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Bisphenol F synthesis over mesoporous aluminosilicate MCM-41 molecular sieves

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Liquid-phase bisphenol F synthesis from phenol and formaldehyde condensation reaction in the presence of water over mesoporous aluminosilicate MCM-41 catalysts ($Si/Al = 50\,mol\,mol^{-1}$) prepared by four different methods: sol–gel, hydrothermal, grafting and template-cation exchange at 90 °C has been investigated. The aluminum-incorporated MCM-41 samples prepared by different methods showed high activity in the bisphenol F synthesis process. However, the procedure of Al introduction into the framework of MCM-41 determines their catalytic activity in the acid-catalyzed phenol and formaldehyde reaction. The Al : MCM-41 prepared by grafting method exhibits the highest activity in the bisphenol F synthesis process.

KEY WORDS: aluminosilicate MCM-41; bisphenol F; phenol; formaldehyde.

1. Introduction

Bisphenol F is an important chemical and/or intermediate for the preparation of industrially useful epoxy resins, phenolic resins, polycarbonates, etc., in the molding, casting, sealing, coating, encapsulating, adhesives, laminating, reinforced plastics, and other industrial chemicals. It is a commercial name of the mixture of 4,4′-, 2,4′-, and 2,2′-dihydroxyphenylmethanes [$CH_2(C_6H_4OH)_2$]. Bisphenol F is a condensation product of 2-mol phenol and 1-mol formaldehyde. During this synthesis process, a small amount of higher molecular weight condensation product (mainly trisphenol isomer) is also formed. The main reaction pathway is shown in scheme 1. The conventional method for the preparation of bisphenol F is based on the condensation reaction of phenol and formaldehyde (formalin) using a liquid protonic acid (e.g., oxalic acid, phosphoric acid, hydrochloric acid, etc.) as catalyst [1–3]. However, the use of homogeneous acid catalysts poses several problems, such as difficulty in separation and recovery, disposal of the spent catalyst, corrosion, high toxicity, etc. Development of easily separable and reusable solid catalysts having high activity in the bisphenol F synthesis process is, therefore, of great practical importance.

To the best of our knowledge, there is only one example of use of a heterogeneous solid acid ($H\beta$) to mediate bisphenol F synthesis disclosed so far [4]. MCM-41 is known to be mesoporous silica with a uniform hexagonal array of cylindrical mesopores along with a very high surface area and hence is expected to be suitable as a catalytic material, particularly for the transformation and/or preparation of large molecules [5]. However, to be catalytically active such silica MCM-41 molecular sieves are modified by framework substitution to create active sites. Modification by incorporation of Al into the electrically neutral siliceous framework generates acid sites and the resultant materials have been reported as good catalysts for a number of acid-catalyzed reactions [6,7]. We report here, our preliminary results, showing high activity of mesoporous aluminosilicate MCM-41 catalysts prepared by four different methods in the synthesis of bisphenol F by condensing phenol with aqueous formaldehyde at 90 °C.

2. Experimental

Mesoporous aluminosilicate MCM-41 molecular sieves used in the present study were prepared by four different methods: sol–gel (Al-MCM-41), hydrothermal (AlMCM-41), grafting (Al : MCM-41) and template-cation exchange (Al/MCM-41) using hexadecyltrimethylammonium bromide as surfactant template similar to the procedures described earlier [8]. Silica MCM-41 was synthesized by a conventional hydrothermal process reported in [9]. Mesoporous MCM-41 samples were characterized for their phase identification and phase purity by XRD, surface area and pore size distribution by nitrogen sorption and acidity by NH_3-TPD similar to that described in reference [8]. Microporous $H\beta$ ($Si/Al = 40.0$, obtained from Zeolyst, Japan) and amorphous silica–alumina (SiO_2–Al_2O_3, $Si/Al = 7.2$) catalysts were used for comparison. Liquid-phase phenol and formaldehyde reactions over

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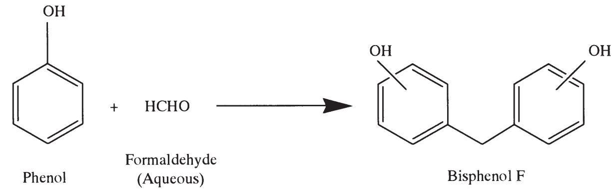

Scheme 1.

different solid catalysts were carried out in a magnetically stirred round-bottomed glass reactor (capacity: 50 cm^3) fitted with a reflux condenser and arrangement for digital temperature controller at the following reaction conditions: reaction mixture = 20-, 10- or 5-g phenol (Kanto Chemical Co., Japan) and 0.60-g aqueous formaldehyde solution (concentration 36–38%; Kanto Chemical Co., Japan), amount of the catalyst = 0.03, 0.006 or 0.0025 g, temperature = 90 °C and reaction period = up to 4 h. The reaction was started by adding the required amount of the catalyst into the reaction mixture containing phenol and formaldehyde, after attaining the reaction temperature. The course of the reaction was followed by measuring quantitatively the yield (sum of bisphenol and higher-boiling trisphenol isomers based on formaldehyde) formed in the reaction by HPLC (Shimadzu LC-VP) as a function of time. Bisphenol F selectivity and the distribution of its isomers in the reaction products were also calculated on a percentage basis based on formaldehyde.

3. Results and discussion

Results of the product yield with reaction time, and bisphenol F selectivity and isomer distribution after the initial reaction period (15 min), in the condensation of phenol with formaldehyde over different mesoporous MCM-41 catalysts reveal the following (table 1).

- Pure silica MCM-41 shows almost no activity in the bisphenol F synthesis process, but its catalytic activity is drastically increased on incorporation of aluminum into the framework of MCM-41. Al-incorporated MCM-41 catalysts prepared by different methods showed high phenol and formaldehyde reaction activity.
- Among the different aluminosilicate MCM-41 catalysts having same Si/Al ratio (Si/Al = 50 mol mol^{-1}), the Al : MCM-41 prepared by a grafting method showed the highest activity. The bisphenol F synthesis activity of the catalysts prepared by different methods is in the following order: Al : MCM-41 > AlMCM-41 > Al-MCM-41 > Al/MCM-41.
- Bisphenol F selectivity and its isomer distribution for all the Al-containing MCM-41 catalysts are similar and almost independent of the catalyst used in the process.

The time course on the product yield, bisphenol F selectivity and isomer distribution over the Al : MCM-41 catalyst (figure 1), which showed highest activity in the phenol and formaldehyde condensation reaction, displayed an initial exponential rise in the product yield with time and then a slow increase in the yield up to the end of the reaction. It is also observed that there is almost no change in bisphenol F selectivity (~90%) over the entire range of the reaction course; however, with increase in the reaction time, the bisphenol F isomer distribution changes drastically.

The influence of the catalyst concentration on product yield, bisphenol F selectivity and its isomers distribution over Al : MCM-41 catalysts are presented in table 2. With increase in the amount of the catalyst in the reaction mixture, the product yield increases linearly, however, bisphenol F selectivity (~92%) almost remains unaffected. No significant change is observed for bisphenol F isomers distribution after the reaction period of 15 min with change in the catalyst concentration under the present reaction condition.

Results showing the effect of phenol/formaldehyde ratio (by changing the amount of phenol only) on bisphenol F synthesis over the Al : MCM-41 catalyst is shown in table 3. The product yield is increased drastically with increase in the phenol/formaldehyde molar ratio from 7.5 to 15; further increase in the phenol/formaldehyde ratio up to 30 results in a very

Table 1
Results on bisphenol F synthesis over mesoporous aluminosilicate MCM-41 catalysts prepared by different methods. [Reaction conditions: phenol/formaldehyde = 30 mol mol^{-1}, catalyst/formaldehyde = 15 wt% and temperature = 90 °C.]

Catalyst	Product yield (%) at the reaction period of		Bisphenol F selectivity (%) at the reaction period of 15 min	Bisphenol F isomers distribution (%) after 15 min of reaction		
	15 min	1 h		4,4′-isomer	2,4′-isomer	2,2′-isomer
Al : MCM-41	27.0	63.2	91.3	40.8	42.5	16.7
AlMCM-41	15.5	44.6	89.4	38.4	43.1	18.5
Al-MCM-41	13.4	43.5	89.6	38.1	44.0	17.9
Al/MCM-41	10.1	40.2	89.7	37.9	44.3	17.8
Si-MCM-41	No reaction up to 1 h					

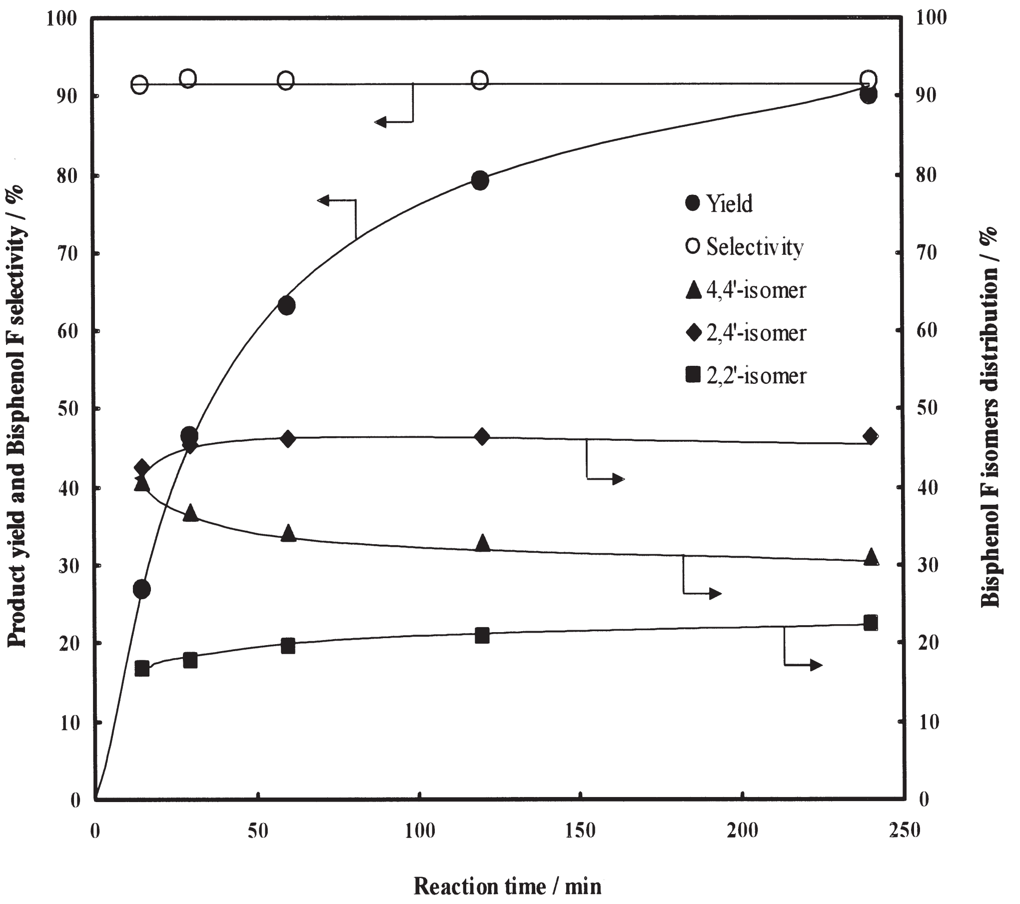

Figure 1. Time course on product yield, bisphenol F selectivity and its isomers (4,4′-, 2,4′-, and 2,2′-isomers) distribution over the Al : MCM-41 catalyst in the bisphenol F synthesis process. [Reaction conditions: phenol/formaldehyde = 30 mol mol^{-1}, catalyst/formaldehyde = 15 wt% and temperature = 90 °C.]

Table 2
Effect of the catalyst concentration on the bisphenol F synthesis process over the Al : MCM-41 catalyst. [Reaction conditions: phenol/formaldehyde = 30 mol mol^{-1} and temperature = 90 °C.]

Catalyst/ formaldehyde ratio (wt%)	Product yield (%) at the reaction period of		Bisphenol F selectivity (%) at the reaction period of 15 min	Bisphenol F isomers distribution (%) after 15 min of reaction		
	15 min	1 h		4,4′-isomer	2,4′-isomer	2,2′-isomer
30	57.6	91.4	91.9	40.0	42.8	17.2
15	27.0	63.2	91.3	40.8	42.5	16.7
7.5	13.1	27.0	93.7	47.4	40.4	12.3

Table 3
Effect of phenol/formaldehyde ratio on the bisphenol F synthesis over the Al : MCM-41 catalyst. [Reaction conditions: catalyst/formaldehyde = 15 wt% and temperature = 90 °C.]

Phenol/ formaldehyde ratio (mol mol^{-1})	Product yield (%) at the reaction period of		Bisphenol F selectivity (%) at the reaction period of 15 min	Bisphenol F isomers distribution (%) after 15 min of reaction		
	15 min	1 h		4,4′-isomer	2,4′-isomer	2,2′-isomer
30	27.0	63.2	91.3	40.8	42.5	16.7
15	26.3	62.6	90.7	49.6	39.4	11.0
7.5	16.6	56.1	94.4	59.1	33.8	7.1

Table 4
Physicochemical properties of Al-containing MCM-41 catalysts prepared by different methods

Catalyst	Method of preparation	XRD pattern	Surface area ($m^2 g^{-1}$)	BJH pore diameter (nm)	Acidity (mmol g^{-1})
Al : MCM-41	Grafting	Regular sharp	988	2.8	0.086
AlMCM-41	Hydrothermal	Regular sharp	967	2.9	0.084
Al-MCM-41	Sol-gel	Single broad	1097	2.5	0.080
Al/MCM-41	Template-cation exchange	Regular sharp	906	2.9	0.071
Si-MCM-41	Hydrothermal	Regular sharp	1060	2.6	—

small increase in the yield. Bisphenol F selectivity is almost not influenced by the use of different phenol/formaldehyde ratio in the reaction mixture. With increase in the phenol/formaldehyde molar ratio, the amount of 4,4′-isomer is decreased markedly and that of 2,4′- or 2,2′-isomer is increased drastically.

Results on the physicochemical characterization of aluminosilicate MCM-41 samples prepared by four different methods are presented in table 4. The X-ray diffraction pattern reveals that the catalyst prepared by the sol–gel method gives only a broad diffraction peak, suggesting lower structural order of the material. However, MCM-41 prepared by other methods exhibits regular hexagonal mesoporous structure. N_2 adsorption studies indicate that Al-containing samples prepared by different methods display high BET surface area from 906 to 1097 $m^2\ g^{-1}$ and BJH pore diameters from 2.5 to 2.9 nm. The observed NH_3-TPD data suggests that the acidic character of the catalysts is in the following order: Al : MCM-41 > AlMCM-41 > Al-MCM-41 > Al/MCM-41. It is interesting to note that the trend for the acidity is similar to that for the bisphenol F synthesis activity of the Al-containing MCM-41 catalysts (table 1) prepared by different methods. The result indicates that there seems to be a correlation between the acidic properties of the Al-incorporated mesoporous catalysts and their bisphenol F synthesis activities. However, it should be noted that the product yield is not increased linearly with increase in the acidity of the catalysts. And, among the different mesoporous catalysts, the Al : MCM-41 prepared by grafting method having higher amounts of Lewis acidity [10] and better acid-site distribution/isolation [11] shows highest bisphenol F synthesis activity. The above observations reveal that, although the total acidity is important, the ratio of Lewis/Brönsted acidity and the acid-site distribution/isolation seems to be more important for the bisphenol F synthesis activities over Al-containing MCM-41 catalysts. It is interesting here to note that all the Al-containing MCM-41 catalysts have moderate acidity, with acid sites mostly of medium strength [8].

The catalytic activity of Al : MCM-41 in the phenol and formaldehyde reaction is higher than that of the microporous Hβ and amorphous silica–alumina catalyst under the present reaction conditions (phenol/formaldehyde = 30 mol mol^{-1}, catalyst/formaldehyde = 15 wt%, temperature = 90 °C, and reaction time = 1 h). For these catalysts, the product yield obtained in the bisphenol F synthesis process is as follows: 43.5% for Hβ zeolite and 7.1% silica–alumina catalyst. The lower activity of highly acidic Hβ than the Al : MCM-41 catalyst may be due to the fact that the bisphenol F synthesis process is catalyzed mostly by moderate acids and hence the strong acidity of Hβ seems to have no significant additional rate enhancement effect on this reaction.

In summary, the mesoporous Al-containing MCM-41 catalyst, particularly that prepared by grafting method has a distinctly higher activity in the phenol and formaldehyde condensation reaction than microporous Hβ zeolite, although it has strong acid sites. This indicates that the number of acid sites is of greater influence than the acid strength. All the above observations suggest that Al-containing MCM-41 catalysts have high potential in moderately acid-catalyzed bisphenol F synthesis process.

4. Conclusions

The results of this work have demonstrated the potential of aluminosilicate MCM-41 molecular sieves in the bisphenol F synthesis process. The activity of the mesoporous Al-containing MCM-41 catalysts can be significantly different, depending on the synthesis process. Among the different aluminosilicate MCM-41 catalysts, the Al : MCM-41 prepared by the grafting method shows the highest activity, which may due to its higher Lewis acidity and better acid-site distribution/isolation properties. The Al : MCM-41 catalyst also shows higher phenol and formaldehyde condensation activity than the commonly used heterogeneous solid acids—such as microporous Hβ and amorphous silica–alumina.

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