Effect of CO_2 addition as an oxidant on the catalytic activity of K/MgO for acrylonitrile synthesis

Jin Mok Hur[a], Byoung-Youl Coh[a], Lianhai Lu[a], Heock-Hoi Kwon[b] and Ho-In Lee[a,*]

[a] *School of Chemical Engineering, Seoul National University, Seoul 151-742, Korea*
[b] *Department of Chemical and Environmental Engineering, Soongsil University, Seoul 156-743, Korea*

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The catalytic behavior of magnesium oxide doped with potassium oxide was investigated for acrylonitrile formation from acetonitrile and methanol. CO_2 was applied as a mild oxidant. Under this oxidative condition, the reaction proceeded via an oxidative dehydrogenation pathway resulting in the increase of both acetonitrile conversion and acrylonitrile selectivity compared with the reaction under a non-oxidative condition.

Keywords: acrylonitrile, acetonitrile, methanol, magnesium oxide, potassium oxide, carbon dioxide

1. Introduction

Acrylonitrile (AN) has been commercially produced by ammoxidation of propylene over multicomponent bismuth molybdate catalysts [1,2]. However, an alternative synthesis method via the reaction of methanol and acetonitrile instead of propylene ammoxidation is possible and promising [3–11]. The overall reaction can be summarized as

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

This process is a solid-base-catalyzed reaction, where the methyl group of acetonitrile (AC) activated by inductive electron withdrawal of the unsaturated substituent, cyano, is converted into a vinyl group by the reaction with methanol. Therefore, methanol can be regarded as a methylating agent. According to Kurokawa et al. [8,9], the reaction consists of three steps: dehydrogenation of methanol to formaldehyde, cross-coupling reaction between AC and formaldehyde, and dehydration of the intermediate to form AN.

Our previous work [10] described that magnesium oxide activated by alkali-metal oxide, specifically potassium oxide, showed high catalytic activity for the above reaction and that an oxidative condition was required to suppress the by-product, propionitrile (PN) which is the hydrogenated form of AN. However, significant amounts of reactants and products were oxidized to form unwanted CO and CO_2 when O_2 was employed as the oxidant. Interestingly, Lin et al. [11] observed the rate enhancement effect of CO_2 for the same reaction over MgO. In addition, it has been reported that CO_2 can be used as a mild oxidant for the oxidative dehydrogenation of ethylbenzene to styrene [12–17], suggesting the possibility of CO_2 as an oxidant in the title reaction.

In this paper, we investigated the role of CO_2 as an oxidant in the AN formation reaction over a K/MgO catalyst.

2. Experimental

The K/MgO catalyst employed in this study was prepared by mixing $Mg(OH)_2$ with aqueous solution of KOH. The mixture was dried at 110 °C for 12 h. The resulting paste was ground and calcined in He flow at 600 °C for 90 min in the reactor and then subsequent assessments of its catalytic properties were carried out *in situ*. The nominal loading of KOH was 15 mol%. The catalytic activity was tested using a continuous-flow system equipped with a quartz reactor (10 mm i.d.) and a tubular furnace at atmospheric pressure. The reactant mixture of AC and methanol was quantitatively introduced into the feed line by a syringe pump and was then vaporized in a preheating zone before entering into the reactor. Helium was used as a carrier gas. The reaction conditions were as follows: partial pressures were AC 1.8 kPa, methanol 16.4 kPa, CO_2 24.8 kPa with a He balance to bring the total pressure up to 101 kPa; weight hourly space velocity 0.89–89.1 h^{-1}; catalyst mass of 200 mg and a reaction temperature of 400 °C were employed. The reaction effluents were analyzed using a gas chromatograph (Donam DS6200, TCD) with a HP-PLOT Q capillary column (30 m) and the performance of catalyst was evaluated using the conversion of AC and the selectivity calculated for each product.

The CO_2-TPD experiments were performed to characterize the behavior of CO_2 on the catalyst. CO_2 was adsorbed at the constant set temperature ranged up to 500 °C and then cooled down to room temperature under He flow. For the TPD, a heating rate of 20 °C/min was employed. The amount of desorbed CO_2 was analyzed by a quadrupole mass spectrometer (QMS; ESS, Quartz 300D). In addition,

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[*] To whom correspondence should be addressed.

a reverse water–gas shift reaction was performed to elucidate the role of CO_2 in this study. An equimolar mixture of CO_2 and H_2 was fed to the reactor and the effluent gases were analyzed by a QMS. Decomposition and oxidation of methanol with CO_2 were studied using a methanol-TPSR (temperature-programmed surface reaction) method. A mixture of methanol of 18.2 kPa, CO_2 of 24.8 kPa with a He balance was premixed before being fed to the reactor. The reaction products were analyzed using a GC-TCD.

3. Results and discussion

Figure 1 compares the catalytic activities and selectivities of K/MgO for AN synthesis from AC and methanol with and without CO_2. Introducing CO_2 to the reaction system imparted enhanced catalytic activity over K/MgO resulting in higher AC conversion as well as higher AN selectivity. PN was observed as a by-product and no other appreciable by-products were detected under the reaction conditions employed in this study.

Although Lin et al. [11] suggested that the rate enhancement effect of CO_2 for the same reaction over MgO was due to the formation of methyl carbonate-like species on the MgO surfaces, the reason is not clear yet. Kurokawa et al. [8,9] reported that AN synthesis from AC and methanol in absence of CO_2 proceeds via formaldehyde intermediate and that the methanol to formaldehyde step is rate determining. Since it is well known that oxidative dehydrogenation of methanol to formaldehyde is thermodynamically more favorable than non-oxidative dehydrogenation, as described elsewhere [10], we believe the activity enhancement resulting from the addition of CO_2 in AN formation is due to its role as an oxidant.

In order to investigate the behavior of CO_2 adsorbed on the catalyst surface a CO_2-TPD experiment was carried out. As illustrated in figure 2, CO_2 adsorbed at 300–450 °C with 50 °C interval showed characteristic desorption peaks which shifted to higher temperatures as the adsorption temperature was increased. These results suggest that the K/MgO catalyst can interact with CO_2 in the temperature range up to ∼450 °C forming surface carbonates. However, the CO_2 dosed sample at 500 °C did not show any significant desorption peak implying that CO_2 does not adsorb on the K/MgO catalyst at ∼500 °C and above. To elucidate the surface state of K/MgO under CO_2 atmosphere, *in situ* FT-IR experiments are currently underway and the results will be reported in the near future.

There are two possible reaction pathways for the oxidation by CO_2, as shown in scheme 1. By pathway 1, CO_2 can directly oxidize methanol to form formaldehyde, H_2O and CO. On the other hand, according to pathway 2, CO_2 may react with the resulting H_2 which formed from non-oxidative dehydrogenation of methanol to form CO and H_2O (reverse water–gas shift reaction). In order to verify the existence of a reverse water–gas shift reaction pathway, TPSR experiments were carried out (figure 3). The oxidation of molecular H_2 to H_2O over a K/MgO catalyst by CO_2 did not take place until the reaction temperature reached ∼450 °C. This implies that the reverse water–gas shift reaction did not occur during the AN formation reaction at 400 °C in figure 1. We believe that the presence of an alternative route for formaldehyde formation when CO_2 was provided contributes to higher yield of AN. Formaldehyde, the intermediate for AN, can be produced only from dehydrogenation of methanol when CO_2 is not provided; however, additional formaldehyde can be supplied via pathway 1 when CO_2 is present as well as via dehydrogenation of methanol.

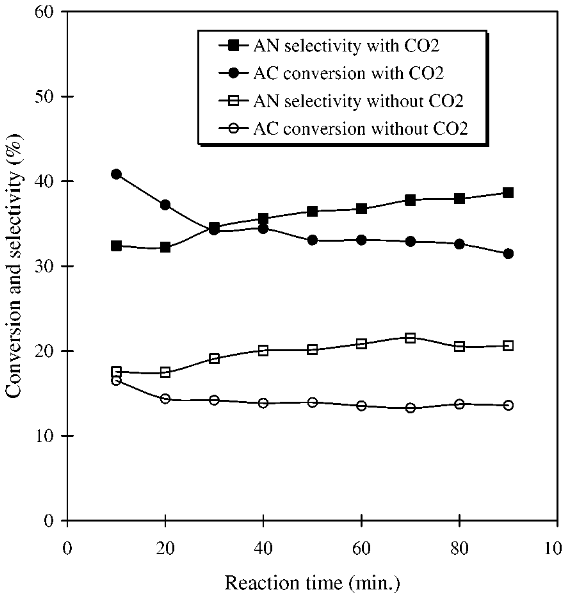


Figure 1. Effects of CO_2 on catalytic activity at 400 °C. Weight hourly space velocity was 0.89 h^{-1}.

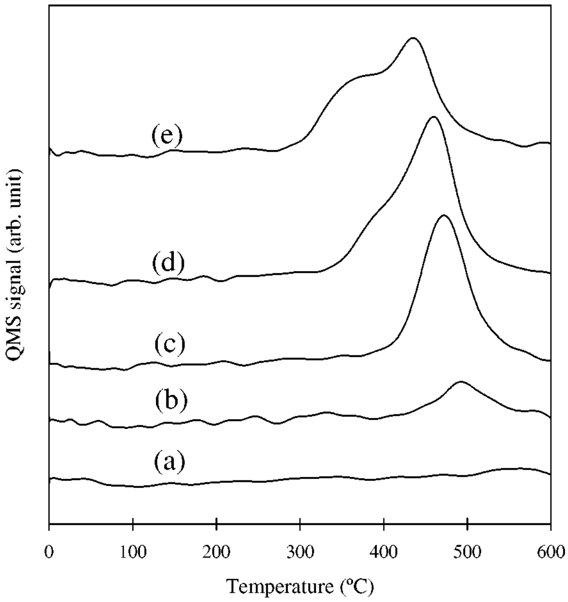
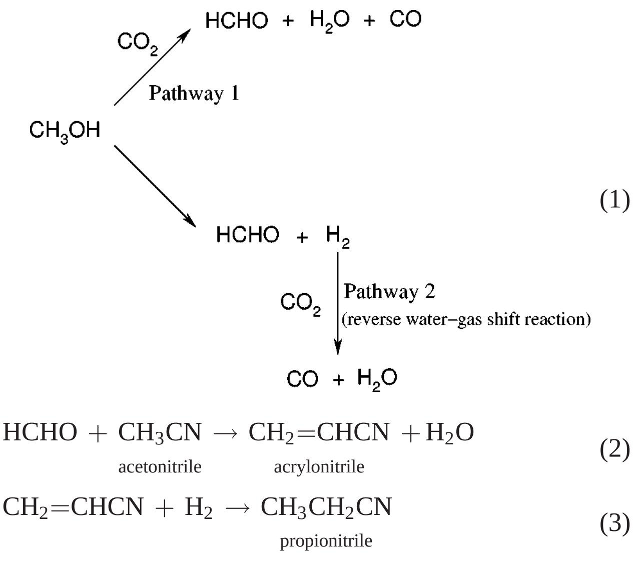


Figure 2. CO_2-TPD spectra over K/MgO. The adsoption temperature of CO_2 was at (a) 500, (b) 450, (c) 400, (d) 350 and (e) 300 °C.



$$HCHO + \underset{\text{acetonitrile}}{CH_3CN} \rightarrow \underset{\text{acrylonitrile}}{CH_2{=}CHCN} + H_2O \qquad (2)$$

$$CH_2{=}CHCN + H_2 \rightarrow \underset{\text{propionitrile}}{CH_3CH_2CN} \qquad (3)$$

Scheme 1.

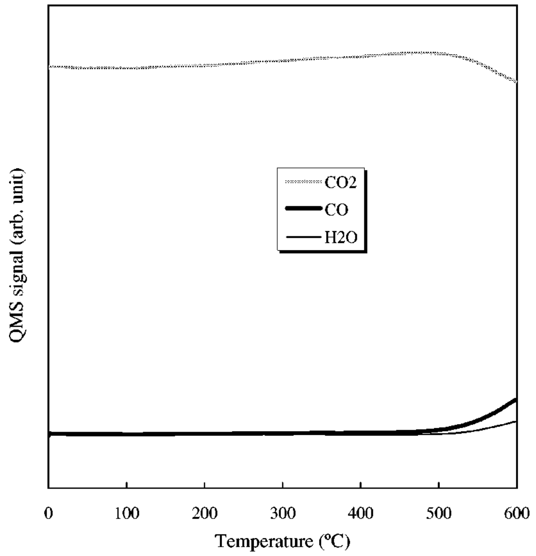


Figure 3. Reverse water–gas shift reaction over K/MgO. The reactant feeds were CO_2 (15 ml min^{-1}) and H_2 (15 ml min^{-1}). Catalyst weight was 0.2 g. Heating rate was 10 °C/min.

Under the non-oxidative conditions in our experiment, methanol decomposed only to CO and H_2, and no H_2O formation was detected in the temperature range of 300–500 °C. However, as shown in figure 4, when CO_2 was introduced as a mild oxidant, H_2O formation was detected from ~350 °C. This phenomenon suggests that the oxygen source for H_2O is CO_2 which exists on the K/MgO surface as carbonate species, and that oxidative dehydrogenation of methanol via pathway 1 outlined in scheme 1 can occur below the temperature where the AN formation reaction takes place. Therefore, it may be concluded that CO_2 functions as a mild oxidant for the oxidative dehydrogenation of methanol (pathway 1) and enhances the catalytic activity of K/MgO for the AN formation reaction from AC and methanol.

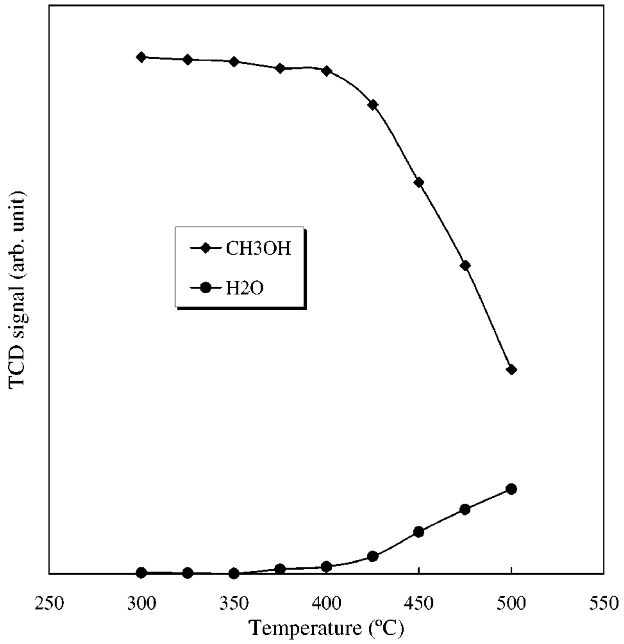


Figure 4. Methanol-TPSR spectra.

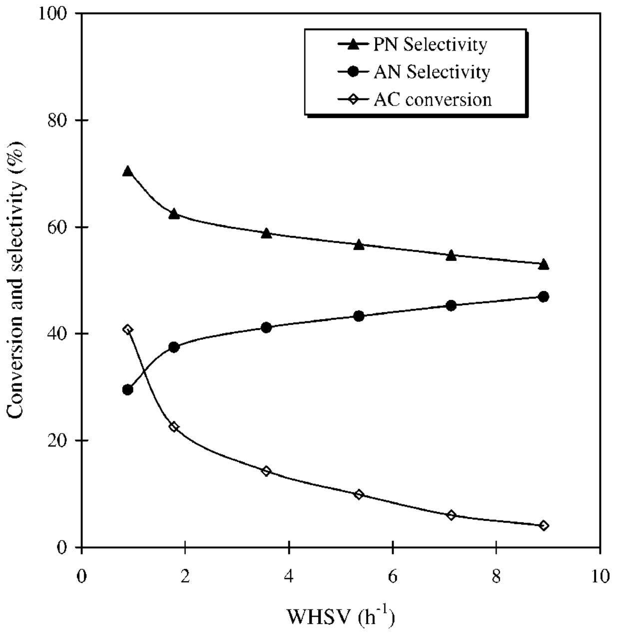


Figure 5. Catalytic activity versus space velocity at 400 °C. The reaction feed was as follows: partial pressure AC 1.8 kPa, methanol 16.4 kPa, CO_2 24.8 kPa and remainder He.

PN formation presumably resulted from AN hydrogenation as shown in scheme 1 and the hydrogen source for AN hydrogenation must be from methanol dehydrogenation. When the methanol conversion to formaldehyde proceeds, in part, via an oxidative dehydrogenation pathway (pathway 1) by introducing CO_2 as a mild oxidant, the hydrogen formation rate should decrease, resulting in lower PN selectivity. The higher AN selectivity resulting under oxidative conditions than that under non-oxidative conditions can be explained accordingly. When the space velocity of reactants was increased, the PN selectivity decreased and AN selectivity increased, as shown in figure 5. This result implies that PN may be formed from hydrogenation of AN and also confirms the validity of the proposed reaction pathway.

4. Conclusion

The effect of CO_2 addition on the catalytic activity and selectivity of K/MgO was investigated for AN formation from AC and methanol. The oxidative dehydrogenation of methanol using CO_2 improved both AC conversion and AN selectivity at 400 °C. The formation of H_2, reagent to hydrogenate AN to PN, was inhibited and/or retarded because of the oxidative dehydrogenation of CH_3OH to form HCHO which resulted in higher AC conversion and AN selectivity. The role of CO_2 in this reaction was that of an oxidant.

Acknowledgement

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