JOURNAL OF CATALYSIS **126**, 199–207 (1990)

Solid Base-Catalyzed Reaction of Nitriles with Methanol to Form α,β-Unsaturated Nitriles

I. Conversion and Selectivity

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Received February 6, 1990; revised May 11, 1990

The synthesis of α,β-unsaturated nitriles from saturated nitriles and methanol was achieved with basic metal oxide catalysts activated by transition metal ions. The methyl or methylene groups at the α-position of saturated nitriles are converted to a vinyl group. The reaction proceeds via dehydrogenation of methanol, cross coupling, and dehydration. Magnesium oxide, activated by manganese ion or chromium ion, has been found to give the most effective catalytic performance. In the conversion of acetonitrile, the selectivity to acrylonitrile was more than 95%. This method was also useful for the conversion of propionitrile to methacrylonitrile.

INTRODUCTION

α,β-Unsaturated compounds are very important chemicals in the chemical industries, especially in polymer industries (*1*, *2*). Production of these compounds has traditionally been accomplished through the catalytic reactions of olefins. For example, acrylonitrile has been synthesized by the ammoxidation of propylene over multicomponent bismuth molybdate catalysts (*3*, *4*). In recent years, however, alternative synthetic methods based on the utilization of C_1 chemicals such as CO, methanol, and CH_4 instead of olefins have become increasingly important (*5–8*). An interesting example is the acrylonitrile synthesis by the oxidative reaction of acetonitrile with methane over metal oxide catalysts (*9*, *10*). Since acetonitrile can be catalytically synthesized from CO, H_2, and NH_3 (*11*), the process may provide a route for acrylonitrile synthesis from C_1 chemicals only.

We recently reported another alternative process to synthesize α,β-unsaturated compounds, where methanol was used as a C_1 material (*12–15*). The general reaction scheme is described as follows:

$$\mathrm{RCH_2Z} + \mathrm{CH_3OH} \xrightarrow[\mathrm{M\text{-}MgO}]{} \mathrm{CH_2{=}CR{-}Z} + \mathrm{H_2} + \mathrm{H_2O} \quad (1)$$

$$\mathrm{Z} = \mathrm{-CN}, \mathrm{-COR'}, \mathrm{-COOR'}, \mathrm{C_6H_5},$$
$$\mathrm{R} = \mathrm{-H}, \mathrm{-CH_3}$$
$$\mathrm{M} = \mathrm{Cr^{3+}}, \mathrm{Fe^{3+}}, \mathrm{Mn^{2+}}, \text{etc.}$$

This process is a solid base-catalyzed reaction, where a methyl or methylene group activated by inductive electron withdrawal by the unsaturated substituent such as carbonyl, cyano, or phenyl group is converted into vinyl group by the reaction with methanol. Methanol can be regarded as a methylenating agent. We found that magnesium oxide modified with metal ions was an effective catalyst for this reaction (*12–15*).

Similar approaches using formaldehyde

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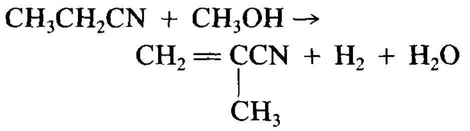
0021-9517/90 $3.00

as well as methanol have been undertaken so far and some patents have already issued (*16–26*). However, no scientific studies of the present reaction have so far been reported with the exception of our previous reports (*12–15*).

In this paper, the following catalytic reactions of nitriles with methanol are described:

$$CH_3CN + CH_3OH \rightarrow CH_2{=}CHCN + H_2 + H_2O \quad (2)$$



$$CH_3CH_2CN + CH_3OH \rightarrow CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CN + H_2 + H_2O \quad (3)$$

$$CH_3CN + CH_3OH \rightarrow CH_3CH_2CN + H_2O. \quad (4)$$

EXPERIMENTAL

Catalyst Preparation

Various metal ion-containing magnesium oxides were employed as catalysts for the reactions. The following impregnation method was used for catalyst preparation. Magnesium oxide powder (Soekawa Rika, 99.92%, surface area 11 $m^2 \cdot g^{-1}$) was placed in contact with a well-stirred aqueous solution containing the appropriate amount of metal nitrate for 12 h at an ambient temperature using a liquid/support ratio of about 25 $cm^3 \cdot g^{-1}$. The mixture was subsequently heated for the evaporation of water. The resulting wet, solid mass was dried in air at 383 K for 24 h, followed by a heat treatment in a nitrogen stream (50 $ml \cdot min^{-1}$) for 2h at 873 K in order to decompose the impregnated metal nitrate and to desorb water and CO_2. Metal ion loadings in the range of 0.05 to 15 wt% on MgO were obtained.

Reaction Apparatus and Procedure

The reaction at atmospheric pressure was carried out in a conventional flow system equipped with a quartz reactor (12-mm i.d.) and a tubular furnace. After the pretreatment of the catalyst at 873 K under a nitrogen stream, the reactant mixture of nitrile and methanol was introduced into the feed line with a syringe pump and vaporized in a preheater tube (323 K). Nitrogen was used as a diluent and carrier. Normal reaction conditions were: partial pressure, methanol 9 kPa and nitrile 0.9 kPa, remainder nitrogen; space velocity (methanol + nitrile + N_2) 58 $ml \cdot g^{-1} \cdot min^{-1}$; catalyst weight 1 g; reaction temperature 623–673 K. The catalysts were usually used in the form of cylindrical pellets. Products were identified by mass spectrometry. Quantitative analysis of the reactants and products was carried out by using gas chromatography Adsorb P-1 (3m, 343 K, He carrier) for methanol and nitriles, and molecular sieve 13 × (0.5m, 298 K, Ar carrier) for H_2, CH_4, and CO.

RESULTS AND DISCUSSIONS

Synthesis of Acrylonitrile from Acetonitrile

Results for the reaction of acetonitrile with methanol over various metal ion-containing magnesium oxide catalysts are given in Table 1. Metal ion loadings of 3 wt% were employed for the reactions. The data listed were collected after steady-state activities were attained. Products were acrylonitrile (AN), propionitrile (PN), and methacrylonitrile (MAN). A small amount of viscous organic material was observed on the outlet surface of the reactor. Since the α,β-unsaturated nitriles are compounds which readily polymerize, it is assumed that the polymerization has taken place on acidic or basic surface of the catalyst or in the gas phase. However, the extent of the polymerization of the unsaturated nitriles was estimated to be very small because the carbon balance was satisfactory in most cases.

A fixed methanol-to-acetonitrile molar ratio of 10 was used in the present study. Small amounts of CH_4 and CO were found at every reaction, suggesting that methanol was consumed to some extent to form CH_4 and CO (<1%). Dimethoxy methane and formaldehyde were not detected. The reaction should be accompanied by the formation of hydrogen and water. The hydrogen formation was confirmed by gas chromatography and mass

TABLE 1

Synthesis of Acrylonitrile by Methylenation of Acetonitrile with Methanol over Various Metal Ion-Containing Magnesium Oxide Catalysts[a]

Catalyst[b]	Conversion of acetonitrile[c] (%)	Selectivity (%)[d]		
		AN[e]	PN[f]	MAN[g]
MgO	0.1	tr	tr	—
Al–MgO	2.5	tr	tr	—
Fe–MgO	11.2	73.2	11.6	tr
Cr–MgO	9.6	94.2	5.4	tr
Mn–MgO	9.1	96.4	2.7	0.9
Ni–MgO	5.5	2.8	33.5	tr
Cu–MgO	2.2	91.0	9.0	—

[a] The reactions were run at 623 K with 1.3 kPa of acetonitrile in N_2 carrier; the methanol/acetonitrile molar ratio was 10 and the space velocity ($CH_3OH + CH_3CN + N_2$) was 80 ml · min^{-1} · g − cat^{-1}.

[b] Loading of added metal ion was 3 wt%.

[c] Conversion (%) = [moles of acetonitrile consumed] × 100/[moles of acetonitrile fed].

[d] Selectivity (%) = [moles of one product] × 100/[moles of acetonitrile consumed].

[e] Acrylonitrile.

[f] Propionitrile.

[g] Methacrylonitrile.

spectrometric analysis; quantitative analyses for hydrogen and water were not carried out.

As shown in Table 1, the conversion of acetonitrile proceeded at 573 K over the metal ion-containing magnesium oxide catalysts and yields AN with minor amounts of PN and MAN. Magnesium oxide itself was virtually inactive. The addition of manganese to magnesium oxide showed the most remarkable effect on the course of the reaction; overall catalytic activity based on acetonitrile conversion increased by a factor of 100 and the highest selectivity to AN was attained. The addition of chromium resulted in a similar effect on the catalytic performance to that of manganese. Replacement of manganese by iron resulted in the highest catalytic activity, while the selectivity to AN was slightly less. Less active catalysts were obtained with nickel and copper because of a rapid loss of activity. Characteristically, magnesium oxide containing nickel gave only a trace amount of AN but gave PN in relatively higher yield than the other catalysts. It seemed that the added nickel ion on the surface of magnesium oxide can catalyze hydrogenation of AN to PN very effectively. In addition, since a good material balance was not made, some of the AN seems to be oligomerized over nickel to form higher molecular weight compounds. The production of PN is mentioned again later. The addition of aluminum did not result in an appreciable change of activity and selectivity. Although a small amount of acetonitrile reacted over this catalyst, only a trace amount of AN was made. At present, the kind of product made is unknown.

The above results strongly suggest that a synergistic or bifunctional property of the binary M–MgO catalysts, depending on the kind of added element, is significant in determining the catalytic activity and selectivity. The drastic increase of catalytic activity by the addition of metal ion to magnesium oxide, in particular Mn or Cr, suggests that the formation of acrylonitrile requires the activation by the added metal ions. At the same time, the basic character of magnesium oxide may also play an important role in the activation of methanol and acetoni-

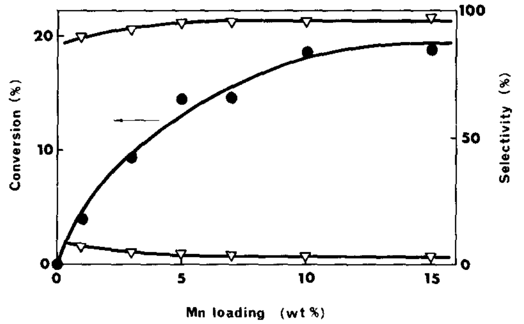


FIG. 1. Addition effect of Mn ion to magnesium oxide on the reaction of acetonitrile with methanol. Reaction conditions are the same as those shown in Table 1. (●) Conversion of acetonitrile. (○) Selectivity to acrylonitrile. (▽) Selectivity to propionitrile.

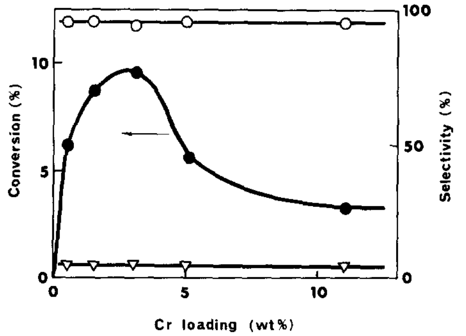


FIG. 2. Addition effect of Cr ion to magnesium oxide on the reaction of acetonitrile with methanol. Reaction conditions are the same as those shown in Table 1. (●) Conversion of acetonitrile. (○) Selectivity to acrylonitrile. (▽) Selectivity to propionitrile.

trile since manganese oxide supported on silica, which shows very weak surface base property, did not catalyze the formation of acrylonitrile.

There are many metal oxides which are well known as solid base oxides, such as CaO, SrO, etc., other than MgO. Although these solids and their activated forms by metal ion showed abilities for catalyzing the reaction, their activities were very poor, mainly because of low surface area of these catalysts. The possibility for improvement of their catalytic performance still remains.

Since the Mn–MgO and Cr–MgO catalysts showed the best catalytic performance, the effects of reaction variables were further investigated. The effects of the amount of metal ion loading were studied in the range of 0 to 15. The results with Mn and Cr systems are shown in Figs. 1 and 2, respectively. The formation of acrylonitrile increased prominently with Mn content up to 10 wt% and further addition did not change the catalytic performance. The selectivity to acrylonitrile also increased slightly with the Mn content. Since the decomposition of methanol took place appreciably over the higher metal loadings, the

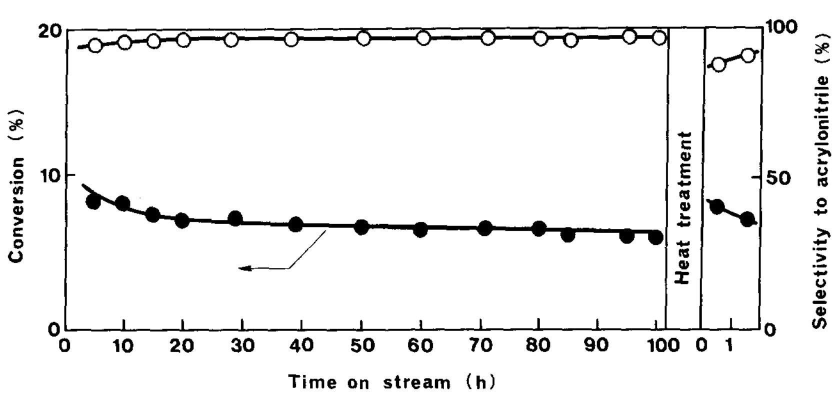


FIG. 3. Activity change of 3 wt% Cr–MgO catalyst for acetonitrile conversion as a function of time. Reaction conditions are the same as those shown in Table 1. After a 100-h reaction, the catalyst was calcined at 873 K for 2 h in air and then activated in a nitrogen stream at the same temperature for 2 h.

TABLE 2

Acrylonitrile Synthesis over 5 wt% Mn–MgO Catalyst at Different Reaction Temperatures[a]

Reaction temperature (K)	Conversion of acetonitrile (%)	Selectivity (%)			
		AN	PN	MAN	Others[b]
573	3.0	97.4	1.9	0.7	—
603	7.8	96.0	2.4	0.8	0.8
623	14.6	94.3	3.2	1.2	1.3
653	29.5	91.6	5.0	1.7	1.7

[a] The reactions were run with 0.9 kPa of acetonitrile in N_2 carrier; the methanol/acetonitrile molar ratio was 10 and the space velocity ($CH_3OH + CH_3CN + N_2$) was 58 ml · min^{-1} · g − cat^{-1}.

[b] Crotononitrile was formed by the skeletal isomerization of MAN.

loading of Mn up to 10 wt% is optimum for attaining high selectivity. In the case of Cr–MgO system (Fig. 2), the formation of acrylonitrile increased with the Cr content and passed through a maximum at 3 wt%. Excess addition caused a decrease in the activity. The selectivity was scarcely affected by the chromium concentration.

These activity changes are not due to changes of the surface area, which with the amount of metal ion loading (e.g., 160 $m^2 \cdot g^{-1}$ for Mn–MgO catalysts and 110 $m^2 \cdot g^{-1}$ for Cr–MgO catalysts), are not appreciable. The magnesium oxide catalyst tested here has a low surface area (11 $m^2 \cdot g^{-1}$), but a higher-surface-area magnesium oxide (140 $m^2 \cdot g^{-1}$), which was prepared by boiling and drying a water–magnesium oxide slurry and heating in a nitrogen stream at 873 K, also showed a very low activity (<1% conversion). The results confirm that the catalytic properties of magnesium oxide are markedly enhanced by the addition of certain transition metal ions.

The stability of the catalyst for the reaction of acetonitrile with methanol was tested. Figure 3 shows the conversion of acetonitrile and the selectivity to acrylonitrile as a function of the reaction time over 3 wt% Cr–MgO catalyst. An initial decrease in the conversion and a slight increase in the selectivity were observed and then the catalyst reached almost a steady state. Further stability tests were conducted up to 100 h on stream. It was found that the activity decreased very slowly with the time on

TABLE 3

Acrylonitrile Synthesis over 5 wt% Mn—MgO Catalyst at 623 K at Different Space Velocities[a]

Space velocity[b] (ml · min^{-1} · g − cat^{-1})	Conversion of acrylonitrile (%)	Selectivity (%)			
		AN	PN	MAN	Others[c]
209	6.2	97.9	1.5	0.6	—
116	12.1	95.5	2.8	1.1	0.6
58	14.6	94.3	3.2	1.2	1.3
29	21.2	91.9	4.7	1.6	1.8

[a] See footnote *a* to Table 2.

[b] $CH_3OH + CH_3CN + N_2$.

[c] See footnote *b* to Table 2.

TABLE 4

Synthesis of Methacrylonitrile by Reaction of Propionitrile with Methanol over Various Metal Ion-Containing Magnesium Oxide Catalysts[a]

Catalyst[b]	Conversion of propionitrile (%)	Selectivity (%)		
		MAN	IBN[c]	CTN[d]
MgO	0.9	65.9	20.9	13.2
Fe–MgO	5.0	94.6	4.6	0.8
Cr–MgO	11.0	88.6	6.8	2.3
Mn–MgO	11.4	97.1	2.2	0.7
Cu–MgO	2.3	87.5	9.4	3.1
Co–MgO	2.2	75.1	20.1	4.8
Ag–MgO	2.3	84.2	12.4	3.4

[a] The reactions were run at 623 K with 0.4 kPa of propionitrile in N_2 carrier; the methanol/propionitrile molar ratio was 10 and the space velocity was 81 ml · min^{-1} · g − cat^{-1}. The definitions of conversion and selectivities were the same as those for the acetonitrile reaction; see footnotes *c* and *d* to Table 1.

[b] Loading of metal ion was 3 wt%.

[c] Isobutyronitrile.

[d] Crotononitrile.

stream. Coke formation on the surface seems to be responsible for the decrease; the catalyst became slightly darker than the initial pale yellow. To confirm this, an air oxidative reactivation was carried out after 100 h on stream: calcination of the used catalyst at 873 K for 2 h, followed by activation under nitrogen at the same temperature for 2 h. This resulted in almost the same activity as that of the fresh catalyst.

Table 2 summarizes the conversion and selectivity data for the acrylonitrile synthesis over 5 wt% Mn–MgO catalyst at different reaction temperatures. As the reaction temperature was elevated, the conversion increased while the selectivity to acrylonitrile decreased. With respect to by-products, the formation of PN, which is the hydrogenated product of AN, is more prominent with increase of the reaction temperature. At the same time, consecutive reaction of PN with methanol to form MAN (Eq. (3)) also took place. The products listed in the last column in the table consist mainly of crotononitrile (CTN). Interestingly, the formation of CTN is due to the skeletal rearrangement of MAN. This novel reaction has been found to be catalyzed by solid bases, which was reported elsewhere (*27*). The reaction mechanism is reported in detail elsewhere (*28*).

Table 3 shows the effect of space velocity on the conversion and selectivities in the AN synthesis over 5 wt% Mn–MgO catalyst at 623 K. The conversion increased with a decrease in the space velocity. The formation of saturated compound (PN) and the appearance of MAN became more appreciable at higher reaction temperatures and also with an increase in the contact time at a fixed reaction temperature. These facts suggest that the selectivity to MAN depends strongly on the conversion of acetonitrile; the by-products increase with the partial pressure of AN. PN is formed by hydrogenation of the AN with molecular hydrogen formed in the reaction and/or by the hydrogen transfer from methanol.

The ratio of methanol/acetonitrile (10/1 to 1/1) had a considerable influence on the conversion of acetonitrile. The conversion increased with increasing methanol/acetonitrile ratio, while the selectivities changed only slightly.

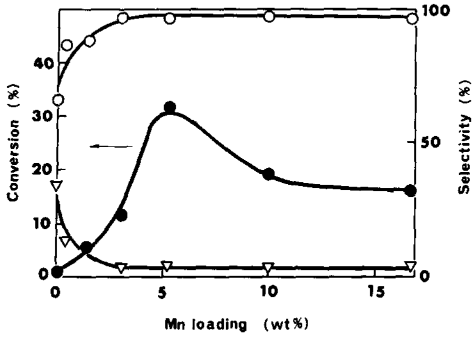


FIG. 4. Addition effect of Mn ion to MgO on the reaction of propionitrile with methanol. Reaction conditions are the same as those shown in Table 4. (●) Conversion of propionitrile. (○) Selectivity to methacrylonitrile. (▽) Selectivity to others.

Synthesis of Methacrylonitrile from Propionitrile

The synthesis of AN was adapted for the synthesis of methacrylonitrile from methanol and propionitrile. The catalytic performance of magnesium oxides activated by various metal ions for the reaction is summarized in Table 4. Almost the same trend in the catalytic performance was observed for MAN synthesis as that for AN synthesis. Thus magnesium oxide without any metal ion additives shows very low catalytic activity. The conversion of PN proceeds smoothly over the activated catalysts at an elevated temperature (>573 K), yielding MAN in high selectivity (>90%). The catalytic activity of magnesium oxide is improved considerably by the addition of Cr, Fe, or Mn as observed in the synthesis of AN. These three catalysts maintained the stable conversion and selectivity after an initial small deactivation which lasted a few hours. By-products were isobutyronitrile (IBN) and CTN, which are formed, respectively, by the consecutive hydrogenation of MAN and by the skeletal isomerization of MAN. It is noteworthy that Mn ion-loaded magnesium oxide shows the best catalytic performance (conversion and selectivity) for both reactions (Tables 1 and 4).

The dependence of the conversion of PN and selectivity to MAN on the manganese ion concentration in the catalyst are shown in Fig. 4. Both conversion and selectivity are improved by the addition of manganese ion and reach the maximum at 5 wt%. Higher manganese concentrations result in a decrease in the catalytic activity and in a small decrease in the selectivity. This activity change observed in the higher concentration region is clearly different from that obtained for the acetonitrile reaction (Fig. 1); the reason is not fully understood at the present time.

Tables 5 and 6 show the effects of reaction temperature and space velocity on the conversion and selectivity of the reaction of propionitrile and methanol. The observed effects were clearly different from those for the reaction of acetonitrile. The selectivity to MAN is not affected by the PN conver-

TABLE 5

Methacrylonitrile Synthesis over 5 wt% Mn–MgO Catalyst at Different Reaction Temperatures[a]

Reaction temperature (K)	Conversion of propionitrile (%)	Selectivity (%)		
		MAN	IBN	CTN
573	2.3	94.5	3.8	1.7
603	13.0	96.6	2.3	0.9
623	31.5	96.8	2.5	0.5
643	31.0[b]	96.3	3.2	0.2

[a] The reactions were carried out under the same conditions shown in Table 4 except the reaction temperature.
[b] Steady-state activity was not attained.

TABLE 6

Methacrylonitrile Synthesis over 5 wt% Mn–MgO Catalyst at 623 K under Different Space Velocities[a]

Space velocity ($ml \cdot min^{-1} \cdot g - cat^{-1}$)	Conversion of propionitrile (%)	Selectivity (%)		
		MAN	IBN	CTN
405	2.1	96.7	2.8	0.7
203	6.1	98.6	1.1	tr
81	11.5	98.3	1.3	0.4
41	31.5	96.8	2.5	0.5

[a] The reactions were carried out under the same conditions shown in Table 4 except the space velocity.

sion under the different reaction conditions, whereas in the reaction of acetonitrile the selectivity to AN decreases appreciably with increasing acetonitrile conversion. The slower rate of hydrogenation of MAN to IBN, relative of that of AN to PN, seems to be responsible for keeping the MAN selectivity high (>95%) and constant.

Synthesis of Propionitrile from Acetonitrile

As mentioned earlier, Ni ion-loaded magnesium oxide favors the formation of saturated nitrile in the reaction of acetonitrile with methanol. The result suggests that Ni ion on the surface of magnesium oxide effectively promotes the hydrogenation with hydrogen produced in the reaction. Utilizing this property of Ni ion, direct synthesis of propionitrile by the reaction of acetonitrile with methanol has been attempted. The results are shown in Table 7. Since Ni ion-loaded magnesium does not result in a very active catalyst, magnesium oxide containing both Ni (1 wt%) and Mn (2 wt%) ion was tested. As can be seen in Table 7, PN was synthesized selectively at high conversion of acetonitrile. Interestingly, the PN selectivity obtained over Ni–Mn–MgO catalyst was much higher than that over Ni–MgO catalyst. Because undesirable side reactions of methanol forming CO and H_2 take place at the same time over Ni ion-loaded catalysts, it is thought likely that the hydrogenation of AN with molecular hydrogen formed by this side reaction occurs predominantly on surface Ni ion sites. However, the hydrogen transfer reaction from methanol to AN and/or a route of direct formation of PN from acetonitrile and methanol are not ruled

TABLE 7

Synthesis of Propionitrile by the Reaction of Acetonitrile with Methanol over Metal Ion-Containing Magnesium Oxide Catalysts[a]

Catalyst[b]	Conversion of acetonitrile (%)	Selectivity (%)		
		AN	PN	MAN
Mn–MgO	22.1	90.6	5.5	1.3
Ni–MgO	5.9	47.4	49.0	0.5
Mn–Ni–MgO	12.8	6.7	88.5	0.4

[a] The reactions were run at 648 K with 1.6 kPa of acetonitrile in N_2 carrier; the methanol/acetonitrile molar ratio was 10 and the space velocity was 63 $ml \cdot min^{-1} \cdot g - cat^{-1}$.

[b] Loading of metal ion was 3 wt%; in Mn–Ni–MgO catalyst, the Mn/Ni weight ratio was 2.

out because no influence by the addition of hydrogen in the reactant gases was observed.

SUMMARY

Heterogeneous catalytic synthesis of α,β-unsaturated nitriles by the reaction of saturated nitriles with methanol as a methylenating agent was achieved using magnesium oxide activated by various transition metal ions. Cr and Mn were found to be particularly effective additives for attaining high conversion and high selectivity to unsaturated nitriles. The reaction consists of dehydrogenation, cross-coupling reaction, and dehydration. The methyl or methylene group at the α-position of saturated nitriles is converted into a vinyl group. This method is widely applicable for the synthesis of various α,β-unsaturated compounds from saturated ketones, esters, and nitriles.

REFERENCES

1. Moser, R. E., and Cassidy, H. G., *J. Polym. Sci., B* **2,** 545 (1964).
2. Ogawa, T., Cedeno, R., and Inoue, M., *Polym. Bull.* **2,** 275 (1980).
3. Callahan, J. L., Grasselli, R. K., Milberger, E. C., and Strecker, H. A., *Ind. Eng. Chem. Prod. Res. Dev.* **9,** 134 (1970).
4. Grasselli, R. K., Burrington, J. D., and Brazdil, J. F., *Faraday Discuss. Chem. Soc.* **72,** 203 (1982).
5. Keim, W., "Catalysis in C_1 Chemistry." Reidel, Dordrecht, 1983.
6. Sheldon, R. A., "Chemicals from Synthesis Gas." Reidel, Dordrecht, 1983.
7. Wender, I., *Catal. Rev. Sci. Eng.* **26,** 303 (1984).
8. Calkins, W. H., *Catal. Rev. Sci. Eng.* **26,** 347 (1984).
9. Khcheyan, Kh. E., Revenko, O. M., Shatalova, A. N., Gel'perina, E. G., Klebanova, F. D., and Arunskaya, L. I., *Neftekhimiya* **17,** 586 (1979).
10. Khcheyan, Kh. E., Shatalova, A. N., Revenko, O. M., and Arinskaya, L. I., *Neftekhimiya* **20,** 876 (1980).
11. Olive, S., and Olive, G., (Monsanto), U.S. Patent 4 179 462, (1979); CA 86-139430j.
12. Ueda, W., Yokoyama, T., Moro-oka, Y., and Ikawa, T., *J. Chem. Soc. Chem. Commun.* 39 (1984).
13. Ueda, W., Yokoyama, T., Moro-oka, Y., and Ikawa, T., *Ind. Eng. Chem. Prod. Res. Dev.* **24,** 340 (1985).
14. Ueda, W. Kurokawa, H. Moro-oka, Y., and Ikawa, T., *Chem. Lett.* 819 (1985).
15. Ueda, W., Yokoyama, T., Kurokawa, H., Moro-oka, Y., and Ikawa, T., *J. Japan. Petrol. Inst.* **29,** 72 (1986).
16. Malinowski, S., *J. Catal.* **2,** 310 (1953).
17. Yamazaki, Y., and Kawai, T., *J. Japan. Petrol. Inst.* **12,** 693 (1969).
18. Vitcha, J. F., and Sims, V. A., *Ind. Eng. Chem. Prod. Res. Dev.* **5,** 50 (1966).
19. Guttmann, A. T., and Grasselli, R. K., (Standard Oil), EP 124380, (1984); CA 102-25215m.
20. Hagemeyer, H. J., Jr., Blood, A. E., and Snapp, T. C., Jr., (Eastman Kodak), U.S. Patent 3 928 458, (1975); CA 84-135070c.
21. Jentsch, C. R., and Schilbach, H. P., (British Petroleum), DE 1 905 763, (1969); CA 72-21340n.
22. Imperial Chemical Industries, Japan Patent, 60-38340, (1985); CA 103-104577e.
23. Merger, F., and Fouguet, G., (BASF, GP), 3 004 467, (1981); CA 95-170036v.
24. Albanesi, G., and Moggi, P., *Appl. Catal.* **6,** 293 (1984).
25. Ai, M., *J. Catal.* **112,** 194 (1988).
26. Ganesan, K., and Pillai, C. N., *J. Catal.* **118,** 371 (1989).
27. Kurokawa, H., Nakamura, S., Ueda, W., Morikawa, Y., Moro-oka, Y., and Ikawa, T., *J. Chem. Soc. Chem. Commun.,* 658 (1989).
28. Kurokawa, H., Nakamura, S., Ueda, W., Morikawa, Y., Moro-oka, Y., and Ikawa, T., *J. Catal.* **126,** 208 (1990).