Preparation of bisphenol-A over zeolite catalysts

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The reaction of phenol and acetone to give bisphenol-A (4,4′-isopropylidenediphenol) has been investigated using zeolite as catalysts. The zeolites are less active and selective than the cation-exchange resin, Amberlyst-15.

Keywords: Synthesis; bisphenol-A; zeolites; cation-exchange resin

1. Introduction

Various catalysts, such as acidic cation-exchange resins [1–5], mineral acids [6–8] and heteropoly compounds [9] have been used for the production of bisphenol-A, a raw material for making polycarbonates and epoxy resins. The use of acidic zeolites for the production of bisphenol-A is of interest. In principle, they should be more shape selective than other catalysts. The present paper describes a comparative study of preparation of bisphenol-A over zeolites and cation-exchange resin, Amberlyst-15 (used commercially at present). The use of zeolites as catalysts in the reaction has not been reported so far.

2. Experimental

Zeolites RE-Y, H-Y, H-mordenite and cation-exchange resin (Amberlyst-15) were obtained from United Catalyst India Limited. H-ZSM-5 was synthesized according to a Mobil patent [10]. The properties of H-ZSM-5, H-mordenite, H-Y and RE-Y zeolites used in this study are presented in table 1. Zeolite samples were heated in air at 673 K for 4 h before use in experiment. Amberlyst-15 was also activated at 393 K for 4 h. All the chemicals used were high purity (AR) grade.

Bisphenol-A was prepared by condensing phenol and acetone (mole ratio 5 : 1) in the presence of zeolites. The reaction was carried out in a 50 ml round

Table 1
Properties of H-ZSM-5, H-mordenite, H-Y and RE-Y zeolites [a]

Zeolite	Channel system		Si/Al ratio	Degree of H^+-exchange (%)	Degree of RE-exchange (%)	Surface area (m^2/g)
	pore dimension (nm)	characteristics				
H-ZSM-5	0.54×0.56 0.51×0.55	three-dimensional channel	30	>98	–	405
H-mordenite	0.67×0.70	uni-dimensional channel	10	>98	–	552
H-Y	0.74	three-dimensional channel	2.4	>98	–	890
RE-Y	0.74	three-dimensional channel	2.4	18	80	750

[a] 100% crystalline zeolite samples.

bottom flask immersed in a thermostated oil bath. A mixture of phenol, acetone and zeolite (20% of reactants) was added to the flask and heated to 363 K. The reaction was carried out at atmospheric pressure under reflux conditions and product samples were drawn periodically. The product was analysed with a gas-chromatograph (Hewlett-Packard model 5890 series II) having a flame ionization detector and 50 m × 0.2 mm capillary column packed with methyl silicon gum. A few samples were also analysed with a Shimadzu GC-MS spectrometer (model GC-MS-QP 2000 A) to provide qualitative identification of the reaction products.

3. Results and discussion

Gas-chromatograph and GC-MS spectrometer analyses of the reaction products revealed the presence of other organic compounds besides bisphenol-A. Bisphenol-A (I), 2,4′-isopropylidenediphenol (II), 4′-hydroxyphenyl-2,2,4-trimethyl chroman I (III) and 4′-hydroxyphenyl-2,4,4-trimethyl chroman II (IV) were the only reaction products present in large quantity. The other compounds (V) were found in trace quantity. The product pattern is generally consistent with the reaction scheme (fig. 1) reported over other acidic catalysts [11,12].

The results show a strong influence of different catalysts on the total conversion of phenol (table 2). The conversions of phenol over RE-Y, H-mordenite, H-Y, H-ZSM-5 and Amberlyst-15 were found to be 4.61, 2.88, 0.51, 0.42, 20.14%, respectively. Table 2 compares the catalytic activity, product distribution and product ratios obtained over different catalysts between 4 and 27 h. In the case of zeolites, RE-Y gave the highest activity while H-Y and H-ZSM-5 possess little activities. The highest activity of RE-Y may be due to its higher

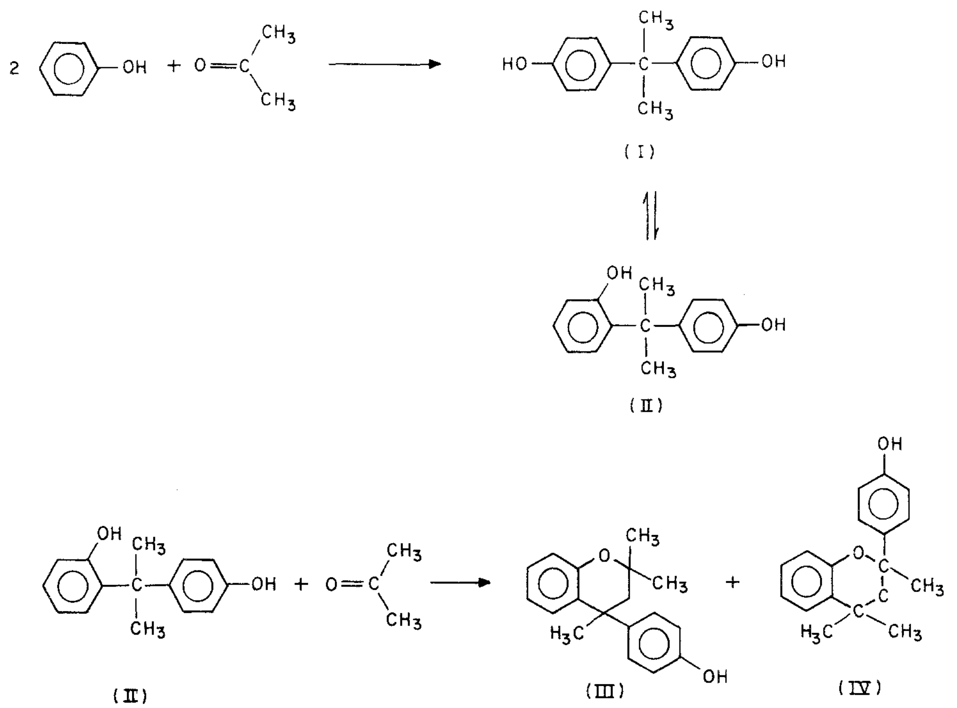

Fig. 1. Reaction scheme for the synthesis of bisphenol-A (I) and other products (II, III, IV).

concentration of acid sites compared to the H-Y, H-mordenite and H-ZSM-5 zeolites. The major product of the reaction is found to be the para isomer, I. The relative activities of various catalysts decrease in the order:

Amberlyst-15 > RE-Y > H-mordenite > H-Y > H-ZSM-5.

Table 2
Results of the reaction of acetone with phenol in the presence of zeolites and cation-exchange resin

Catalyst	Reaction time (h)	Conversion of phenol (wt%)	Product distribution [a] (wt%)				Product ratios	
			I	II	III+IV	V	II/I	III+IV/I
Re-Y	5	1.08	59.26	16.02	4.62	20.10	0.27	0.08
	17	4.35	60.00	19.08	11.49	9.43	0.32	0.19
	27	4.61	57.91	19.10	15.19	7.80	0.32	0.26
H-mordenite	4	1.12	38.13	28.59	8.00	25.28	0.75	0.21
	16	2.52	37.42	29.56	9.35	23.67	0.79	0.25
	27	2.88	36.80	31.25	11.12	20.83	0.84	0.30
Amberlyst-15	5	8.74	85.37	3.41	2.56	8.66	0.04	0.03
	17	19.50	88.72	4.44	3.54	3.30	0.05	0.04
	27	20.14	89.57	5.06	3.54	1.83	0.06	0.04

[a] See text for the identity of products I–IV.

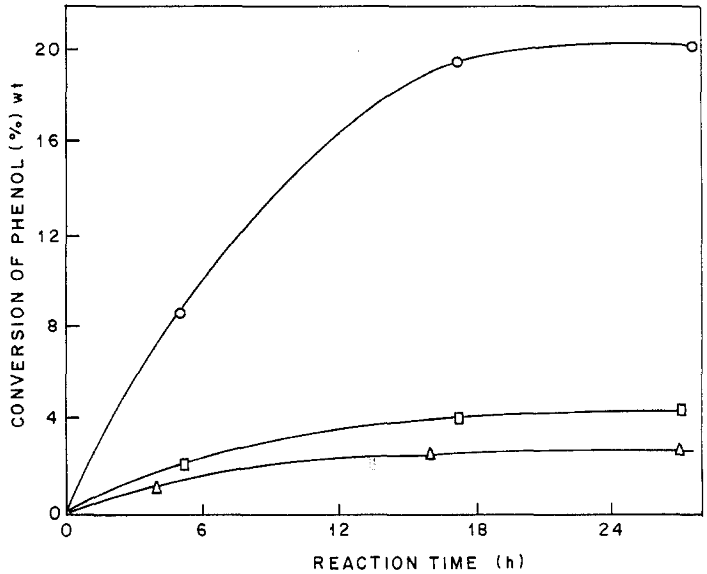

Fig. 2. Conversion of phenol as a function of reaction time over RE-Y (□), H-mordenite (△) and Amberlyst-15 (○).

The measured product ratios of II/I over Amberlyst-15, RE-Y and H-mordenite at 27 h reaction time were found to be 0.06, 0.32 and 0.84, respectively. The corresponding product ratios of III + IV/I were 0.04, 0.26 and 0.30, respectively. The results obtained over zeolites indicate that the increase in the concentration of 2,4′-bisphenol-A (II) and chroman isomers (III + IV) in the reaction products may be attributed to the further isomerization of I to II and condensation of acetone with II, respectively (fig. 1) [13,14]. Thus the concentration of the undesired products (II, III, IV) increases in the order:

Amberlyst-15 < RE-Y < H-mordenite.

The influence of various catalysts (Amberlyst-15, RE-Y, H-mordenite) on phenol conversion was studied over a period of 27 h (fig. 2). The conversion of phenol increases steadily with time (fig. 2).

4. Conclusions

The data indicate that acidic zeolites with large pore openings (> 7.0 Å) are active in this process. Their activity for the formation of bisphenol-A is, however, lower than that of the cation-exchange resins. Hence, either the reaction occurs on the external surface of the zeolite crystals or factors other than geometric control the selective formation of bisphenol-A.

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