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ISOMERIZATION AND HYDROGENATION OF NITROGEN-CONTAINING ORGANIC COMPOUNDS CATALYZED BY HETEROGENEOUS CATALYSTS

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Abstract—— The double-bond isomerization of 1-N-pyrrolidino-2-propene  and N,N-dimethyl-2-propenylamine ($C{=}C{-}C{-}N{<}^{C}_{C} \longrightarrow C{-}C{=}C{-}N{<}^{C}_{C}$) were studied at 40°C over MgO, CaO, SrO, BaO, La_2O_3, ThO_2, ZrO_2, ZnO etc. It was found that MgO and CaO which have strong basic sites on the surfaces exhibited a high catalytic activity, the selectivity for the formation of 1-N-pyrrolidino-1-propene being more than 80 %. The double-bond migration of the allylamines is suggested to proceed via anionic intermediates in which the cis form is much more stable than the trans form. For the hydrogenation of N,N-dimethyl-2-propenylamine ($C{=}C{-}C{-}N{<}^{C}_{C} + H_2 \longrightarrow C{-}C{-}C{-}N{<}^{C}_{C}$), the activity as well as the selectivity of nickel catalysts supported on MgO, CaO, La_2O_3, ThO_2, TiO_2, ZrO_2 etc. was examined at 0°C. Nickel on MgO was found to give 100 % conversion and almost 100 % selectivity for the formation of N,N-dimethyl-propenylamine. It is suggested that nickel catalyst becomes active when supported on basic oxides. The reaction path is discussed on the basis of experiments using deuterium as a tracer.

INTRODUCTION

The potential use of enamines has expanded in organic synthesis[1], because of the general ability of enamines for the acylation and alkylation of carbonyl compounds. Base-catalyzed double-bond isomerization of allylamines is one of the ways to prepare enamines. By this method, stereospecific synthesis is possible. Although heterogeneous catalysts have several advantages compared with homogeneous catalysts, only a few solid base catalysts such as K/Al_2O_3[2] and KNH_2/Al_2O_3[3] have been examined for the isomerization of allylamine. However, there remained some problems such as requirement of high reaction temperature and activity degradation during the reaction. Thus, we have attempted to examine the catalytic actions of solid bases such as MgO[4], CaO[5], SrO[6], BaO[7], La_2O_3[8], ThO_2[9] etc., whose basic property was studied in our oaboratory for the isomerization of allylamines to enamines. Regarding the hydrogenation of unsaturated compounds containing nitrogen, not much study has been made over heterogeneous catalyst. Although NiB and boronhydride-reduced Pd have been reported to be quite active and selective for such a hydrogenation[10,11], poisoning by the reactant and complexities of hydrogenolysis are unavoidable for conventional metal catalysts such as Pt, Pd, and Ni[12,13]. A selection of materials for supports is considered to be crucial in preparation of excellent supported-metal catalysts. In the present work, we have studied the effects of supports(mainly basic oxides) on Ni catalysts for the hydrogenation of N,N-dimethyl-2-propenylamine.

EXPERIMENTAL

Catalysts and Reagents: The MgO, CaO, SrO, and BaO catalysts were prepared from $Mg(OH)_2$, $Ca(OH)_2$, $SrCO_3$, and granular BaO by thermal decomposition under a helium stream. The ThO_2 catalyst was prepared from $Th(C_2O_4)_2$ by thermal decomposition at 500°C in air. The La_2O_3 and ZrO_2 catalysts were obtained by thermal decomposition of $La(OH)_3$ at 700°C under a helium stream, and $Zr(OH)_4$ at 700°C in air, respectively, the hydroxides being prepared by hydrolysis of an aqueous solution of $La(NO_3)_3$ or $ZrOCl_2$ with aqueous ammonia, followed by washing with deionized water and drying at 120°C. The ZnO, SiO_2, and Al_2O_3 catalysts were prepared by hydrolysis of each aqueous solution of $Zn(NO_3)_2$, ethyl orthosilicate and an alcoholic solution of aluminium isopropoxide with aqueous ammonia, followed by washing and calcination at 450°C(ZnO) or 500°C(SiO_2 and Al_2O_3) in air. The SiO_2-Al_2O_3catalyst was type SA-N of Nikki Chemical Industry Co. Prior to the reaction, all catalysts were pretreated at proper temperatures in a reactor under a helium stream for 3 h. Supported Ni catalysts were prepared by impregnating various metal oxides, which had been calcined at 500°C in air for 3 h, with aqueous $Ni(NO_3)_2$ followed by drying over a water bath and decomposition by heating at 500°C in air for 3 h. Prior to the reaction, the catalysts were reduced under a hydrogen stream at 500°C. The content of Ni was 10% by weight for all catalysts.

1-N-Pyrrolidino-2-propene was prepared from allyl bromide and pyrrolidine by condensation according to the method of Sauer and Prahl.[14] N,N-Dimethyl-2-propenylamine was purchased from Tokyo Kasei Kogyo Co. Ltd. Amines were distilled under a reduced pressure and purified by passage through KOH column.

Reactions: A microcatalytic pulse reactor was employed to carry out the isomerization of 1-N-pyrrolidino-2-propene at 40°C and the hydrogenation of N,N-dimethyl-2-propenylamine at 0°C. The products were trapped by liquid nitrogen before being flash evaporated into a gas chromatographic column, which was directly connected to a mass spectrometer. Apiezone L on KOH-treated Chromosorb was packed in a 3-m glass column which was operated at 100°C.

Stereoselectivity in the isomerization of N,N-dimethyl-2-propenylamine over CaO was examined by NMR spectroscopic analysis. An all-glass static reactor was employed. Calcium oxide was outgassed at 500°C in a reactor and sealed. A reactant was introduced through a breakable seal. The products in the cell were kept at liquid nitrogen temperature to prevent the produced enamine from undergoing cis-trans isomerization, and melted immediately before NMR measurement. The NMR spectrum was recorded on an R 20B Hitachi spectrometer at 60 MHz.

Deuteration of N,N-dimethyl-2-propenylamine was carried out in a recirculation reactor with Ni/MgO and Ni/SiO_2-Al_2O_3 catalyst. The numbers and location of D atoms in the product were determined by NMR, in which Eu-FOD was added to separate the NMR peaks.

RESULTS AND DISCUSSION

1 Isomerization of 1-N-pyrrolidino-2-propene

The compositions of the products for each catalyst are shown in Table 1. Although a main product was 1-N-pyrrolidino-1-propene, considerable amounts of pyrrolidine and propionaldehyde were produced over all catalysts. The formation of propionaldehyde was facile especially at the first pulse. Since neither the reactant nor the carrier gas contained oxygen atoms, the oxygen atom in propionaldehyde should originate from the catalyst surface.

Magnesium oxide and CaO showed high activities when they were pretreated at proper temperatures. The activities were so high that the percentage of 1-N-pyrrolidino-1-propene was almost independent of the change in flow rate and did not decrease with increase of pulse number. The selectivity for the formation of 1-N-pyrrolidino-1-propene was more than 80 % over MgO. Activities of MgO and CaO

Table 1

Double-Bond Migration of 1-*N*-Pyrrolidino-2-propene at 40°C

Catalyst	Pretreatment temperature (°C)	Specific surface area (m^2/g)	Weight of catalyst (mg)	Pulse No.	Flow rate (ml/min)	Percentage of each product			
						1-*N*-Pyrrolidino-2-propene	1-*N*-pyrrolidino-1-propene	Pyrrolidine	Propionaldehyde
MgO	600	135	30	1	30	0	79.8	9.9	10.3
				3	30	0.1	85.6	11.5	2.7
				5	88	1.0	83.9	12.3	2.7
CaO	400	81	30	1	30	4.4	64.3	25.5	5.7
				3	30	28.5	49.9	18.8	2.8
				5	30	56.0	35.1	7.1	1.8
CaO	700	52	34	1	30	0.5	61.2	26.1	11.7
				3	30	0.2	81.8	15.7	2.2
				5	113	0.4	76.7	19.8	3.2
SrO	1000	10	302	1	30	0.2	77.7	11.8	10.3
				3	30	62.4	31.2	5.3	1.2
				5	30	86.3	12.9	0.6	0.1
BaO	800	0.2	313	1	30	0.4	71.9	19.1	8.7
				2	30	96.5	2.9	0.4	0.2
ThO_2	700	59	102	1	30	16.6	50.8	17.0	15.6
				3	30	50.8	40.6	5.9	2.4
				5	120	72.2	19.7	5.2	2.8
La_2O_3	700	27	31	1	30	0.6	67.9	19.3	12.2
				3	30	71.9	20.8	5.6	1.7
				4	30	97.8	0.4	1.8	0

varied with pretreatment temperature of the catalysts and the maximum activities were obtained when pretreated in the temperature range, 400∿1000°C for MgO and at 700°C for CaO. With SrO, BaO, and La_2O_3, the activity degradation with the pulse number was prominent. Thorium oxide gradually lost its activity with successive pulses. No activity was observed with ZrO_2, ZnO, Al_2O_3, and SiO_2-Al_2O_3. Magnesium oxide, CaO, SrO, BaO, La_2O_3, and ThO_2 which showed activities at least in the first pulse are known to possess basic sites[4-9]. This seems to indicate that the basic sites are active sites. On the other hand, ZrO_2[15] and ZnO[16] which have both acidic and basic sites and Al_2O_3[17] and SiO_2-Al_2O_3[17] which have strong acidic sites were inactive. Therefore, it is considered that the acidic sites on the catalysts interact with a lone pair of nitrogen atom of the reactant and become inactive or interfere the isomerization over basic sites[18,19].

2 Isomerization of N,N-dimethyl-2-propenylamine

Stereochemistry was examined for the double-bond migration of N,N-dimethyl-2-propenylamine over CaO. Since N,N-dimethyl-2-propenylamine has a molecular structure in which a methine group of 4-methyl-1-pentene is replaced by a nitrogen atom, stereochemistry in the double-bond migration of 4-methyl-1-pentene was also studied for comparison. The cis/trans ratio of N,N-dimethyl-1-propenylamine was obtained from the intensities of quartet peaks ($CH_3(1)$) at 0.95 ppm for the cis isomer and at 0.86 ppm for the trans isomer.

Percentages of the cis isomer in N,N-dimethyl-1-propenylamine produced are plotted

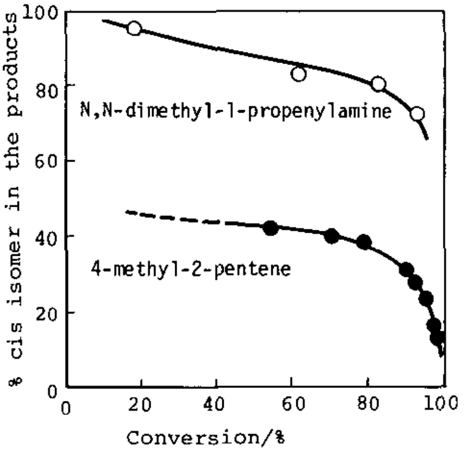
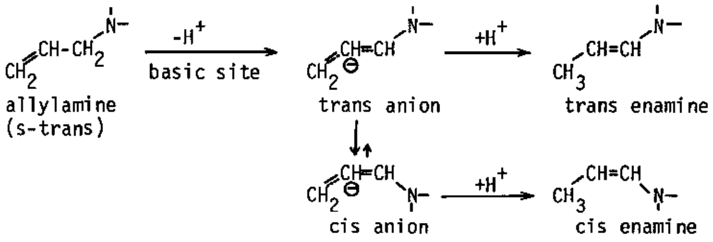


Fig. 1 Percentages of cis isomer in isomerized products for the double bond isomerization of N,N-dimethyl-2-propenylamine and 4-methyl-1-pentene. Reaction temperature; 25°C.

against the conversion in Fig. 1. Extrapolation to zero conversion gives 100% cis-N,N-dimethyl-1-propenylamine. Percentages of the cis isomer in 4-methyl-2-pentene from 4-methyl-1-pentene are also shown in Fig. 1. The percentage at zero conversion was about 50%. The percentages of cis isomers decreased with conversion for both reactions as the equilibria favor for the trans isomers. A high cis-selectivity in N,N-dimethyl-2-propenylamine isomerization compared with cis-selectivity in 1-methyl-1-pentene isomerization suggests that the energy difference between cis and trans forms of the intermediate is greater for the former reaction than the latter one. The intermediates for the double-bond migration of allylamine and of olefin are considered to be anionic.[19] The reaction scheme could be drawn as follows for allylamine.



3 Hydrogenation of N,N-dimethyl-2-propenylamine

The main product over Ni supported on basic oxides was N,N-dimethylpropylamine. The other products such as propane and dimethylamine were negligibly small. N,N-Dimethyl-1-propenylamine which might result from double-bond migration was not detected in a microcatalytic pulse reactor. As shown in Fig. 2, Ni supported on MgO, CaO, La_2O_3, and ThO_2 exhibited high activities from the first pulse. Especially, Ni/MgO gave 100 % conversion and almost 100 % selectivity for the formation of N,N-dimethylpropylamine[20]. Nickel on SiO_2-Al_2O_3 also showed a high activity after the 4th pulse. Following them, the activities were in the order of $Ni/ZrO_2 > Ni/Al_2O_3 > Ni/TiO_2 > Ni/SiO_2$. Since MgO, CaO, La_2O_3, and ThO_2 have basic sites on their surfaces and Ni supported on these oxides showed high activities, it is suggested that Ni catalyst becomes active when supported on basic oxides, though there is an exception for Ni/SiO_2-Al_2O_3. On the other hand, the effect of supports is entirely different in the hydrogenation of 1-butene which does not contain nitrogen as shown in Fig. 3. The different effect of support was most prominent for Ni/SiO_2, which showed the highest activity for the hydrogenation of 1-butene and the lowest activity for the hydrogenation of N,N-dimethyl-2-propenylamine. Further studies are needed to clarify the reasons.

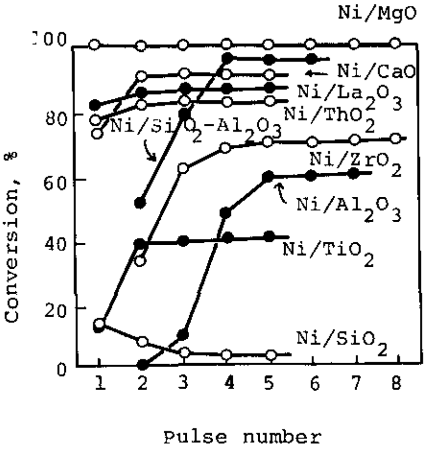


Fig. 2 Hydrogenation of N,N-dimethyl-2-propenylamine

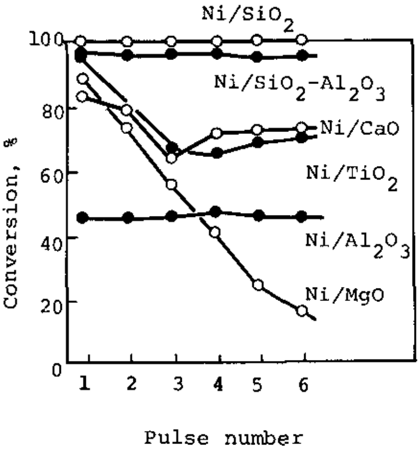


Fig. 3 Hydrogenation of 1-butene.

The effect of the amount of Ni supported on MgO on the conversion of N,N-dimethyl-2-propenylamine is shown in Table 2.

Table 2. Change in hydrogenation activity with Ni content in Ni/MgO

Ni wt, %	0	5	7	9	20	30	50
Conversion of N,N-dimethyl-2-propenylamine, %	0	31	70	100	100	98	94

The optimum amount of Ni was 10∿30 wt. %. Over the catalysts on which 5 or 7 % of Ni was supported, the formation of N,N-dimethyl-1-propenylamine (enamine) was observed. The time course of the reaction of N,N-dimethyl-2-propenylamine over Ni(9 %)/MgO which was carried out in a closed recirculation reactor is shown in Fig. 4. The enamine forms at the initial stage of the reaction, but changes to the hydrogenated compound, as the reaction proceeds. However, no enamine was formed over Ni/SiO_2-Al_2O_3 during the reaction. The adsorption of CO_2 caused to stop the reaction over Ni/MgO, but did not affect the activity of Ni/SiO_2-Al_2O_3. In order to examine the reactivity of enamine toward hydrogenation, MgO that is active for the double-bond migration of allylamine to enamine and Ni/SiO_2 which is inactive for the hydrogenation of allylamine were put in series in a reactor and the hydrogenation of allylamine was carried out. The conversion was 95 %, indicating that Ni/SiO_2 is active for the hydrogenation of enamine. The high conversion is due to the fact that *basic sites are unnecessary for the* hydrogenation of enamine. Isotopic distributions of the products in the deuteration of N,N-dimethyl-2-propenylamine over Ni/MgO, and Ni/SiO_2-Al_2O_3 are summarized in Table 3. Over Ni/MgO, about two D atoms were included in the product. About one D atom was located at carbon atom 2 and the rests were equally located at carbon atoms 1 and 3. On the contrary, about two D atoms were included in the product over Ni/SiO_2-Al_2O_3, the positions of D atoms being limited to carbon atoms 2 and 3. These suggest that in the case of Ni/MgO, Ni/CaO, Ni/La_2O_3, and Ni/ThO_2, allylamine isomerizes to enamine on basic sites of supports and the formed enamine is successively hydrogenated on Ni, while in the case of Ni/SiO_2-Al_2O_3, Ni/ZrO_2, Ni/TiO_2, Ni/Al_2O_3, and Ni/SiO_2, allylamine is hydrogenated directly to alkylamine without passing through enamine.

The postulated reaction schemes are drawn as follows.

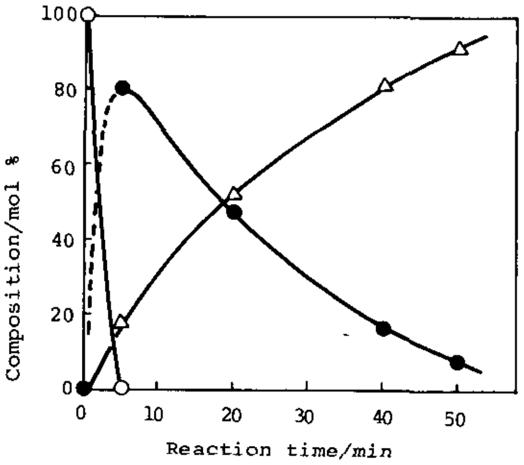


Fig. 4 Time dependence of the hydrogenation of N,N-dimethyl-2-propenylamine over Ni/MgO ○;reactant, ●;N,N-dimethyl-1-propenylamine, △;N,N-dimethylpropylamine.

Table 3. Number of D atoms located at different carbon atoms of N,N-dimethylpropylamine in the deuteration of N,N-dimethyl-2-propenylamine.

Catalyst	Position		
	C(1)	C(2)	C(3)
Ni/MgO	0.36	1.11	0.49
Ni/SiO_2-Al_2O_3	0.03	0.80	1.17

$$CH_2{=}CH{-}CH_2{-}N{<} \xrightarrow[\text{basic site}]{} CH_3{-}CH{=}CH{-}N{<} \xrightarrow[\text{Ni}]{} CH_3{-}CH_2{-}CH_2{-}N{<} \text{ (on Ni/MgO)}$$

$$CH_2{=}CH{-}CH_2{-}N{<} \xrightarrow[\text{Ni}]{} CH_3{-}CH_2{-}CH_2{-}N{<} \quad \text{(on Ni/}SiO_2\text{-}Al_2O_3\text{)}$$

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