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ZEOLITE-CuNaY CATALYZED DECOMPOSITION OF ARYLDIAZOMETHANE

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Decomposition of aryldiazomethanes is catalyzed by copper ion-exchanged Y-type zeolite to afford **cis**-1,2-diarylethylenes in high selectivity. The catalytic activity and selectivity are found to be affected by the exchange level of copper ions in zeolite and the solvent used.

Recently there have been a lot of studies on gas-phase catalytic reactions induced by transition metal ion-exchanged zeolites such as reduction, oxidation, carbonylation, and so on. The transition metal ions in zeolite are held to the zeolite framework by coordinating lattice oxide ions, hence the zeolite framework is considered to be a mono to polydentate macro ligand to the transition metal ion.1)

In the present study we applied copper(II) ion-exchanged Y-type zeolite (CuNaY: sodium ions in NaY were partly exchanged for copper ions) to decomposition of aryldiazomethane in a liquid phase.

Decompositions of aryldiazomethanes to 1,2-diarylethylenes were reported to be catalyzed by ceric ammonium nitrate,2) lithium bromide,3) copper(II) salts (perchlorate and bromide),4) rhodium(II) acetate,5) iodorhodium(III) tetraphenylporphyrin,5) and to be induced by photolysis.6) In the study of rhodium complexes, the ligand around the rhodium ion greatly affected the catalytic activity and the **cis/trans** selectivity of the product.5)

As compared with an organic ligand like porphyrin, the rigid framework of zeolite containing metal cations is expected to work as an inorganic macro ligand to regulate catalysis of the metal more effectively. Thus we compared catalyses of CuNaY, copper salts supported on Al_2O_3, and $Cu(ClO_4)_2$ on decomposition of aryldiazomethane.

$$\mathrm{ArCHN_2} \xrightarrow{\text{Cat.}} \underset{\underline{1}}{\mathrm{ArCH{=}CHAr}} + \underset{\underline{2}}{\mathrm{ArCH{=}N{-}N{=}CHAr}}$$

CuNaY was prepared by the treatment of sodium ion-exchanged Y-type zeolite (NaY: a reference catalyst from the Catalysis Society of Japan, JRC-Z-Y4.8, SiO_2/Al_2O_3=4.8) with an aqueous $CuCl_2$ solution according to an ion-exchange technique. The content of copper ions was determined by atomic absorption

Table 1. Decomposition of p-chlorophenyldiazomethane by various copper catalysts

Run	Catalyst	Solv.	Temp/°C	Time/h	Product yields/%[a]			
					1(cis/trans)[b]	2	3[c]	4[d]
1	NaY[e]	CH_2Cl_2	-72	9.0[f]	6 (21)	1	0	0
2		$PhCH_3$	0	45	8 (9.7)	2	24	44
3	CuNaY-1[g]	CH_2Cl_2	-72	1.0	64 (22)	1	11	2
4		$PhCH_3$	0	2.0	57 (4.6)	6	15	8
5	CuNaY-5[g]	CH_2Cl_2	-72	6.0	91 (27)	6	0	0
6		$PhCH_3$	0	2.0	57 (5.3)	8	12	6
7		n-Hexane	0	5.0	8 (4.9)	1	4	0
8		Et_2O	0	0.5	47 (8.3)	8	13	4
9	CuNaY-22[g]	CH_2Cl_2	-72	7.5	81 (23)	2	3	2
10		$PhCH_3$	0	8.0	57 (2.4)	9	10	7
11	CuNaY-65[g]	CH_2Cl_2	0	7.5	47 (2.0)	5	8	1
12		$PhCH_3$	35	45	70 (2.5)	9	9	2
13	$CuCl_2/Al_2O_3$[g]	CH_2Cl_2	-72	4.5	46 (4.3)	21	9	9
14		$PhCH_3$	-30	0.25	47 (3.4)	11	11	8
15	$CuSO_4/Al_2O_3$[g]	CH_2Cl_2	-72	4.5	44 (4.7)	17	16	16
16		$PhCH_3$	-30	0.2	48 (3.0)	13	15	13
17	$Cu(ClO_4)_2$[h]	CH_3CN	20	0.2	90 (3.4)	2	0	0
18		CH_3CN	-30	0.2	93 (3.8)	1	0	0

a) Isolated yields. b) Determined by GLC analysis. c) $p\text{-}ClC_6H_4CH_2OH$. d) $(p\text{-}ClC_6H_4CH_2)_2O$. e) NaY (0.9 g) was used. f) The reaction was stopped after 9 h owing to low catalytic activity of NaY. g) Cu^{2+}, 10 mol%. h) 0.7 mol%.

spectroscopy. "n" in CuNaY-n represents the degree (%) of copper ion exchange. $CuCl_2/Al_2O_3$ and $CuSO_4/Al_2O_3$ were prepared by the impregnation of $CuCl_2 \cdot 2H_2O$ (0.5 wt%) and $CuSO_4 \cdot 5H_2O$ (1.0 wt%) on γ-alumina (Woelm-200-neutral), respectively. CuNaY, $CuCl_2/Al_2O_3$, and $CuSO_4/Al_2O_3$ were all dried at 150 °C/0.1 Torr for 24 h prior to use. $Cu(ClO_4)_2$ was dried at 90 °C/0.1 Torr for 2 h.

To a suspended mixture of a copper catalyst (10 mol% of Cu^{2+}) and a solvent (3 ml) (except for a homogeneous mixture of $Cu(ClO_4)_2$ (0.6-0.9 mol%) in CH_3CN) was added a solution of aryldiazomethane (1.0 mmol) in the same solvent (7 ml), and the

Table 2. Decompositions of various aryldiazomethanes by use of $Cu(ClO_4)_2$ and CuNaY-5

Run	Ar	Method$^{a)}$	Time/h	Product yields/%$^{b)}$		
				1	(cis/trans)$^{c)}$	2
1	C_6H_5	A	1	70	(1.7)	7
2		B	7	65	(19)	3
3	o-ClC_6H_4	A	0.2	90	(1.6)	1
4		B	3.5	77	(4.8)	1
5	m-ClC_6H_4	A	0.2	96	(2.8)	0
6		B	4	72	(8.3)	1
7	p-ClC_6H_4	A	0.2	90	(3.4)	2
8		B	6	91	(27)	6
9	o-MeC_6H_4	A	0.2	72	(1.7)	5
10		B	8	63	(6.4)	3
11	m-MeC_6H_4	A	0.3	90	(4.2)	1
12		B	7	68	(18)	1
13	p-MeC_6H_4	A	0.3	81	(1.7)	3
14		B	7	60	(25)	1

a) Method A: Reaction was carried out by use of $Cu(ClO_4)_2$ (0.6-0.9 mol%) at 20 °C.

Method B: Reaction was carried out by use of CuNaY-5 (Cu^{2+}, 10 mol%) at -72 °C.

b) Isolated yield.

c) Determined by GLC analysis.

resulting mixture was stirred until the red color of the diazo compound disappeared. After the addition of benzene (20 ml) and water (20 ml), the mixture was refluxed for 0.5 h in order to desorb organic products from zeolite completely. The organic products were extracted, purified by TLC, and analyzed by GLC and NMR. Main products were olefin (1), azine (2), alcohol ($ArCH_2OH$, 3), and ether ($(ArCH_2)_2O$, 4). Compounds 3 and 4 were derived from the reaction of a diazo compound with residual water in inorganic solids.

The study on decomposition of p-chlorophenyldiazomethane in Table 1 reveals several features. (1) The decomposition was promoted by the homogeneous catalyst ($Cu(ClO_4)_2$) more effectively than by the heterogeneous catalysts (CuNaY,

$CuCl_2/Al_2O_3$, and $CuSO_4/Al_2O_3$). (2) The catalysis of CuNaY was dependent on the exchange level of copper ions in zeolite. The zeolites with low exchange levels (1-22%) of copper ions showed much higher catalytic activities than CuNaY-65. (3) CuNaY-5 showed the highest **cis/trans** selectivity among the catalysts employed. (4) The solvent greatly influenced the yield and selectivity of p,p'-dichlorostilbene in case of CuNaY. (5) Among the heterogeneous catalysts examined, CuNaY proved to be a more effective and selective catalyst than $CuCl_2/Al_2O_3$ and $CuSO_4/Al_2O_3$. Zeolite-encapsulated copper ions thus exhibit catalysis different from that of simple oxide(alumina)-bound copper ions.

Table 2 summarizes decompositions of various aryldiazomethanes catalyzed by $Cu(ClO_4)_2$ and CuNaY-5. In general, with the heterogeneous catalyst of CuNaY, yields of 1,2-diarylethylenes were lower, but their selectivities were higher in comparison with the homogeneous catalyst of $Cu(ClO_4)_2$. It should be noted that a substituent on a benzene ring had a pronounced influence on the enhancement of **cis/trans** selectivity of 1,2-diarylethylene by CuNaY. Phenyldiazomethane and p-substituted phenyldiazomethanes yielded the **cis** olefins in very high selectivities compared with o- and m-substituted ones.

The studies on the location of exchanged-copper ions in zeolite Y reveal that the copper ions occupy the positions which are near or face supercages of zeolite.$^{7)}$ Oshima and Nagai proposed that copper carbenoid intermediates were involved in copper-catalyzed decomposition of aryldiazomethane.$^{4)}$ Similarly it is assumed that in the present reactions organocopper intermediates were formed in narrow supercages (about 13 Å in diameter),$^{8)}$ and the stabilities of the intermediates leading to **cis** or **trans**-1,2-diarylethylene were greatly affected by the restricted circumstances around the copper ions to govern the **cis/trans** selectivity.

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