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Selective O-methylation of phenol with dimethyl carbonate over X-zeolites

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The O-methylation of phenol with dimethyl carbonate proceeds selectively in the vapor phase over alkali ion exchanged X-zeolites. Thus, a 76% yield of anisole was obtained with a 93% selectivity over NaX at 553 K. The participation of basic sites in the O-methylation is suggested.

Keywords: Anisole; dimethyl carbonate; methylation; phenol; zeolite

1. Introduction

Aryl alkyl ethers, of which anisole is the simplest member, are important industrial chemicals and are extensively used as starting materials for the production of dyes and agrochemicals, as antioxidants for oils and grease, as stabilizers for plastics.

The vapor-phase methylation of phenol with methanol using metal oxides or zeolites as catalysts has been extensively studied [1–5]. The products are usually mixtures of anisole (the product of O-methylation) and the products of ring methylation (cresols and xylenols), the selectivity being strongly dependent on the catalyst. Reports on the selective O-methylation, however, have been very limited. Pierantozzi and Nordquist [1] obtained a 94% selectivity for anisole at a 12% yield over $La_2(HPO_4)_3$ at 573 K. Renaud et al. [2] obtained a 80% selectivity with an anisole yield in the range of 20–30%.

Anisole could be obtained by the Williamson ether synthesis, which requires methyl halide and a stoichiometric amount of sodium hydroxide. Dimethyl sulfate could also be used as a methylation reagent. In these methods, the toxic and corrosive properties of the halides or the sulfate cause problems.

Dimethyl carbonate (DMC) can also be a useful methylation reagent as a substi-

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tute for these reagents. For example, we have shown that aniline can be selectively monomethylated with DMC over alkali-exchanged zeolites [6].

DMC has also been used for O-methylation of phenol. Tundo et al. [7] reported that a supported phase-transfer catalyst (K_2CO_3 coated with polyethylene glycol) gave no trace of C-alkylation products even at a high conversion level. A patent describes that anisole was obtained in a 82% yield together with a selectivity of 94% selectivity with a zeolite catalyst at 556 K, though no details of the reaction such as catalyst life and type of the zeolite used were given [8].

This paper is concerned with the vapor-phase synthesis of anisole from phenol and DMC using alkali ion exchanged faujasites as the catalysts.

2. Experimental

Alkali-ion exchanged zeolites were prepared by a conventional ion-exchange procedure using an 1 M aqueous solution of a corresponding chloride or nitrate with a solid–liquid ratio of 0.02 g cm^{-3}. After ion exchange, the zeolites were washed with deionized water. The alkali ion content of the zeolites was determined by atomic absorption spectrometry. The main characteristics of the catalysts used are given in table 1.

The reactions were carried out with a continuous flow reactor at atmospheric pressure. The catalysts (16–32 mesh) were packed in a reactor of silica tubing (10 mm i.d.) placed in a vertical furnace and heated under an air stream at 773 K for 1 h. The mixture of phenol and DMC was fed into the reactor by means of a motor driven syringe. The contact time was expressed as W/F, where W is the weight of the catalyst used and F is the flow rate of the total feed (DMC + phenol + N_2). The products were trapped and analyzed by a gas chromatograph.

3. Results and discussion

The catalytic activities of various zeolites on the methylation of phenol with DMC were compared at 553 K. Fig. 1 shows the change in the yield of anisole with time on stream over various zeolites at 553 K. Alkali-exchanged zeolites show the high catalytic activity for anisole formation, while the zeolites containing alkali

Table 1
Main characteristics of zeolites

	LiX	NaX	KX	CsX	CaX	NaY	MgY
SiO_2/Al_2O_3	2.5	2.5	2.5	2.5	2.5	5.6	5.6
ion exchange (%)	49	–	62	59	72	–	62

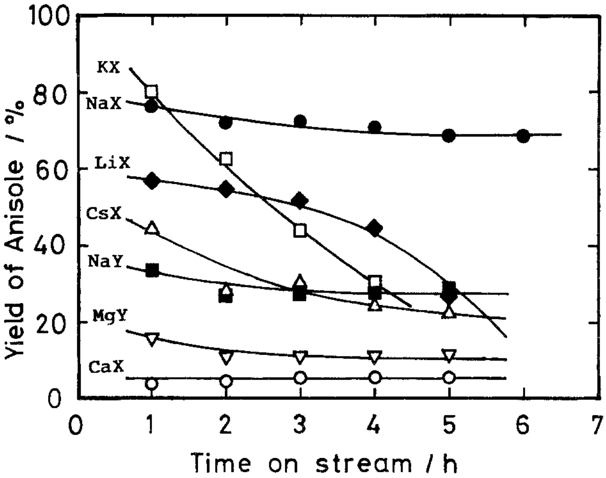

Fig. 1. The change in anisole yield with time on stream in the methylation of phenol with DMC over various zeolites. Reaction conditions: temperature: 553 K; phenol pressure: 24.7 kPa; DMC/phenol molar ratio: 1; W/F: 12.0 g h mol^{-1}.

earth metal cations (CaX, MgY) gave low yields of anisole. This indicates that the basicity is essential for the O-methylation of phenol [9–11].

Among alkali-exchanged zeolites, only NaX gave a high and stable activity. KX showed higher activity than NaX, but the activity lowered quickly with time on stream. The deactivation may be caused by the strong adsorption of phenol or carbon dioxide at basic sites. CsX has the highest basic strength among alkali-exchanged zeolites [10,11]. The activity of CsX was, however, lower than KX or NaX. This may be caused by a steric hindrance due to the high density of the large cations in the supercages in CsX [11].

The selectivity for anisole did not change with time on stream, though the activities decayed except for NaX. The highest selectivity was observed for KX (94%). NaX also showed a high selectivity (93%). Thus, the yield of anisole was 76%. The other products were methyl tolyl ethers (4.0%) and cresols (1.2%). On the other hand, the selectivity was low for CaX (47%) and MgY (48%). This indicates that basic nature of the zeolites is essential for O-methylation of anisole.

Fig. 2 shows the dependence of anisole yield on the reaction temperature in the reaction over NaX. A stable activity was observed at 553 K. Deactivation is slow at 523 K, while it was faster at 493 and 583 K. Thus, the optimum reaction temperature is around 550 K.

Fig. 3 shows the effect of DMC partial pressure on the anisole yield. The selectivity for anisole was about 90% at each DMC pressure. At DMC partial pressure of 49.4 kPa (DMC/phenol = 2), the anisole yield decayed with time on stream. The activity was stable with time on stream at 12.4 kPa (DMC/phenol = 0.5) and 24.7 kPa (DMC/phenol = 1). Thus, the favorable DMC pressure for yielding anisole was 24.7 kPa (DMC/phenol = 1).

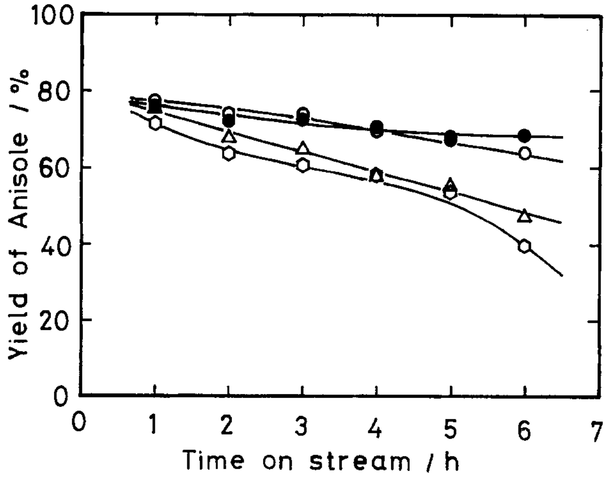

Fig. 2. Effect of reaction temperature on the anisole yield in the methylation of phenol with DMC over NaX. Reaction conditions: temperature: 493 K (△), 523 K (○), 553 K (●), 583 K (⬡); phenol pressure: 24.7 kPa; DMC/phenol molar ratio: 1; W/F: 12.0 g h mol^{-1}.

As for the mechanism of anisole formation, the base-catalyzed scheme may be expressed as follows.

$$PhOH + BZ \rightarrow PhO^- + H^+BZ,$$

$$PhO^- + DMC \rightarrow PhOCH_3 + CO_2 + CH_3O^-,$$

$$CH_3O^- + H^+BZ \rightarrow CH_3OH + BZ.$$

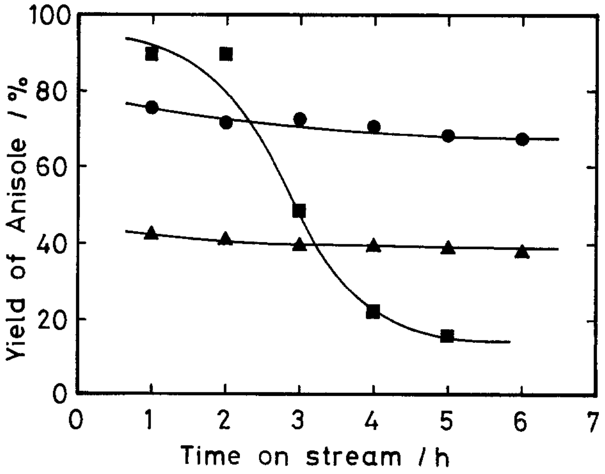

Fig. 3. Effect of DMC partial pressure on the anisole yield in the methylation of phenol with DMC over NaX. Reaction conditions: temperature: 553 K, phenol pressure: 24.7 kPa; DMC pressure: 12.4 kPa (▲), 24.7 kPa (●), 49.4 kPa (■); W/F: 12.0 g h mol^{-1}.

Here, BZ denotes a basic site on the zeolite surface. The basic sites interact with phenol molecules to form PhO^- ions, which, in turn, react with DMC molecules to generate CH_3O^- ions. The CH_3O^- ions react with protons to form methanol to regenerate the basic sites.

In conclusion, NaX is an active and selective catalyst for the formation of anisole from phenol and DMC. Thus, an anisole selectivity of 93% was obtained at phenol conversion of 82% at 553 K. The anisole yield was much higher in the methylation with DMC than in that with methanol.

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