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Synthesis of a Novel Heterogeneous Strong Acid Catalyst from p-Toluenesulfonic Acid (PTSA) and its Catalytic Activities

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Abstract A novel heterogeneous strong acid catalyst has been synthesized through the copolymerization of *p*-toluenesulfonic acid and paraformaldehyde with sulfuric acid as catalyst. The novel catalyst owns the strong acidity as much as 4.0 mmol/g, while Nafion and Amberlyst-15 only has the acidity of about 0.8 mmol/g. Furthermore, the catalyst possesses the advantages of the high thermal stability (200 °C) and low cost for the simple synthetic procedure. The catalytic activities of the novel catalyst were taken through esterification of acetic acid and ethanol and acetalization of benzolaldehyde and 1,2-ethandiol. The results showed that the novel catalyst showed much higher activities than the Amberlyst-15 and owned even the comparative activity to sulfuric acid, which made the catalyst hold great potential for the replacement of the traditional homogeneous catalyst for the green process.

Keywords Novel heterogeneous strong acid catalyst · High activity · High stability · Green process

1 Introduction

Acid-catalyzed reactions are one of the most important reactions in chemical industry and the catalysts play the key role during the processes. Over 15 million tons of sulfuric acid is annually consumed as “an unrecyclable catalyst”—which requires costly and inefficient separation of the catalyst from homogeneous reaction mixtures—for the production of industrially important chemicals, thus resulting in a huge waste of energy and large quantities of waste products [1–8]. From the view of green process, many heterogeneous catalysts such as organic acid/inorganic solid oxide hybrids and strong acidic cation-exchangeable resins were used for the replacement of the catalyst [9–13]. Nafion is one of the most famous heterogeneous acid catalysts from Du Pont. Nafion owned excellent heat-resistant properties which can be used at 200 °C. But the catalyst owned low acidity of about 0.8 mmol/g. Moreover, most of the acid sites were inside the catalyst that cannot take effect during the reaction due to its low BET surface (0.02 m^2/g). Also the high price made the catalyst impossible for the wider application in chemical industry [14–16]. Amberlyst-15 is another famous acidic cation-exchangeable resin commercial available. The catalyst owned a higher acidity and BET surface (45 m^2/g) than that of Nafion. However, the low thermal instability (< 120 °C) limited its application area [17]. So there is a great desire for the heterogeneous acid catalysts that possessed both the high acidity and stability. In order to achieve the object above, here we present a simple procedure for the preparation of a novel heterogeneous strong acid catalyst. The novel catalyst was synthesized through the copolymerization of *p*-toluenesulfonic acid (PTSA) and paraformaldehyde using sulfuric acid as catalyst (Scheme 1). The comparative study on the catalytic activities of the novel catalyst and other common catalysts were taken through esterification of acetic acid and ethanol and acetalization of benzolaldehyde and 1, 2-ethandiol. The results showed that the novel catalyst showed much higher activities than the Amberlyst-15 and owned even the comparative activity to sulfuric acid.

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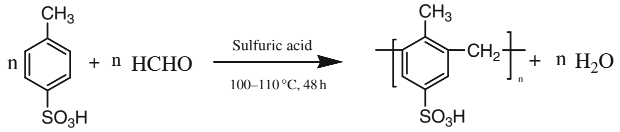

Scheme 1 The synthetic route of the novel catalyst

2 Experimental

All organic reagents were commercial products with the highest purity available (>98%) and used for the reaction without further purification. Benzaldehyde, 1,2-ethaniol, acetic acid, and ethanol were purchased from Shanghai Chemicals Co. Amberlyst-15 was obtained from Fluck. GC measurements were taken on a Shimadzu (GC-14B) gas chromatograph. GC-MS measurements were performed on an American Agilent 6890/5973N instrument.

2.1 Synthesis of the Catalyst

The catalyst was synthesized through the polymerization of *p*-toluenesulfonic acid (PTSA) and paraformaldehyde catalyzed by sulfuric acid (Scheme 1). In the typical procedure: The mixture of *p*-toluenesulfonic acid (10 g), paraformaldehyde (2 g) and sulfuric acid (0.2 g) was heated in a three necked round bottomed flask equipped with a magnetic stirrer, a thermometer and a funnel. The reaction mixture was kept in the range of 100–110 °C for 48 h to form black solid. Sulfuric acid is absolutely necessary here and the polymerization would not take out efficiently without the sulfuric acid. The solid was washed with hot water (>80 °C) and filtrated until no SO_4^2 was detected in the filtrate. The catalyst was obtained after drying at 120 °C in an oven overnight.

2.2 Characterization of the Catalyst

The acidity of the catalyst was determined through the neutralization titration and thermodesorption of chemisorbed ammonia (NH_3-TPD). The structure was investigated through IR spectrum on Nexus 670 Nicolet FT-IR, element analysis on the Varioel3 from German Elementar and Quancachrome BET 02108-KR-1. The thermal stability was determined by thermogravimetric analysis (TG) on Tgalsdta851e/5Fl1100.

2.3 Catalytic Reactions

2.3.1 The Esterification of Acetic Acid and Ethanol

The esterification of acetic acid and ethanol was carried out as a testing reaction for the novel acid catalyst. A mixture of ethanol (0.02 mol) and acetic acid (0.02 mol) were reacted over different catalysts (0.05 g) at room temperature. The products were analyzed by gas chromatography using an inner standard method. Here the comparative studies of the novel catalyst with different catalysts were taken. On completion, the catalyst was recovered by filtering and washing with acetone, then dried in an oven at 453 K for about 1 h. The reusability of the novel catalyst was investigated and the element analysis of the recycled catalyst was performed.

2.3.2 The Acetalization of the Benzoldehyde and 1,2-Ethandiol

The acetalization of the benzoldehyde and 1,2-ethandiol was carried out as another testing reaction for the novel acid catalyst. Benzoldehyde 0.1 mol,10 mL cyclohexane, 1,2-ethandiol 0.1 mol and the catalyst 0.05 g were mixed together in a three necked round bottomed flask equipped with a magnetic stirrer and a thermometer, and a Dean-Stark apparatus was used to remove the water continuously from the reaction mixture. The process of the reaction was monitored by GC analysis. On completion, the catalyst was recovered by filtering off and washing with acetone, then dried in an oven at 453 K for about 1 h. The reusability of the novel catalyst was investigated and the element analysis of the recycled catalyst was performed.

3 Results and Discussion

3.1 Characterization of the Novel Catalyst

3.1.1 The Acid Properties of the Novel Catalyst

The average molecular weight of the novel catalyst was 5,800 with average number of the polymer 32 using the oil-well cementing services according to the method provided by Miller [18]. The acidic amount of the novel catalyst determined through the neutralization titration gave the results of 4.0 mmol/g, a little lower than that of pure PTSA (5.8 mmol/g). The catalyst owned much higher acidity than that of the common heterogeneous acid catalysts such as Nafion and Amberlyst-15 (0.8 mmol/g). It can be seen from Scheme 1 that the acidity of the catalyst originated from the sulfonic groups of the PTSA molecular, so the acidity in the novel catalyst was strong, which was confirmed by thermodesorption of chemisorbed ammonia (NH_3-TPD). The results showed that the catalyst had high acid strength in which ammonia desorbed ranging from 673 to 873 K a little higher than that of the pure PTSA. NH_3-TPD gave the acidity of 5.0 mmol/g, which indicated that many acid sites might hide inside the novel catalyst (Fig. 1). And the BET surface area using nitrogen adsorption isotherms at the

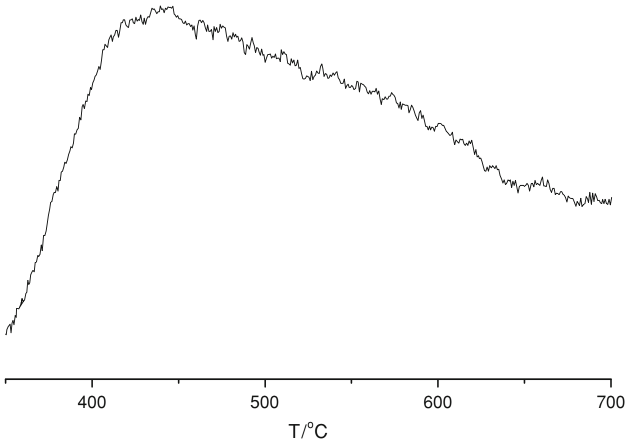

Fig. 1 The NH_3-TPD profile of the novel catalyst

temperature of liquid nitrogen which gave the result of 23 m^2/g also support the results above. Also it can be seen from Scheme 1 that almost every benzyl ring was attached with the sulfuric groups. As a result, the catalyst should own the acidity as high as 5.4 mmol/g in theory. Here some sulfonic groups might drop from PTSA molecular and not only the linear chains but also some branches or cross-linked structures were formed during the process. It was in accordance with the results of the element analysis. The elemental analysis gave the results: C 54.3%; H 5.3%; S 16.2%; O 24.2% with the theoretic results: C 52.1%; H 4.3%; S 17.4%; O 26.2%. The results indicating that the almost all the element S existed in the catalyst in the form of sulfonic groups according to the result of NH_3-TPD. The carbon and hydrogen content was a little more than the theoretic value, which indicated the more CH_2 groups in the catalyst, namely some branches or cross-linked structures in the catalyst. But the main structure should be as shown in Scheme 1.

3.1.2 The TG Curve of the Novel Catalyst

The thermal stability of the catalyst was an important property for the catalyst. TG curve for the catalyst was shown in Fig. 2. The decrease in gravity began at about 200 °C which indicated the decomposition of the catalyst. The catalyst showed very high thermal stability compared to Amberlyst-15 below 120 °C. The covalent chemical bonds connection made the catalyst owned high thermal stability. This discovery made it possible that the catalyst could be used for the high temperature applications.

3.1.3 The IR Spectra of the Novel Catalyst

The IR spectra of the catalyst and PTSA were compared (Fig. 3). The results showed that the differences between them were not obvious. It can be seen from Scheme 1 that the catalyst owned the similar structure to that of PTSA. The sulfuric group absorbability at 1,040 and 1,195 cm^{1} existed in both of them. The PTSA showed stronger absorbability than the novel catalyst and the peaks during 500–1,000 were different with each other due to the polysubstitution benzyl rings of the catalyst.

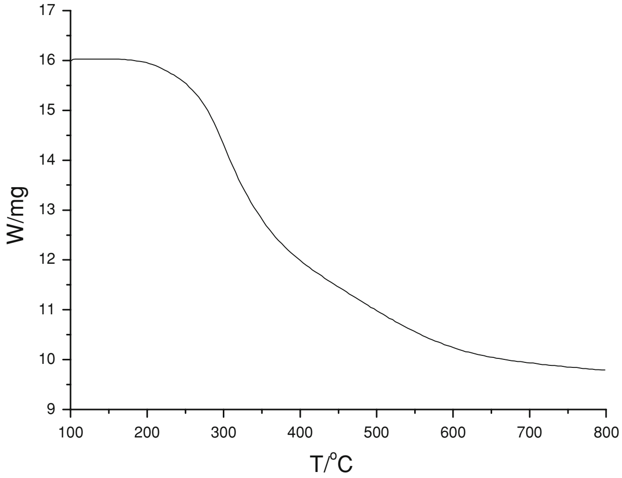

Fig. 2 The TG curve of the novel catalyst

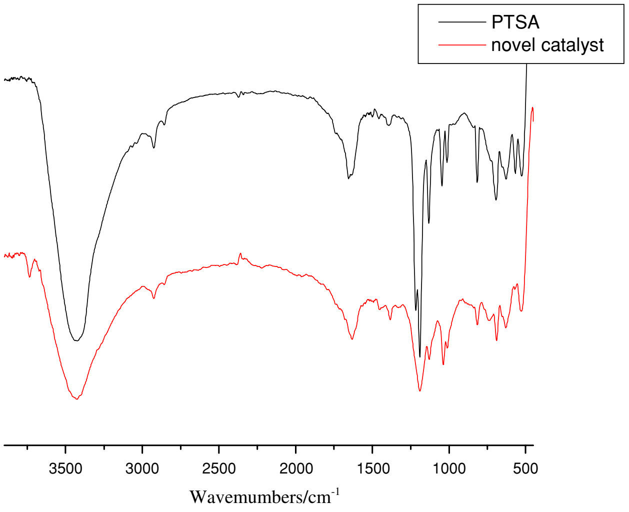

Fig. 3 The IR spectra of the novel catalyst

3.2 Catalytic Reactions of the Catalyst

3.2.1 The Esterification of Acetic Acid and Ethanol

For comparison, the results of concentrated sulfuric acid (>96%), PTSA and Amberlyst-15 were also shown (Fig. 4). Amberlyst-15 was obtained from Fluck with the acidity of 0.8 mmol/g. The novel catalyst exhibited an extremely high activity for the formation of ethyl acetate. The activity is much higher than that of Amberlyst-15 and is comparative to that of sulfuric acid and PTSA. After the

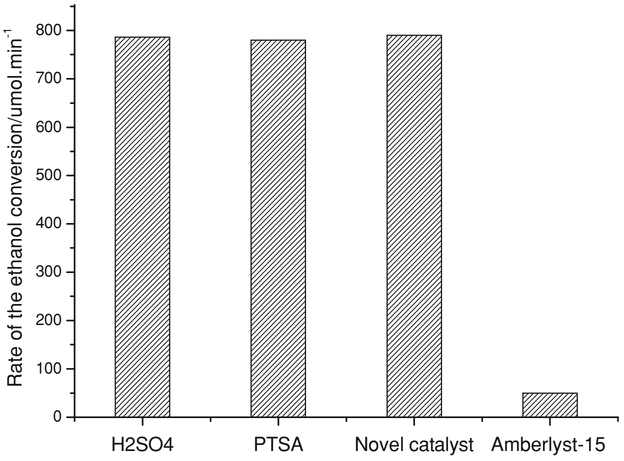

Fig. 4 The esterification of acetic acid and ethanol (rates were measured in the early stage of the reaction (1 h)). The reaction was carried out R.T. (25 °C) ethanol (0.02 mol), acetic acid (0.02 mol), catalyst (0.5 g). The conversion and selectivity were determined by GC using an internal standard

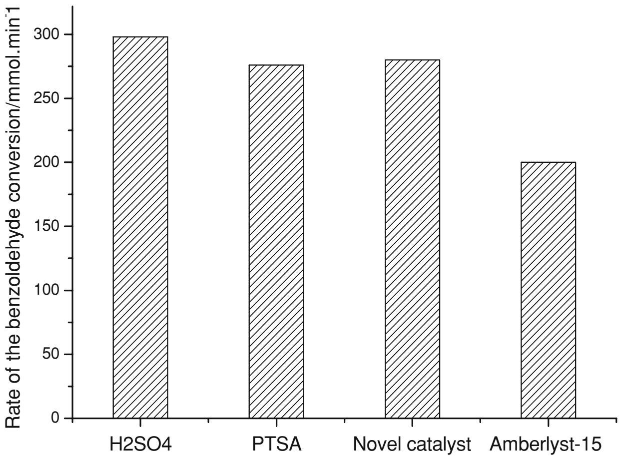

Fig. 5 The acetalization of benzoldehyde and 1,2-ethandiol (rates were measured in the early stage of the reaction (1 h)). The reaction was carried out under Dean–Stark conditions: Benzoldehyde 0.1 mol, 10 mL cyclohexane, 1,2-ethandiol 0.1 mol and the catalyst 0.05 g. The conversion and selectivity were determined by GC using an internal standard

reaction had reached equilibrium (4–6 h), the novel catalyst was recovered by filtration and recycled for tenth reaction. The results showed that both the activity for the formation of ethyl acetate and the sample composition remained unchanged, even after the sample had been recycled for a tenth time, which confirmed the high stability of the novel catalyst once more. In order to confirm that no H_2SO_4 remained in the catalyst, the catalyst was stirred with water for 12 h at room temperature. After catalyst separation by filtering, the liquid phase was tested for the reaction and no product was formed in this situation. Meanwhile, there was no SO_4^2 was detected in the liquid phase.

3.2.2 The Acetalization of Benzoldehyde and 1,2-Ethandiol

Figure 5 showed the comparative study of the different catalysts for the acetalization of benzoldehyde and 1,2-ethandiol. Amberlyst-15 showed relatively low activity for the reaction. The novel catalyst showed even a little higher activity than that of the homogeneous catalyst PTSA because of its higher acid density. On competition (2 h), the novel catalyst was recovered by filtration and recycled for 10th reaction. It was also confirmed that both the activity for the formation of ethyl acetate and the sample composition remained unchanged, even after the sample had been recycled for a 10th time.

4 Conclusion

A novel heterogeneous strong acid catalyst has been prepared through a simple procedure. The catalyst owns the advantages of high strength and density of the acid sites and high thermal and chemical stability. The novel catalyst has the comparative catalytic activities for the esterification and acetalization to the homogeneous acid catalysts such as H_2SO_4 and PTSA. Furthermore, the low cost through simple procedure made the catalyst hold great potential for the replacement of the homogeneous catalysts for the green process.

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