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DEMETHYLATION OF 2,3-XYLIDINE TO m-TOLUIDINE

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Hydrocracking of 2,3-xylidine to m-toluidine over various metal oxide-supported nickel catalysts was examined. m-Toluidine was obtained in 65.3% of selectivity at 52.6% of 2,3-xylidine conversion by using basic nickel-magnesia catalyst. Nickel catalysts supported on strongly acidic metal oxides caused considerable extents of side reactions.

Selective demethylation of nuclear-methylated aromatic amines has not yet been successfully carried out, because the reaction is usually accompanied by a considerable amount of deamination.[1] At present, no investigations concerning with these selective demethylation have been reported except for only a few patents.[2,3] The present authors have found that the demethylation of 2,3-xylidine over nickel catalysts supported on metal oxides yielded selectively m-toluidine, which is a useful intermediate for some synthetic coloring materials.

The reactions were carried out in a continuous flow reactor made of stainless steel pipe of internal diameter of 2.5 cm equipped with an internal thermocouple well. Twenty ml of catalyst was packed in a middle part of the reactor and the upper part was filled with inert Rashig rings which served as a preheater. The catalysts were prepared by impregnating the aqueous solution of nickel nitrate or chromium nitrate on metal oxide carriers[4] followed by calcination at 550°C in air. Prior to use, all catalysts were reduced for 3 hours at 500°C with hydrogen gas. 2,3-Xylidine and hydrogen gas were supplied at a controlled rate from the top of the reactor. The reaction mixture was collected through a back pressure controll valve into an ice-cooled receiver and the liquid products were analyzed by GC and GPC. Defects in the mole-balance between the feed and the recovered liquid were due to the formation of coke and gaseous products.

At first, the thermal hydrocracking of 2,3-xylidine under an atmospheric pressure was examined and the results were summerized in Table 1. The thermal hydrocracking yielded a large amount of o-toluidine and coke and it was revealed to be unsatisfactory for the preparation of m-toluidine.

Although many catalysts for hydrocracking have been known to be active, in the present study, Ni, Pd, Pt, Cu, Cr and Co were tested. Among them, Ni was found to be most effective for the preparation of m-toluidine.

Table 1. Thermal hydrocracking[a)]

Reaction Temp.	Conv. of 2,3-Xyl.[b)]	Selectivity of products (%)						
		BTX[c)]	Aniline	o-Tol.[d)]	m-Tol.[e)]	Isomers[*)]	Others	Coke,gas
650°C	4.7 (%)	10.5	0.4	21.6	45.6	2.8	19.1	0
730	48.7	10.9	3.8	13.3	30.2	0.7	2.7	39.4

Table 2. Catalytic hydrocracking[f)]

Catalyst	Conv. of 2,3-Xyl.[b)]	Selectivity of products (%)						
		BTX[c)]	Aniline	o-Tol.[d)]	m-Tol.[e)]	Isomers[*)]	Others	Coke,gas
Cr_2O_3-α-Al_2O_3[g)]	80.5(%)	98.2	0	0.1	0.5	0.2	1.0	—
Ni-MgO	52.6	16.2	11.2	2.6	65.3	2.7	0.5	1.5
Ni-Al_2O_3	64.9	28.0	4.9	2.3	40.0	20.5	4.3	—
Ni-SiO_2-Al_2O_3	61.0	33.7	4.7	4.0	28.5	24.5	4.7	—
Ni-TiO_2	16.0	12.7	2.6	2.9	71.1	9.9	0.8	—
Ni-ZrO_2	74.4	46.6	16.4	1.3	31.8	1.6	2.3	—
Ni-ZnO	14.0	15.6	1.1	4.7	66.7	10.9	1.0	0

a) H_2/2,3-xylidine = 6, LHSV of 2,3-xylidine = 0.3 hr^{-1} b) 2,3-xylidine c) benzene, toluene, xylene d) o-toluidine e) m-toluidine *) isomers of 2,3-xylidine f) reaction temp. = 550°C, pressure = 10 kg/cm^2, LHSV(2,3-xyl.) = 1.0 hr^{-1}, H_2/2,3-xyl. = 3.0 g) reaction temp. = 480°C

Table 2 shows the results over Cr_2O_3-α-Al_2O_3, which gave very high selectivity for deamination rather than demethylation though contrary to the present purpose. Ni-MgO showed the highest selectivity for the formation of m-toluidine at relatively high conversion.

The selectivity of m-toluidine is influenced by side reactions, that is, the isomerization, the demethylation of meta-methyl group, the deamination, etc. The extent of isomerization over Ni catalysts can be related to the acidic character of each metal oxide carriers as indicated in terms of H_0,max proposed by Yamanaka and Tanabe[5)] in Table 3. The isomerizations became significant over carriers of H_0,max ≤ -3.0 and the extent of those over basic carriers of H_0,max ≥ 3.3 became similar order to that in the thermal hydrocracking. The product ratio of o-toluidine to m-toluidine also seems to be related to the acidity of carriers.

Table 3. The relation between the acidity of the carriers and the side reactions

Catalyst carriers	Acidity*) H_0,max	Isomerization / Demethylation	o-Toluidine / m-Toluidine	Deamination / Demethylation
SiO_2-Al_2O_3	-5.6	0.66	0.14	0.90
Al_2O_3	-3.0	0.43	0.058	0.59
TiO_2	4.8	0.13	0.041	0.22
ZnO	6.8	0.15	0.07	0.22
ZrO_2	3.3	0.032	0.041	0.94
MgO	6.8	0.034	0.04	0.20
Thermal hydrocracking**)		0.015	0.44	0.23

*) H_0,max of metal oxides was measured by the method proposed by Yamanaka and Tanabe.[5] Before the measurement metal oxides were calcined at 550°C in air for 3 hours. **) at 730°C

As indicated in Table 3, carriers of $H_0,\max \geq -3.0$ gave nearly the same ratios. Strongly acidic silica-alumina gave high ratio though lower than that of the thermal hydrocracking. These observations may be explained by a deduction that the strong acidic surface of the catalyst interacts with benzene ring in a fashion that m-methyl group approaches to the surface active sites.

Table 3 also indicates that the deamination occurred to a larger extent over acidic catalysts than over basic catalysts except for Ni-ZrO_2 (ZrO_2 used in this work had weak acidic sites). In the case of hydrocracking of cresol, Moghul et al.[6] have reported that the acidic catalysts facilitate dehydroxylation and basic catalysts facilitate demethylation. It may be thought that the mechanism of hydrocracking of aromatic amines is similar to that of alkyl phenols.

Sonnemans et al.[7] have reported that in the deamination of pentylamine over acidic catalyst, disproportionation was predominant to direct hydrocracking. Aniline is also known to form diphenylamine through the disproportionation over various acidic catalysts.[8] However, no significant amount of diphenylamine derivatives were found in the hydrocracking product of 2,3-xylidine even over acidic catalysts. The deamination of 2,3-xylidine, therefore, is considered to proceed through direct hydrocracking with little disproportionation. The demethylation is also considered to proceed through direct hydrocracking with little disproportionation of methyl group, because trimethylaniline were detected only in very small amounts in the products.

Figure 1 shows the first order plot of 2,3-xylidine in the range of relatively low conversion over Ni-MgO under constant hydrogen pressure. The rate of 2,3-xylidine conversion was clarified to be of first order in 2,3-xylidine concentration. The catalytic hydrocracking of both toluene[9,10] and cresols[6] were also reported to be of first order in their concentrations. Figure 2 shows the Arrhenius plot of

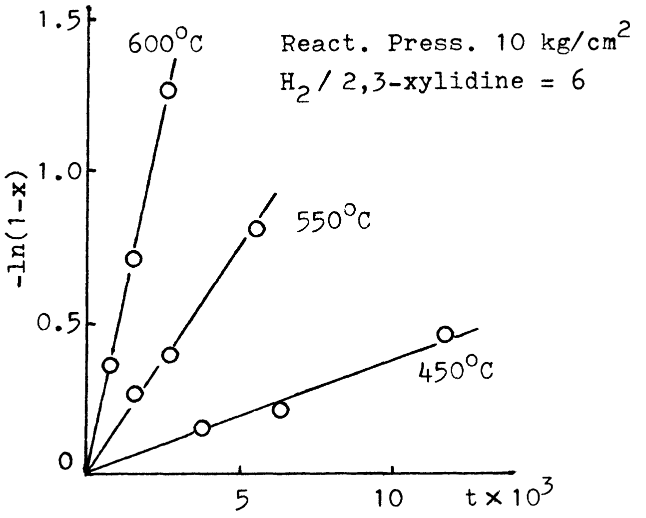

Fig. 1. First order plot of 2,3-xylidine conversion

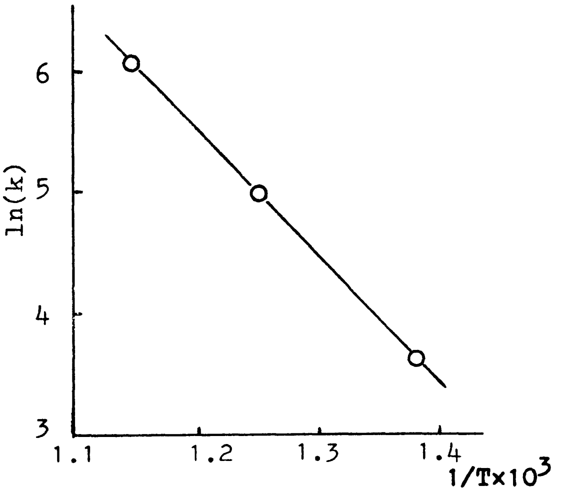

Fig. 2. Arrhenius plot of first order rate constant

the first order rate constant. The activation energy was calculated to be 22 kcal/mole. Further study is required for the clarification of the reaction mechanism.

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