Letter

Promotion effects of alkali metal halides on the oxidative methylation of toluene with methane over KY zeolite catalysts

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Abstract

Effects of alkali metal halides promoter on the oxidative methylation of toluene with methane over KY zeolite catalysts were systematically studied. In terms of the catalytic activity for the oxidative methylation of toluene with methane over those catalysts, the following order was observed: NaBr/KY>KBr/KY>NaCl/KY. The C_8 products containing much styrene were gained over alkali metal bromide promoted KY zeolite catalysts. The acidity and basicity of these catalysts were studied by using NH_3-TPD and formic acid-TPD. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The oxidative methylation of toluene with methane which has been investigated by Khcheyan et al. [1] is an attractive method for the production of styrene and ethylbenzene because of the low prices of the two starting materials compared with the currently used benzene–ethene process. Recently, several research groups have employed some metal oxides for the oxidative methylation of toluene with methane [2–5].

It is known that zeolite is the focus of the catalytic chemistry. In contrast to extensive studies of the acidity of zeolites, less attention has been given to the studies of base catalysis of zeolites. Applying basic zeolites to catalytic synthesis of organic compounds is one of the new attempts which have potentially economical effectiveness and great theory value. In this research, KY zeolites promoted with alkali metal halides, an oxidative methylation of toluene with methane was studied. It was found that the basic zeolites were very effective for the oxidative methylation.

2. Experimental

2.1. Catalyst preparation

Zeolite NaY (raw powder) was supplied from Wenzhou Chemical Plant. Sample KY was prepared by ion-exchange of NaY with 0.5 M KNO_3 aqueous

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solution at 358 K for 2 h. The ion-exchange procedures were repeated four times. The zeolite sample was filtered, washed with deionized water, and then dried at 398 K, followed by calcination in air at 773 K for 5 h. NaBr, KBr and NaCl – promoted KY zeolites were further prepared by an impregnation method. The promoted catalysts were calcined in air at 773 K for 5 h. The powder zeolites were pressed into pellets, crushed, and then sieved. As catalyst, 40–60 Tayler mesh part of the granulated sample was used.

2.2. Catalyst screening and product analysis

The experiments in this work were carried out using a conventional fixed bed flow reactor of quartz glass (6 mm i.d.). The typical experimental conditions were as follows: reaction temperature=973 K, CH_4 flow rate=24 ml/min, toluene flow rate=2.33 ml/min(g), weight of catalyst/total feed rate (W/F)=2.14 g h/mol, and $CH_4/O_2/C_6H_5CH_3/N_2$ (diluent)=24:6:2.33:20 in ml/min. Toluene was introduced by passing the gas mixture of CH_4, O_2 and N_2 through a toluene vapor saturator located just before the inlet of reactor. Liquid products condensed using an ice-salt bath were analyzed by a gas chromatograph equipped with a SE-30 capillary column and flame ionization detection (FID). Products were styrene (ST), ethylbenzene (EB), and benzene and trace amounts of xylene and water.

3. Results and discussion

3.1. Effect of NaCl loading

The effect of NaCl loading on the KY catalyst has been investigated. In Fig. 1(a) and (b), with the increase in NaCl loading, the toluene conversion decreased through a maximum at 4 wt%, while the total C_8-selectivity increased, and become almost constant above the 4 wt% loading. In addition, a noticeable difference between the EB-selectivity and ST-selectivity was observed with the increase of NaCl loading. The EB-selectivity showed a change trend similar to that of the total C_8-selectivity, while the ST-selectivity remained almost unchanged with the increase of NaCl loadings.
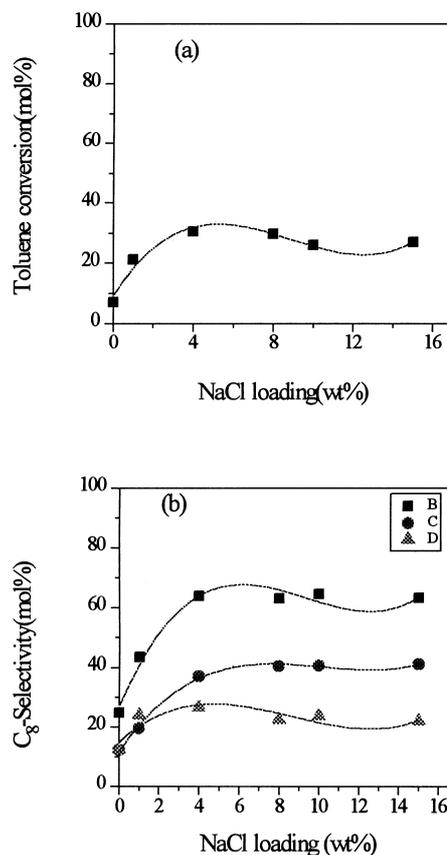

Fig. 1. Effects of NaCl loading on toluene conversion (a) and C_8 selectivity (b). [(B) Total C_8, (C) Ethylbenzene, (D) Styrene.]

3.2. Effects of KBr loading

Effects of KBr loading on the toluene conversion and C_8-selectivity are shown in Fig. 2(a) and (b). With increasing in KBr loading, the toluene conversion and the total C_8-selectivity increased, remaining almost constant for loading higher than 8 wt% KBr. With the increase in KBr loading, the ST-selectivity and EB-selectivity showed different changes, and the ST-selectivity exhibited a similar behavior to that of the total C_8-selectivity, while the EB-selectivity decreased slightly.

3.3. Effects of NaBr loadings

Fig. 3(a) and (b) showed variation of the toluene conversion and the C_8 selectivity at 973 K with
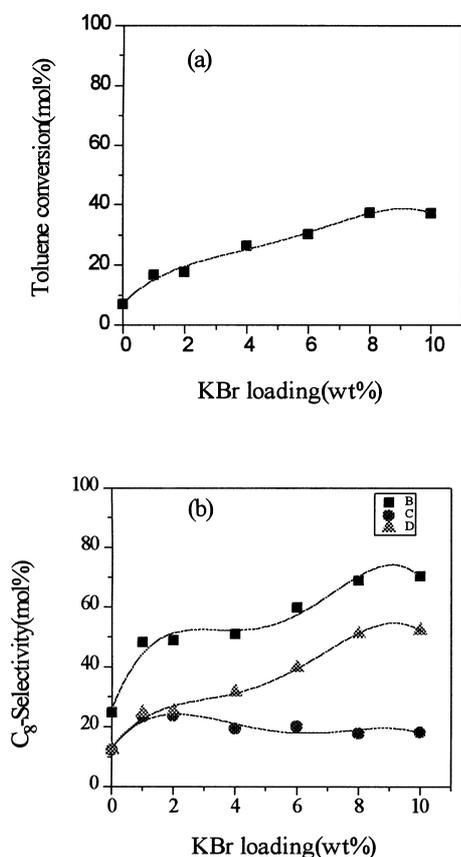
Fig. 2. Effects of KBr loading on toluene conversion (a) and C_8 selectivity (b). [(B) Total C_8, (C) Ethylbenzene, (D) Styrene.]

Fig. 3. Effects of NaBr loading on the toluene conversion (a) and the C_8 selectivity (b). [(B) Total C_8, (C) Ethylbenzene, (D) Styrene.]

increasing in the loading level of NaBr on KY. The toluene conversion resulted in a maximum (72%) at the NaBr loading of 12.5 wt% followed by a decrease. With increasing NaBr loadings, the total C_8-selectivity showed a noticeable increase up to the NaBr loading, but above it was unchanged. In addition, EB and ST-selectivities show quite different behaviors. With increasing NaBr loading, the ST-selectivity indicated a similar pattern to that of the toluene conversion, whereas the EB-selectivity increased through a minimum at 12.5 wt% NaBr loading. The decrease in ST-selectivity with the increase in EB-selectivity suggests that styrene is a secondary product formed by an oxidative dehydrogenation of ethylbenzene.

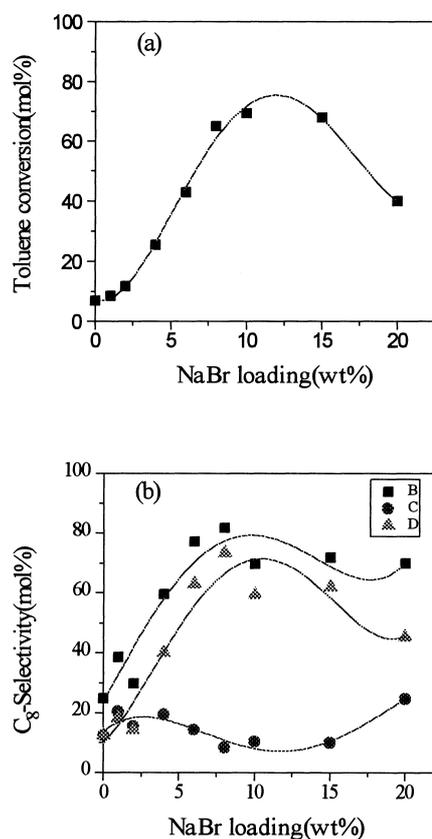Furthermore, acidity and basicity of KY zeolite promoted with alkali metal halides were studied by NH_3-TPD and formic acid-TPD, respectively. It was found that NH_3-TPD patterns of KY zeolite promoted with alkali metal halides had one desorption peak in the temperature range 451–458 K, which indicates that the alkali metal halide-promoted KY zeolite had weak Lewis acidic centers. TPD plots of formic acid desorbed from the alkali metal halide-promoted KY zeolite were low and wide curves, and these wider desorption peaks appear in the temperature range 483–613 K. The results indicated that the alkali metal halide-promoted KY zeolite had moderately strong Lewis basic centers. It was found that the alkali metal halide-promoted KY zeolites had weak Lewis acidic centers and moderately strong Lewis basic centers. It seems likely that these weak Lewis acidic centers and strong Lewis basic centers are active centers for oxidative methylation of toluene with methane.

The stability with time-on-stream of NaBr-promoted KY zeolite catalyst was also investigated. The results showed that the toluene conversion suffered 40–50% decrease compared to the initial value after 50 h of reaction. In contrast, the total C_8-selectivity remained almost unchanged.

Among the alkali metal halide-promoted KY zeolites examined in this work, the toluene conversion and the C_8-selectivity decreased in the following order: NaBr/KY>KBr/KY>NaCl/KY. It was found that the most effective catalytic system was KY zeolite promoted with NaBr, which gave the highest toluene conversion (72%) and the C_8-selectivity (77%). Moreover, the C_8 products containing much styrene were obtained on alkali metal bromide promoted KY zeolite catalysts. In addition, the increase in the ST selectivity strongly suggests that styrene is formed through oxidative dehydrogenation of ethylbenzene.

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