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A novel solid acid for synthesis of bisphenol A

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A novel solid acid was prepared from boric, phosphorous and sulfuric acid by a simple method, and characterized by FT-IR, XRD and TG. Surprisingly, the prepared solid acid is an effective catalyst for the synthesis of bisphenol A from condensation of phenol with acetone. The high conversion of acetone (91.8%) and selectivity of bisphenol A (93.4%) were achieved in the presence of the novel catalyst.

KEY WORDS: bisphenol A; solid acid; synthesis; catalyst.

1. Introduction

Bisphenol A [2, 2-bis (4-hydroxyphenyl) propane, BPA] is a very important feedstock for the production of epoxy resins, polycarbonate and numbers of other polymers. The widely used method for its preparation is the acid-catalyzed condensation of phenol with acetone (scheme 1). In this process of the preparation, mineral acid catalysts, conventionally used in acidic catalysis, should be avoided due to their environmentally unfriendly nature [1]. It was reported that ion exchange resins or modified ion exchange resins are worldwide used to produce BPA in industry [2–5], and they show good catalytic functions. But, there are some problems, such as fouling and thermal stability for these resin catalysts in the reaction process. In order to overcome these drawbacks, many solid acid catalysts were attempted for BPA synthesis. Although these solid acid catalysts, such as zeolites [6], heteropoly acid ($H_3PW_{12}O_{40}$) [7], heteropoly acid supported on K-10 clay [2] or encapsulated in MCM-41 [8], and sulfonic acid functionalized mesoporous MCM silica [9], etc., were reported to be active for BPA synthesis, these systems also have disadvantages of low conversion, higher reaction temperature or prolonged reaction time, etc. Besides, Lewis acid ionic liquid Et_3NHCl–$AlCl_3$ has been used as catalyst for bisphenol A synthesis in liquid phase reaction [10], it could be accomplished with high yield and good selectivity, but the product separation from catalyst is more difficult. Preparation of new solid acid catalysts with good catalytic performance is, therefore, a very important task for BPA synthesis. In the present study, a novel solid acid was prepared from three usual acids by a simple method, and its high catalytic activity for phenol and acetone condensation to BPA in the liquid phase was presented for the first time.

2. Experimental

2.1. Preparation and characterization

Concentrated sulfuric, boric and phosphoric acid are efficiently mixed at room temperature according to an appropriate molar ratio for an hour. The mixture becoming thickness and blocky was dried at 100 °C for 24 h under vacuo; and then a solid acid was obtained when it was cooled down to the room temperature.

IR spectrum of the prepared solid acid was recorded on Nicolet 360 FT-IR spectrophotometer with pressed KBr pellet in the 4000–400 cm^{-1} region, its thermal stability was analyzed with thermogravimetric analysis, which was performed on a PE Diamond instrument (Perkin–Elmer) in static air with a heating rate of 5 °C/min from 30 to 600 °C. Powder X-ray diffraction pattern of the sample was recorded on a D/max-rB X-ray diffractometer (RIGAKU) using CuK_α radiation.

2.2. Synthesis of BPA

An appropriate amount of the prepared solid acid, phenol and acetone were charged in a glass reactor provided with a flux condenser, and a magnetic stirrer and then the reactor was heated to a desired temperature in an oil bath. After the reaction was performed in homogeneous phase for some hours, the reaction mixture was cooled down to about 45 °C, the catalyst was automatically precipitated, and separated from the reaction solution through immediate filtration. The solution samples were analyzed by a HPLC (LC-6A, Shimudzu) and LC-MS (Agilent 1100) with a column of CenturySIL BDS, 5 μ, 250×4.6 mm and methanol–water (63:37, V/V) used as the mobile phase with the

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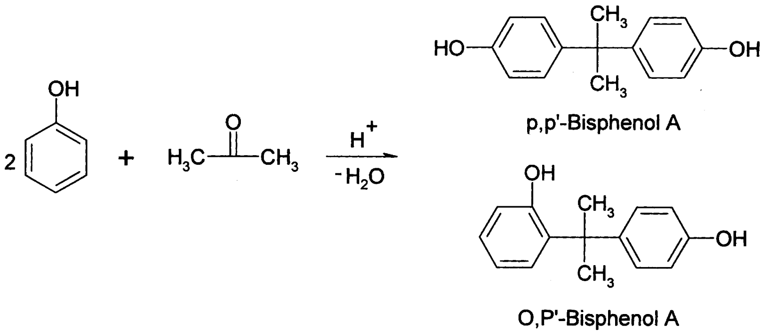

Scheme 1.

flow rate of 1 mL min^{-1}. IR spectra of the target product were also recorded on Nicolet 360 FT-IR spectrophotometer with pressed KBr pellet in the 4000–400 cm^{-1} regions, and ^1H NMR spectrum was measured on a AV 300 spectrometer (400 MHz) in CD_3COCD_3.

3. Results and discussion

3.1. *Characterization of the solid acid*

Powder XRD pattern of the sample indicated that B_2O_3 crystal with cubical structure may exist in the prepared solid acid, as shown in figure 1, which was confirmed by the diffraction peaks observed at $2\theta = 15°$ and 28° [11]. However, BPO_4 crystal in the solid acid may be also recognized by the peaks at 24°, 29°, 40°, 48°, 60° and 63°, while BPO_4 is a copolymer of boric oxide and phosphorous oxide, its crystal structure composed of BO_4 and PO_4 tetrahedrons is, similar to that of silica [12,13]. These findings showed that the crystal of the solid acid was composed of boric and phosphorous oxides.

The infrared spectrum of the prepared solid acid is given in figure 2. As shown, the absorption bands at 1466.6 cm^{-1} is attributed to B–O stretching vibration associated with trigonal BO_3, which is a fundamental building block in the structure of B_2O_3 [14]. However, the bands at 1081.2, 925.5, 622.7 and 555.5 cm^{-1} are ascribed to B–O and P–O stretching, O–B–O and O–P–O bending vibration in BO_4 and PO_4 tetrahedrons, respectively [13]. These findings indicate that two kinds of fundamental building blocks, trigonal BO_3 and tetrahedral BO_4, coexist in the solid acid, which is in agreement with the result obtained by the XRD pattern. It is worthy to note that wide and strong band observed at 1000–1220 cm^{-1}, which is the feature of S=O stretching vibration [15]. And the absorption band at 1641.0 cm^{-1} is due to the H_2O adsorbed on the surface. Furthermore, a very wide and strong band observed at 3100–3500 cm^{-1} is attributed to stretching vibration of hydroxyl that may be assigned to borate–OH, phosphate–OH and less water in the solid acid, which may also be approved by the following thermal analysis.

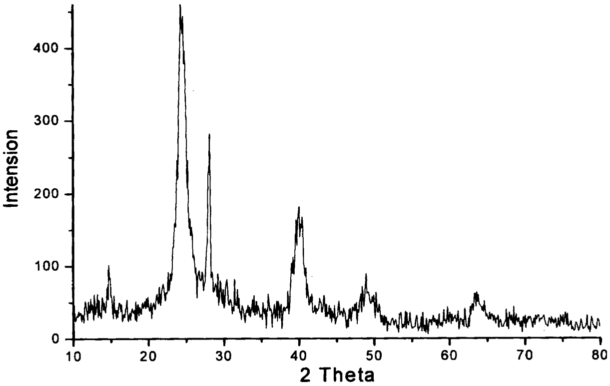

Figure 1. XRD pattern of the prepared solid acid.

There are two stages of weight loss in a typical thermogram for the solid acid sample, as shown in figure 3. The first one was evidently observed in the range of temperatures from 110 to 200 °C, showing that the weight loss may result from the removal of the water formed between hydroxyls and less free water. Moreover, the second one from 200 to 300 °C may be attributed to the water removal between other parts of hydroxyls and decomposition of sulfate ions, which reveals that abundant hydroxyls are included in the solid acids.

Through the above spectral analysis, a conclusion was obtained that the prepared solid acid is a polymer of boric oxide and phosphorous oxide supported by SO_4^{2-}, which can be denoted as $SO_4^{2-}/BO_x–PO_x$. It is the existence of surface sulfur complexes formed by the interaction of oxides with sulfate ions in SO_4^{2-}/BO_xPO_x that endows the solid acid with superacidic properties [16,17]. This superacidic nature was completely presented by the synthesis reaction of BPA from phenol and acetone catalyzed by the solid acid.

3.2. *Catalytic performance of solid acids*

The solid acid prepared from Boric acid, sulfuric acid and phosphoric acid catalyses the condensation of phenol with acetone at 70 °C to yield a mixture of bisphenol A and its *o*, *p*′- or/and *m*, *p*′-isomer. The other by-products, such as mesityl oxide and chroman

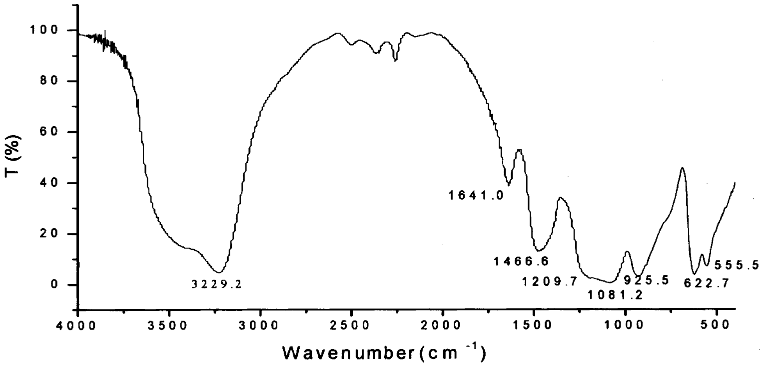

Figure 2. IR spectrum of prepared solid acid.

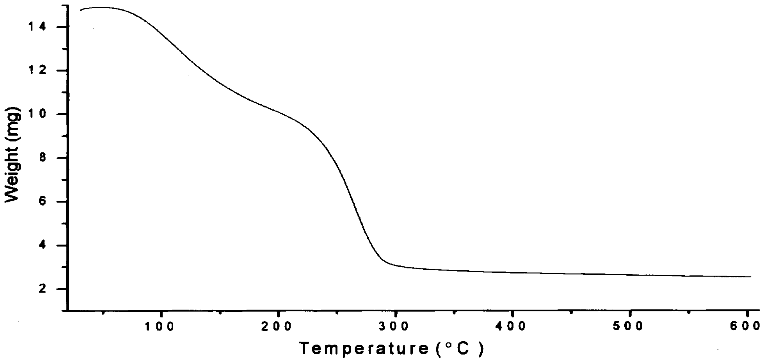

Figure 3. the TG curve of the solid acid.

derivatives, etc., were not detected. The catalytic reaction was performed in homogeneous phase due to the solubility of the solid acid in the reaction system. The activities of the solid acids prepared at various amounts of acids and calcination temperatures are summarized in table 1, in which n_P, n_B and n_S denote molar ratio of phosphoric, boric and sulfuric acid used in the preparation process. As easily seen, no activity for the synthesis reaction was presented without H_2SO_4 added during the preparation of the catalyst (Entry 1), and the conversion of acetone was evidently increased and the selectivity of BPA slightly decreased with the increase in the molar ratio of H_2SO_4. When the molar ratio in the solid acid was increased from 0.33 to 0.50, the conversion was increased from 79.9% to 91.0%, while the selectivity was decreased from 82.4% to

Table 1
Conversion and selectivity of BPA synthesis with various catalysts

Entry	Catalysts	$T_{\text{calcin.}}$ (K)	Conver (%)	Select. (%)	Yield (%)
1	n_P:n_B:n_S = 1:1:0	373	0	0	0
2	n_P:n_B:n_S = 1:1:1	373	79.9	82.40	65.8
3	n_P:n_B:n_S = 1:1:2	373	91.0	80.1	72.9
4	n_P:n_B:n_S = 1:2:3	373	91.8	88.9	81.6
5	n_P:n_B:n_S = 1:2:1	373	84.5	80.1	67.7
6	n_P:n_B:n_S = 1:3:1	373	80.8	80.3	64.9
7	n_P:n_B:n_S = 1:2:3	393	58.5	85.0	49.7
8	n_P:n_B:n_S = 1:2:3	413	49.9	88.5	44.2
9	n_P n_B:n_S = 1:2:3	433	46.9	90.0	42.2
10	n_P:n_B:n_S = 1:2:3	453	49.1	93.4	45.9
11	P_2O_5		3.5	77.0	2.7
12	H_3BO_3		0	0	0.
13	P_2O_5 + H_3BO_3		0	0	0
14	Reused catalyst	373	1.8	100	1.8

Conditions: Reaction temperature 343 K, time 7 h, molar ratio of phenol/acetone 8:1, catalyst 2 g.

80.1%. This phenomenon suggested that stronger acidity of the catalyst is disadvantageous to selectivity of BPA, because it may result in continuous reaction of the target product to produce a by-product, and the supported sulfate ions play a crucial role for the acidity of the solid acid indeed. However, when the ratio of H_2SO_4 holds unchangeable, the amount of boric acid is basically independent of the conversion and selectivity (Entry 2, 5 and 6), showing that its amount has not to do with the acidity of the catalyst, but it can shorten the solidification time of the catalytic material and Brönsted acid from sulfate ions in the catalyst plays a main role for the reaction, rather than Lewis acid from boric oxide. For the catalyst prepared at n_P:n_B:n_s = 1:2:3 and calcined at temperature of 373 K, the conversion of acetone reached to maximum 91.8% with the BPA selectivity of 88.9%, which is almost the maximum conversion and selectivity for BPA synthesis using solid acids as catalysts that have been reported so far. As the calcination temperature increased above 373 K, the selectivity of BPA was remarkably increased, although the activity was almost constant (Entry 7–10), which may be ascribed to the reduction of the acidity due to the decomposition of sulfate ions at higher treatment temperatures. Finally, the selectivity of BPA reached up to 93.4% (Entry 10). In addition, when the catalytic system is only made of P_2O_5, H_3BO_3 or a mixture of P_2O_5 + H_3BO_3, as shown in Entry 11–13, a very poor activity to the reaction is obtained for P_2O_5 catalyst, the conversion was only 3.5%, and no activity for H_3BO_3 or a mixture of P_2O_5 + H_3BO_3. This result further testifies that the prepared material is not a simple mixture of P_2O_5 and H_3BO_3, while it is really a copolymer composed of PO_x and BO_y supported by SO_4^{2-}.

The white crystal of BPA was obtained with the purity of about 100% and has fully been identified by IR and ^{1}H NMR spectrum. IR spectrum: 3100–3500, 2970.0, 1666.7, 1588.8, 1510.2, 1447.9, 1401.2, 1244.7, 1182.4, 823.5, 542.5 cm^{-1}; ^{1}H NMR: δ = 1.59, 6.71, 6.74, 7.04, 7.07, 8.06 ppm.

3.3. *Effect of reaction conditions*

For the catalytic system using the catalyst shown in Entry 4 of table 1, the conversion increased rapidly with reaction time in the range from 3 to 7 h. After 7 h of reaction time, the acetone conversion reached at the maximum 91.8%, with a BPA selectivity of 88.9% (figure 4). Thereafter, as the time increases, the catalyst deactivation manifests with a decrease of conversion, and the selectivity displays small changes. After 9 h, the conversion of acetone is 62.9%, while the selectivity of BPA is 90.1%. After 11 h, conversion is 48.2%, selectivity drops to 81.8%. The deactivation of the catalyst was likely ascribed to the interaction of the catalyst with water produced during the reaction.

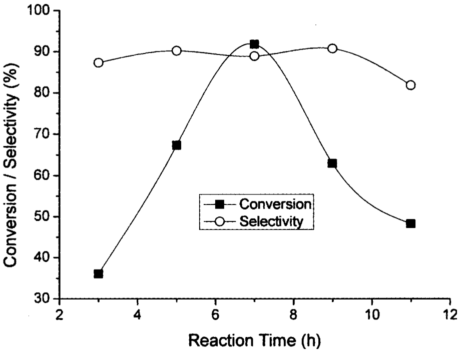

Figure 4. The conversion of acetone and selectivity of BPA on reaction time phenol/acetone = 8:1 (mol ratio), T = 70 °C, P_{catalyst} = 10%.

As the raise of reaction temperature, the conversion and selectivity increased from 85.4% and 81.3% at 60 °C to 91.8% and 88.9% at 70 °C, respectively, and then rapidly fell to 61.1% and 78.3% at 100 °C (figure 5). This changing rule of the conversion with the temperature is maybe attributed to the thermodynamic and kinetic character of the synthesis reaction. In order to discuss the character, the heat of the reaction was calculated by means of formation heats of various compounds involved in the reaction, in which the formation heat of BPA was estimated by additivity rules reported by S. W. Benson *et al.* [18]. As a result, the heat of the reaction was obtained to be $\Delta rH^{\emptyset}$ = 69.2 KJ/mol, indicating that it is an endothermic reaction. Consequently, in view of the thermodynamics, the increase of the reaction temperature is of a great advantage to the generation of BPA. Similarly, raise of the reaction temperature can generally accelerate the reaction and shorten the reaction time approaching to the equilibrium from a kinetics point of view. Therefore, the speedy decrease of the conversion as the temperature increased from 70 to 100 °C was indeed ascribed to the deactivation of the catalyst. This can also be validated by the discussion of the following section.

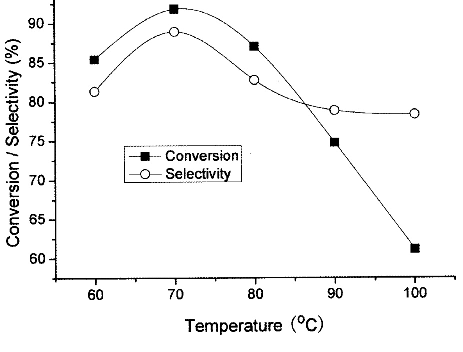

Figure 5. The conversion of acetone and selectivity of BPA on reaction temperature phenol/acetone 8:1 (mol ratio), t = 7 h, P_{catalyst} = 10%.

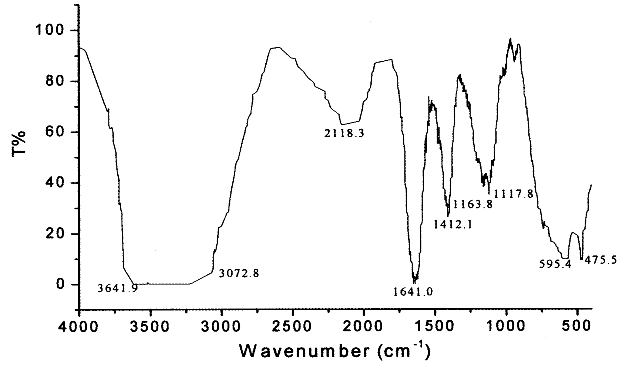

Figure 6. IR spectrum of reused catalyst.

3.4. *Deactivation of the catalyst*

To investigate the deactivation, the catalyst was extracted by filtration under reduced pressure in the end of reaction and then reused for the next run after being dehydrated. It was found that the activity of the reused catalyst was negligible (Entry 14 in table 1); the conversion was only 1.8%. Thus, it was directly concluded that the catalyst was deactivated in the course of the reaction. This reason of deactivation could be explained by IR spectrum of the reused catalyst as shown in figure 6. As compared with fresh catalyst, the strong and wide absorption band at 1000–1220 cm^{-1}, which is the feature of S = O stretching vibration, was substituted by two split bands at 1163.8 and 1117.8 cm^{-1}. These two bands may be attributed to B–O–B bending vibration associated with trigonal BO_3 and B–O stretching vibration in BO_4 tetrahedron, respectively. The characteristic bands associated with S = O stretching vibration disappeared, which suggested loss of sulfate ions by means of dissolving out of the solid acid into the reaction solution in the reaction process. It is the loss of sulfate ions that result in reduction acidity, as well as deactivation of the catalyst. At the same time, a weak and wide band at 2118.3 cm^{-1} appears in IR spectrum of reused catalyst, which is probably attributed to combined phosphate hydroxyls [19]. The appearance of the combined hydroxyl bands implied that the structure or composition of the catalyst was changeable, as compared with that of fresh catalyst. It was another reason of rapid deactivation of the catalyst. Consequently, loss of sulfated ions and, formation of combined phosphate hydroxyls greatly led to conversion falling down, especially at higher reaction temperatures and prolonged reaction time. However, the detail deactivation mechanism of the catalyst needed to be further investigated.

4. Conclusion

A novel solid acid catalyst was prepared from boric acid, concentrated sulfuric acid and phosphoric acid by a simple method, and it was affirmed as a polymer containing boric oxide, phosphorous oxide with supported SO_4^{2-}, by IR, XRD and TG. Therefore, it possesses stronger acidity due to the interaction of oxides with supported SO_4^{2-} and it is an effective catalyst for the synthesis of bisphenol A by condensation of phenol with acetone. The high yield and selectivity of bisphenol A were obtained. In addition, deactivation of the catalyst was discussed; the deactivation reason was recognized as loss of sulfated ions and formation of combined phosphate hydroxyls by comparison of IR spectrum of reused catalyst with that of fresh one.

Acknowledgments

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References

[1] P. Michele, C. Giuseppe, B. Pedido BR 7,903,483 (1979).
[2] G.D. Yadav and N. Kirthivasan, Appl. Catal. A Gen. 154 (1997) 29.
[3] A.E. Donald, B.R. Lawrence, C. Ye-mon, and J. R. Lawrence WO 9,734,688 (1997).
[4] K. Jeřábek, L. Hanková, Z. Prokop and E.G. Lundquist, Appl. Catal. A Gen. 232 (2002) 181.
[5] M. Kawase, Y. Inoue, T. Araki and K. Hashimoto, Catal Today 48 (1999) 199.
[6] A.P. Singh, Catal. Lett. 16 (1992) 431.
[7] M.N. Timofeeva, G.M. Maksimov, V.A. Utkin and V.A. Likholobov, Kinet. Catal. 41 (2000) 767.
[8] K. Nowinska, and W. Kaletn, Appl. Catal. A Gen. 203 (2000) 91.
[9] D. Das, J. Lee and S. Cheng, J. Catal. 223 (2004) 152.
[10] L.J. Jia, C.Y. Hua, L.Y. Dai and Y.K. Shan, React. Kinet. Catal. Lett. 81 (2004) 235.
[11] Z.P. Li, and L. Gao, J. Inorg. Mater. (in Chinese) 19 (2004) 249.
[12] A. Baykal, M. Kizilyalli, M. Toprak and R. Kniep, Turk. J. Chem. 25 (2001) 425.
[13] Z. Shan, Chem World (in Chinese) (2003) 289.
[14] B.Q. Xu, and S.B. Cheng, Acta Phys. Chim. Sin (in Chinese) 17 (2001) 443.
[15] J.R. Sohn, and S.H. Lee, Appl. Catal. A Gen. 266 (2004) 89.
[16] J.R. Sohn, W.C. Park and H.W. Kim, J. Catal. 209 (2002) 69.
[17] T. Jin, T. Yamaguchi and K. Tanabe, J. Phys. Chem. 90 (1986) 4194.
[18] S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haugen, H.B. O'neal, A.S. Rodgers, R. Shaw and R. Walsh, Chem. Rev. 69 (1969) 279.
[19] G.B. Rong and S.Z. Zhu, *Spectral Data-Structural Analysis of Organic Compounds*. (East China University of Science and Technology Press, Shanghai, 2002) p. 207 (in Chinese).