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A study on the alkali metal-promoted magnesium oxide system used as a catalyst for acrylonitrile synthesis from methanol and acetonitrile

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Abstract

Alkali metal-promoted MgO catalysts such as Li/MgO, Na/MgO, K/MgO, and Cs/MgO were studied for the acrylonitrile synthesis from methanol and acetonitrile in the range 300–500°C. The doping of alkali metal with larger cationic radius than that of Mg^{2+} increased the basic strength of MgO and facilitated the formation of acetonitrile carbanion, a reaction intermediate for acrylonitrile synthesis. Thermodynamic analysis showed that oxidative conditions were necessary to suppress the production of propionitrile, the main product under non-oxidative conditions. The doping of alkali metal also decreased the Lewis acid strength of MgO and consequently inhibited complete oxidation of anionic intermediates to CO and CO_2. The catalytic activity for acrylonitrile production under oxidative conditions was in the order of $K/MgO > Na/MgO > Cs/MgO > Li/MgO$.

Keywords: K/MgO; Acrylonitrile; Methanol; Acetonitrile; Propionitrile

1. Introduction

Acrylonitrile is one of very important chemicals in the chemical industries, especially in polymer industries. Generally, it has been synthesized by the ammoxidation of propylene [1,2]. However, an alternative synthetic method based on the utilizations of methanol, a C_1 chemical, and acetonitrile instead of propylene is possible and promising [3–9].

$$CH_3OH + CH_3CN \rightarrow CH_2{=}CHCN + H_2 + H_2O \qquad (1)$$

This process is a solid base-catalyzed reaction, where a methyl group activated by inductive electron withdrawal of the unsaturated substituent, cyano, is converted into vinyl group by the reaction with methanol. The catalysts so far reported for acrylonitrile synthesis from methanol and acetonitrile are alkali metals supported on silica gel [3], alkali or alkali earth metal supported on silica [4,5], and transition metal-promoted MgO [6–9].

In this paper, we studied the performance of alkali metal-promoted MgO such as Li/MgO, Na/MgO, K/MgO, and Cs/MgO in the acrylonitrile synthesis from methanol and acetonitrile at reaction temperatures in the range 300–500°C and characterized alkali metal-promoting effects on MgO in relation to the reaction. Recent efforts have focused on the syntheses of valuable organic materials via solid–base catalysis [10–12] and this study was carried out as the extension of them.

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2. Experimental

2.1. Preparation and characterization of the catalysts

The alkali metal-promoted catalysts used in this study were prepared by mixing $Mg(OH)_2$ with the corresponding aqueous solution of alkali hydroxide. The mixture was dried at 110°C for 12 h. The resultant paste was ground and calcined in He flow at 600°C for 90 min at the reactor and then in situ applied to the catalytic test to prevent catalyst deactivation by CO_2 and water. The nominal loading of alkali hydroxide was 15 mol%.

FT-IR (MIDAC, Prospect IR) analyses of the catalysts and methanol temperature-programmed desorption (TPD) experiments were performed to characterize acid–base properties of each catalyst. For the FT-IR experiments, the spent catalysts after the catalytic tests were placed in He flow at 100°C for 1 h to remove physisorbed material and then collected for the analyses. All the IR spectra were normalized based on the weight of pellet to allow comparisons. For TPD measurements, samples were calcined at 600°C for 90 min in He flow and in situ exposed to methanol vapor for 1 h at room temperature, after which physisorbed methanol was removed in He flow for 30 min. TPD experiments were run at a heating rate of 20°C/min. Desorbed gases were analyzed by a quadrupole mass spectrometer (QMS; ESS, Quartz 300D) and peak intensities were normalized to that of He which was constantly introduced into the system as an internal standard. BET surface area of the catalyst was measured by N_2 adsorption using a Micromeritics Pulse Chemisorption Unit (ASAP 2000). Differential thermal analysis (DTA) was performed in He flow to detect the dehydration temperature of the hydroxide precursor of corresponding catalyst during the calcination process.

2.2. Catalytic test

Catalytic test was carried out in a continuous flow system equipped with a quartz reactor (10 mm i.d.) and a tubular furnace at atmospheric pressure. The reactant mixture of methanol and acetonitrile was introduced into the feed line by a syringe pump and vaporized in a preheating part before being co-fed into the reactor. He was used as a carrier gas. The reaction conditions were as follows: partial pressures of methanol 16.4 kPa, acetonitrile 1.82 kPa, with(=oxidative condition)/without(=non-oxidative condition) O_2 24.5 kPa; the balance He; space velocity, 61.1 $cm^3\,g^{-1}\,min^{-1}$; catalyst loading, 200 mg; reaction temperatures from 300 to 500°C at a heating rate of 5°C/min. Catalytic activity was analyzed by using a gas chromatograph (HP 5890, TCD) with packed columns, Chromosorb 102 (3.64 m) and Porapak Q (3.64 m), and calculated by the conversion of acetonitrile and the selectivity for each product.

3. Results and discussion

3.1. Catalytic activity under non-oxidative condition

Figs. 1 and 2 show the catalytic activities as a function of temperature over various catalysts under non-oxidative condition. Promotion of MgO with alkali hydroxide except LiOH imparted high catalytic activity to MgO. However, acrylonitrile, the target material, was the minor product and propionitrile, the hydrogenated form of acrylonitrile, was the main product from the alkali metal-promoted catalysts. We

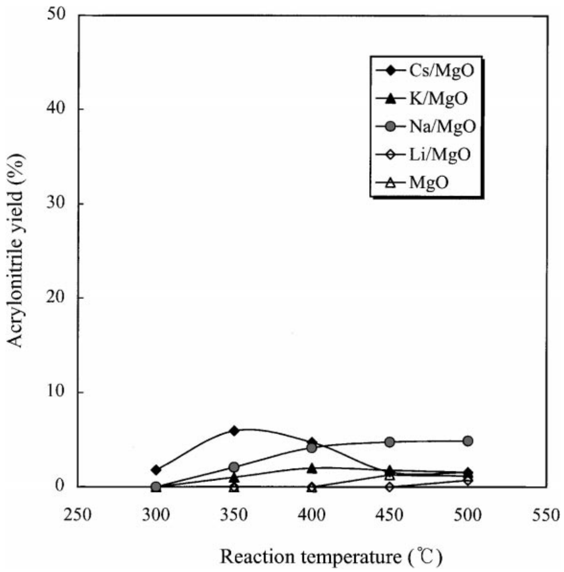

Fig. 1. Acrylonitrile yield versus reaction temperature over MgO and alkali metal-promoted catalysts under non-oxidative conditions.

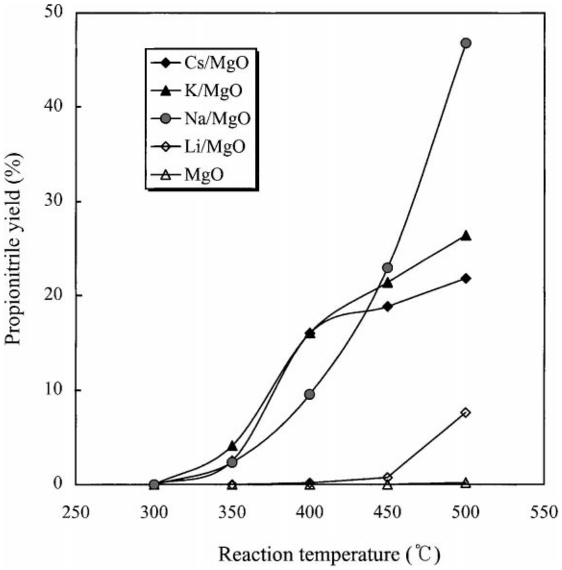

Fig. 2. Propionitrile yield versus reaction temperature over MgO and alkali metal-promoted catalysts under non-oxidative conditions.

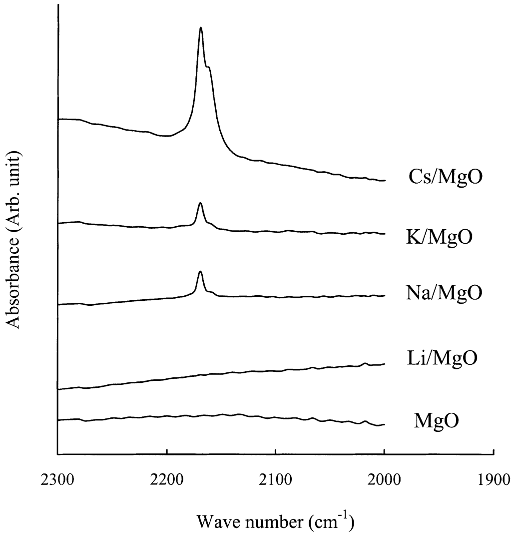

Fig. 3. FT-IR spectra of used catalysts for the identification of acetonitrile carbanion. (The samples were collected after reaction under non-oxidative conditions.)

will discuss later the reason for this phenomenon. In terms of propionitrile yield, the following activity sequence for the alkali metal-promoted catalysts was observed at 500°C of reaction temperature: Na/MgO > K/MgO > Cs/MgO > Li/MgO.

As suggested by Kurokawa et al. [9], acrylonitrile synthesis from methanol and acetonitrile may proceed via acetonitrile carbanion intermediate. This suggests that basic sites strong enough to rupture a C–H bond and to form an acetonitrile carbanion should be present on the catalyst surface in order to be an active catalyst in this reaction. From the FT-IR analyses of used catalysts shown in Fig. 3, $\nu(\mathrm{C{\equiv}N})$ peak attributed to the formation of acetonitrile carbanion was observed only on Na/MgO, K/MgO, and Cs/MgO. Consequently, the lower activities of MgO and Li/MgO could be explained in this sense.

The variation of the basic strength of MgO by alkali metal doping could be explained in viewpoint of the ionic radius of doped alkali metal cation. Kurokawa et al. [9] reported that the basic strength of MgO increased when a transition metal ion with a radius larger than that of Mg^{2+} was incorporated into the MgO lattice because it caused the localization of electron on an oxygen atom. However, when a transition metal ion with a radius far larger than that of Mg^{2+} was added, its effect weakened because the cation could not effectively incorporate into the lattice. That concept may also be applied to the alkali metal-promoted catalysts. As shown in Table 1, the ionic radius of Li^+ is similar to that of Mg^{2+} and the ionic radii of K^+ and Cs^+ are far larger than that of Mg^{2+}. So, the basic strengths of the alkali metal-promoted catalysts were considered to be in the order of Na/MgO > K/MgO > Cs/MgO > Li/MgO. Such a trend was in agreement with that of catalytic activity at 500°C of reaction temperature (Figs. 1 and 2).

In Table 1, the BET surface areas of the catalysts and the dehydration temperatures of the hydroxide precursors to form the corresponding oxide structures during the calcination process are also included. Alkali metal doping on MgO caused a decrease of BET surface area suggesting that acid–base properties are much more important than surface area in this catalytic reaction.

The DTA results confirmed that the radius of doped alkali cation has a significant effect on the basic strength of MgO. Li/MgO showed a single strong dehydration peak at ca. 320°C which is similar to that of MgO (ca. 350°C). So, it could be inferred that MgO and Li/MgO have similar properties. On the other hand, Na/MgO had a single strong dehydration

Table 1
Properties of MgO and alkali metal-promoted catalysts

Catalyst	BET surface area (m^2/g)	DTA peak maximum (°C)[a]	Ionic radius of doped alkali cation (Å)
MgO	170.7	348 s	0.66 (Mg^{2+})
Li/MgO	30.3	319 s	0.68
Na/MgO	15.3	128 s	0.97
K/MgO	42.7	216 m, 281 w	1.33
Cs/MgO	25.3	244 m, 279 w	1.67

[a] Dehydration of metal hydroxide precursor to the corresponding metal oxide. s: strong; m: medium; w: weak.

peak at 128°C which is much lower than that of MgO suggesting that Na^+ drastically changed the properties of MgO matrix and facilitated the formation of metal oxide whose basic strength is stronger than that of metal hydroxide. K/MgO and Cs/MgO showed two separated dehydration peaks, respectively, proving again that a metal ion with a far larger ionic radius than that of Mg^{2+} could not effectively incorporate into the MgO lattice. CO and CO_2 resulting from complete oxidation of reactants and products were not appreciably produced even at high reaction temperature (500°C) under non-oxidative condition.

3.2. Themodynamic analysis

Calculation of ΔG_r to elucidate a thermodynamically favorable reaction route for acrylonitrile synthesis from acetonitrile was performed, and the results under non-oxidative and oxidative conditions are shown in Figs. 4 and 5, respectively. ΔG_f's at various temperatures were calculated by using the equation $\Delta G_f = A + BT + CT^2$. The correlation constants (A, B, and C) are found in Ref. [13].

CH_3OH, HCHO, and CH_4 have been considered as a methylating agent for acrylonitrile synthesis from acetonitrile. However, it was proved that acetonitrile methylation by CH_4 is thermodynamically unfavorable under non-oxidative conditions as shown in Fig. 4(c). When CH_3OH or HCHO is used as a methylating agent, acrylonitrile can be produced because ΔG_r is negative in the range 250–550°C as shown in Fig. 4(a) and (b). However, acrylonitrile will be readily transformed into propionitrile under non-oxidative conditions as inferred from Fig. 4(d), and this could explain why propionitrile is the main product under non-oxidative conditions.

When the acrylonitrile synthesis reaction is performed under oxidative conditions, ΔG_r becomes more negative and even acetonitrile methylation by CH_4 is thermodynamically favorable as shown in Fig. 5(a) and (b). Propionitrile production is also suppressed because dehydration of propionitrile occurs readily under oxidative condition as inferred from Fig. 5(c). So, high yield of acrylonitrile production can be expected under oxidative conditions.

3.3. Catalytic activity under oxidative condition

Figs. 6–8 show the catalytic activities under oxidative conditions. In agreement with thermodynamic

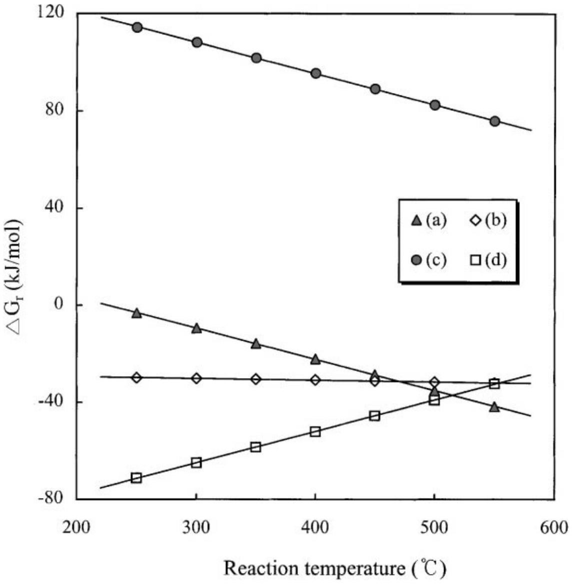

Fig. 4. ΔG_r at various temperatures under non-oxidative conditions: (a) $CH_3OH + CH_3CN \leftrightarrow CH_2{=}CHCN + H_2 + H_2O$; (b) $HCHO + CH_3CN \leftrightarrow CH_2{=}CHCN + H_2O$; (c) $CH_4 + CH_3CN \leftrightarrow CH_2{=}CHCN + 2H_2$; (d) $CH_2{=}CHCN + H_2 \leftrightarrow CH_3CH_2CN$.

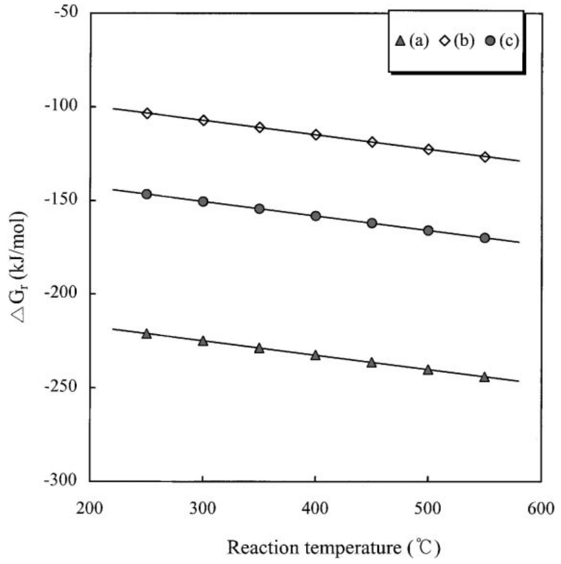

Fig. 5. ΔG_r at various temperatures under oxidative conditions: (a) $CH_3OH + CH_3CN + \frac{1}{2}O_2 \leftrightarrow CH_2{=}CHCN + H_2 + 2H_2O$; (b) $CH_4 + CH_3CN + \frac{1}{2}O_2 \leftrightarrow CH_2{=}CHCN + H_2 + H_2O$; (c) $CH_3CH_2CN + \frac{1}{2}O_2 \leftrightarrow CH_2{=}CHCN + H_2O$.

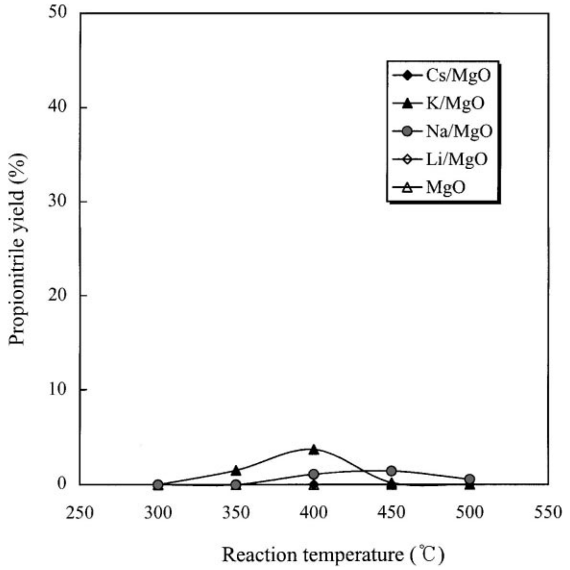

Fig. 7. Propionitrile yield versus reaction temperature over MgO and alkali metal-promoted catalysts under oxidative conditions.

predictions, the acrylonitrile yields were higher than the propionitrile ones over Na/MgO, K/MgO, and Cs/MgO, and the highest acrylonitrile yield of 28.3% was obtained over K/MgO at 400°C. However, the complete oxidation of reactants and products to CO and CO_2 increased in accordance with the reaction temperature resulting in a bell-shaped trend of

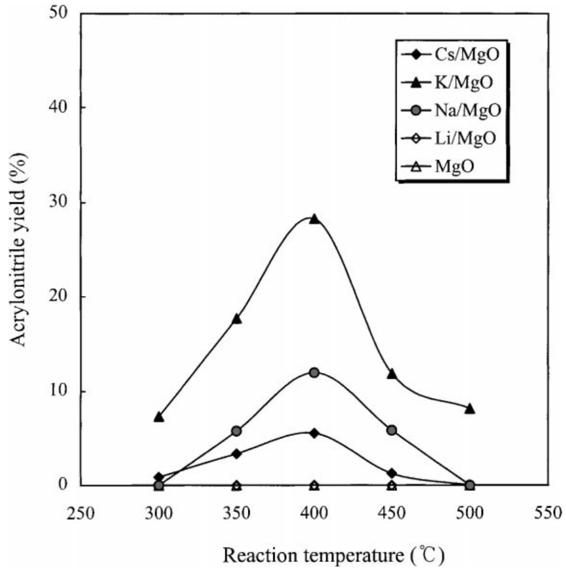

Fig. 6. Acrylonitrile yield versus reaction temperature over MgO and alkali metal-promoted catalysts under oxidative conditions.

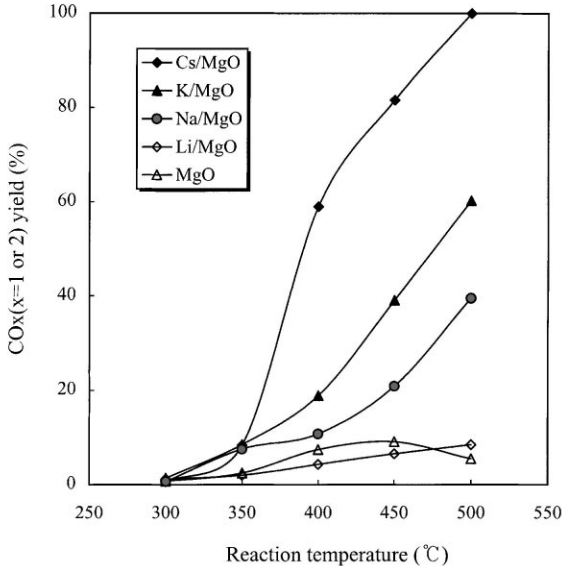

Fig. 8. CO_x $(x = 1 \text{ or } 2)$ yield versus reaction temperature over MgO and alkali metal-promoted catalysts under oxidative conditions.

acrylonitrile yield in the range 300–500°C. As shown in Table 1, the BET surface area of Na/MgO (15.3 m^2/g) is much lower than that of K/MgO (42.7 m^2/g) and its basic strength is higher than that of K/MgO as discussed previously. Consequently, the deactivation and sintering of Na/MgO by exposure to CO_2 under oxidative conditions might be more severe than those of K/MgO. As a result, in terms of acrylonitrile yield, the catalytic activity was in the order of $K/MgO > Na/MgO > Cs/MgO$ as shown in Fig. 6.

MgO and Li/MgO did not show any catalytic activity for acrylonitrile synthesis, which may be attributed to the fact that the basic strengths of MgO and Li/MgO are not strong enough to form acetonitrile carbanion as discussed previously. Therefore, CO_x $(x = 1 \text{ or } 2)$ productions over MgO and Li/MgO were considered as a result of reactant's complete oxidation. Mn/MgO reported as an effective catalyst for this reaction under non-oxidative conditions also caused complete oxidation of reactants at the reaction temperatures above 400°C.

As mentioned previously, the formation of acetonitrile carbanion on a catalyst is important to the acrylonitrile synthesis from methanol and acetonitrile. In order to stabilize the acetonitrile carbanion, cationic adsorption sites (Lewis acid sites) are necessary. So, Lewis acidity of a catalyst might also play an important role in the acrylonitrile synthesis. To elucidate Lewis acidity variation of MgO by alkali metal doping, the methanol-TPD was performed. Methoxide can be formed by dissociative chemisorption of methanol on a Lewis acid site [14]. The methoxide may adsorb more strongly as the Lewis acid strength of the catalysts increases. Fig. 9 shows that the peak temperature of methanol-TPD was in the order of $Na/MgO < K/MgO < Cs/MgO < Li/MgO < MgO$. Accordingly, it was deduced that the order of Lewis acidity might be the same. These results confirmed again that the basic strengths of alkali metal-doped MgO catalysts are in the order of $Na/MgO > K/MgO > Cs/MgO > Li/MgO$ because the strength of Lewis acid site will decrease as the strength of nearby base site increases.

Once the acetonitrile carbanion is formed on the surface of catalyst, more strongly adsorbed species will have higher possibility to interact with methanol, resulting in a better chance of forming products. This may explain why Cs/MgO and K/MgO have higher catalytic activity than Na/MgO below 400°C of under non-oxidative conditions (Figs. 1 and 2). However, under oxidative conditions, the strong adsorption may cause acetonitrile carbanion's complete oxidation to CO_x, and explains why the catalytic activity in terms of CO_x yield was in the order of $Cs/MgO > K/MgO > Na/MgO$ (Fig. 8).

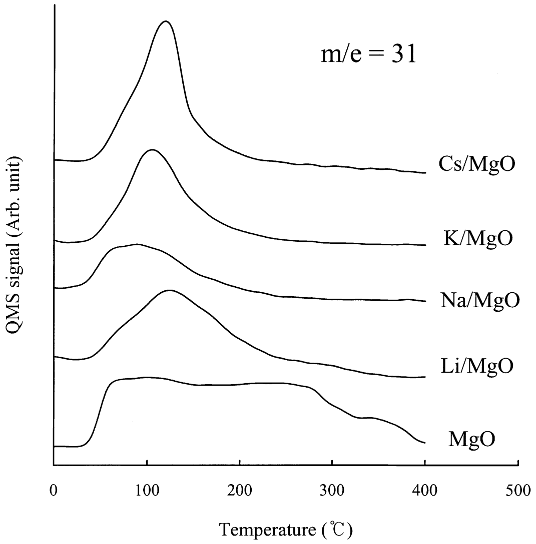

Fig. 9. Methanol-TPD profiles from MgO and alkali metal-promoted catalysts.

4. Conclusions

The doping of alkali metal with larger cationic radius than that of Mg^{2+} imparted high catalytic activity to MgO. However, propionitrile was the main product produced over these catalysts under non-oxidative conditions. It was found that oxidative conditions are necessary to suppress the production of propionitrile. Alkali metal doping facilitated the formation of acetonitrile carbanion, a reaction intermediate for acrylonitrile synthesis and also restrained complete oxidation of the anionic intermediate. The catalytic activity for acrylonitrile production under oxidative conditions was in the order of $K/MgO > Na/MgO > Cs/MgO > Li/MgO$.

Acknowledgements

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