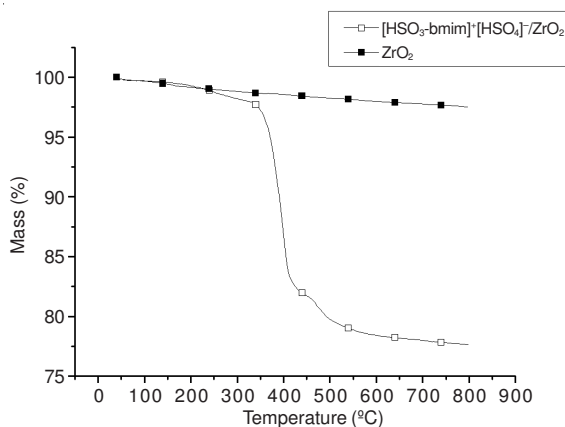


Fig. 3. TG analysis of ZrO<sub>2</sub> and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> samples

**Surface appearance of ZrO<sub>2</sub> and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub>:** Fig. 4 are the SEM photos of ZrO<sub>2</sub> and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub>, in which (a) and (b) are SEM photos of ZrO<sub>2</sub>, the others are SEM photos of [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub>. The contrast of (a), (b), (c) and (d) shows that after loading ionic liquid, the surface appearance of ZrO<sub>2</sub> turns rough, which indicates ionic liquid is truly loaded on ZrO<sub>2</sub>. This not only increase the dispersity of ionic liquid, improve the catalytic activity, but also reduce the loss of ionic liquid and enhance the reutilization rate, which is good for the stability of the catalyst. In photos (c) and (d), there are obvious honeycomb multi-hole loosened structure, which is beneficial to improve the superficial area and the surface free energy of the catalyst and then improve its catalytic activity.

**Loading rate of [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub>:** The elementary analysis of [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> shows that the quality scores of C, H, N are 7.37, 2.12 and 1.86 %, respectively. According to the analytical result of nitrogen content, the quality scores of [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> in catalyst [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> can be calculated to be 21.01 %.

**Catalytic property of [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> in esterification reaction:** The influences of different conditions for the esterification reaction between 0.05 M maleic anhydride and 0.2 M *iso*-octanol are listed in Table-1. The contrast of entry 1 and 2 shows that under the same conditions ZrO<sub>2</sub> has certain catalysis to the esterification reaction, for it can improve the conversion rate of maleic anhydride. entry 3-5 show that ionic liquid [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> both have excellent catalysis to the reaction, while the auxoaction of which there is toluene is better

than that of cyclohexane, which may be caused by the low boiling point of cyclohexane. Data from entry 6 to entry 9 show that the conversion rate of maleic anhydride continuously improve with the increase of [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub>, until the dosage of catalyst reach to 0.8 g. As a result, the best addition amount of catalyst is 0.8 g. Entry 10, 11, 12 and 13 shows the influence of different addition amount of toluene to the conversion rate of maleic anhydride. The result indicates that the best addition amount of toluene is 6 g. Entry 14, 15, 16, 17 and 18 shows the conversion of maleic anhydride versus time, from which we can see the reaction reaches to balance in 100 min, so that the best reaction time is 100 min.

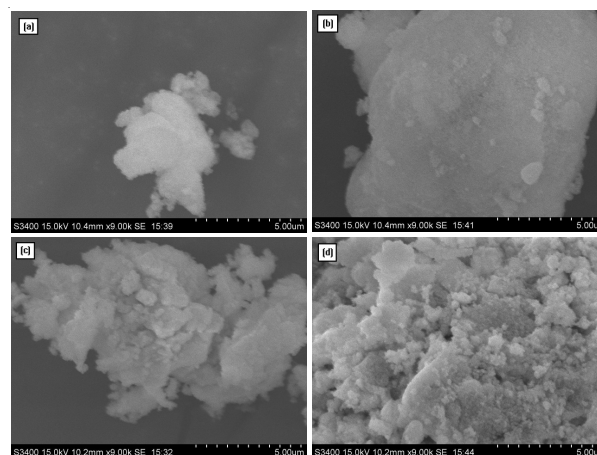


Fig. 4. SEM analysis of ZrO<sub>2</sub> and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> samples

Fig. 5 shows the reutilization property of [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub>. The result indicates that after being reused for 3 times, the catalytic property of [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> starts to reduce obviously, which is probably caused by the loss of ionic liquid, while the catalytic property of [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> doesn't reduce obviously after being reused for 9 times and the conversion rate of maleic anhydride is still up to 94.9 %. The result shows that the load of [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> on ZrO<sub>2</sub> is firm and the catalyst can be reused without any activation treatment, also there are no catalyst poisoning problems.

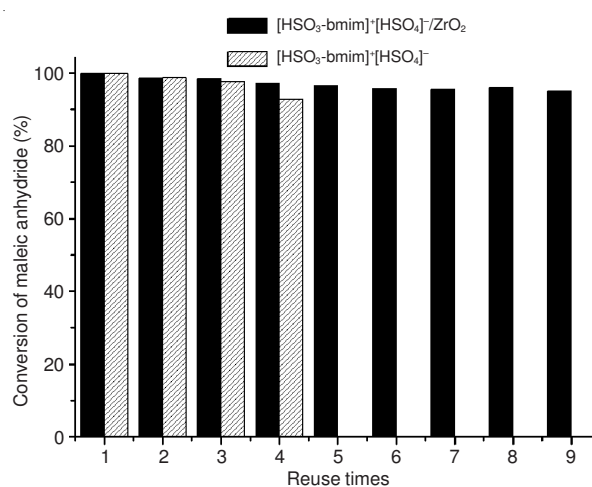


Fig. 5. Catalytic performance of catalyst reused of [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> and [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> samples

TABLE-1  
EFFECT OF DIFFERENT FACTORS ON ESTERIFICATION OF MALEIC ANHYDRIDE AND *ISO*OCTANOL

Entry	Catalyst	Catalyst dosage (g)	Reaction temp. (°C)	Reaction time (min)	Water-carrying agent	Water-carrying agent dosage/g	Conversion of maleic anhydride/%
1	-	-	140	100	Toluene	6	70.3
2	ZrO <sub>2</sub>	0.8	140	100	Toluene	6	86.4
3	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup>	0.2	130	75	Cyclohexane	6	99.2
4	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup>	0.2	140	75	Toluene	6	99.8
5	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.8	130	100	Cyclohexane	6	99.4
6	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.4	140	100	Toluene	6	90.5
7	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.6	140	100	Toluene	6	93.4
8	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.8	140	100	Toluene	6	99.8
9	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	1.0	140	100	Toluene	6	99.8
10	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.8	140	100	Toluene	4	97.6
11	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.8	140	100	Toluene	5	98.3
12	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.8	140	100	Toluene	6	99.8
13	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.8	140	100	Toluene	8	96.2
14	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.8	140	25	Toluene	6	81.4
15	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.8	140	50	Toluene	6	94.3
16	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.8	140	75	Toluene	6	98.5
17	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.8	140	100	Toluene	6	99.8
18	[HSO <sub>3</sub> -bmim] <sup>+</sup> [HSO <sub>4</sub> ] <sup>-</sup> /ZrO <sub>2</sub>	0.8	140	125	Toluene	6	99.8

## Conclusion

An ionic liquid [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup> is loaded on ZrO<sub>2</sub> through immersion method to prepare a novel catalyst [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>/ZrO<sub>2</sub> with good thermal stability and reutilization property. Under the following reaction conditions: 140 °C, 0.05 mol maleic anhydride, 0.2 mol *iso*-octanol and 0.8 g catalyst, after reacting for 100 min, the conversion rate of maleic anhydride can reach to 99.8 % without any treating and the conversion rate of maleic anhydride is still up to 94.9 % after catalyst being reused for 9 times, which is much more than ionic liquid [HSO<sub>3</sub>-bmim]<sup>+</sup>[HSO<sub>4</sub>]<sup>-</sup>.

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