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Dehydrogenation of Alkylamines on Acid-Base Hybrid Catalyst

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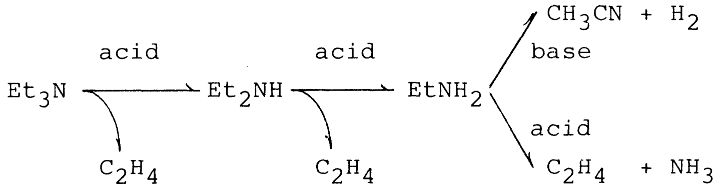
A peparation of hybrid catalysts of $SiO_2 \cdot Al_2O_3$-MgO (SA/MgO) and silanized MgO (SiOx/MgO) was attempted for the purpose of obtaining a new category of the acid-base bifunctional catalyst. The resultant catalyst was applied to the catalytic decomposition of alkylamines to yield acetonitrile via a dealkylation-dehydrogenation reaction.

Recently we found that ZrO_2 exhibited higher activity for the formation of acetonitrile from triethylamine than a strongly acidic $SiO_2 \cdot Al_2O_3$ (SA) or a strongly basic MgO through TPD experiments, and such a specific catalytic behavior of ZrO_2 was attributed to its acid-base bifunctional properties.[1,2]

Decomposition of alkylamines may involve dealkylation, deamination, and dehydrogenation reactions. Dealkylation and deamination may be catalyzed by a solid acid, and a dehydrogenation reaction may take place over a solid base catalyst.



Thus the catalytic activity and selectivity for alkylamine conversion may be influenced by acid-base properties of catalysts. In our preceding papers, we showed $SiO_2 \cdot Al_2O_3$ was effective for the deamination reaction, and MgO exhibited a high selectivity for the dehydrogenation of primary alkylamines.[2] This paper deals with an intention of the construction of a new category of acid-base bifunctional catalysts by the combination of a typical solid acid and solid base on the one hand and by the addition of acidic properties to a solid base by a deposition of silica overlayers on the MgO surface using tetramethoxysilane (TMS) on the other.

Zirconium dioxide was prepared by hydrolysis of zirconium oxynitrate with concentrated ammonia water followed by drying the washed precipitate at 393 K and calcining in air at 873 K for 24 h. Silica-alumina was N631(L) of Nikki Co. Ltd., which was calcined in air at 773 K for 5 h. Magnesium oxide was MgO of Merck Co.

Ltd., which was evacuated at 1073 K for 2 h prior to use. The surface areas of ZrO_2, MgO, and SA were 30, 93, and 396 m^2g^{-1}, respectively. A hybrid catalyst of SA/MgO was prepared by mechanically grinding a mixture of desired amounts of SA and MgO in an agate mortar. The obtained mixture was evacuated in a reaction vessel for several hours at 773 K. SA/MgO(1:2), SA/MgO(1:4), etc. denote that the mixing ratio of SA and MgO was 1:2, 1:4, and so on by weight. A layered SA/MgO(1:4) catalyst was prepared by such a way that a 80 mg of MgO was placed on a 20 mg of SA in a catalyst bed and was evacuated at 773 K. The reactant gas, which flows from the bottom to the top of the catalyst, first contacts with SA layer and then MgO layer. SiOx/MgO was prepared by the adsorption of gaseous TMS at room temperature onto MgO evacuated at 773 K, followed by the oxidation and evacuation at 773 K. An adsorption-oxidation cycle was repeated until a desired amount of deposited Si was obtained. SiOx(4)/MgO and SiOx(8)/MgO denote that such a cycle was repeated 4 and 8 times, respectively, and contained 23.4 and 32.6 mg of Si on g of MgO, respectively, which was revealed by X-ray fluorescence analysis.

Triethylamine (Et_3N), diethylamine (Et_2NH) and n-propylamine (n-$PrNH_2$) purchased from Wako Pure Chem. Ind. Ltd. were purified by repeated freeze-thaw cycles and a trap-to-trap distillation.

The catalytic conversion of alkylamines was carried out by using 100 - 300 mg of catalyst at 673 - 773 K in a closed recirculation reaction system at an initial pressure of 5.34 kPa. Product analysis was performed by using a gas chromatograph

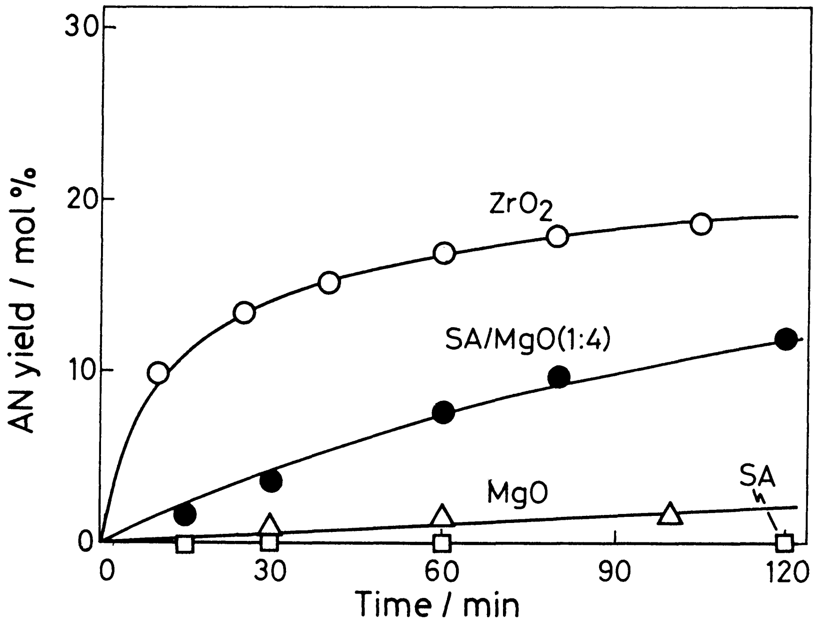


Fig. 1. Formation of acetonitrile over acid-base hybrid catalyst (SA/MgO). (Reaction temperature = 673 K, amount of catalyst: see text)

equipped with a 3 m column of Amipak 141 and FID detector.

Figure 1 shows reaction time courses of the formation of acetonitrile (AN) from Et_3N over SA (50 mg), MgO (300 mg), ZrO_2 (300 mg), and SA/MgO(1:4)(100 mg) at 673 K. Though SA was quite active for the decomposition of Et_3N, the reaction was found to be limited to the dealkylation-deamination reaction and no AN was found. A production of intermediate products such as Et_2NH and $EtNH_2$ was high. MgO exhibited a fairly high activity and selectivity for the dehydrogenation of $n-PrNH_2$ to yield propionitrile, but this was not the case in Et_3N. ZrO_2 was very active and selective (80 - 90% selectivity) for the decomposition of Et_3N to yield AN and this specific action was attributed to its acid-base bifunctional properties.[2)] It is clear from Fig. 1 that the hybridization of SA, which has a high activity in dealkylation-deamination reaction, and MgO, which is active for the dehydrogenation of primary amines such as $n-PrNH_2$, acquired a pronounced activity for the AN formation, though selectivity to AN was slightly low (60 - 70%). A partial suppression in the basic properties of MgO by the hybridization was found by a decrease in the dehydrogenation reaction of $n-PrNH_2$. Since the reaction to yield AN from Et_3N proceeds via a dealkylation by acidic sites and a dehydrogenation by basic sites, SA/MgO hybrid catalyst retains, at least, a part of their original acidic and basic properties. Thus, an acid-base bifunctional catalyst was successfully obtained by a simple combination of solid acid and solid base.

A catalytic performance of the layered SA/MgO catalyst for the decomposition

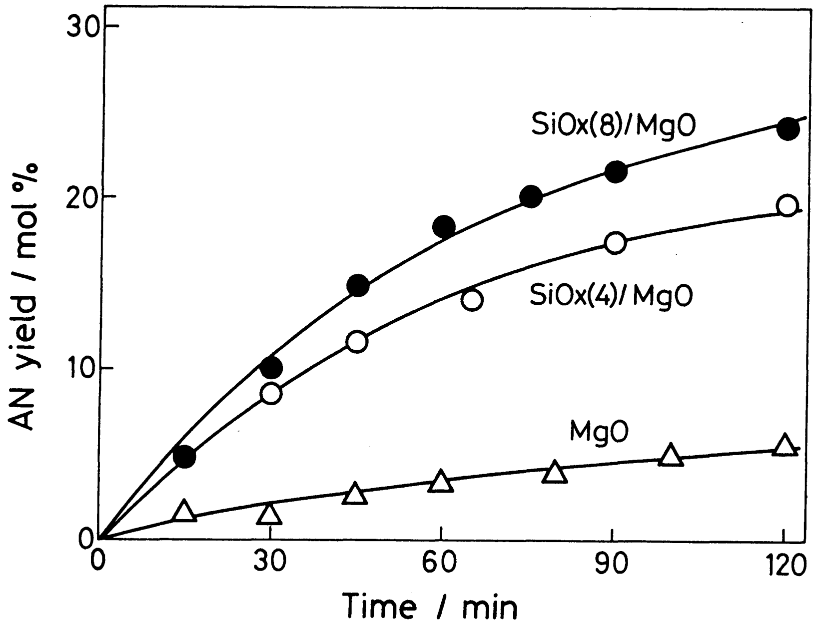


Fig. 2. Formation of acetonitrile over SiOx/MgO catalyst.
(Amount of catalyst 100 mg, reaction temperature = 773 K)

of Et_3N was examined at 723 K and compared with the hybrid SA/MgO catalyst. An acetonitrile yield on the layered SA/MgO catalyst was 12%, which is lower than that on the hybrid SA/MgO catalyst (21% at the same condition). A production of Et_2NH and $EtNH_2$ was found to be high on the layered catalyst. Since the production of such intermediate products was typically found on SA catalyst, the layered catalyst may keep the original acidic properties of SA, however, the presence of a second layer of MgO shifts the reaction toward the dehydrogenation to yield AN, instead of the deamination reaction. Since the layered SA/MgO catalyst system is composed of the separated two layers, SA and MgO, a larger distance between acidic sites and basic sites may result in the lower yield of AN.

It is known that an enhancement in the acidic properties was frequently found for the mixed metal oxides prepared by a coprecipitation method.3) An acid-base bifunctional catalyst could be obtained by a similar manner, however, a recent report4) suggests that a new category of an acid-base bifunctional catalyst may be obtained by a controlled deposition of silica on MgO by using TMS, by keeping a part of the original basic properties of MgO. Figure 2 shows the reaction time courses of the formation of AN from Et_3N at 773 K on the SiOx(4)/MgO and SiOx(8)/MgO catalysts. This clearly indicates the deposition of a silica phase on MgO surface generated acidic property and hence enhanced the activity for the overall reaction of Et_3N to AN.

References
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