Rate Enhancing Effect of Carbon Dioxide in the Reaction of Acetonitrile with Methanol to Acrylonitrile over Magnesium Oxide Catalyst

Yi Wen Lin,† Makoto Ishii, Wataru Ueda,* and Yutaka Morikawa†
Department of Environmental Chemistry and Engineering, Tokyo Institute of Technology, Yokohama 226
†*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Yokohama 226*

(Received June 6, 1995)

Carbon dioxide greatly enhanced the formation rate of acrylonitrile in the gas-phase reaction of acetonitrile with methanol over magnesium oxide catalyst. The reaction in the presence of carbon dioxide was accompanied by the reaction of methanol with carbon dioxide to give carbon monoxide and water. An adsorbed carbon dioxide species on the basic surface of magnesium oxide seems to afford an active methanol-derived species for the reaction with acetonitrile.

We previously reported the following base-catalyzed reaction to synthesize unsaturated nitriles from acetonitrile, where methanol was used as a reagent for C=C bond formation.[1]

$$CH_3CN + CH_3OH \longrightarrow CH_2{=}CHCN + H_2 + H_2O$$

The catalysts used for this reaction are based on metal oxides, which are well-known solid-base materials, such as MgO, CaO, La_2O_3, and so forth. These metal oxides themselves are, however, virtually inactive for this reaction, so that these basic oxides should be modified with small amounts of additive transition metal cations. The effective metal cations were Mn^{2+}, Fe^{3+}, and Cr^{3+}. Recently, we found that the above catalytic reaction was able to take place over MgO without the additive metal cations when a small amount of carbon dioxide was fed in the reactants. In this letter we wish to report the reaction features in the presence of carbon dioxide and some aspects on the role of carbon dioxide in the course of the reaction.

The MgO catalyst was prepared by the following procedure: Commercial MgO (Soekawa Rika, 99.92%, surface area 11m^2 • g^{-1}) was dispersed in a distilled water with stirring for 12 h at ambient temperature and for another 12 h at 80 °C. The water was then evaporated by heating, followed by drying in air at 110 °C for 24 h. The gas-phase reaction was carried out using a conventional flow reactor at atmospheric pressure. 2 g of the precursor $[Mg(OH)_2]$ having a size of 1 mm was mounted in the reactor and was heat-treated prior to use for the reaction. Heat treatment of the dried solid (precursor) at 600 °C for 2 h under a nitrogen stream (80 mL•min^{-1}) gave the MgO-phase catalyst having a high surface area (ca. 200 m^2 • g^{-1}). The reactant mixture was 1.25 mol% of acetonitrile, 7.5 mol% of methanol, 0-11.3 mol% of CO_2, and remainder of nitrogen. The total flow rate was 80 mL•min^{-1}(STP). The reaction temperature was 360 °C.

The effect of CO_2 addition on the reaction of acetonitrile and methanol over the MgO catalyst is demonstrated in Figure 1, where the conversions of acetonitrile, methanol and CO_2 and the selectivity of acrylonitrile formation are plotted against the reaction time. Without CO_2 the reaction took place very slowly to form acrylonitrile with the selectivity of more than 90%. Another product was propionitrile and a trace amount of CO was detected under this condition. When CO_2 was fed in the reactant, both the conversions of methanol and acetonitrile remarkably increased, while the selectivity to acrylonitrile was unchanged. The conversions and the selectivity continued for several hours without any changes. Once the addition of CO_2 was ceased, the reaction rate immediately decreased. When CO_2 was fed again, the same conversions and the same selectivity recovered, as shown in Figure 1. Since no reaction took place without the MgO catalyst even in the presence of CO_2 in the system, it is obvious that CO_2 involves in the course

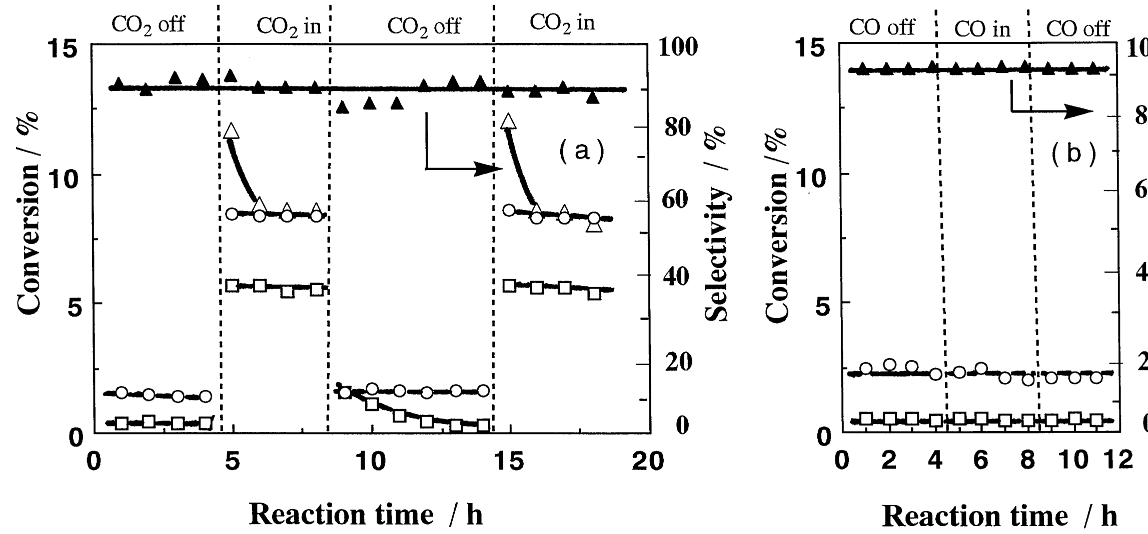

Figure 1. Addition effects of CO_2 (a) and CO (b) in the reaction of acetonitrile and methanol over MgO catalyst (2.0 g) at 360 °C. The reactant feed was methanol (6 ml·min^{-1}), acetonitrile (1 ml·min^{-1}), CO_2 (or CO) (3 or 0 ml·min^{-1}), and N_2 (70 or 73 ml·min^{-1}). Methanol conversion (□), acetonitrile conversion (○), CO_2 conversion (△), and acrylonitrile selectivity (▲).

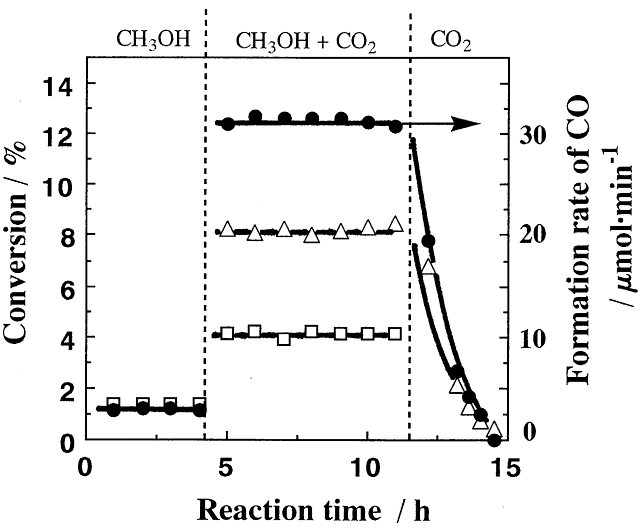

Figure 2. Reaction of methanol and CO_2 over MgO catalyst (2.0 g) at 360 °C. The reactant feed was methanol (7 ml·min^{-1}), CO_2 (3 or 0 ml·min^{-1}), and N_2 (70 or 73 ml·min^{-1}). Methanol conversion (□), CO_2 conversion (△), and CO formation rate (●).

of the surface reaction of acetonitrile with methanol.

It should be noteworthy in Figure 1 that the conversion of methanol (5.6%) was extremely higher than the stoichiometric conversion (ca. 1.4% at 8.5% conversion of acetonitrile) when CO_2 was added in the reactant and also that the conversion of CO_2 was observed and a large amount of CO was formed. Obviously a side reaction occurred at the same time. For clarifying this reaction, we conducted the reaction of methanol and CO_2 over the MgO catalyst under the similar reaction condition to the acetonitrile reaction. Results are shown in Figure 2. Without CO_2 in the feed, methanol decomposed slowly, giving small amount of CO. When methanol was reacted with CO_2 over the catalyst, the conversions of both methanol and CO_2 were observed and CO was formed in twice molar of the reacted CO_2. The result clearly indicates that CO_2 reacts with methanol, and CO was formed from both CO_2 and methanol over the MgO catalyst, as reported for a copper-zinc catalyst.[2] When the methanol feed was stopped, CO_2 still converted and then the CO formation gradually decreased, suggesting that the CO formation takes place through the reaction of CO_2 with a strongly adsorbed methanol-derived species.

On the basis of the above results, one would consider that CO formed by the reaction of CO_2 and methanol can be the effective alkylating reagent in the reaction of acetonitrile with methanol. We, therefore, tested the addition effect of CO on the reaction. Results are illustrated in Figure 1 as well. The figure clearly showed that CO had no effects.

Table 1 summarizes the rate enhancement for the acrylonitrile formation under different partial pressures of CO_2. At a lower partial pressure of CO_2, the rate enhancement was still remarkable but at a higher region the CO_2 effect was saturated, because of the strong adsorption of CO_2. The selectivity to acrylonitrile was almost independent of the CO_2 pressure added. As a consequence, the formation of CO_2-derived species on MgO surface are responsible for the rate enhancement of acrylonitrile formation in the reaction of acetonitrile with methanol.

Table 1. Effect of CO_2 in the reaction of acetonitrile and methanol

CO_2 addition /kPa	Conversion /% CH_3OH	Conversion /% CH_3CN	Formation rate of AN[a]/μmol•min^{-1}	Sel. to AN[a] /%
0	0.4	1.5	0.6	90
1.4	3.6	6.6	2.6	90
2.8	4.3	8.5	3.4	90
3.9	5.6	8.5	3.4	89
6.0	7.0	8.6	3.4	89
11.3	10.0	8.7	3.5	90

[a] Acrylonitrile.

Although the precise feature of the CO_2 enhancement effect is not explicable at the present stage, the following mechanism would be proposed on the basis of previously reported results: Recently, it was reported that addition of CO_2 increased yields in the substitution of halogenated aromatics with sodium methoxide or ammonia over copper-based catalysts.[3,4] It was presumed that CO_2 forms an adduct with the methoxide anion like $(MeO)CO_2^-Na^+$, thereby acting as a cocatalyst. In fact, it is known by FT-IR study that an adsorbed methanol on solid-base metal oxide, like thoria and ceria, reacts with CO_2 at room temperature, leading to the formation of methyl carbonate like species on the surface.[5,6] Except that acetonitrile is present in the system, the situation in our experiments seems to be similar to those; thus, an adsorbed methanol over the MgO surface may react with CO_2 at the reaction temperature, forming the similar methyl carbonate species. This species may be unstable, easily decomposing to CO. It is, however, plausible that the surface methyl carbonate species can alkylate acetonitrile to acrylonitrile more effectively than simple adsorbed methanol, in analogy to that dimethyl carbonate is a well-known alkylating reagent.[7] FT-IR studies for the CO_2 effect over the MgO catalyst are undertaken now.

References

1 W. Ueda, *J. Jap. Petrol. Inst.*, **36**, 421(1993).
2 A. Ya. Rozovskii, G. I. Lin, S.M. Loktev, Yu. B. Kagan, and A.N. Bashkirov, *Kinet. Katal.*, **17**, 1071(1976).
3 D. Nobel, *J. Chem. Soc., Chem. Commun.*, 419(1993).
4 M.H.W. Burgers and H. van Bekkum, *Catal. Lett.*, **25**, 365(1994).
5 J. Lamotte, V. Moravek, M. Bensitel, and J.C. Lavalley, *React. Kinet. Catal. Lett.*, **36**, 113(1988).
6 A.A. Tsyganenko and E.A. Trusov, *Zh. Fiz. Khim.*, **59**, 2602(1985).
7 Z.-H. Fu and Y. Ono, *J. Catal.*, **145**, 166(1994).