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Catalytic Reactions of Pyridines. IV.[1] Heterogeneous Vapor-phase Side-chain Alkylation of Pyridines with Alcohols over Na^+, K^+, Rb^+, and Cs^+ Exchanged Zeolites

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The heterogeneous vapor-phase alkylation of pyridine with methanol over Na^+, K^+, Rb^+, or Cs^+ exchanged X- or Y-type zeolite in an atmosphere of nitrogen resulted in the formation of 2- and 4-ethylpyridines and 2- and 4-vinylpyridines together with picolines and lutidines.

Next, the alkylation of α-, β-, and γ-picolines with methanol was studied over alkali cation exchanged zeolites and was found to produce mainly the side-chain methylated derivatives: ethylpyridines and vinylpyridines. However, considerable amounts of ring-alkylated derivatives (lutidines) were formed simultaneously. In general, the catalytic activity became observable under reaction conditions involving both a high temperature and a small flow rate of carrier gas (N_2). The yields of ethylpyridines were highest when the CsY catalyst was used at 450°C, whereas the yields of vinylpyridines were highest when the CsX catalyst was used at 425°C.

This catalytic side-chain alkylation over alkali cation exchanged zeolites was successfully applied to a variety of picolines, lutidines, and ethylpyridines with either methanol or ethanol.

Keywords——side-chain alkylation; catalyst; cesium cation exchanged zeolite; pyridine; picoline; lutidine; ethylpyridine; vinylpyridine; propylpyridine; alcohol

Beginning with the extensive studies by Pines and coworkers,[2,3] many reports have appeared regarding the side-chain alkylation of aromatic hydrocarbons with olefins, aldehydes, or alcohols in the presence of alkali catalysts both in the vapor phase and in the liquid phase. In particular, the alkali cation (such as Na^+, K^+, Rb^+, or Cs^+) exchanged zeolites are well-known to be one of the most effective catalysts for the side-chain alkylation of aromatic compounds,[4] and have been used, for instance, in the alkylation of methylnaphthalene[5] or toluene[6,7] with methanol. In addition, Yashima *et al.*[7] studied in detail the side-chain alkylation of toluene in the vapor phase using alkali cation exchanged zeolites, and suggested that the active sites for this side-chain alkylation might be the solid base sites.

In contrast, relatively few papers have appeared on the catalytic side-chain alkylation of aromatic compounds containing pyridine rings, though the side-chain alkylation[8—11] and the side-chain aralkylation[12] of 2- and 4-alkylpyridines with olefins on alkali metals were studied in some detail in the liquid phase.

Meanwhile, the side-chain alkylation of pyridines has not been investigated thus far in the vapor phase. If the heterogeneous vapor-phase alkylation is carried out, however, the product distribution would probably differ from that in the liquid-phase alkylation even if the same catalyst is used. Also, a reaction can be operated continuously for as long as the catalyst remains active. Furthermore, the separation of desired products is simple, because only liquid compounds at the trap temperature need be post-treated. As regards the heterogeneous vapor-phase alkylation of pyridine, the authors reported previously the α-alkylation of pyridine and picolines with either methanol or ethanol over Ni^{2+} exchanged zeolites at 350°C.[13]

The authors found thereafter that in the vapor phase at higher temperature (450°C), 2- and 4-ethylpyridines and 2- and 4-vinylpyridines were produced together with α-, β-, and

γ-picolines in the alkylation of pyridine over Na^+, K^+, Rb^+, and Cs^+ exchanged zeolites. In comparison with the side-chain alkylation of toluene over alkali cation (except Li^+) exchanged zeolites,[6,7] the formation of ethylpyridines observed here was considered to result from the side-chain methylation of α-picoline and γ-picoline produced at first by the ring methylation of pyridine with methanol. From this point of view, we then carried out the alkylation of α-, β-, and γ-picolines with methanol using Na^+, K^+, Rb^+, and Cs^+ exchanged X- and Y-type zeolites (metal cation exchanged X-type zeolite is abbreviated hereafter as MX, and metal cation exchanged Y-type zeolite is abbreviated as MY, where M is the chemical symbol of the metal used). Moreover, this side-chain alkylation over alkali cation exchanged zeolites was applied to the production of 2- and 4-propylpyridines either from picolines with ethanol or from ethylpyridines with methanol, as well as that of ethylmethylpyridines from lutidines with methanol, and so forth.

Incidentally, not side-chain alkylation but β-alkylation was observed in the methylation of pyridines with alcohols over LiX and LiY catalysts. A comprehensive study on this β-alkylation will be presented in a subsequent paper. Therefore, lithium will be excluded from alkali metals throughout this report.

Experimental

Materials——Pyridine, α-, β-, and γ-picolines, lutidines, ethylpyridines, vinylpyridines, propylpyridines, and ethylmethylpyridines, having a purity of over 99%, were commercial products, and were used after being distilled and confirmed to be gas chromatographically pure. Other chemical reagents were of commercial GR grade and were used without further purification.

Catalysts——The K^+, Rb^+, or Cs^+ exchanged X- or Y-type zeolite was prepared by a conventional cation exchange procedure using a saturated aqueous solution of alkali nitrate and either 13X (raw NaX) or SK-40 (raw NaY).[13] The degrees of cation exchange were measured by X-ray fluorescence analysis and were found to be 90, 75, and 81% for KX, RbX, and CsX, and 90, 77, and 79% for KY, RbY, and CsY, respectively. The cation exchanged zeolites were calcined at 500°C for 3 h before reaction.

Analysis——The liquid reaction mixture was analyzed by a gas chromatography[14] using a 3 mm × 5 m stainless steel column with polyethylene glycol (PEG) (400) 15% + Uniport B 85%. The carrier gas was H_2 and the analysis temperature was 110°C. The gaseous products were analyzed by gas chromatography using a 3 mm × 2 m stainless steel column with active carbon (80—100 mesh). The carrier gas was N_2 and the analysis temperature was 25°C.

Apparatus and Procedure——Experiments were carried out in a fixed bed type apparatus with a continuous flow system at atmospheric pressure. The catalyst was placed in an electrically heated reactor and, after the air had been replaced with nitrogen, the catalyst was calcined at 500°C for 3 h, then brought to the reaction temperature *in situ*. A mixture of a pyridine and an alcohol was fed *via* a microfeeder and was carried by nitrogen gas to the catalyst bed. The product was captured in a methanol trap (−30°C).

Unless otherwise specified, the following set of reaction conditions was employed as the optimal conditions: reaction temperature, 450°C; molar ratio of alcohol and pyridine ([alcohol]/[pyridine]), 8.0; feed rate of reactants (a pyridine and an alcohol), 4.0 ml/h; flow rate of carrier gas (N_2), 15 ml/min; amount of catalyst, 3.0 g; calcination conditions of catalysts, 500°C for 3 h. When examining the influence of reaction conditions on catalytic activities, however, only one condition was varied from the above values and other conditions were kept unchanged. Unless otherwise noted, the catalytic activity was discussed on the basis of the analysis of a liquid mixture obtained from 0 to 1 h after reaction: the average yields of alkylpyridines correspond to those obtained within 1 h after the start of the reaction.[13] Gaseous compounds were of course produced by the decomposition of both pyridines and alcohols. The recovery of pyridines by the methanol trap (−30°C) was found to be 90%.[13] Thus the yield of a gaseous compound formed by the decomposition of the pyridine ring was calculated from the difference in molar amount of alkylpyridines between the value estimated from the recovery in the methanol trap and the value actually recovered.[13] The yield of an alkylpyridine was calculated by considering the formation of both liquid and gaseous compounds from a starting pyridine. The conversion of a pyridine shown in this report therefore indicates the conversion of a pyridine to both liquid and gaseous compounds. Experimental data are the means of 3 runs.

Results and Discussion

Alkylation of Pyridine with Methanol

A mixed vapor of pyridine and methanol was passed through a fixed bed of 3.0 g of Na^+, K^+, Rb^+, or Cs^+ exchanged X- or Y-type zeolite under various reaction conditions. Under the optimal conditions, the liquid products were 2-ethylpyridine, 4-ethylpyridine, 2-vinylpyridine, 4-vinylpyridine, α-picoline, β-picoline, γ-picoline, 2,4-lutidine, and 2,6-lutidine. In addition, trace amounts ($<0.1\%$) of 3-ethylpyridine and 2,5-lutidine were produced. Gaseous products were identified as CH_3OCH_3, CO_2, CO, CH_4, H_2, and H_2O. Generally speaking, catalytic activities became observable under reaction conditions involving both a high temperature ($>400°C$) and a small flow rate of carrier gas (N_2) (<20 ml/min). Catalytic activities of zeolites appeared at about 350°C, increased with temperature, and reached their maxima at about 450°C.

Table I summarizes the results of heterogeneous vapor-phase reaction of pyridine with methanol over NaX, KX, RbX, CsX, NaY, KY, RbY, or CsY in an atmosphere of nitrogen at 450°C. As can be seen from Table I, a Y-type zeolite gives a larger conversion of pyridine than the corresponding X-type zeolite. Furthermore, as far as the alkali metals are concerned, catalytic activities are in the following order of magnitude: Cs>Rb>K>Na. Therefore, CsY exhibited the highest activity among the 8 catalysts examined. On the other hand, a Y-type zeolite shows rather smaller selectivities to α-picoline, 2-ethylpyridine, and 2-vinylpyridine than the corresponding X-type zeolite.

The total yield of alkylpyridines in Table I is less than the value calculated from the conversion of pyridine. This difference corresponds to the total yield of gaseous compounds formed by the thermal decomposition of the pyridine ring. Thermal decomposition of pyridine appeared at about 370°C and increased with temperature. The total yield of gaseous compounds in the alkylation of pyridine with methanol at 375, 400, 425, 450, 475, or 500°C was found to be 3, 9, 14, 20, 28, or 37% for CsX, and 4, 14, 22, 31, 45, or 59% for CsY, respectively. Fortunately, it was almost independent of the kind of alkali cation.

The yield of γ-picoline in the methylation of pyridine is greater than expected in view of the yields of α- and γ- picolines and 2- and 4-ethylpyridines shown in Table I. Furthermore, 3-ethylpyridine and 3-vinylpyridine are hardly produced despite the presence of β-picoline. In addition, when a mixed solution of α-, β-, γ-picolines and methanol (1: 1: 1: 24) was passed through a catalyst bed of CsY, methylation of α- and γ-picolines was observed, (the former occurs in preference), whereas β-picoline was almost unreactive. This indicates the following order of side-chain methylation: α-picoline>γ-picoline>β-picoline.

Although not shown in Table I, the yields of alkylpyridines were found to be dependent on the molar ratio of methanol and pyridine ([methanol]/[pyridine]) in a starting liquid mixture.

TABLE I. Conversion of Pyridine and Yields of Alkylpyridines in the Alkylation of Pyridine with Methanol over Alkali Cation Exchanged Zeolites[a]

Catalyst[b]	Conversion[c] (%)	Yield (%)								
		α-Picoline	β-Picoline	γ-Picoline	2,4-Lutidine	2,6-Lutidine	2-Ethylpyridine	4-Ethylpyridine	2-Vinylpyridine	4-Vinylpyridine
NaX	45	5.8	0.8	1.2	0.5	0.5	9.5	1.5	4.8	0.6
KX	46	5.2	0.7	1.2	1.3	0.5	10.1	1.8	5.0	0.7
RbX	56	7.6	1.3	2.1	0.7	0.7	15.8	2.4	4.7	0.7
CsX	58	6.5	1.4	1.8	0.7	0.4	18.6	2.5	5.3	0.8
NaY	65	5.4	2.9	4.4	2.0	1.1	11.2	1.6	4.1	0.6
KY	66	5.3	2.7	4.9	1.4	2.5	12.3	0.9	4.6	0.3
RbY	79	8.2	3.7	5.2	2.5	1.4	18.5	4.3	3.4	0.9
CsY	82	6.5	3.1	5.0	0.9	0.6	22.2	5.3	5.5	1.4

a) Reaction conditions: temperature, 450 °C; [methanol]/[pyridine], 8.0; feed rate of the mixture of pyridine and methanol, 4.0 ml/h; flow rate of carrier gas (N_2), 15 ml/min; amount of catalyst, 3.0 g; calcination conditions of catalysts, 500 °C for 3 h.

b) Degree of cation exchange: KX, 90%; RbX, 75%; CsX, 81%; KY, 90%; RbY, 77%; CsY, 79%.

c) Conversion of pyridine to both alkylpyridines and gaseous compounds.

Major products were found to be particularly dependent on [methanol]/[pyridine]. Namely, when [methanol]/[pyridine]<0.4, α-picoline>γ-picoline were mainly produced, whereas when [methanol]/[pyridine]>1.0, 2-ethylpyridine was produced as a major product. Moreover, the conversion of pyridine and the yield of 2-ethylpyridine tended to increase with decrease in the flow rate of carrier gas (N_2).

In the alkylation of toluene over Na^+, K^+, Rb^+, and Cs^+ exchanged zeolites in the vapor phase, ethylbenzene and styrene were produced selectively, but xylenes were not produced.[7] In the alkylation of pyridine, these alkali cation exchanged zeolites could catalyze not only the formation of ethylpyridines and vinylpyridines but also that of lutidines. The formation of ethylpyridines and vinylpyridines can be rationally accounted for in terms of the side-chain methylation of corresponding picolines produced at first by the ring methylation of pyridine with methanol.

Alkylation of Picolines with Methanol

The alkylation of α-picoline with methanol over alkali cation exchanged zeolites resulted in the formation of 2-ethylpyridine, 2-vinylpyridine, 2,4-lutidine, and 2,6-lutidine. In addition, considerable amounts of β-picoline, γ-picoline, and pyridine and small amounts of 2,5-lutidine, 3-ethylpyridine, 4-ethylpyridine, and 4-vinylpyridine were produced. The alkylation of β-picoline with methanol over alkali cation exchanged zeolites led to the formation of 3-ethylpyridine, 3-vinylpyridine, and 2,5-lutidine. In addition, considerable amounts of α-picoline and 2,6-lutidine and small amounts of pyridine, γ-picoline, 2,3-lutidine, 2,4-lutidine, 2-ethylpyridine, 2-vinylpyridine, and 4-ethylpyridine were produced simultaneously. The alkylation of γ-picoline with methanol resulted in the formation of 4-ethylpyridine, 4-vinylpyridine, and 2,4-lutidine. In addition, considerable amounts of α-picoline, 2,6-lutidine and small amounts of pyridine, β-picoline, 2-ethylpyridine, and 2-vinylpyridine were formed. Although the alkylation of picolines with methanol yielded ethylpyridines and vinylpyridines as major products, lutidines were formed simultaneously to a considerable extent. The co-occurrence of ring alkylation is the fundamental distinction between the side-chain alkylation of toluene[7] and that of picolines. In analogy with the alkylation of pyridine with methanol, gaseous products in the alkylation of picolines were found to be CH_3OCH_3, CO_2, CO, CH_4, H_2, and H_2O.

The catalytic activities of the alkali cation exchanged zeolites in the side-chain alkylation of picolines with methanol appeared at about 350°C, increased with temperature, reached their maxima at 450°C, and decreased at higher temperatures. It was above 400°C that the yields of ethylpyridines and vinylpyridines began to surpass those of lutidines. The results for the alkylation of α-picoline, β-picoline, and γ-picoline with methanol over alkali cation exchanged zeolites under the optimal reaction conditions are summarized in Tables II, III, and IV, respectively. The yields of alkylpyridines in the alkylation of γ-picoline are somewhat lower, and the yields of alkylpyridines in the alkylation of β-picoline are considerably lower than those of alkylpyridines in the alkylation of α-picoline. As far as alkali metals are concerned, catalytic activities are in the following order of magnitude: Cs>Rb>K>Na. Although a Y-type zeolite shows larger conversions of picolines and higher yields of ethylpyridines than the corresponding X-type zeolite, it provides rather smaller selectivities to ethylpyridines and vinylpyridines than the corresponding X-type zeolite. Although not shown in these tables, maximal yields of vinylpyridines were attained at 425°C, which was slightly lower than the optimal temperature for the formation of ethylpyridines (450°C). For example, 18.4% 2-ethylpyridine and 6.6% 2-vinylpyridine, 6.4% 3-ethylpyridine and 2.1% 3-vinylpyridine, and 16.0% 4-ethylpyridine and 6.2% 4-vinylpyridine were obtained in the methylation of α-, β-, and γ-picolines, respectively, over CsY at 425°C. In general, the yields of 2-vinylpyridine from α-picoline, 3-vinylpyridine from β-picoline, and 4-vinylpyridine from γ-picoline were highest when CsX was used at 425°C, and were found to be 9.9, 2.9, and 7.7%, respectively. In general, optimal conditions for the formation of vinylpyridines were slightly milder than those for the formation of ethylpyridines.

In the next place, as can be seen from Tables I, II, and IV, the yield ratio of either 2-ethylpyridine to 2-vinylpyridine or 4-ethylpyridine to 4-vinylpyridine in the alkylation of either α- or γ-picoline is considerably greater than the corresponding yield ratio in the alkylation of pyridine with methanol. This can be accounted for by the fact that the yield of hydrogen in gaseous products in the alkylation of a picoline was greater than that in the alkylation of pyridine by a factor of about 1.3. Moreover, when hydrogen was used as a carrier gas in place of nitrogen, the yields of ethylpyridines increased to some extent, but the yields of vinylpyridines became very low in the alkylation of both pyridine and picolines.

Although not shown in Tables II, III, and IV, the yields of ethylpyridines decreased with the passage of time on-stream. For example, they were reduced to about one-half of their initial values at 30 h on-stream. However, they were restored to more than 90% of the maximal values by recalcining the catalysts at 700°C for 3 h in an atmosphere of oxygen even after 30 h on-stream. In contrast, the yields of vinylpyridines reached maxima at 4—5 h on-stream, and thereafter decreased very slowly. Next, the yields of ethylpyridines decreased remarkably with increase in the flow rate of carrier gas (N_2), provided that the flow rate was

TABLE II. Conversion of α-Picoline and Yields of Alkylpyridines in the Alkylation of α-Picoline with Methanol over Alkali Cation Exchanged Zeolites[a)]

Catalyst[b)]	Conversion[c)] (%)	Yield (%)				
		2,4-Lutidine	2,6-Lutidine	2-Ethylpyridine	2-Vinylpyridine	Others[d)]
NaX	47	1.4	2.7	15.9	3.8	3.2
KX	49	1.2	2.9	17.4	3.5	4.1
RbX	56	1.1	3.2	23.0	4.0	4.7
CsX	61	0.8	2.9	28.3	4.5	4.5
NaY	70	1.6	4.3	19.9	3.5	9.7
KY	71	1.2	4.8	22.0	3.6	8.4
RbY	77	1.4	5.5	25.3	3.2	10.6
CsY	83	3.6	7.3	30.2	3.1	7.8

a) Reaction conditions: see Table I.
b) Degree of cation exchange: see Table I.
c) Conversion of α-picoline to both alkylpyridines and gaseous compounds.
d) Pyridine, other picolines, other lutidines, and other ethylpyridines.

TABLE III. Conversion of β-Picoline and Yields of Alkylpyridines in the Alkylation of β-Picoline with Methanol over Alkali Cation Exchanged Zeolites[a)]

Catalyst[b)]	Conversion[c)] (%)	Yield (%)			
		2,5-Lutidine	3-Ethylpyridine	3-Vinylpyridine	Others[d)]
NaX	28	1.5	4.0	1.2	1.3
KX	30	1.7	5.8	1.4	1.1
RbX	34	2.5	8.1	1.7	1.7
CsX	38	3.1	11.3	2.0	1.6
NaY	43	3.7	5.3	1.2	1.8
KY	45	4.8	6.7	1.1	1.4
RbY	50	7.4	8.7	1.1	1.7
CsY	52	6.3	10.7	1.3	2.7

a) Reaction conditions: see Table I.
b) Degree of cation exchange: see Table I.
c) Conversion of β-picoline to both alkylpyridines and gaseous compounds.
d) Pyridine, other picolines, other lutidines, and other ethylpyridines.

TABLE IV. Conversion of γ-Picoline and Yields of Alkylpyridines in the Alkylation of γ-Picoline with Methanol over Alkali Cation Exchanged Zeolites[a]

Catalyst[b]	Conversion[c] (%)	Yield (%)			
		2,4-Lutidine	4-Ethylpyridine	4-Vinylpyridine	Others[d]
NaX	43	4.6	11.7	3.9	2.8
KX	47	4.9	16.5	3.8	1.9
RbX	50	5.1	18.9	4.2	1.8
CsX	55	4.6	24.9	4.2	1.4
NaY	63	11.8	13.4	3.5	3.2
KY	66	12.3	17.5	3.2	2.1
RbY	70	12.5	19.5	3.1	3.9
CsY	77	13.8	27.1	3.7	1.4

a) Reaction conditions: see Table I.
b) Degree of cation exchange: see Table I.
c) Conversion of γ-picoline to both alkylpyridines and gaseous compounds.
d) Pyridine, other picolines, other lutidines, and other ethylpyridines.

greater than 20 ml/min. However, the yield ratios of vinylpyridines to ethylpyridines increased with increase in the flow rate. Further, the yields of ethylpyridines and vinylpyridines increased slightly with decrease in the flow rate in the region of 20—10 ml/min, and then decreased with decrease in the flow rate at below 10 ml/min. Next, the yields of ethylpyridines and vinylpyridines increased with increase in the partial pressure of methanol. However, the yield ratios of vinylpyridines to ethylpyridines tended to decrease with increase in [methanol]/[picoline]. Moreover, the yields of ethylpyridines increased remarkably with the percentage of cation exchange ($Na^+ \rightarrow Cs^+$). However, beyond 60%, they increased only very slowly with increase in the degree of cation exchange. In contrast, the yields of vinylpyridines were not influenced very much by the percentage of cation exchange. Further, the yields of alkylpyridines were independent of calcination temperature of zeolites in the region of 500—750°C.

Other Reactions

The alkylation of pyridine with ethanol was carried out over CsY and was found to give 5.9% 2-ethylpyridine, 1.1% 3-ethylpyridine, 3.2% 4-ethylpyridine, 1.3% 2-vinylpyridine, and 1.1% 2,6-lutidine under the optimal reaction conditions. In addition, considerable amounts of α-, β-, and γ-picolines and small amounts of 2,4-lutidine, 2,5-lutidine, 3-vinylpyridine, and 4-vinylpyridine were produced. Contrary to expectation, diethylpyridines and butylpyridines were not produced.

The alkylation of picolines with ethanol was examined over CsY and was found to give 1.5% 2-propylpyridine from α-picoline and 0.9% 4-propylpyridine from γ-picoline as major products under the optimal conditions. However, 3-propylpyridine was not formed from β-picoline due to its instability at elevated temperature. In general, catalytic activities of zeolites in the alkylation of pyridines with ethanol were much smaller than those in the alkylation of pyridines with methanol.

The alkylation of ethylpyridines with methanol was investigated over CsY and was found to give 6.2% 2-propylpyridine from 2-ethylpyridine and 5.1% 4-propylpyridine from 4-ethylpyridine under the optimal conditions. However, 3-propylpyridine was not formed from 3-ethylpyridine. Although propylpyridines were mainly obtained, considerable amounts of pyridine, picolines, and lutidines were formed.

Next, the alkylation of lutidines with methanol was carried out using CsY and was found to result in the formation of ethylmethylpyridines containing 2- or 4-ethyl group. However, the yields of ethylmethylpyridines containing 3-ethyl group were less than 0.1%. Actually, under the optimal conditions, this alkylation gave 4.9% 2-ethyl-3-methylpyridine from 2,3-lutidine, 5.2% 2-ethyl-4-methylpyridine and 2.4% 4-ethyl-2-methylpyridine from 2,4-lutidine, 7.3% 2-ethyl-5-methylpyridine from 2,5-lutidine, 8.8% 2-ethyl-6-methylpyridine from 2,6-lutidine, and 7.0% 4-ethyl-3-methylpyridine from 3,4-lutidine. However, almost no ethylmethylpyridine was produced from 3,5-lutidine. In addition, the yields of diethylpyridines and methylvinylpyridines were very low.

The alkylation of pyridine with propyl alcohol was carried out over CsY and was found to give 1.3% 2-propylpyridine and 0.6% 4-propylpyridine at 450°C as major products. In addition, picolines, lutidines, and ethylpyridines were formed simultaneously. However, the alkylation of pyridine with isopropyl alcohol, butyl alcohol, *sec*-butyl alcohol, or *tert*-butyl alcohol occurred over CsY, but no isopropylpyridine, butylpyridine, *sec*-butylpyridine, or *tert*-butylpyridine was produced.

Consideration on the Active Sites for the Side-chain Alkylation of Pyridines

The side-chain alkylation of alkylpyridines has been studied in the presence of basic catalysts, such as alkali metals.[8-11] In addition, Yashima *et al.*[7] considered in detail the side-chain alkylation of toluene with methanol or formaldehyde over alkali cation exchanged zeolites and suggested that the active sites were solid base sites. In the alkylation of toluene over alkali cation exchanged zeolites, ethylbenzene and styrene were produced selectively, and xylenes were not produced simultaneously.[7] On the other hand, in the alkylation of picolines, not only ethylpyridines and vinylpyridines but also lutidines were produced. Moreover, pyridine itself was alkylated with alcohol over an alkali cation (except Li^+) exchanged zeolite. Thus, the most striking characteristic of the side-chain alkylation of pyridines is that it is always accompanied by ring alkylation.

As far as the alkylation of a picoline with methanol over CsY was concerned, the formation of an ethylpyridine and a vinylpyridine became undetectable when about 1 mol % of hydrogen chloride, a typical acidic reagent, was added to the reaction system. In this case, the formation of lutidines decreased remarkably, but did not cease completely. On the other hand, when about 1 mol % of aniline, a typical basic reagent, was added to the reaction system, the yields of the ethylpyridine and the vinylpyridine increased to some extent. In addition, the yields of lutidines also increased but only slightly. Therefore, the active sites for both side-chain alkylation and ring alkylation of pyridines over Na^+, K^+, Rb^+, and Cs^+ exchanged zeolites can be concluded to be the solid base sites. In contrast to the alkylation of toluene,[7] some of the solid base sites can catalyze the ring alkylation of pyridines.

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