



High Selective Alkylation of Aniline with Methanol to *N*-Methylaniline over [Fe]-KL Molecular Sieves

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Abstract. In the alkylation of aniline with methanol, [Al]-KL zeolite exhibits a much higher NMA (*N*-methylaniline) selectivity (>95%) and more stable activity with time on stream than NaX, NaY and Na β under the same experimental conditions. Incorporation of an appropriate amount of Fe into the framework of zeolite L can enhance the reaction activity without loss of high NMA selectivity. This improvement is attributed to an increase in the basicity of the zeolite as shown by pyrrole-IR spectra. The high NMA selectivity of zeolite L may be due to its one-dimensional channel structure with no large cavities and its lower number of accessible acid sites.

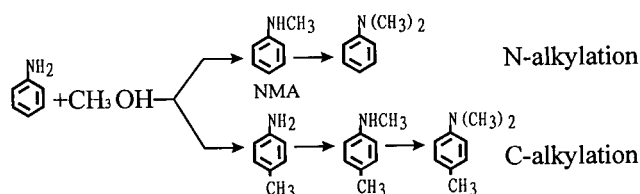
Key words: selective alkylation, zeolite L, Fe incorporation, *N*-methylaniline.

1. Introduction

N-methylaniline (NMA) is one of the major products in the alkylation of aniline with methanol and is used as an important intermediate in organic synthesis and in the dyestuff industry. Liquid-phase alkylation, commercialized in 1866, has been extensively used in industry to prepare NMA. However, corrosion and pollution problems cannot be avoided due to the use of strong acid as catalyst at high temperatures and pressures. The unreacted raw materials can also not be recycled and many undesired by-products are obtained as well in the liquid-phase system. Therefore, it was considered desirable to replace this system by a vapor-phase system, and different types of catalysts have been employed in such vapor-phase systems [1–5]. After the 1980's, zeolite molecular sieves were investigated. The studies focused on faujasite, ZSM-5 and modified ZSM-5 zeolites [6–10]. In recent years, Barthomeuf's group investigated the use of more extensive zeolite materials including EMT, beta, L and mordenite [11, 12], and focused on the relationship between the selectivity of the product and the acid-base properties of the zeolites employed.

It has been shown that the vapor-phase alkylation process gives two types of products – *N*-alkylated and C-alkylated products:

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The products are complex and the selectivity depends strongly on the experimental conditions and on the nature of the catalyst. In particular, it is more difficult to control the reaction for obtaining NMA with a high selectivity. In the present paper, we report the alkylation of aniline with methanol over [Al]-KL and [Fe]-KL zeolites. It was found that the introduction of Fe into the framework not only apparently improves the activity of zeolite L but also retains its high NMA selectivity.

2. Experimental

[Al]-KL and [Fe]-KL samples were prepared by hydrothermal synthesis. The detailed procedures were described in our previous work [13]. The method employed to synthesize [Fe]-KL was similar to that used to prepare [Al]-KL, except for partially substituting potassium aluminate by ferric nitrate as source material and using a relatively longer crystallizing period. NaX, NaY and Na β were obtained by ion-exchanging commercial zeolites X, Y and beta with NaCl solutions, respectively. Before exchange, the zeolite beta was calcined at 550 °C for 12 h in an oxygen flow to remove the template.

The Si/Al ratios of the samples were determined by conventional chemical analysis, and the contents of other elements were analyzed by the inductively coupled plasma technique. The detailed characterizations of [Al]-KL and [Fe]-KL, including XRD, IR, TG/DTA, N₂ sorption and Mössbauer spectroscopy, have been reported in our previous work [13]. The characterizations showed that the incorporated Fe atoms were almost completely located at the framework positions.

The IR spectra of pyrrole adsorbed on zeolites L were recorded on a Nicolet 510P FTIR spectrometer. Self-supporting wafers (~ 6 mg/cm²) were heated to 450 °C at a rate of 5 °C/min under vacuum, contacted with O₂ at that temperature for 20 min, and further evacuated at the same temperature for 3 h. The surface-cleaned samples were cooled to room temperature and exposed to pyrrole vapor for 10 min, followed by evacuation at a given temperature for 50 min, then the spectra were recorded at room temperature. For the spectra shown below, background spectra have been subtracted.

The catalytic test was carried out in a fixed bed micro-reactor containing 50 mg of zeolite sample. The sample was activated in a N₂ flow at 500 °C for 2 h and then cooled to reaction temperature. A mixture of aniline and methanol, in which the molar ratio of methanol to aniline was 3 : 1, was continuously fed by a syringe

Table I. Composition of samples

Sample	Si/Al	Si/Al+Fe	Fe/Al+Fe
NaX	1.4	–	–
NaY	2.4	–	–
Na β	19.0	–	–
[Al]-KL	2.9	–	–
[Fe]-KL-1	3.2	2.9	0.1
[Fe]-KL-2	3.5	2.8	0.2
[Fe]-KL-3	4.1	2.9	0.3
[Fe]-KL-4	4.5	2.8	0.4

pump. The carrier gas (N₂) flow and WHSV (weight hour space velocity) were 10 mL/min and 7.1 h⁻¹, respectively. The reaction effluents were trapped and then analyzed by gas chromatograph with a SE-30 column.

3. Results and Discussion

The composition data for zeolite L, beta and faujasite are listed in Table 1. The conversion of aniline and the NMA selectivity over various types of zeolites are shown in Figures 1 and 2. It can be seen that the reactivity on zeolite L is quite different from that of NaX, NaY or Na β . On the one hand, the activity on zeolite L is essentially stable over the reaction period although the initial activity is not high (Figure 1), on the other hand, almost solely NMA forms on zeolite L so that its selectivity is higher than 95% (Figure 2), whereas on faujasite and zeolite beta, C-alkylation products and *N,N*-dimethylaniline form in considerable amount. This special reactivity on zeolite L may reflect the following two aspects: (i) zeolite L possesses a one-dimensional channel structure which is open and does not have large cavities formed by channel cross. This pore structure not only favors the diffusion and escape of NMA and hence avoids secondary alkylation, but also provides no large space for the formation of bulky products, such as *N,N*-dimethylaniline and *N,N*-dimethyltoluidine etc. (ii) [Al]-KL zeolite possesses weak acidity. It is well-known that the acidic strength of alkali cations, which act as Lewis acid sites in alkali zeolites, is weak. It is also reported recently that the number of accessible cations on [Al]-KL zeolite is much less than that on faujasite [12], i.e., the effective acidic sites on [Al]-KL are few as well. So weak acidity must be unfavorable to C-alkylation.

Although high NMA selectivity occurs on [Al]-KL, its activity for *N*-alkylation is still low. When Fe atoms are introduced into the framework of KL, the conversion of aniline is enhanced significantly (Figure 3). A twice higher activity is observed on [Fe]-KL-1 with no loss of the high NMA selectivity. In addition, no notable

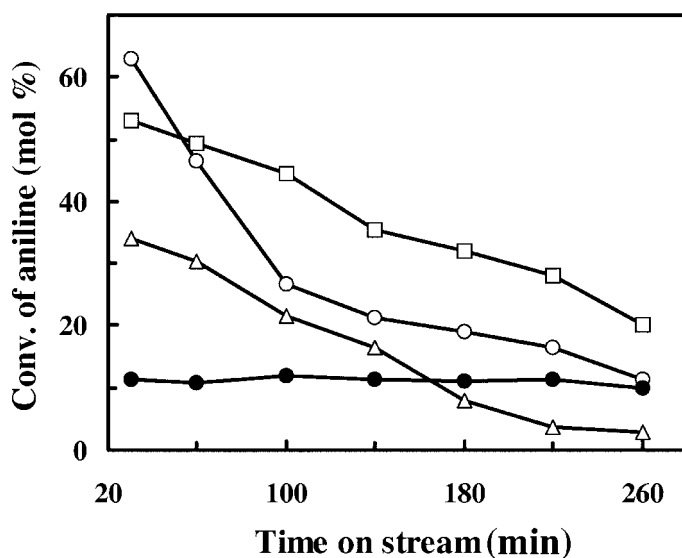


Figure 1. Change of conversion of aniline with time on stream (●)KL, (Δ)NaY, (○)Naβ, (□)NaX.

change in activity and selectivity takes place over the reaction period. On [Fe]-KL-1, the yield of NMA is as high as ~30%, higher than that on faujasite or beta. However, when more Fe is incorporated (sample [Fe]-KL-2, -3 and -4), the activities at the later stage of the reaction period decrease though the initial activities on

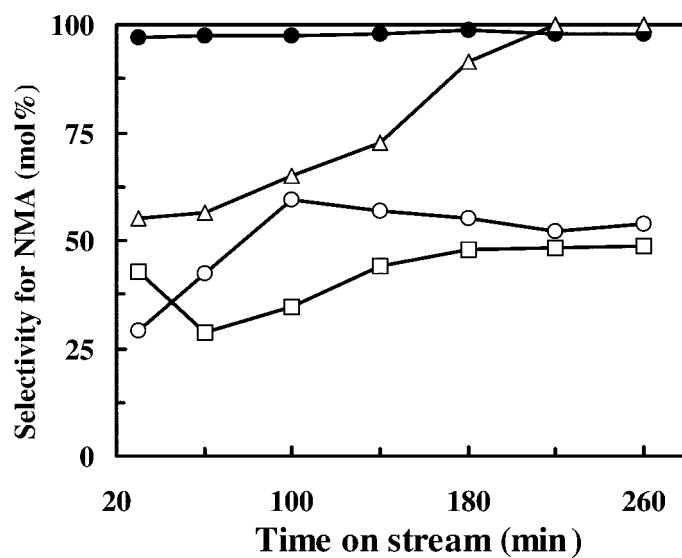


Figure 2. Change of NMA selectivity with time on stream (●)KL, (Δ)NaY, (○)Naβ, (□)NaX.

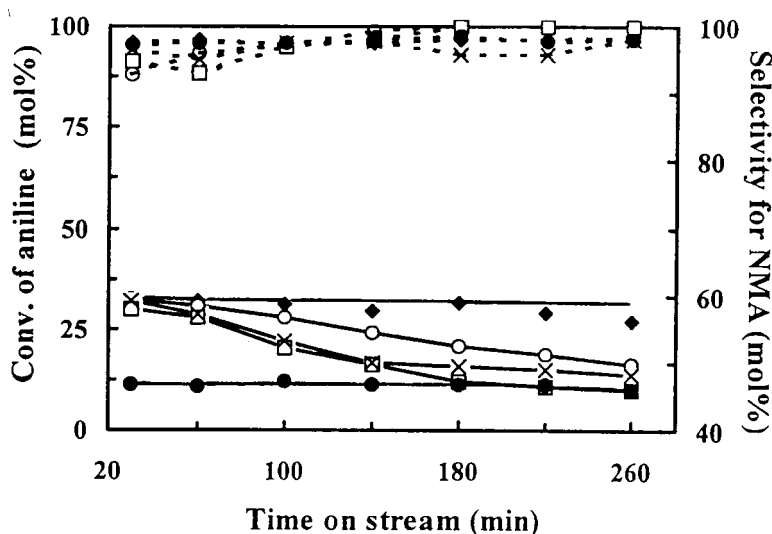


Figure 3. Change of conversion and selectivity with time on stream on KL zeolites. (◆)[Fe]-KL-1, (○)[Fe]-KL-2, (×)[Fe]-KL-3, (□)[Fe]-KL-4, (●)[Al]-KL, — conversion of aniline, ····· NMA selectivity.

these samples are close to that on [Fe]-KL-1 (Figure 3). That is, the deactivation occurs on the samples with higher Fe contents, and the higher the Fe content, the more quickly the deactivation develops. Therefore, the amount of incorporated Fe should be limited in order to maintain stable activity.

Further improvement of reaction activity may be realized by changing the reaction conditions. When the reaction temperature was elevated to 460 °C (Figure 4), the initial activity and NMA yield on [Fe]-KL-1 reached 54% and 50%, respectively; but a higher reaction temperature also led to the deactivation of the sample and a slight decrease in NMA selectivity (see Figure 4).

Why would the incorporation of Fe result in enhancement of the activity for *N*-alkylation? The answer to this question involves consideration of the acid-base property of the catalyst and the reaction mechanism. After making a systematic investigation of the basicities of heteroatom zeolites, we find that the introduction of B, Ga or Fe atoms into the framework of a zeolite can increase the basic strength of the framework oxygen. This increase is indicated by the bathochromic shift of the NH-stretching frequency in the IR spectrum of adsorbed pyrrole on the sample [14–18]. For the non-acidic zeolite samples, for which the 1490 cm^{-1} band characteristic of pyrrole adsorbed on acid sites [15] is not found, the basic strength corresponds to the extent of the bathochromic shift of the NH band. The pyrrole-IR spectra for [Al]-KL and [Fe]-KL-3 in the NH-stretching region and in the ring vibration region are shown in Figure 5A and B, respectively. It can be seen that, even though the Si/Al + Fe ratios of these two samples are similar, the NH band (at 3200–3500 cm^{-1}) for [Fe]-KL-3 is quite different from that for [Al]-KL. The latter

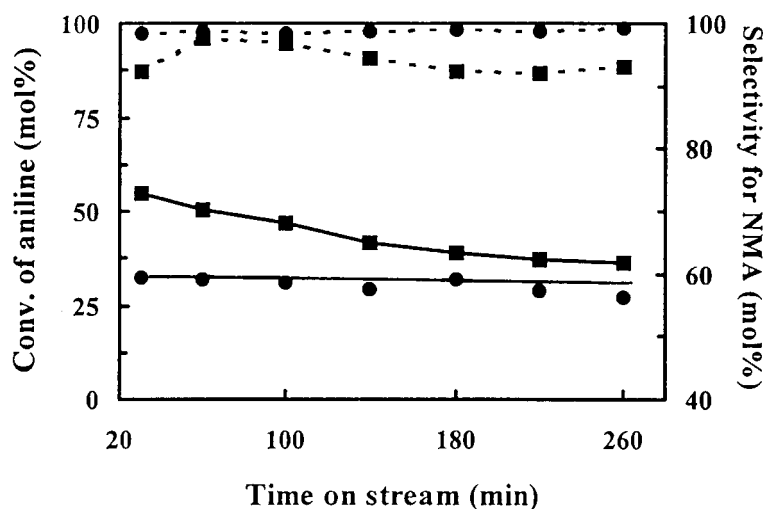


Figure 4. Change of conversion and selectivity with time on stream on [Fe]-KL-1 at different temperature. (●) 400 °C, (■) 460 °C, — conversion of aniline, ····· NMA selectivity.

is essentially symmetrical (Figure 5a), while the former exhibits a shoulder on the lower frequency side (3300 cm^{-1}), although no notable change in the original NH frequency is observed (Figure 5b). This suggests that the incorporation of Fe does not modify the basic strength of the original base sites but rather gives rise to new base sites with stronger basicity. As the evacuating temperature increases (Figure 5c), the intensity of the original NH band clearly decreases because the pyrrole molecules adsorbed on the weaker base sites are removed, leading to an increase in the relative intensity of the shoulder corresponding to the stronger base sites. These results thus reveal that the introduction of Fe into the zeolite L (to replace Al) enhances the basicity of oxygen in some special positions to produce new sites with higher base strength.

As for the reaction mechanism, it is well-known that C-alkylation occurs *via* electrophilic substitution involving carbonium ion and is accelerated by an increase in acid strength, whereas *N*-alkylation corresponds to a nucleophilic $\text{S}_{\text{N}}2$ mechanism. In this $\text{S}_{\text{N}}2$ reaction, the reaction velocity depends on the nucleophilicity of aniline and the “removability” of the OH group of methanol. Since the acidity and the basicity of the catalyst aid the removal of the OH group and increase the nucleophilicity of the NH_2 group, respectively, both the acidity and the basicity may be favorable to *N*-alkylation. However, the selectivity for *N*-alkylation will tend to be low using a catalyst with both acidic and basic properties, because the acidity will promote C-alkylation simultaneously. The previously reported results [6, 8–10] are consistent with this proposal, i.e., C-alkylation is catalyzed by the acid sites of the zeolite [6, 8], while *N*-alkylation is found to correlate with the base sites [6, 9, 10]. Strong basicity can enhance the activity and selectivity for *N*-alkylation. In our case, zeolites X, Y and beta possess either high cation densities or stronger acidity,

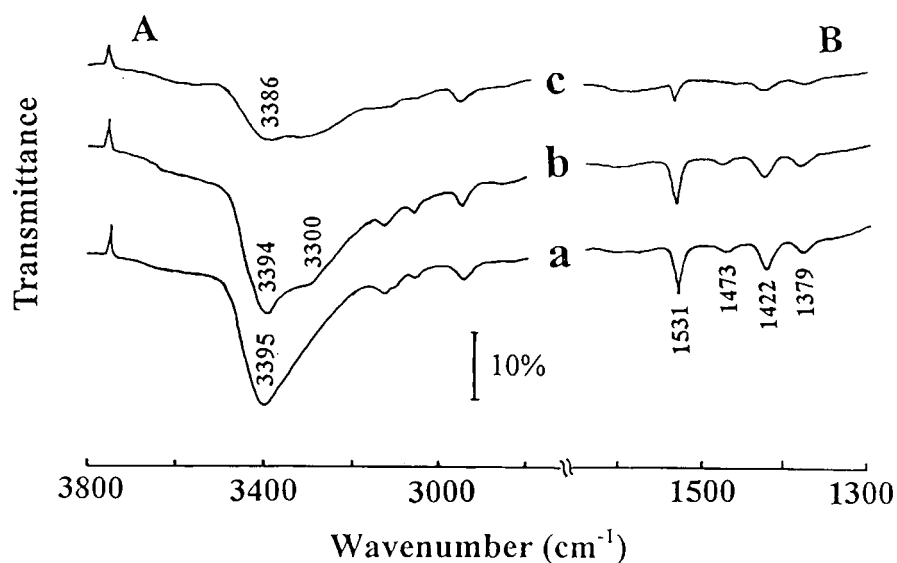


Figure 5. IR spectra of pyrrole adsorbed on KL zeolites. (a) [Al]-KL evacuated at 80 °C, (b) [Fe]-KL-3 evacuated at 80 °C, (c) [Fe]-KL-3 evacuated at 120 °C.

therefore, they show a high activity for C-alkylation and a low selectivity for *N*-alkylation. On zeolite L, C-alkylation is suppressed due to the zeolite structure and the lack of accessible cation sites, as mentioned above. Thus the selectivity for *N*-alkylation is very high. When Fe atoms are incorporated into zeolite L, a distinct increase in basicity occurs, resulting in not only high *N*-alkylation selectivity but also improved *N*-alkylation activity. However, “over-basicity” may bring about deactivation resulting from an anionic polymerisation reaction involving aniline and methanol, as proposed by Barthomeuf *et al.* [10–12].

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