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Catalytic Reactions of Pyridines. VI.[1] Heterogeneous Vapor-phase Ring Alkylation of Pyridines with Alcohols over H^+-, Li^+-, and Alkaline Earth Cation-Exchanged Zeolites

HIROSHI KASHIWAGI,* YUJI FUJIKI, and SABURO ENOMOTO

Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University, 2630, Sugitani, Toyama-shi, Toyama, 930-01, Japan

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The heterogeneous vapor-phase alkylation of pyridine with methanol was examined over metal cation-exchanged X- and Y-type zeolites in an atmosphere of nitrogen. β-Methylation was observed over H^+- or Li^+-exchanged zeolites, whereas α- and γ-methylation (the former occurred in preference) were observed over alkaline earth cation-exchanged zeolites. For example, at 400°C, the yields of α-, β-, and γ-picolines over the HY catalyst were 2.6, 12.2, and 2.6%, whereas those over the BaY catalyst were 22.7, 3.8, and 7.6%, respectively.

This catalytic ring alkylation over metal cation-exchanged zeolites was also examined by the use of pyridine with ethanol and picolines with either methanol or ethanol.

Keywords——alkylation; catalyst; H^+-exchanged zeolite; Li^+-exchanged zeolite; alkaline earth cation-exchanged zeolite; pyridine; picoline; lutidine; methanol; ethanol

Metal cation-exchanged zeolites (metal cation-exchanged X- or Y-type zeolite is abbreviated henceforth as MX or MY, respectively, where M is the chemical symbol of the metal used) have hitherto been used as catalysts in various reactions, especially in the vapor phase.[2] For example, Venuto *et al.*[3,4] and Minachev *et al.*[5] studied the alkylation of a variety of aromatic compounds catalyzed by metal cation-exchanged zeolites. As regards reactions of aromatic compounds over zeolites, alkylations of alkylbenzenes were described most frequently.[6-9] In contrast, the heterogeneous vapor-phase alkylation of pyridines was not investigated until the appearance of our reports on the α-alkylation of pyridines with alcohols over NiX or NiY at 350 °C[10] and the side-chain alkylation of pyridine derivatives over alkali cation-exchanged zeolites at 450°C.[11]

A different attachment of a methyl or ethyl group to the pyridine ring was found for the alkylation of pyridines with alcohols over H^+-, Li^+-, and alkaline earth cation-exchanged zeolites under reaction conditions involving both a high temperature (about 400°C) and a low flow rate of carrier gas (N_2) (about 20 ml/min).

Experimental

Reagents——Pyridine, α-, β-, and γ-picolines, lutidines, ethylpyridines, ethylmethylpyridines, each 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——A metal cation-exchanged X- or Y-type zeolite was prepared by a conventional cation-exchange procedure using a saturated aqueous solution of a metal nitrate and either 13X(raw NaX) or SK-40 (raw NaY).[11] As an exception, HX or HY was prepared by the deammoniation of NH_4X or NH_4Y upon heating at 500°C for 3 h after the cation-exchange ($Na^+ \rightarrow NH_4^+$) procedure. Degrees of cation exchange, determined by means of X-ray fluorescence analysis, were found to be 75—91%.

Analysis——Liquid and gaseous products were analyzed by gas chromatography. The chromatographic conditions were as described in our previous paper.[11]

Apparatus and Procedure——Experiments were carried out in a fixed bed type apparatus in the manner described previously.[11] Unless otherwise specified, the following set of reaction conditions was employed as the optimal conditions: reaction temperature, 400°C for methylation and 420°C for ethylation; 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), 20 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 usual value and other conditions were kept unchanged. The catalytic activity was usually discussed on the basis of analysis of a liquid mixture accumulated within 1 h after the start of the reaction.[10,11] The yields of alkylpyridines and the conversions of pyridines were calculated as described in the previous paper.[11] Experimental data are the means of three runs.

Results and Discussion

Alkylation of Pyridine with Methanol

A mixed vapor of pyridine and methanol was passed through a fixed bed of a metal cation-exchanged X- or Y-type zeolite under various reaction conditions. Generally speaking, formations of products became observable at 320 °C, and increased with temperature, reaching their maxima at about 400 °C. Further, if the flow rate of carrier gas (N_2) was greater than 25 ml/min, the conversions of pyridine and the yields of alkylpyridines decreased remarkably with increase in the flow rate. In general, a pronounced catalysis was seen under reaction conditions involving both a high temperature (about 400°C) and a low flow rate of carrier gas (about 20 ml/min).

Table I summarizes the results for heterogeneous vapor-phase reactions of pyridine with methanol over various metal cation-exchanged zeolites in an atmosphere of nitrogen at 400 °C. In general, a Y-type zeolite provides larger conversions of pyridine and higher total yield of alkylpyridines, but smaller selectivities to picolines than the corresponding X-type zeolite. The position of methylation is dependent on the metal cation. Namely, β-methylation over HX, HY, LiX, and LiY and α- and γ-methylation (the former occurs in preference) over other metal cation-exchanged zeolites are observed. As far as the present experiments are concerned, the yields and selectivities to α- and γ-picolines are influenced by the metal cations and are particularly high for alkaline earth cation-exchanged zeolites. Furthermore, the conversion of pyridine and the yields of α- and γ-picolines were examined for Al, Cr, Mn, Cu, Zn, Ag, Cd, Ce, Hg, or Pb cation-exchanged zeolites, but were found to be considerably lower than those for the alkaline earth cation-exchanged zeolites. Although NiY mainly produces α-picoline and 2,6-lutidine even under this set of reaction conditions, their yields and selectivities are much lower than the values described in the previous paper.[10] In this case, considerable amounts of other picolines, lutidines, and ethylpyridines are formed as by-products. In particular, as in our previous report,[11] alkali cation-exchanged zeolites give rise to the formation of significant amounts of 2- and 4-ethylpyridines even under this set of reaction conditions. Next, 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.[11] Gaseous products in this reaction were found to be CH_3OCH_3, CO_2, CO, CH_4, H_2, and H_2O.[12]

The conversion of pyridine and the yields of the picolines were found to decrease with the passage of time on-stream. The yields of picolines became 30—50% of the initial values at 30 h on-stream. However, they were restored to more than 90% of the initial values by recalcining the catalysts at 700°C for 3 h in an atmosphere of oxygen even after 30 h on-stream. The conversion of pyridine and the yields of picolines also increased with both decrease in the flow rate of carrier gas and increase in the partial pressure of methanol. In contrast to the yields of major picolines, the selectivities to the major picolines increased with decrease of reaction temperature and with increases of flow rate of carrier gas and of partial pressure of methanol. Further, the conversions of pyridine and the yields of alkylpyridines were almost independent of degree of cation exchange in the region of 60—100% and of calcination temperature of catalysts in the region of 500—750°C.

Table I. Conversion of Pyridine and Yields of Alkylpyridines in the Alkylation of Pyridine with Methanol over Various Metal Cation-Exchanged Zeolites[a]

Catalyst	Conversion[b] (%)	Yield (%)								
		α-Picoline	β-Picoline	γ-Picoline	2-Ethylpyridine	3-Ethylpyridine	4-Ethylpyridine	2,4-Lutidine	2,5-Lutidine	2,6-Lutidine
HX	25	2.5	10.0	2.5	0.5	0	0	0	3.0	0.8
HY	32	2.6	12.2	2.6	0.6	0	0	0	4.8	1.3
LiX	24	2.9	7.9	1.9	0.7	0.5	0	0.2	2.9	1.0
LiY	31	3.7	9.0	2.2	1.2	0.9	0	1.2	2.8	1.9
FeY	35	13.7	2.5	4.9	0	0	0	2.1	0.7	3.5
CoY	37	14.4	2.2	5.6	0	0	0	2.2	0.7	3.7
NiY	44	20.0	1.9	7.1	0	0	0	1.4	0.5	6.1
MgX	29	12.2	2.6	5.8	0	0	0	1.2	0	2.0
MgY	48	20.2	4.9	8.3	0	0	0	4.7	0	3.2
CaX	36	15.1	3.2	6.8	0	0	0	2.2	0	3.2
CaY	57	21.5	3.9	8.0	0	0	0	8.1	0	8.6
SrX	39	17.2	3.9	8.2	0	0	0	1.6	0	3.5
SrY	62	22.3	3.8	7.4	0	0	0	10.8	0	10.9
BaX	41	19.7	4.1	9.0	0	0	0	2.1	0	2.5
BaY	63	22.7	3.8	7.6	0	0	0	10.7	0	10.7
NaY	25	6.5	1.8	2.0	1.8	0	0.3	1.5	0	2.0
KY	26	6.8	1.8	2.3	2.3	0	0.6	1.8	0	2.5
RbY	26	6.8	1.8	2.3	2.3	0	0.6	1.6	0	2.5
CsY	30	6.9	2.1	3.0	3.0	0	0.3	2.4	0	3.3

a) Reaction conditions: temperature, 400°C; [methanol]/[pyridine],, 8.0; feed rate of the mixture of pyridine and methanol, 4.0 ml/h; flow rate of carrier gas, 20 ml/min; amount of catalyst, 3.0 g; calcination conditions of catalysts, 500°C for 3 h.

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

Alkylation of Picolines with Methanol

The alkylation of α-, β-, and γ-picolines with methanol over HY or LiY at 400 °C resulted in the formation of 1.8 or 6.2% 2,5-lutidine from α-picoline, 1.3 or 1.7% 3,5-lutidine from β-picoline, and 1.4 or 2.9% 3,4-lutidine from γ-picoline, respectively. Next, the alkylation of picolines with methanol over CaY or BaY at 400°C led to the formation of 5.2 or 4.4% 2,4-lutidine and 8.8 or 11.5% 2,6-lutidine from α-picoline, 4.1 or 4.9% 2,5-lutidine and 0.6 or 0.9% 3,4-lutidine from β-picoline, and 10.9 or 12.8% 2,4-lutidine from γ-picoline, respectively. In addition, small amounts of pyridine, other picolines, other lutidines, and ethylpyridines were obtained in the reaction mixture. In general, β-methylation over H^+- or Li^+-exchanged zeolites and α- and γ-methylation over alkaline earth cation-exchanged zeolites were also observed in this case.

Alkylation of Pyridine with Ethanol

A mixture of pyridine and ethanol was passed through a fixed bed of HY, LiY, CaY, or BaY. The yields of 2-, 3-, and 4-ethylpyridines in the alkylation of pyridine with ethanol at 420 °C were 0.9, 3.7, and 1.7% for HY, 0.9, 4.2, and 4.0% for LiY, 6.3, 1.8, and 3.9% for CaY, and 7.4, 1.9, and 4.8% for BaY, respectively. Generally speaking, β-ethylation over H^+- and Li^+-exchanged zeolites and α- and γ-ethylation over alkaline earth cation-exchanged zeolites were observed. Further, considerable amounts of 2,4- and 2,6-lutidines and α-, β-, and γ-picolines were produced.

Alkylation of Picolines with Ethanol

The reaction of α-, β-, and γ-picolines with ethanol over HY or LiY at 420°C led to the formation of 0.8 or 0.6% 5-ethyl-2-methylpyridine from α-picoline, 0.4 or 0.4% 3-ethyl-5-

methylpyridine from β-picoline, and 0.5 or 0.4% 3-ethyl-4-methylpyridine from γ-picoline, respectively. Next, the alkylation of the picolines with ethanol over CaY or BaY at 420 °C resulted in the formation of 3.8 or 4.3% 2-ethyl-6-methylpyridine and 1.4 or 1.5% 4-ethyl-2-methylpyridine from α-picoline, 2.7 or 3.0% 2-ethyl-5-methylpyridine and 0.7 or 0.9% 4-ethyl-3-methylpyridine from β-picoline, and 3.8 or 4.4% 2-ethyl-4-methylpyridine from γ-picoline, respectively. In addition, pyridine, other picolines, lutidines, and ethylpyridines were formed to a considerable extent. As a rule, β-ethylation over H^+- or Li^+-exchanged zeolites and α- and γ-ethylation over alkaline earth cation-exchanged zeolites were observed. The yields of alkylpyridines in the vapor-phase alkylation of picolines with ethanol over the cation-exchanged zeolites were maximized at 420°C and were found to be much lower than those in the alkylation of picolines with methanol.

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12) Thermal decomposition of the pyridine ring appeared at about 380°C and increased with temperature. When pyridine vapor was passed through a fixed bed of BaY or HY at 400°C, gaseous compounds, such as CO_2, CO, CH_4, H_2, and H_2O, were generated. Almost independent of the kinds of metal cations, the conversions of the pyridine ring to gaseous products at 400°C were 11% for a Y-type zeolite and 7% for a X-type zeolite. On the other hand, 46% of methanol was converted to gaseous compounds, such as CH_3OCH_3, CO_2, CO, and H_2O, when methanol vapor was passed through a fixed bed of BaY or HY at 400°C. Therefore, large proportions of the CH_3OCH_3, CO_2, CO, and H_2O were derivedf rom methanol.