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Selective Dehydrogenation of Alkylamines to Nitriles over Metal Oxide Catalysts

Bo-Qing XU, Tsutomu YAMAGUCHI,* and Kozo TANABE
Department of Chemistry, Faculty of Science,
Hokkaido University, Sapporo 060

Decomposition of alkylamines over ZrO_2, SiO_2-Al_2O_3, and MgO were examined in a closed recirculation reactor. ZrO_2 showed the highest activities and selectivities for the formation of nitriles, especially in di- and trialkylamine decomposition. In contrast, SiO_2-Al_2O_3 catalyzed dealkylation and deamination reactions exclusively. MgO exhibited high selectivity for the dehydrogenation of primary alkylamine. The high activity of ZrO_2 is attributed to its acid-base bifunctional properties.

A weakly acidic and weakly basic zirconium dioxide exhibits specific catalytic actions.[1,2] For instance, Yamaguchi et al. reported a selective formation of α-olefin from sec-alcohol[3] and a unique isotopic exchange reaction between surface H atoms of ZrO_2 and methyl-D in 2-propanol-d_8.[4] Satoh et al. reported that ZrO_2 showed a highest activity for the production of 1-butene from 2-butylamine among various metal oxide catalysts.[5] Recently we found that ZrO_2 exhibited higher activity for the formation of acetonitrile from triethylamine than a strongly acidic SiO_2-Al_2O_3(SA) and a strongly basic MgO through TPD experiments, and attributed such specific catalytic behavior of ZrO_2 to its acid-base bifunctional properties.[6] Decomposition of alkylamines may involve dealkylation, deamination and dehydrogenation reactions. Dealkylation reaction may be catalyzed by a solid acid while a dehydrogenation reaction may take place over solid base catalysts. So the catalytic activity and selectivity for alkylamine conversion may be influenced by the acid-base properties of oxides. This paper deals with the characteristic catalytic action of ZrO_2 for the decomposition of alkylamines and the results are compared with that of SA or MgO in terms of their acid-base properties.

Zirconium dioxide was prepared by hydrolysis of zirconium oxynitrate, $ZrO(NO_3)_2$, with concentrated ammonia water (28%) followed by drying the washed precipitate at 393 K and calcining in air at 873 K for 24 h. XRD pattern showed that a monoclinic ZrO_2 was obtained with a little tetragonal phase. Silica-alumina was N631(L) SiO_2-Al_2O_3 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. The BET surface areas of the three catalyst samples are given in Table 1.

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 by passing successively through molecular sieves 3A and

KOH.

The catalytic conversion of alkylamine was carried out at 673 K in a closed recirculation reaction system at an initial pressure of 5.34 kPa. Catalyst pretreatment is described in our previous report.6) Gas analysis was performed by using a gas chromatograph equipped with a 3 m column of Amipak 141.

When n-$PrNH_2$, a primary amine, was allowed to contact with oxide catalysts, propionitrile and propene were formed (Table 1); the former is a dehydrogenation product and the latter a deamination product (Eqs. 1 and 2).

$$n\text{-}C_3H_7NH_2 \longrightarrow C_2H_5CN + 2H_2 \qquad (1)$$

$$n\text{-}C_3H_7NH_2 \longrightarrow C_3H_6 + NH_3 \qquad (2)$$

The catalytic activity was found to be in the order of ZrO_2 > MgO > SA. Table 1 clearly indicates that both ZrO_2 and MgO catalyze effectively the dehydrogenation reaction to yield propionitrile, while SA catalyzes the deamination reaction exclusively. It is worth mentioning that a weakly acidic and basic ZrO_2 is a better catalyst for the production of propionitrile than a strongly basic MgO.

Table 1. Conversion of n-Propylamine over Oxide Catalysts

Catalyst (mg)	Pretreat. temp/K	Surface area/m^2g^{-1}	Reaction time/min	Conv./%	Composition/mol%		
					CH_3CH_2CN	C_3H_6	C_{4+}
ZrO_2 (200)	873	30	35	98.7	94.4	1.9	3.7
MgO (100)	1073	93	60	94.1	94.8	1.6	3.6
SA (100)	773	293	60	68.1	1.0	70.5	28.5

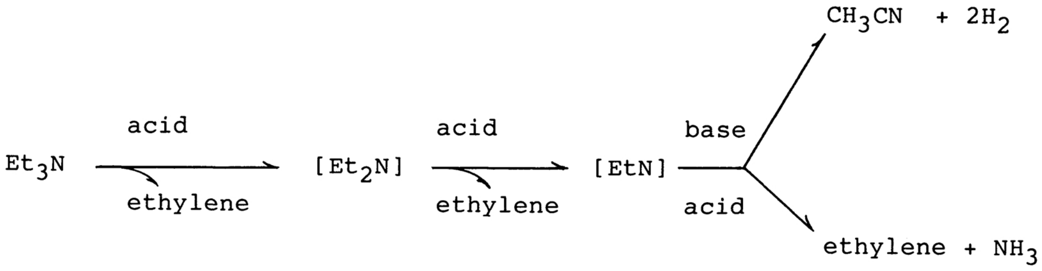
Catalytic decomposition of Et_3N over ZrO_2, MgO, and SA is summarized in Table 2. SiO_2-Al_2O_3 was found to be quite active for the decomposition of tertiary amine but the reaction is limited to the deamination reaction as in the case of primary amine. An extensive production of C_{4+} from n-$PrNH_2$ and C_{3+} from Et_3N on SA could be obtained from the acid-catalyzed oligomerization-cracking reaction of olefins produced. MgO exhibits fairly low activity for the decomposition of tertiary amine, which is in a marked contrast to the case of the decomposition of primary amine. On the other hand, ZrO_2 showed a good activity for the production of nitriles. Since a formation of nitriles from Et_3N may proceed via a stepwise dealkylation-dehydrogenation process (Scheme 1), the acid-catalyzed C-N bond dissociation should take place prior to the base-catalyzed dehydrogenation reaction. Hence acidic property of catalyst is necessary for the over-all reaction sequence.

Table 2. Conversion of Triethylamine over Oxide Catalyst

Catalyst (mg)	Reaction time min	Conv./%	Composition/mol%					
			C_2H_4	C_{3+}	Et_2NH	$EtNH_2$	CH_3CN	C_3H_7CN
ZrO_2 (200)	120	38.6	68.1	-	4.2	-	24.6	3.1
MgO (100)	120	12.1	52.1	-	21.5	6.6	19.8	-
SA (100)	120	96.7	39.8	28.4	13.4	18.4	-	-

The low activity of MgO for the Et_3N conversion can be interpreted in terms of its weak acidity or its low activity for the dealkylation reaction, while a high activity of ZrO_2 can be attributed to the acid-base bifunctional properties.

Reactivities of primary, secondary, and tertiary amines on ZrO_2, MgO, and SA are



Scheme 1.

Table 3. Catalytic Activity and Selectivity of Oxide Catalysts for Alkylamine Conversion

Catalyst (mg)	Reactant	Reaction time min	Conv./%	Composition/mol%	
				Nitriles	Others
ZrO_2	n-$PrNH_2$	20	95.8	94.2	5.8
(200)	Et_2NH	120	60.3	66.3	33.7
	Et_3N	120	38.6	27.9	72.1
MgO	n-$PrNH_2$	20	74.1	93.3	6.7
(100)	Et_2NH	120	21.9	42.9	57.1
	Et_3N	120	12.1	19.8	80.2
SA	n-$PrNH_2$	60	68.1	1.0	99.0
(100)	Et_3N	120	96.7	0	100

compared in Table 3. Reactivities on ZrO_2 and MgO are in the order of primary > secondary > tertiary amine, while tertiary amine was the most reactive on SA. When an oxide catalyst is a typical solid acid, the decomposition mainly proceeds via dealkylation-deamination reaction. When a catalyst is basic, the main reaction is a dehydrogenation reaction, and the dealkylation reaction is not facile. Thus the primary amine is the most reactive and the secondary amine comes next. This is the case on MgO. However, if the catalyst has an acidic property in addition to basic property, the preceding dealkylation reaction becomes facile and thus the nitrile formation becomes pronounced. This is the case on ZrO_2.

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