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Addition of Amines to Conjugated Dienes Catalyzed by Solid Base Catalysts

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Addition of amines to conjugated dienes to yield unsaturated amines was carried out over solid base catalysts such as MgO, CaO, SrO, La_2O_3, ThO_2, and ZrO_2. Dimethylamine, ethylamine, piperidine, aniline, and triethylamine were used as amines, and 1,3-butadiene, and 2-methyl-1,3-butadiene were used as dienes. From all the reactions examined, CaO exhibited the highest activity, while ZrO_2 was inactive. The activities of catalysts varied with the pretreatment temperature. For the addition of dimethylamine to 1,3-butadiene, the pretreatment temperatures which gave the maximum activities were 600°C for CaO, 650°C for La_2O_3, 700°C for MgO(I) (prepared from $Mg(OH)_2$), and 500°C for MgO(II) (prepared from commercial MgO). The reactivities of amines are in the order: dimethylamine > ethylamine > piperidine ≫ aniline, triethylamine. In the addition of dimethylamine to 1,3-butadiene, primary products consisted mainly of *N*,*N*-dimethyl-2-butenylamine which resulted from 1,4-addition of a dimethylamino group and an H to the diene for all catalysts. As the reaction proceeded, the 1,4-addition product underwent double-bond migration to the enamine over CaO, MgO(II), and SrO. The double-bond migration was slow over MgO(I), La_2O_3, and ThO_2. In particular, double-bond migration was not appreciable over La_2O_3. In the reaction of 2-methyl-1,3-butadiene with dimethylamine, *N*,*N*-dimethyl-3-methyl-2-butenylamine, which resulted from 4,1-addition of the amino group and an H, was produced as the main product for all catalysts except for MgO(I). Exchange of dimethylamine with D_2 was studied over CaO. Only one D atom was incorporated into dimethylamine, suggesting that amines dissociate into an H^+ and an amide ion on the catalyst surface. Based on these results, the reaction mechanisms were discussed, and it is proposed that addition of amines to conjugated dienes on basic catalysts proceeds via the amino allylic carbanion intermediates which result from addition of amide ions to the dienes.

INTRODUCTION

Addition of primary and secondary amines to conjugated dienes to yield unsaturated amines has been studied with homogeneous catalysts. As catalysts, alkali metals (*1*, *2*), Li-amide (*3*), and transition metal complexes such as $Ni[P(OC_2H_5)_3]_4$ (*4*), Ni acetylacetonate (*5*), $PdBr_2$ $(Ph_2PCH_2CH_2PPh_2)$ (*6*), and $(Ph_3P)_3RhCl$ (*7*) have been reported. With alkali metals and Li-amide, the products consisted mostly of 1,4-addition products (*1–3*), while a mixture of 1,2 adducts, 1,4 adducts, and telomer was produced with transition metal complex catalysts (*4–7*).

Although heterogeneous catalysts have many advantages as compared with homogeneous catalysts, only graphite–Al_2O_3–K (*8a*) and complexes comprising graphite and alkali metals (*8b*) have been reported as heterogeneous catalysts active for addition of amines to conjugated dienes. Alkali metals and Li-amide being active suggests that certain metal oxides having basic properties are also active for the reaction. We have reported a preliminary study which reveals solid base catalysts show activities for addition of amines to 1,3-butadiene (*9*). In the present work, the catalytic properties of certain solid base catalysts for addition of several kinds of amines to 1,3-butadiene and 2-methyl-1,3-butadiene are examined in detail, and the reaction mechanisms over solid base catalysts are discussed.

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TABLE 1

Surface Areas of Catalysts (m^2/g)

Catalyst	Pretreatment temperature (°C)								
	300	400	500	600	700	800	900	1000	1100
MgO(I)	—	—	145	135	117	93	43	—	—
MgO(II)	22	34	68	55	54	—	33	—	28
CaO	—	—	71	72	52	36	32	—	—
SrO	—	—	—	—	—	—	—	10	—
La_2O_3	—	—	37	34	27	21	17	—	—
ThO_2	—	—	62	59	—	—	—	—	—
ZrO_2	176	109	65	32	21	11	10	—	—

EXPERIMENTAL METHODS

Catalysts. Two kinds of MgO were obtained by heating different starting materials in a vacuum. The MgO(I) catalyst was prepared from $Mg(OH)_2$ (Kanto Chemicals), and the MgO(II) from MgO (E. Merck, Darmstadt). The CaO and SrO catalysts were similarly prepared from $Ca(OH)_2$ (Kanto Chemicals) and $SrCO_3$ (E. Merck, Darmstadt). The La_2O_3 catalyst was obtained by high temperature evacuation of $La(OH)_3$ which was obtained by precipitation from an aqueous solution of $La(NO_3)_3$ with aqueous ammonia. The ThO_2 and ZrO_2 catalysts were prepared from $Th(OH)_4$ and $Zr(OH)_4$ by decomposition in air at 500°C. The $Th(OH)_4$ and $Zr(OH)_4$ were obtained by precipitation from aqueous solutions of $Th(NO_3)_4$ and $ZrOCl_2$, respectively, with aqueous ammonia. Prior to the reaction, all catalysts were pretreated in a reactor at elevated temperatures in a vacuum for 3 h. Surface areas were measured by the BET method and summarized in Table 1.

Materials. 1,3-Butadiene was purchased from Takachiho Chemicals, and 2-methyl-1,3-butadiene and dimethylamine from Tokyo Kasei. These were purified by passage through 4-Å molecular sieves kept at the dry-ice temperature. Ethylamine (Tokyo Kasei) and aniline (Wako Pure Chemicals) were purified by passage through well-degassed MgO at room temperature. Piperidine (Wako Pure Chemicals) and triethylamine (Tokyo Kasei) were purified by passage through a series of columns containing KOH and 3-Å molecular sieves at room temperature. Deuterium was obtained by decomposition of D_2O with a magnesium ribbon at 500°C, and was purified by passage through a mixture of well-degassed MgO and 13X molecular sieves at the liquid nitrogen temperature.

Reaction procedures. A closed recirculation reactor equipped with greaseless valves was used for the reactions of dimethylamine, ethylamine, and triethylamine with 1,3-butadiene or 2-methyl-1,3-butadiene. The volume of the reactor was 250 ml. A mixture containing equal amounts of amine and diene was allowed to react over 100–500 mg catalyst. Total pressures were 100 Torr (1 Torr = 133.3 Pa) for the reactions of dimethylamine and ethylamine (amines and dienes, 620 μmol each), and 60 Torr for the reaction of triethylamine (amine and diene, 370 μmol each).

The reactions of aniline and piperidine with 1,3-butadiene were carried out in a sealed glass reactor. Catalyst (200 ~ 650 mg) was placed in a quartz or Pyrex glass reactor, and pretreated in a vacuum. After treatment, the reactor was sealed. A mixture of aniline (0.05 ml) or piperidine (0.05 ml) and 1,3-butadiene (0.05 ml) was introduced into the reactor through breakable seal. A known amount of hexane was also introduced into the reactor as an internal standard for calculation of the conversion.

For the exchange reaction of dimethylamine with D_2, a closed recirculation reactor was employed. A mixture containing about 10 Torr of dimethylamine and 50 Torr of D_2 was allowed to react at 0°C.

For the reactions carried out in a closed recirculation reactor, a part of the reaction mixture was withdrawn periodically and subjected to gas chromatographic analysis. For the reactions in a sealed glass reactor, the reaction was quenched in 10 min, and the products were analyzed by gas chromatography. A 3-m glass column packed with 28% Penwalt Amine Packing and a 3-m stainless-steel column packed with Apiezon

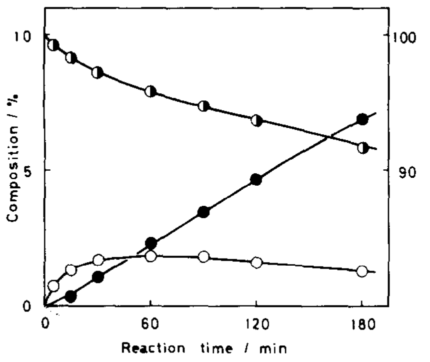


FIG. 1. Time dependence of composition in the reaction of 1,3-butadiene with dimethylamine at 0°C over the MgO(II) pretreated at 700°C. Catalyst, 500 mg; 1,3-butadiene, 50 Torr; dimethylamine, 50 Torr; ◑, 1,3-butadiene; ○, *N*,*N*-dimethyl-2-butenylamine; ●, *N*,*N*-dimethyl-1-butenylamine.

L on KOH-treated Chromosorb were operated at 125–145°C. For identification of the products, the products were separated by a gas chromatographic column and trapped in liquid nitrogen. Each separated product was analyzed by ^{1}H NMR in deuterio benzene or in deuterio chloroform.

For analysis of isotopic distribution of dimethylamine, a mass spectrometer (Hitachi M-52) was used with an ionization voltage of 9 eV.

RESULTS

Addition of Dimethylamine to 1,3-Butadiene

The reaction proceeded at 0°C over the MgO(I), MgO(II), CaO, SrO, and La_2O_3 catalysts, and at 50°C over ThO_2. The composition of the products varied with the types of catalysts.

Time dependence of the composition in the reaction over the MgO(II) catalyst outgassed at 700°C is shown in Fig. 1. In the initial stage of the reaction, *N*,*N*-dimethyl-2-butenylamine that resulted from 1,4-addition of a dimethylamino group and an H to 1,3-butadiene was produced as the main product. As the reaction proceeded, *N*,*N*-dimethyl-2-butenylamine underwent double bond migration to *N*,*N*-dimethyl-1-butenylamine (enamine) which is thermodynamically more stable. The rate of the double-bond migration was strongly dependent on the pretreatment temperature. The double-bond migration scarcely occurred when the MgO(II) catalyst was outgassed at high temperatures (1000–1100°C).

The MgO(I) catalyst showed an activity different from that of the MgO(II) catalyst. The double-bond migration was much slower for the MgO(I) catalyst than for the MgO(II) catalyst when compared under the same pretreatment condition. The main product over the MgO(I) catalyst was 1,4-addition product throughout the reaction. In particular, the formation of the enamine was not appreciable when the MgO(I) catalyst was pretreated at high temperatures (900–1000°C).

The La_2O_3 catalyst showed a high selectivity for the addition regardless of the pretreatment temperature. As shown in Fig. 2, the formation of the enamine was not observed at 0°C. Only 1,4-addition took place. The pressure dependence of the rate of conversion was determined over the La_2O_3 catalyst outgassed at 600°C. The reaction order was determined by the method of initial rates, in which the initial rates were measured with varying the initial pressure of 1,3-butadiene (or dimethylamine) over the range 15–60 Torr while the initial pressure

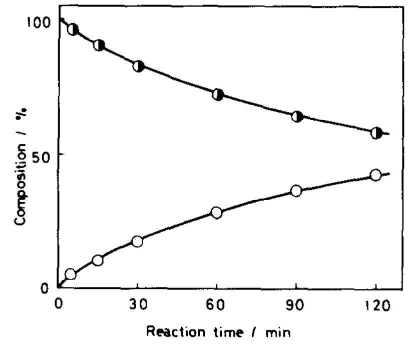


FIG. 2. Time dependence of composition in the reaction of 1,3-butadiene with dimethylamine at 0°C over the La_2O_3 pretreated at 600°C. Catalyst, 500 mg; 1,3-butadiene, 50 Torr; dimethylamine, 50 Torr. Symbols are the same for Fig. 1.

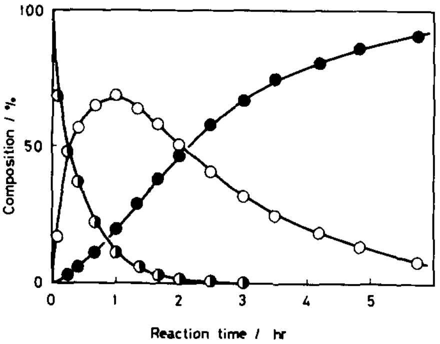


FIG. 3. Time dependence of composition in the reaction of 1,3-butadiene with dimethylamine at 0°C over the CaO pretreated at 600°C. Catalyst, 100 mg; 1,3-butadiene, 15 Torr; dimethylamine, 20 Torr. Symbols are the same for Fig. 1.

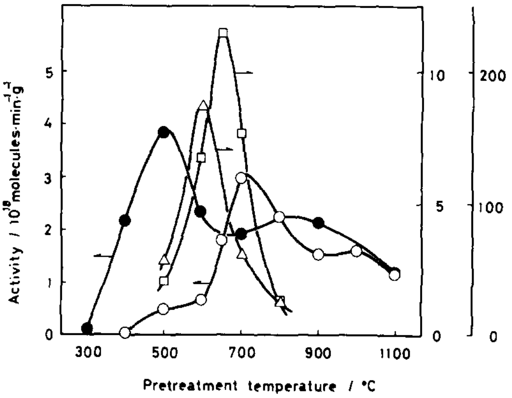


FIG. 5. Variations of activity as a function of pretreatment temperature for the reaction of 1,3-butadiene with dimethylamine. Catalyst, MgO(I)(○); MgO(II)(●); CaO (△); La_2O_3 (□).

of the other reactant, dimethylamine (or 1,3-butadiene) was kept constant at 30 Torr. The reaction order was 0.67 in 1,3-butadiene and −0.8 in dimethylamine.

The CaO catalyst was highly active. Time dependence of the composition in the reaction over the CaO catalyst outgassed at 600°C is shown in Fig. 3. The double-bond migration also occurred at a considerable rate.

The SrO catalyst was selective for the formation of the enamine. As shown in Fig. 4, the products consisted exclusively of enamine (*N*,*N*-dimethyl-1-butenylamine). The formation of 1,4-addition product was slightly observed only in the initial stage of the reaction.

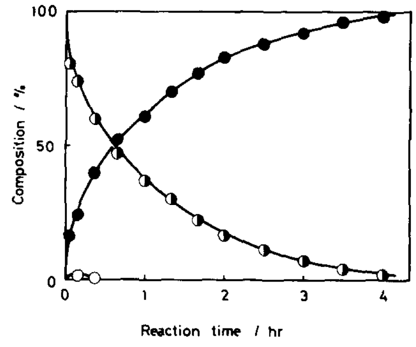


FIG. 4. Time dependence of composition in the reaction of 1,3-butadiene with dimethylamine at 0°C over the SrO pretreated at 1000°C. Catalyst, 250 mg; 1,3-butadiene, 13 Torr; dimethylamine, 20 Torr. Symbols are the same for Fig. 1.

The ThO_2 catalyst did not show any appreciable activity at the reaction temperature of 0°C. At 50°C, formation of the 1,4-addition product was observed, but enamine was not produced.

The ZrO_2 catalyst was inactive even at 100°C.

Activity Dependence on Pretreatment Temperature of Catalyst

The variations of the activity (rate of conversion of 1,3-butadiene) as a function of the pretreatment temperature are shown in Fig. 5 for the MgO(I), MgO(II), CaO, and La_2O_3 catalysts. Maximum activities were observed at the pretreatment temperature of 500°C for the MgO(II), 600°C for the CaO, 650°C for the La_2O_3, and 700°C for the MgO(I). It is noted that MgO catalysts prepared from different starting materials exhibited different variations of the activity with the pretreatment temperature. In Table 2 are summarized the maximum activities of those catalysts on unit weight basis. The order of catalytic activity is: CaO(57.7) > SrO(5.5) > La_2O_3(3.8) > MgO(II)(1.3) > MgO(I)(1) $\gg$ ThO_2, where relative activities are given in parentheses. The activity of the CaO catalyst is such an activity that it takes

TABLE 2

Activities for Addition of Dimethylamine to 1,3-Butadiene Catalytic Activities of Various Oxides

Catalyst	Catalyst weight (mg)	Pretreatment temp. (°C)	Reaction temp. (°C)	Activity (10^{18} molecules · min^{-1} · g^{-1})
MgO(I)	500	700	0	3.0
MgO(II)	500	500	0	3.9
CaO	100	600	0	173.2
SrO	300	1000	0	16.4
La_2O_3	500	650	0	11.4
ThO_2	500	500	50	1.4
ZrO_2	500	800	100	0
SiO_2–Al_2O_3	500	500	150	0

1.1 h for 1 g of CaO to convert 1 g of 1,3-butadiene.

Addition of Dimethylamine to 2-Methyl-1,3-butadiene

The activities of the catalysts for addition of dimethylamine to 2-methyl-1,3-butadiene are given in Table 3. The catalysts were pretreated at the temperatures which gave the maximum activities. The product compositions obtained by extrapolation to zero conversion are also included. Except for

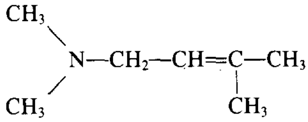
TABLE 3

Activities and Selectivities for Addition of Dimethylamine to 2-Methyl-1,3-butadiene

Catalyst	Pretreatment temperature (°C)	Reaction temperature (°C)	Activity (10^{18} molecules · min^{-1} · g^{-1})	Percentage of each product at zero conversion[a]		
				1	2	3
MgO(I)	700	0	0.3	44	56	0
MgO(II)	500	0	0.8	91	9	0
CaO	600	0	22.0	61	39	0
SrO	1000	0	8.5	75	19	6
La_2O_3	650	0	1.6	73	27	0
ThO_2	500	50	0.6	95	5	0

[a] Products:

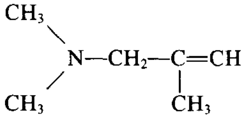
(1) *N,N*-dimethyl-3-methyl-2-butenylamine



$(CH_3)_2N—CH_2—CH{=}C(CH_3)—CH_3$

(4,1-addition product).

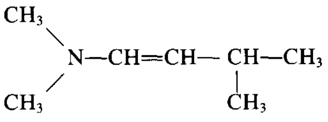
(2) *N,N*-dimethyl-2-methyl-2-butenylamine



$(CH_3)_2N—CH_2—C(CH_3){=}CH—CH_3$

(1,4-addition product).

(3) *N,N*-dimethyl-3-methyl-1-butenylamine



$(CH_3)_2N—CH{=}CH—CH(CH_3)—CH_3$

(enamine).

TABLE 4

Activities for Addition of Ethylamine to 1,3-Butadiene at 100°C

Catalyst	Pretreatment temperature (°C)	Activity (10^{18} molecules · min^{-1} · g^{-1})
MgO(I)	700	1.78
MgO(II)	500	1.96
MgO(II)	600	2.10
MgO(II)	700	1.31
CaO	600	6.68
CaO	700	7.31
CaO	800	6.32
SrO	1000	0.56
La_2O_3	650	0.45
La_2O_3	700	0.51
ThO_2	500	1.60[a]

[a] Reaction temperature 130°C.

ThO_2, the reaction proceeded at 0°C. The rates for the reaction of dimethylamine with 2-methyl-1,3-butadiene were 0.5–0.1 of the rates for the reaction of dimethylamine with 1,3-butadiene. In the initial stage of the reaction, the 4,1-addition product (*N,N*-dimethyl-3-methyl-2-butenylamine) predominated over the 1,4-addition product (*N,N*-dimethyl-2-methyl-2-butenylamine) except for the MgO(I) catalyst. The MgO(I) catalyst gave products containing almost equal amounts of the 1,4-addition and 4,1-addition products. Over the CaO, and SrO catalysts, the 1,4- and 4,1-addition products underwent double-bond migration to the enamine, whereas the formation of the enamine was not appreciable over the MgO(I), La_2O_3, and ThO_2 catalysts.

Addition of Ethylamine to 1,3-Butadiene

The addition of ethylamine to 1,3-butadiene proceeded at 100°C. The activities of catalysts are summarized in Table 4. For this reaction too, the CaO catalyst exhibited the highest activity. For the MgO(II), CaO, and La_2O_3 catalysts, activity dependence on the pretreatment temperature was examined. The temperatures which gave the maximum activities were 600°C for the MgO(II), and 700°C for the CaO and La_2O_3. These temperatures were 50–100°C higher than those which gave the maximum activities for the addition of dimethylamine to 1,3-butadiene.

Addition of Piperidine to 1,3-Butadiene

The addition of piperidine to 1,3-butadiene proceeded above 180°C. The activities of catalysts determined from the number of molecules produced in 10 min divided by 10 min and by weight of catalyst are given in Table 5. The compositions of the products in 10 min are also included. The CaO catalyst exhibited the highest activity. The products consisted of the 1,4-addition product (1-*N*-piperidino-2-butene) and the enamine (1-*N*-piperidino-1-butene). For all catalysts, considerable amounts of the enamine formed, probably because the reaction temperature was high. The ThO_2 catalyst was inactive even at 200°C. The variations of the activities as a function of the pretreatment temperature were examined for the MgO(II) and CaO catalysts. The pretreatment temperatures which gave the maximum activities were 500°C for the MgO(II) catalyst and 600°C for the CaO catalyst, which coincided with the temperatures which gave the maximum activities for the reaction of dimethylamine with 1,3-butadiene.

Addition of Aniline or Triethylamine to 1,3-Butadiene

The addition of aniline or triethylamine to 1,3-butadiene were tried over the CaO catalyst at 200°C. However, the formation of addition products was not appreciable. Only polymerized products of 1,3-butadiene formed.

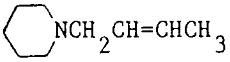
Exchange of Dimethylamine with Deuterium

Exchange of dimethylamine with D_2 was carried out at 0°C over the MgO(II), CaO, and La_2O_3 catalysts. Only monodeuterio dimethylamine was formed. This indicates

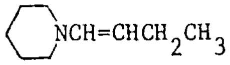
TABLE 5

Activities and Selectivities for Addition of Piperidine to 1,3-Butadiene

Catalyst	Pretreatment temperature (°C)	Reaction temperature (°C)	Activity (10^{18} molecules · min^{-1} · g^{-1})	Percentage of each product[a]		
				1	2	3
MgO(I)	700	180	0.01	24	70	6
MgO(II)	500	180	0.12	18	81	1
CaO	600	180	0.43	38	59	3
SrO	1000	180	0.18	2	98	0
La_2O_3	650	180	0.03	43	50	7
ThO_2	500	200	0	—	—	—

[a] Products: (1) 1-piperidino-2-butene 

(1,4-addition product).

(2) 1-piperidino-1-butene 

(enamine).

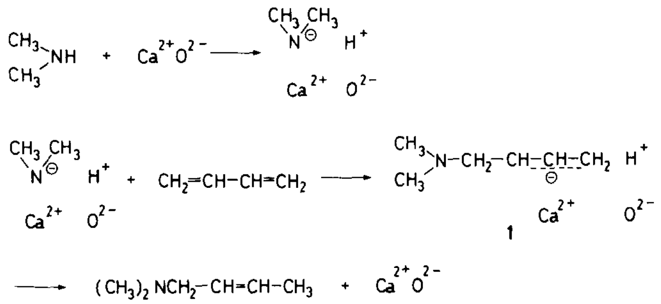
(3) unknown products.

that the H atom bonded to N atom was exchanged with a D atom, and that a methyl H was not exchanged. The exchange was very slow as compared with the addition of dimethylamine to 1,3-butadiene.

DISCUSSION

Magnesium oxide, CaO, SrO, La_2O_3, and ThO_2 are known to act as basic catalysts for certain reactions such as butene isomerization (*10–12*), double-bond migration of unsaturated compounds containing O or N atoms (*13, 14*), and hydrogenation of conjugated dienes (*15–17*). These reactions proceed by the allylic anion mechanisms in which basic sites are involved. Removal of CO_2 and H_2O from the surfaces by pretreatment at relatively high temperature is needed for these catalysts to become active for these reactions. The variations of the activity for addition of amines to conjugated dienes as a function of the pretreatment temperature are similar to those for the base-catalyzed reactions mentioned above. Therefore, it is suggested that the active sites for addition of amines to dienes are basic sites. Although the ZrO_2 acts as a basic catalyst for butene isomerization (*18*), the ZrO_2 did not show any activity for addition of amines to conjugated dienes. Since the active sites of the ZrO_2 catalyst for butene isomerization were strongly poisoned by ammonia (*18*), the strong adsorption of amines may cause the ZrO_2 being inactive for addition of amines to dienes. Two types of MgO prepared from different starting materials showed different catalytic properties. These differences were also observed with MgO catalyst for other reactions, e.g., butene isomerization (*19*), 1,3-butadiene hydrogenation (*20*). The degree of removal of CO_2 and H_2O from different starting materials may not be the same, which result in generation of different arrangements of Mg^{2+} and O^{2-} on the surfaces. However, a definite conclusion cannot be made at present.

Negative reaction order in amine and positive reaction order in diene suggests that amine is more strongly adsorbed on the active sites than diene. Incorporation of only one D atom into dimethylamine in the exchange with D_2 suggests that dimethyl-



SCHEME 1. Addition of dimethylamine to 1,3-butadiene over CaO

amine is dissociatively adsorbed into the amide ion and an H^+ as shown below.

$$(CH_3)_2NH \rightarrow (CH_3)_2N^- + H^+$$

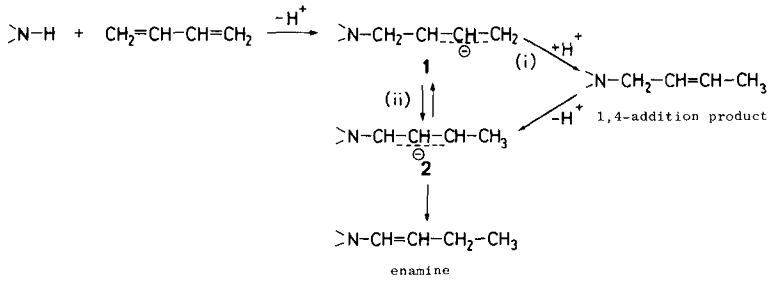
The H^+ is abstracted by a basic site on the catalyst. The amide ion is stabilized on the cationic site. The reaction scheme for the addition of dimethylamine to 1,3-butadiene over the CaO catalyst can be drawn as shown in Scheme 1. The amide ion attacks the terminal carbon atom of 1,3-butadiene to form amino allylic anion **1**, since the electron density in the anion **1** is the highest on the carbon atom 4, the proton selectively attacks the carbon atom 4 and finally yields the 1,4-addition product. This scheme is analogous to that proposed for 1,3-butadiene hydrogenation over basic catalysts, in which 1,4-addition of an H^+ and an H^- occurs selectively (*15–17*).

For the formation of enamine, the following two pathways are possible.

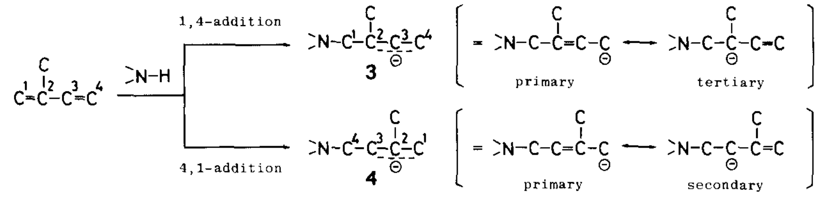
(i) Consecutive reaction of 1,4-addition of amine to diene and double-bond migration of the 1,4-addition product to enamine.

(ii) Direct formation of enamine involving the conversion of allylic anion **1** to allylic anion **2**.

In the reaction of dimethylamine with 1,3-butadiene over the MgO(II) pretreated at 700°C, the concentration vs time curve for the 1,4-addition product showed a maximum and that for the enamine exhibited an S type shape. It is suggested that the formation of the enamine occurs mostly by pathway (i) over the MgO(II) catalyst. On the contrary, with the SrO catalyst, negligible amounts of the 1,4-addition product were formed, and the formation of the enamine was not of an S type shape. Probably the formation of the enamine on SrO proceeds by pathway (ii) in which H transfer within the allylic anion intermediates is fast. The catalyst dependence of enamine formation may arise from the differences in the rate of protonation. If protonation proceeds fast, allylic anion **1** would give 1,4-addition prod-



SCHEME 2. Formation of enamine



SCHEME 3. Addition of amines to 2-methyl-1,3-butadiene

uct before it converts to allylic anion **2**. On the other hand, if protonation is slow, allylic anions **1** and **2** would be equilibrated and nonselective formation of 1,4-addition product and enamine would be observed.

For the reaction of 2-methyl-1,3-butadiene with dimethylamine, the anionic mechanism accounts for the selective occurrence of 4,1-addition rather than 1,4-addition. If the conformational differences are not taken into account, two types of anionic intermediates are possible; one is formed by addition of the amide ion to carbon atom 4 in 2-methyl-1,3-butadiene, and the other by addition to carbon atom 1 as shown in Scheme 3. The allylic anion **3** is a resonance hybrid of a primary anion and a tertiary anion, while the allylic anion **4** is a resonance hybrid of a primary anion and a secondary anion. The order of stability is primary > secondary > tertiary for anion. Therefore, the allylic anion **4** is more stable than the allylic anion **3**. The predominant occurrence of 4,1-addition which was observed for all catalysts except for the MgO(I) is likely due to the difference in the stabilities of the allylic anion **4** over the allylic anion **3** This explanation is similar to that discussed for base-catalyzed isomerization of olefins (*21, 22*) and for alkali metal-catalyzed reactions of 2-methyl-1,3-butadiene with alkylaromatics (*22, 23*). It should be noted that the $C^1{=}C^2$ double bond is more sterically hindered and more electron rich than is the $C^3{=}C^4$ double bond. This situation also favors nucleophilic addition of amide ion to carbon atom 4. It is uncertain why the selectivity for 4,1-addition was low over the MgO(I) pretreated at 700°C.

The reactivities of amines with 1,3-butadiene were in the order dimethylamine > ethylamine > piperidine $\gg$ aniline, triethylamine. The conversion rate is considered to be controlled by several factors. Three important factors are (i) adsorption strength of amines, (ii) acidity of amines, and (iii) basic strength of active sites.

The negative reaction order with respect to amine suggests that the conversion rate decreases as the adsorption of amine becomes strong. The low activities of piperidine and aniline are probably due to strong adsorption of the amines on the active sites.

Factors (ii) and (iii) are closely related to each other. The acidities of secondary amines are generally stronger than those of primary amines (*24*). Proton is liberated more easily for secondary amines than for primary amines. Primary amines need stronger basic site to be dissociatively adsorbed than secondary amines do. The pretreatment temperatures which resulted in the highest activities were higher for the reaction with primary amine (ethylamine) than those with secondary amines (dimethylamine, piperidine). A possible explanation for this may be an appearance of stronger basic sites on pretreatment at higher temperatures. As mentioned earlier, the mechanisms for hydrogenation of conjugated dienes are analogous to those for addition of amines to conjugated dienes. The maximum activities for the hydrogenation were observed when the MgO(I) and CaO were pretreated at 1100 and at 800°C, respectively (*25*).

Dissociation of hydrogen molecule to H^+ and H^- is more difficult than that of amines to H^+ and amide ion. Appearance of the maximum activities for the hydrogenation at higher temperature is explained if the basic strength increases with an increase in the pretreatment temperature. Therefore, both for addition of amines and for hydrogenation, variations of the activities with pretreatment temperature are explained in terms of capability of dissociating the reacting molecules.

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