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Cyanoethylation of alcohols over solid base catalysts

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Abstract

Cyanoethylation of alcohols with acrylonitrile to form 3-alkoxypropanenitriles proceeds effectively over solid base catalysts such as alkaline metal oxides and hydroxides, lanthanum oxide, and alumina supported potassium fluoride and hydroxide at a reaction temperature below 323 K. The order of the reactivity of alcohols varied with the types of catalyst. With magnesium hydroxide and calcium hydroxide, the reactivity of alcohol decreased: methanol>ethanol>2-propanol, while with the alkaline earth oxides, lanthanum oxide, and alumina supported KOH and KF, the reactivity order was opposite. The reactivity orders are interpreted by the acidity of alcohol combined with the basic strength of the catalysts. The catalytic activity of solid base catalysts were scarcely affected by exposure of the catalyst to air before use for the reaction. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Cyanoethylation; Solid base catalyst; 3-alkoxypropanenitrile

1. Introduction

Acrylonitrile undergoes cyanoethylation with a variety of compounds containing an active hydrogen to form nitriles of different types. The resulting nitriles can be converted to different types of carboxylic acids by hydrolysis, and amines by reduction. Therefore, cyanoethylation is one of the important reactions for the synthesis of drug intermediates and organic compounds of industrial interest. In general, cyanoethylation proceeds in the presence of a base [1,2]. The catalysts so far reported for cyanoethylation of alcohols are alkali hydroxides [2], alkali alkoxides [3], and tetraalkylammonium hydroxides [3] as homogeneous catalysts, and anion exchange resins as heterogeneous catalysts [4–6]. Although there are many types of metal oxides showing basic properties on the surfaces, and the use of metal oxides has many advantages as compared with the ion exchange resins, there have been no reports of the metal oxides used for cyanoethylation.

In the present paper, we report that cyanoethylation of alcohols with acrylonitrile to 3-alkoxypropanenitrile proceeds below 323 K over the metal oxide type solid base catalysts such as alkaline metal oxides and hydroxides, lanthanum oxide, and alumina supported potassium fluoride and hydroxide.

2. Experimental

2.1. Catalysts

Alkaline earth hydroxides and carbonates used for the catalysts and starting materials for alkaline earth oxides were commercially available. $Ca(OH)_2$, $Sr(OH)_2 \cdot 8H_2O$, $Ba(OH)_2 \cdot 8H_2O$, $CaCO_3$, $SrCO_3$, and

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$BaCO_3$ were purchased from Kanto Chem., $Mg(OH)_2$ and $MgCO_3$ were purchased from E. Merck and Wako Pure Chem., respectively. MgO, CaO, SrO, and BaO, were prepared by decomposition of $Mg(OH)_2$, $Ca(OH)_2$, $SrCO_3$, and $BaCO_3$, respectively, at elevated temperature in a vacuum. La_2O_3 was prepared from $La(OH)_3$ which was prepared from an aqueous solution of $La(NO_3)_3$ by hydrolysis with an aqueous ammonia, followed by washing with distilled water and drying at 373 K. ZrO_2 and ZnO were prepared from $Zr(OH)_4$ and $Zn(OH)_2$, respectively, by decomposition at elevated temperatures in a vacuum. KF/alumina was purchased from Fluka Chem., and KF content of 8.2 mmol/g was determined by XRF. Alumina used for the catalyst and the support for KOH/alumina was supplied from the Catalysis Society of Japan (JRC-ALO4). KOH/alumina was prepared by impregnation of the alumina with an aqueous solution of KOH, the content of KOH was 3.6 mmol/g.

2.2. Reaction procedures

Acrylonitrile and alcohols were purchased from Tokyo Kasei, and purified by passage through 4A molecular sieves to remove water and carbon dioxide exclusively from the reactants. The types of alcohol used were methanol, ethanol as a primary alcohol, 2-propanol as a secondary alcohol and 2-methyl-2-propanol as a tertiary alcohol. Cyanoethylation of alcohol with acrylonitrile to 3-alkoxypropanenitrile is shown in Fig. 1 together with the structures of alcohols such as methanol, ethanol, 2-propanol and 2-methyl-2-propanol.

The reaction was carried out in a H-shaped glass batch reactor. The two branches of the reactor were separated by a breakable seal. A sample of the catalyst precursor was placed in one branch, outgassed at an elevated temperature for 2 h, and sealed. A mixture of purified acrylonitrile (4 mmol) and alcohol (12 mmol) was stored in the other branch until it was introduced through the breakable seal by distillation into the branch containing the catalyst thermostated at liquid nitrogen temperature. Reaction was initiated by melting the reactant mixture at a reaction temperature followed by stirring. The products were analyzed by GC with a TC-5 capillary column. The products were also identified by ^{1}H-NMR, MS, GC–MS and elemental analysis.

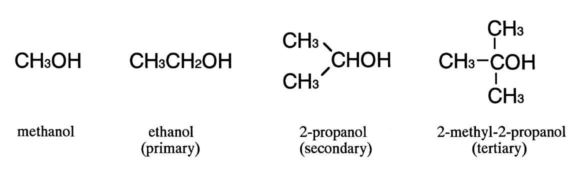


Fig. 1. Cyanoethylation of alcohol with acrylonitrile to 3-alkoxypropanenitrile.

3. Results and discussion

3.1. Catalytic activity of solid base catalyst for cyanoethylation of methanol

The conversions of acrylonitrile are listed in Table 1 when the reaction was carried out for 120 min over different types of solid base catalysts at a reaction temperature of 323 K. In the table, the temperature for catalyst pretreatment and the surface areas of the catalysts are also included. The products consisted exclusively of 3-methaoxypropanenitrile. The selectivity for cyanoethylation exceeded 99% for all the active catalysts.

All the alkaline earth oxides exhibited high conversions. The conversions obtained with MgO, CaO, and SrO exceeded 90%. Even with BaO which has a small surface area of 2 m^2/g, conversion of 78.2% was obtained. The alkaline earth hydroxides also exhibited high conversions. The surface areas are smaller for the hydroxides than for the oxides with all the alkaline earth elements. Considering the small surface areas of alkaline earth hydroxides, the activities of the alkaline earth hydroxides appear to be comparable to those of the alkaline earth oxides on the unit surface area basis. The alkaline earth carbonates, however, were inactive except for $MgCO_3$ which showed only a low conversion of 1.3%.

Although La_2O_3, ZrO_2, and ZnO show basic properties and catalyze a number of base-catalyzed reactions [7], they are not so active as the alkaline earth oxides or hydroxides for cyanoethylation of methanol with acrylonitrile; La_2O_3 gave a conversion of 8.1%, and ZrO_2 and ZnO were inactive.

Table 1
Activities of solid base catalysts for cyanoethylation of methanol

Catalyst	Catalyst weight (mg)	Pretreatment temperature (K)	Surface area (m^2/g)	Conversion[a] (%)
MgO	100	1073	223	98.7
$Mg(OH)_2$	144	—	74	62.4
$MgCO_3$[b]	210	—	38	1.3
CaO	100	873	62	94.7
$Ca(OH)_2$	132	—	6	30.6
$CaCO_3$	179	—	2	0
SrO	100	1073	10	98.9
$Sr(OH)_2{\cdot}8H_2O$	248	—	1	65.0
$SrCO_3$	143	—	5	0
BaO	100	1273	2	78.2
$Ba(OH)_2{\cdot}8H_2O$	206	—	1	68.5
$BaCO_3$	129	—	2	0
La_2O_3	100	873	33	8.1
ZrO_2	100	873	42	0
ZnO	100	873	2	0
γ-Alumina	100	773	170	0
KF/alumina	100	623	38	52.3
KOH/alumina	100	873	91	85.3

Acrylonitrile, 4 mmol; methanol, 12 mmol; reaction temperature, 323 K; reaction time, 120 min.

[a] Conversion was calculated by the decrease in acrylonitrile percentage.

[b] Containing small impurities of MgO.

Alumina itself was inactive, but KF/alumina and KOH/alumina exhibited high conversions. The conversions were not so high as those observed for MgO, CaO, and SrO, but comparable to those for alkaline earth hydroxides and BaO.

3.2. Reactivity of different alcohols for cyanoethylation

Reactivity of different alcohols for cyanoethylation varied with the types of solid base catalysts. Fig. 2 shows the conversions of acrylonitrile for cyanoethylation with different alcohols when alkaline earth hydroxides were used as catalysts. With $Mg(OH)_2$ and $Ca(OH)_2$, the reactivity was in the order: methanol>ethanol>2-propanol. With $Sr(OH)_2{\cdot}8H_2O$ and $Ba(OH)_2{\cdot}8H_2O$, ethanol is most reactive and 2-propanol is least reactive.

The order of the reactivity of alcohol over MgO, CaO, SrO, BaO, La_2O_3, KF/alumina and KOH/alumina was different from those observed for alkaline earth hydroxides as shown in Fig. 3. The order was methanol<ethanol<2-propanol.

In a homogeneous system, cyanoethylation of alcohol with acrylonitrile is believed to proceed by three steps [1]. In step 1, the function of the base is to abstract an H^+ from hydroxyl group of alcohol and generate an alkoxide anion. The alkoxide anion reacts with acrylonitrile to form 3-alkoxypropanenitrile anion in step 2. The 3-alkoxypropanenitrile anion

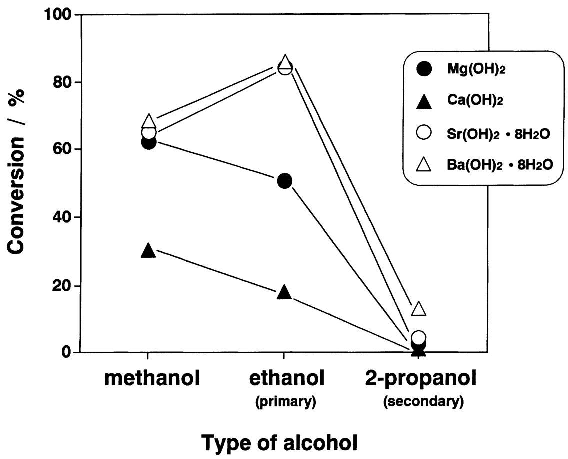


Fig. 2. Reactivity of alcohol for cyanoethylation over alkaline earth hydroxides: Acrylonitrile, 4 mmol; alcohol, 12 mmol; reaction temperature, 323 K; reaction time, 120 min.

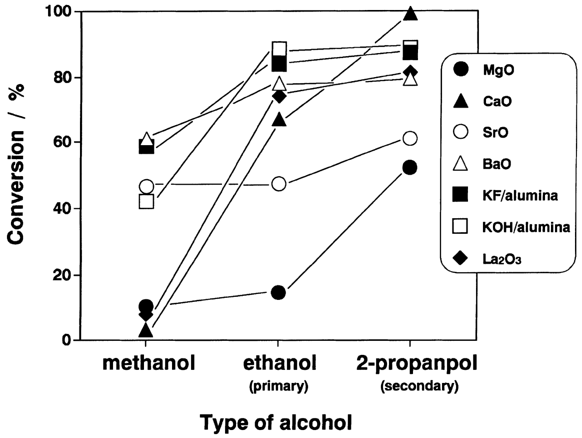


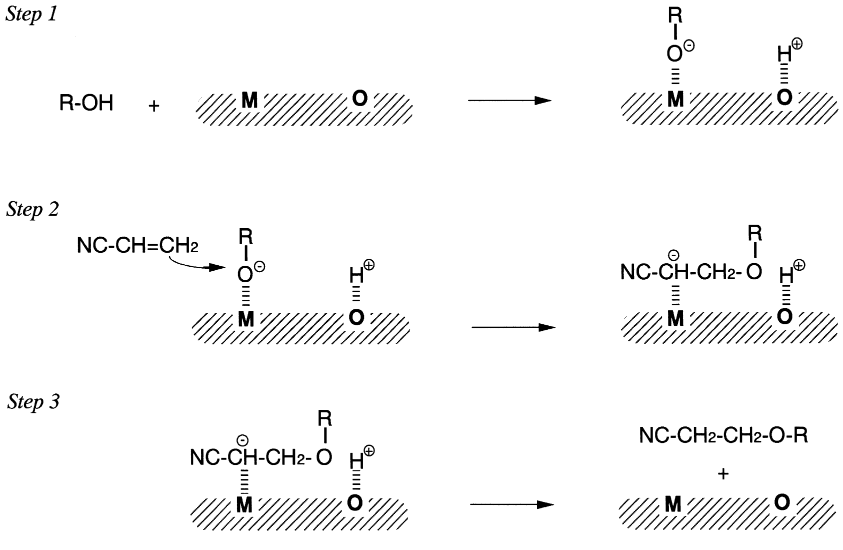
Fig. 3. Reactivity of alcohol for cyanoethylation over solid bases: Catalyst, 100 mg; acrylonitrile, 4 mmol; alcohol, 12 mmol SrO; reaction temperature, 273 K; reaction time, 10 min MgO, CaO, BaO, KF/alumina, KOH/alumina; reaction temperature, 273 K; reaction time, 120 min La_2O_3; reaction temperature, 323 K; reaction time, 120 min.

picks up an H^+ from the base to yield 3-alkoxypropanenitrile in step 3.

By analogy, with a homogeneous system, cyanoethylation of alcohols with acrylonitrile is suggested to proceed as illustrated in Scheme 1. In step 1, an H^+ is abstracted from hydroxyl group of alcohols by a basic site of the catalyst to form surface alkoxide anion. The alkoxide anion is believed to be stabilized on the surface metal cation. The alkoxide anion reacts with acrylonitrile to form 3-alkoxypropanenitrile anion in step 2. The 3-alkoxypropanenitrile anion picks up an H^+ from the surface to yield 3-alkoxypropanenitrile in step 3.

The acidity of alcohols in liquid phase is in the order: methanol>ethanol>2-propanol. If step 1 is the slow step in cyanoethylation, the reactivity would be in accordance with the ease of abstraction of H^+ from alcohol, that is, acidity. This case would occur for the weakly basic catalysts. Actually, the reactivities decreased with the decrease in acidity of alcohols for $Mg(OH)_2$ and $Ca(OH)_2$ whose basic sites are weaker than those of MgO and CaO.

For the strong basic catalyst, however, the abstraction of an H^+ should be rapid, and step 2 will be the slow step. If step 2 is a slow step, the reactivity of alcohols would be determined by the stability of alkoxide anion. The stable alkoxide would react slowly with acrylonitrile. The stability of alkoxides is in the order: methoxide>ethoxide>2-propoxide. Therefore, the reactivity for cyanoethylation will be in the order; 2-propanol>ethanol>methanol. This reactivity order was observed for MgO, CaO, SrO, BaO, La_2O_3, KF/alumina and KOH/alumina, whose basic sites are strong.



Scheme 1. Reaction route of cyanoethylation of alcohol.

Table 2
Activities of solid base catalysts for cyanoethylation of 2-methyl-2-propanol

Catalyst	Pretreatment temperature (K)	Conversion[a] (%)
MgO	1073	1.3
CaO	873	2.6
SrO	1073	6.9
BaO	1273	1.0
KF/alumina	623	6.3
KOH/alumina	873	3.4

Catalyst, 100 mg; acrylonitrile, 4 mmol; 2-methyl-2-propanol, 12 mmol; reaction temperature, 323 K; reacton time, 120 min.
[a]Conversion was calculated by the decrease in acrylonitrile percentage.

The maximum reactivity for ethanol was observed for $Sr(OH)_2{\cdot}8H_2O$ and $Ba(OH)_2{\cdot}8H_2O$. For these catalysts, the basic sites are not strong enough to easily abstract an H^+ from 2-propanol, but strong enough to abstract an H^+ from methanol and ethanol. The slow steps over these hydroxides are step 1 for 2-propanol and step 2 for methanol and ethanol.

3.3. *Catalytic activity of solid base catalysts for cyanoethylation of 2-methyl-2-propanol*

The results of cyanoethylation of 2-methyl-2-propanol is shown in Table 2. At a reaction temperature of 323 K and for a reaction time of 120 min, SrO and KF/alumina exhibited a low activity. The conversion obtained for SrO and KF/alumina were 6.9% and 6.3%, respectively. One of the reasons for low reactivity of 2-methyl-2-propanol is the weak acidity of 2-methyl-2-propanol. Abstraction of an H^+ for 2-methyl-2-propanol is difficult even for strongly basic catalysts. The other reason is a steric hindrance of 2-methyl-2-propoxide anion on the surface. Attack of acrylonitrile to O atom in 2-methyl-2-propoxide is hindered by methyl groups.

3.4. *Dependence of catalytic activities of MgO and CaO on pretreatment temperature*

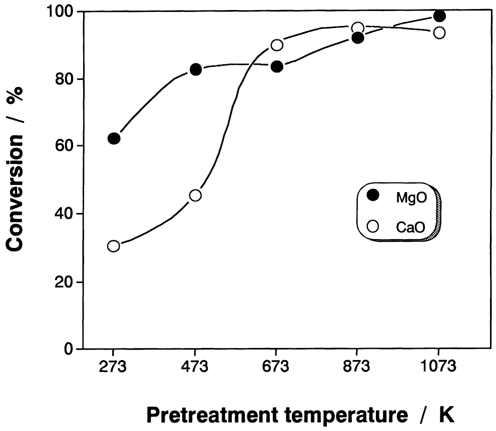


Fig. 4. Variation of activities of MgO and CaO for cyanoethylation of methanol as a function of pretreatment temperature: Acrylonitrile, 4 mmol; methanol, 12 mmol; reaction temperature, 323 K; reaction time, 120 min.

As reported elsewhere, the catalytic activities of MgO for several base-catalyzed reactions such as a double bond isomerization of 1-butene [8] and 5-vinylbicyclo[2.2.1]hept-2-ene [9], condensation of acetone [10] and *n*-butyraldehyde [11], and Michael addition of methyl crotonate [12], strongly depend on the pretreatment temperature. Fig. 4 shows the dependence of the conversions of cyanoethylation of methanol on the pretreatment temperature of MgO and CaO. The activities of MgO and CaO for cyanoethylation of methanol do not so strongly depend on the pretreatment temperature as compared to those for the other base-catalyzed reactions listed above. Below a pretreatment temperature of 673 K, the surface of MgO and CaO may be mostly covered with OH groups, even though considerable activities were observed on such surfaces. The OH groups are the candidates for the active sites of MgO and CaO pretreated below 673 K. It was reported that the OH groups on MgO and CaO are the active sites for aldol condensation of acetone [10], whereas they are inactive for 1-butene [8] and 5-vinylbicyclo[2.2.1]hept-2-ene [9] isomerization.

The basic strength of the OH groups is considered to be lower than that of the O^{2-} ions on the MgO surface. The acidity of methanol is higher than those of 1-butene and 5-vinylbicyclo[2.2.1]hept-2-ene. It is, therefore, possible that weakly basic sites of the OH groups can abstract an H^+ from methanol to act as actives for the cyanoethylation of methanol, but cannot abstract an H^+ from 1-butene and 5-vinylbicyclo[2.2.1]hept-2-ene.

3.5. *Effect of exposure of solid base catalysts to air on activity for cyanoethylation*

The catalytic behaviors of solid base catalysts examined in this study for cyanoethylation are different in the sensitivity to poisons from those for other base-catalyzed reactions [7] such as 1-butene isomerization, CH_4–D_2 exchange and 1,3-butadiene hydrogenation. For these reactions, the active sites are completely eliminated if the pretreated catalysts are exposed to air, because water and carbon dioxide in air are strongly adsorbed on the active sites. However, for the cyanoethylation of methanol and 2-propanol over solid base catalysts, the activity was scarcely decreased by the exposure to air.

The conversions in cyanoethylation of methanol at different reaction times over the pretreated MgO are compared with those obtained for the MgO pretreated and then exposed to air, and shown in Fig. 5. In the initial stage of the reaction, a short induction period was observed for the MgO exposed to air. The conversion rate accelerated with the reaction time and approached those for the pretreated MgO in 10 min.

Table 3 presents the effects of exposure of solid base catalysts to air on the activity for cyanoethylation of methanol. The conversions in 120 min were not affected much by exposure to air for all catalysts examined. Similar results were obtained for cyanoethylation of 2-propanol over MgO and CaO, and are shown in Table 4. The conversions were not changed by exposure of the catalysts to air.

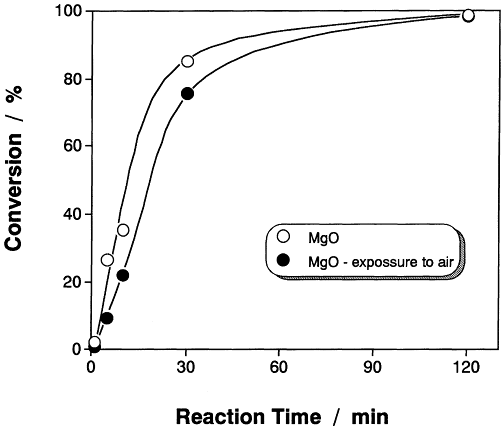


Fig. 5. Effect of exposure of MgO to air on activity for cyanoethylation of methanol: (○) MgO pretreated at 1073 K in vacuum; (●) MgO pretreated at 1073 K in vacuum and exposed to air for 30 min followed by evacuation at room temperature. Catalyst, 100 mg; acrylonitrile, 4 mmol; methanol, 12 mmol; reaction temperature, 323 K.

Table 3
Effect of exposure of solid base catalysts to air on activity for cyanoethylation of methanol

Catalyst	Pretreatment temperature (K)	Reaction temperature (K)	Conversion[a] (%)
MgO	1073	323	98.7
MgO	—[b]	323	98.1
MgO	1073	273	10.3
MgO	—[b]	273	9.8
CaO	873	323	94.7
CaO	—[c]	323	95.2
CaO	873	273	3.2
CaO	—[c]	273	4.3
KF/alumina	623	323	52.3
KF/alumina	—[d]	323	51.1
KOH/alumina	873	323	85.3
KOH/alumina	—[e]	323	87.6

Catalyst, 100 mg; acrylonitrile, 4 mmol; methanol, 12 mmol; reaction time, 120 min.

[a] Conversion was calculated by the decrease in acrylonitrile percentage.

[b] MgO pretreated at 1073 K in a vacuum and exposed to air for 30 min followed by evacuation at room temperature.

[c] CaO pretreated at 873 K in a vacuum and exposed to air for 30 min followed by evacuation at room temperature.

[d] KF/alumina pretreated at 623 K in a vacuum and exposed to air 30 min followed by evacuation at room temperature.

[e] KOH/alumina pretreated at 873 K in a vacuum and exposed to air 30 min followed by evacuation at room temperature.

Table 4
Effect of exposure of MgO and CaO to air on activity for cyanoethylation of 2-propanol

Catalyst	Pretreatment temperature (K)	Reaction temperature (K)	Conversion[a] (%)
MgO	1073	323	83.1
MgO	—[b]	323	83.1
CaO	873	323	95.7
CaO	—[c]	323	98.6

Catalyst, 100 mg; acrylonitrile, 4 mmol; 2-propanol, 12 mmol; reaction time, 120 min.

[a] Conversion was calculated by the decrease in acrylonitrile percentage.

[b] MgO pretreated at 1073 K in a vacuum and exposed to air for 30 min followed by evacuation at room temperature.

[c] CaO pretreated at 873 K in a vacuum and exposed to air for 30 min followed by evacuation at room temperature.

For many base-catalyzed reactions, solid base catalysts are easily poisoned by carbon dioxide and water. The high sensitivity to these molecules has prevented the solid base catalysts from being used in a practical process. For cyanoethylation of alcohols, however, the solid base catalysts are tolerant to water and carbon dioxide. Probably, the alcohols are able to replace CO_2 and H_2O on the catalysts surface, because alcohols are adsorbed more strongly than CO_2 and H_2O. Appearance of the activity in the presence of CO_2 and H_2O enables the solid base catalysts to be used in a practical cyanoethylation process.

Acknowledgements

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