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ADDITION OF AMINES TO CONJUGATED DIENES CATALYZED BY SOLID BASE CATALYSTS

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Addition of dimethylamine, ethylamine, and piperidine to 1,3-butadiene or 2-methyl-1,3-butadiene effectively occurred over solid base catalysts such as MgO, CaO, SrO, La_2O_3, and ThO_2. Among these catalysts, CaO exhibited the highest activity.

As the catalysts active for addition of amines to conjugated dienes to produce unsaturated amines, Li-amide,$^{1)}$ Na metal,$^{2)}$ and transition metal complexes such as $Ni[P(OEt)_3]_4$,$^{3)}$ Ni acetylacetonate,$^{4)}$ $PdBr_2(Ph_2PCH_2CH_2PPh_2)$,$^{5)}$ and $(Ph_3P)_3RhCl$,$^{6)}$ have been reported. These catalysts act in a homogeneous system. Although heterogeneous catalysts have many advantages as compared with homogeneous catalysts, there have been no reports of heterogeneous catalysts active for the reaction. The Li-amide catalyst and the Na metal catalyst being active suggests that solid base catalysts are also active for addition of amines to conjugated dienes. In this paper, we wish to report the catalytic behaviors of solid base catalysts such as alkaline earth metal oxides, La_2O_3, ThO_2, and ZrO_2 for addition of several kinds of amines to 1,3-butadiene or 2-methyl-1,3-butadiene.

The MgO, CaO, and SrO catalysts were prepared by decomposition of $Mg(OH)_2$ (Kanto Chemicals Co.), $Ca(OH)_2$ (Kanto Chemicals Co.), and $SrCO_3$ (E. Merck) at elevated temperatures under a vacuum. The La_2O_3 catalyst was similarly prepared from $La(OH)_3$ which was obtained by precipitation from aqueous solution of $La(NO_3)_3$ with aqueous ammonia. The ThO_2 and ZrO_2 catalysts were prepared from $Th(OH)_4$ and $Zr(OH)_4$, respectively, by decomposition in air at 500 °C followed by outgassing 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. Amines and

Table 1 Addition of Amines to 1,3-Butadiene or 2-Methyl-1,3-butadiene

Reaction	Catalyst	Pretreat. temp./°C	Reaction temp./°C	Activity $/10^{18}$ molecules$\cdot$min$^{-1}\cdot$g^{-1}
Dimethylamine (6650 Pa) + 1,3-Butadiene (6650 Pa)	MgO	700	0	3.0
	CaO	600	0	173
	SrO	1000	0	16.4
	La_2O_3	650	0	11.4
	ThO_2	500	50	1.1
	ZrO_2	800	100	0
Dimethylamine (6650 Pa) + 2-Methyl-1,3-butadiene (6650 Pa)	MgO	700	0	0.3
	CaO	600	0	22.3
	SrO	1000	0	8.5
	La_2O_3	650	0	1.6
	ThO_2	500	50	0.6
Ethylamine (6650 Pa) + 1,3-Butadiene (6650 Pa)	MgO	700	100	1.8
	CaO	700	100	7.3
	SrO	1000	100	0.6
	La_2O_3	700	100	0.5
	ThO_2	500	130	1.6
Piperidine (0.05 ml) + 1,3-Butadiene (0.05 ml)	MgO	700	180	0.010
	CaO	600	180	0.432
	SrO	1000	180	0.177
	La_2O_3	650	180	0.029
	ThO_2	500	200	0
Triethylamine (4000 Pa) + 1,3-Butadiene (4000 Pa)	CaO	600	200	0
Aniline (0.05 ml) 1,3-Butadiene (0.05 ml)	CaO	700	200	0

dienes were purified by passage through 4A molecular sieves. For the reactions of dimethylamine, ethylamine, and triethylamine with 1,3-butadiene or 2-methyl-1,3-butadiene, a closed recirculation reactor was employed. The reactions of aniline and piperidine with 1,3-butadiene were carried out in a sealed glass reactor. In the latter case, catalyst was activated in a glass tube and sealed. A mixture of aniline or piperidine and 1,3-butadiene was introduced into the reactor through breakable seal. n-Hexane was also introduced as an internal standard to obtain conversion.

The results are summarized in Table 1. Since the activities of catalysts varied with the pretreatment temperature of catalysts, the data given in Table 1 are those when catalysts were pretreated at the temperature which gave the maximum activities. Over the MgO, CaO, SrO, La_2O_3 and ThO_2 catalysts, dimethylamine, ethylamine, and piperidine underwent addition to 1,3-butadiene while trimethylamine, and aniline did not. The ZrO_2 catalyst showed no activity. The reactivities of the amines were in the following order:

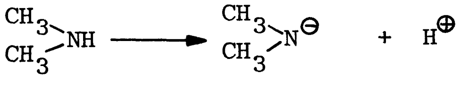
dimethylamine > ethylamine > piperidine ≫ aniline ≈ trimethylamine

The rates of the addition of dimethylamine to 2-methyl-1,3-butadiene over the catalysts were about $1/2\sim1/10$ times those to 1,3-butadiene. For all reactions, the CaO catalyst exhibited the highest activities.

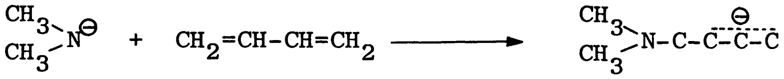
In the reaction of dimethylamine with 1,3-butadiene, the main product in the initial stage of the reaction was N,N-dimethyl-2-butenylamine which resulted from 1,4 addition of the dimethylamino group and the hydrogen atom to 1,3-butadiene. As the reaction proceeded, N,N-dimethyl-2-butenylamine underwent double bond migration to form N,N-dimethyl-1-butenylamine over the MgO, CaO, and SrO catalyst. The double bond migration did not occur over the La_2O_3 and ThO_2 catalysts.

In the reaction of dimethylamine with 2-methyl-1,3-butadiene, the products consisted mainly of N,N-dimethyl-3-methyl-2-butenylamine which resulted from 4,1 addition of the amino group and the hydrogen atom to 2-methyl-1,3-butadiene over the CaO, SrO, La_2O_3, and ThO_2 catalysts. The MgO catalyst gave mainly the 1,4 addition product. The successive double bond migration of N,N-dimethyl-3-methyl-2-butenylamine was observed for the CaO and SrO catalysts to some extent, whereas the migration did not take place over the La_2O_3 and ThO_2 catalysts.

A plausible reaction mechanisms could be drawn for the reaction of dimethylamine with 1,3-butadiene as follows:



$$(CH_3)_2NH \longrightarrow (CH_3)_2N^{\ominus} + H^{\oplus}$$



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}N^{\ominus} + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}{>}N{-}C{-}\overset{\ominus}{C{\cdots}C{\cdots}C}$$

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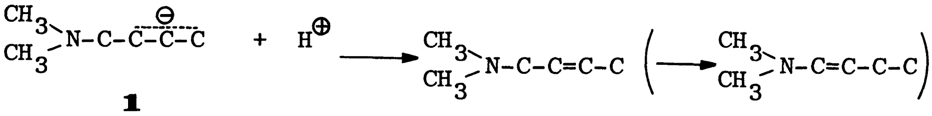

$$\underset{\mathbf{1}}{\begin{matrix}CH_3\\CH_3\end{matrix}{>}N{-}C{-}\overset{\ominus}{C{\cdots}C{\cdots}C}} + H^{\oplus} \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}{>}N{-}C{-}C{=}C{-}C \left(\longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}{>}N{-}C{=}C{-}C{-}C\right)$$

Since the electron density on carbon atom 4 is higher than that of carbon atom 2 in the allylic carbanion **1**, predominant 1,4 addition would occur.

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