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Selective α-Monomethylation of Phenylacetonitrile with Dimethyl Carbonate or Methanol over Alkali-Exchanged Faujasites

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Phenylacetonitrile was found to be selectively methylated into α-methylphenylacetonitrile (MPAN) in the vapor phase with dimethyl carbonate or methanol by using alkali ion-exchanged zeolites as catalysts. When methanol was used as a methylating agent, a 27% yield of MPAN was obtained over CsX at 623 K. Dimethyl carbonate is far more effective as a methylating agent, and the methylation proceeds at a much lower temperature. A 72% yield of MPAN was obtained over NaY at 533 K. The effects of the reaction variables are described and the raction scheme is discussed.

INTRODUCTION

Alkylation of active methylene compounds is a widely used procedure in organic synthesis. For example, the α-monomethylation of phenylacetonitrile (PAN, or benzene-acetonitrile) is a very important step for the synthesis of the arylacetic acid moieties, used in drugs, natural products etc.

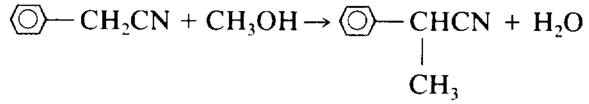
The alkylation of PAN has been carried out using alkyl halides as alkylating agents in the presence of strong bases (1–9). These reaction systems usually require more than a stoichiometric amount of strong bases such as $NaNH_2$ and NaOH. The reactions are carried out in a single phase (1–3) or in a two-phase system using phase-transfer catalysts (4–8). Furthermore, the reactions are not selective, noticeable amounts of dialkyl derivatives being formed as by products (1–6, 8).

Though alkyl halides are usually used as alkylating agents, they are toxic and corrosive. Therefore, the use of less toxic and noncorrosive alkylation agents is desirable.

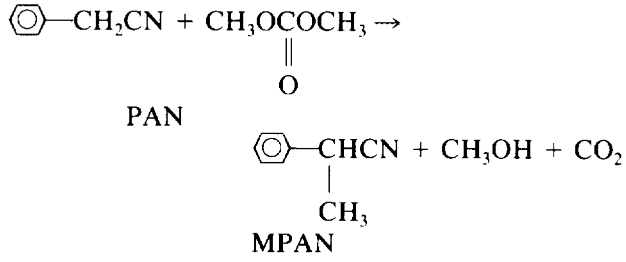
A further disadvantage of these reaction systems is that the reactions are carried out in the liquid phase. Therefore, tedious procedures may be required for separation of the catalyst, excess base, and products.

Some efforts have been reported to avoid the disadvantages described above. Sukata reported that alkali metal hydroxides impregnated on alumina act as efficient bases for selective α-alkylation of PAN in benzene (9). Tundo *et al.* observed very high selectivity in monomethylation of PAN when dimethyl carbonate (DMC) was used as an alkylating agent under gas–liquid phase-transfer catalysis conditions (10). DMC is a noncorrosive and much less toxic methylating agent compared with methyl halides.

In this work, we examined the possibility of methylating PAN into α-methylphenylacetonitrile (MPAN) with methanol and dimethyl carbonate in the vapor phase with use of solid base catalysts:



[1]



[2]

This reaction system should eliminate almost all of the disadvantages of liquid-phase methylation using alkyl halides and stoichiometric amounts of bases.

Alkali-exchanged zeolites are known to act as solid bases (11–14) and to catalyze side-chain alkylation of toluene with methanol (15, 16). Thus, we examined the catalytic activities of alkali-exchanged zeolites for methylation of PAN with methanol, which has been widely used as a safe alkylating agent (17).

We also used dimethyl carbonate (DMC) as a methylating agent over alkali-exchanged zeolites. We have shown that DMC is a selective alkylating agent in N-monoethylation of aniline (18) and O-methylation of phenol (19) in combination with the use of alkali ion-exchanged zeolites as catalysts.

The effects of the reaction variables on rate and selectivity were exmained and the capacities of methanol and DMC as alkylating agents are compared.

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EXPERIMENTAL METHODS

Zeolites used were NaX(SiO_2/Al_2O_3 = 2.5), NaY(SiO_2/Al_2O_3 = 5.6), KL, and NaZSM-5 (SiO_2/Al_2O_3 = 43.5). Alkali ion-exchanged faujasites were prepared from the Na and NH_4 forms of faujasites by a conventional ion-exchange procedure using a 1 *M* aqueous solution of a corresponding chloride or nitrate. The degrees of ion exchange of LiX, KX, RbX, CsX, KY, CsY, and CaY were 49%, 62%, 50%, 59%, 98%, 59%, and 55%, respectively. The zeolites were pelleted, crushed, and sized into 16–32 mesh. HY was obtained by calcining NH_4Y at 773 K under an air stream. Hydrotalcite ($Mg_6AP_2(OH)_{16}CO_3^{2-} \cdot 4H_2O$) was prepared according to the method described by Miyata (20) and the structure was confirmed by XRD powder pattern.

Reactions were carried out in a fixed-bed flow reactor (10 mm i.d.) at atmospheric pressure. The zeolite catalyst was pretreated under an air stream at 773 K for 1 h prior to the reaction. The hydrotalcite (16–32 mesh) was calcined in an air stream at 773 K, or 1023 K. The mixture of PAN and DMC was fed by a motor-driven syringe to the preheating zone of the catalyst bed. The products were collected in an ice trap and analyzed by gas chromatography equipped with a flame ionization detector. The values of the MPAN yields are determined with experimental errors of ±7%. The weight hourly space velocity (WHSV) was defined as grams of feed (DMC + PAN or MeOH + PAN)/gram of catalyst.

The yield of MPAN was expressed by a percentage yield based on PAN.

RESULTS AND DISCUSSION

A. Methylation of PAN with Methanol

Catalytic activities of alkali ion-exchanged zeolites. The methylation of PAN with methanol over alkali ion-exchanged faujasites was carried out at 673 K. Over every catalyst, MPAN was the only product; the formation of dimethylation product α,α-dimethylphenylacetonitrile (DMPAN) was not observed. A separate experiment showed that the dehydration of methanol to dimethyl ether was less than 5% at 623 K. The change in the MPAN yield with time on stream is shown in Fig. 1. Among X-type zeolites, the order of the initial MPAN yield (at 1.0 h of time on stream), was CsX > RbX > NaX > LiX, which is consistent with the order of base strength (13, 14). The activity of CsX was higher than CsY. NaY showed no activity. The higher activity of X-zeolites in comparison with Y-zeolites is again consistent with the order of base strength. These facts indicate that the methylation is promoted by the basic sites of faujasites.

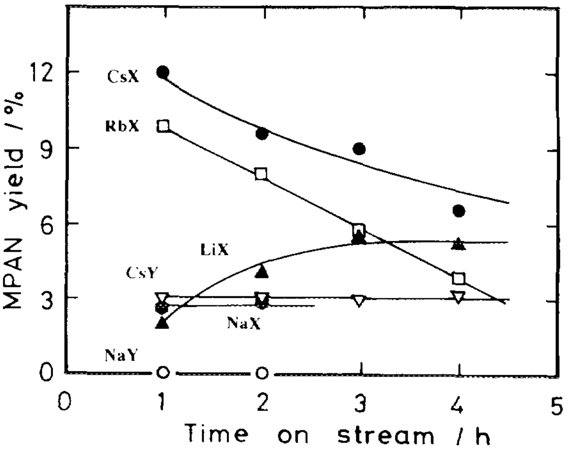


FIG. 1. Change in the MPAN yield with time on stream in the methylation of PAN with methanol over alkali ion-exchanged faujasites. Reaction conditions: 673 K, CH_3OH/PAN = 1.0, WHSV = 1.89 h^{-1}, N_2 = 8.0 ml min^{-1} (S.T.P.).

Effect of reaction variables. The effect of the reaction temperature on the MPAN yield over CsX is shown in Fig. 2. Catalyst activity was higher at higher temperatures, but deactivation was observed above 648 K. Stable activity was only observed at and below 623 K. At any temperature, the dimethylation product was not observed.

Figure 3 shows the effect of methanol pressure on the MPAN yield over CsX at 623 K. Methanol pressure was varied from 14.0 to 42.0 kPa, while PAN pressure was kept at 14.0 kPa. The MPAN yield increased with increasing methanol pressure; the MPAN yield of 22% was obtained at methanol pressure of 42.0 kPa.

The rate of MPAN formation only slightly depended on the PAN pressure in the reaction over CsX at 623 K.

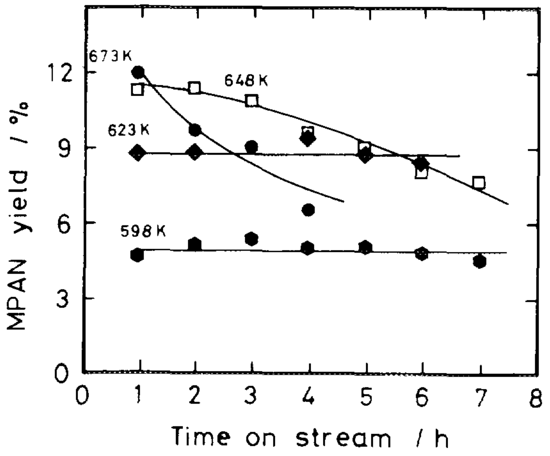


FIG. 2. Change in the MPAN yield with time on stream in the methylation of PAN with methanol over CsX at various temperatures. Reaction conditions: CH_3OH/PAN = 1.0, WHSV = 1.89 h^{-1}, N_2 = 8.0 ml min^{-1} (S.T.P.).

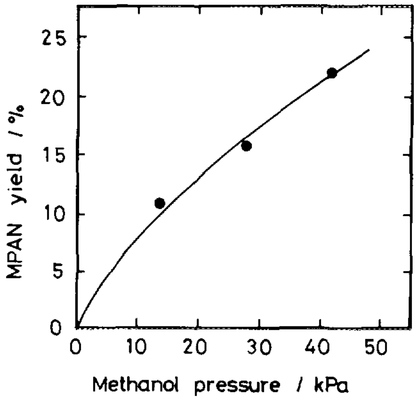


FIG. 3. Dependence of the MPAN yield on the methanol partial pressure in the methylation of PAN with methanol over CsX. Reaction conditions: 623 K, PAN = 14.0 kPa, catalyst = 1.0 g, total flow rate (CH_3OH + PAN + N_2) = 46.7 mmol h^{-1}.

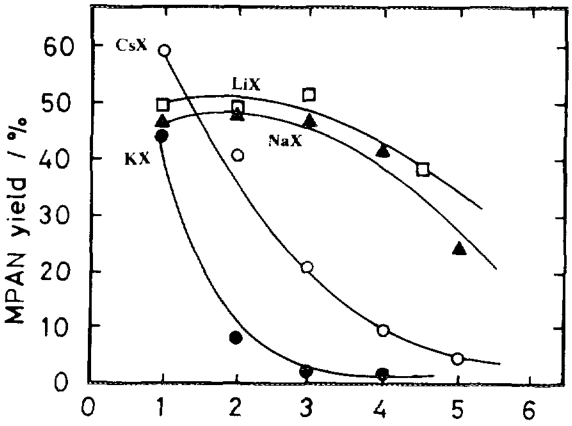


FIG. 5. Change in the MPAN yield with time on stream over alkali ion-exchanged X-zeolites in the methylation of PAN with DMC. Reaction conditions: 523 K, DMC/PAN = 1.0, WHSV = 1.85 h^{-1}, N_2 = 8.0 ml min^{-1} (S.T.P.).

In Fig. 4 is shown the effect of 1/WHSV on the MPAN yield over CsX under the following reaction conditions: PAN pressure = 14.0 kPa, methanol to PAN molar ratio = 3.0, and at 623 K. With increasing 1/WSHV from 0.37 to 1.12 h, the MPAN yield increased from 11% to 27%.

As described above, PAN can be methylated with methanol over CsX. At 623 K, the MPAN yield of 27% was obtained without forming the dimethylation product.

B. Methylation of PAN with DMC

Catalytic activities of alkali ion-exchanged zeolites. The methylation of PAN with DMC was carried out with alkali ion-exchanged X- and Y-zeolites at 523 K. The results are shown in Figs. 5 and 6 for X- and Y-zeolites, respectively. As shown in Fig. 5, the initial activities of alkali ion-exchanged X-zeolites were very high for methylation at this temperature. The activities, however, decayed with time on stream especially in the case of CsX and KX. The initial activities of Y-zeolites are lower than those of X-zeolites. In the case of NaY, the yield of MPAN was low, but it increased with time on stream and reached a steady value of 28%.

The product over NaY gave only the monomethylation product, the dimethylation product, DMPAN, was not found. However, over the other catalysts, the formation of DMPAN was observed. For example, the yields of MPAN and DMPAN were 59% and 7%, respectively, at 1.0 h of time on stream over CsX.

The activities of catalysts other than alkali-ion-exchanged zeolites were also examined. Acidic zeolites, HY and CaY, showed no activity, indicating that basicity is

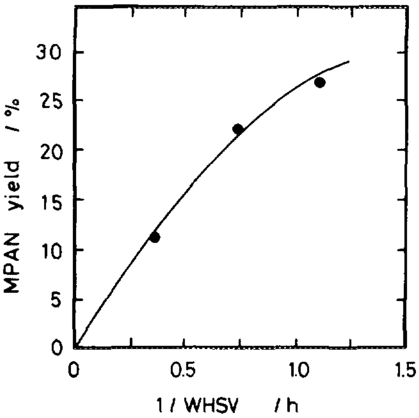


FIG. 4. Dependence of the MPAN yield on 1/WHSV in the methylation of PAN with methanol over CsX. Reaction conditions: 623 K, CH_3OH/PAN = 3.0, PAN = 14.0 kPa.

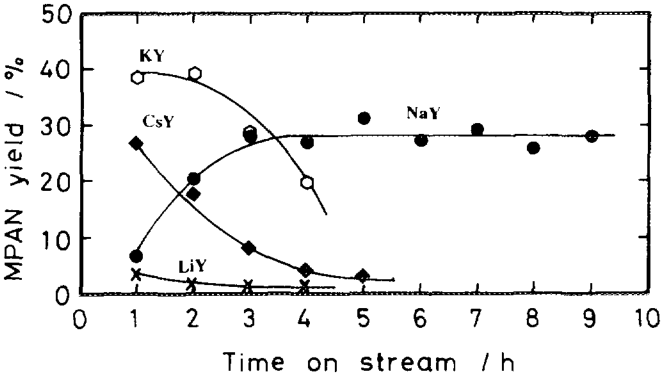


FIG. 6. Change in the MPAN yield with time on stream over alkali ion-exchanged Y-zeolites in the methylation of PAN with DMC. Reaction conditions: 523 K, DMC/PAN = 1.0, WHSV = 1.85 h^{-1}, N_2 = 8.0 ml min^{-1} (S.T.P.).

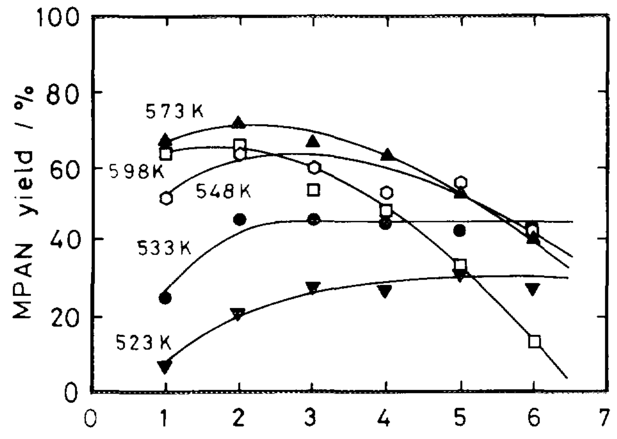


FIG. 7. Change in the MPAN yield with time on stream in the methylation of PAN with DMC over NaY at various temperatures. Reaction conditions: DMC/PAN = 1.0, WHSV = 1.85 h^{-1}, N_2 = 8.0 ml min^{-1} (S.T.P.).

essential for methylation. However, Na-ZSM-5 and KL showed no activity for methylation.

DMC completely decomposed into dimethyl ether and carbon dioxide when only DMC was fed to NaY. The decomposition of DMC was suppressed when DMC was fed with PAN. Thus, the selectivity for MPAN with respect to DMC was ca. 70% over NaY, the highest among alkali-ion-exchanged zeolites.

Basic oxides, MgO, ZrO_2 and Al_2O_3, were also inactive. It is known that these oxides are easily poisoned with carbon dioxide.

Mixed oxides prepared by calcining hydrotalcite at 773 and 1023 K gave MPAN yields of 23% and 21%, respectively. These mixed oxides are known to work as base catalysts (21–24).

Effects of reaction variables over NaY. The effect of reaction temperature on the MPAN yield over NaY is shown in Fig. 7. The initial MPAN yield was higher at higher reaction temperatures; the activity decayed with time on stream at higher temperatures. The stable activity was observed at 523 and 533 K. The MPAN yield was 45% at 533 K. The selectivity for MPAN with respect with DMC was ca. 80% at 533 K. No dimethylation occurred at 533 K, while it was observed at higher temperatures.

The effect of DMC partial pressure on the MPAN yield was studied at 533 K. DMC partial pressure was varied in the range from 10.9 to 31.4 kPa, while PAN partial pressure was kept constant (23.1 kPa). As shown in Fig. 8, the MPAN yield was almost proportional to the DMC partial pressure. At a DMC pressure of 31.4 kPa (DMC/PAN = 1.36), the MPAN yield reached ca. 60%. Under these reaction conditions, only monomethylation occurred and the selectivity for MPAN with respect to DMC was ca. 80%.

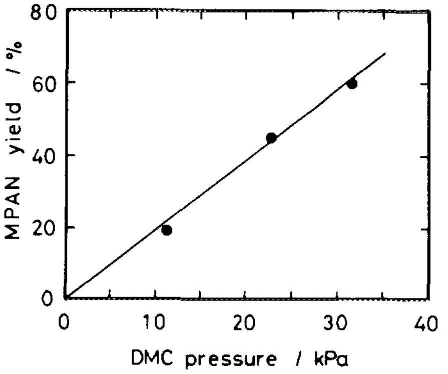


FIG. 8. Dependence of the MPAN yield on the DMC partial pressure in the methylation of PAN with DMC over NaY. Reaction conditions: 533 K, PAN = 23.1 kPa, catalyst = 1.0 g, total flow rate (DMC + PAN + N_2) = 39.2 mmol h^{-1}.

The effect of PAN partial pressure was also examined. PAN partial pressure was varied in the range from 11.8 kPa to 29.2 kPa, while DMC partial pressure was kept constant (23.1 kPa). The rate of MPAN formation was independent of PAN partial pressure.

Figure 9 shows the effect of 1/WHSV on the MPAN yield over NaY at 533 K. The MPAN yield increased with increasing 1/WHSV. At 1/WHSV of 1.50 h, the MPAN yield reached 72%. Under the reaction conditions, only monomethylation occurred and the selectivity for MPAN with respect to DMC was ca. 80%. The rate of MPAN formation over NaY was 2.3 mmol g^{-1} h^{-1}. This value is much higher than the rate reported for supported phase-transfer catalysts (0.2 mmol g^{-1} h^{-1}).

C. Reaction scheme. The active sites for the methylation are the basic sites in the zeolites in both cases. The

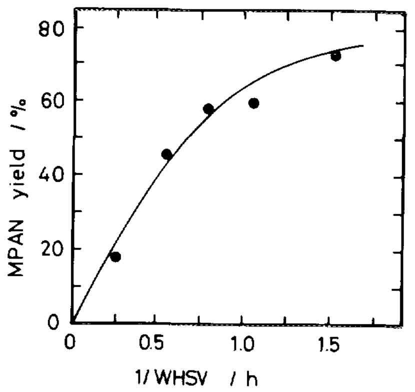


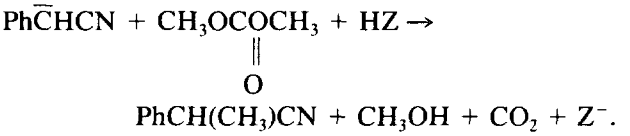
FIG. 9. Dependence of the MPAN yield on 1/WHSV in the methylation of PAN with DMC over NaY. Reaction conditions: 533 K, DMC/PAN = 1.0, PAN = 23.1 kPa.

rate of the reactions were almost independent of the PAN partial pressure. This indicates that the adsorption of PAN on the basic sites is strong and most of the basic sites are saturated with the anions formed from PAN:

$$\mathrm{PhCH_2CN + Z^- \rightarrow Ph\bar{C}HCN + HZ.} \quad [3]$$

Here, Z^- denotes the basic sites on the zeolites. The reaction was first order with respect to the methylating agent, methanol or DMC, indicating that the reaction with the anionic intermediate and the methylating agent is the rate determining step:

$$\mathrm{Ph\bar{C}HCN + CH_3OH + HZ \rightarrow PhCH(CH_3)CN + H_2O + Z^-} \quad [4]$$



$$\mathrm{Ph\bar{C}HCN + CH_3O\underset{\underset{O}{\|}}{C}OCH_3 + HZ \rightarrow PhCH(CH_3)CN + CH_3OH + CO_2 + Z^-.} \quad [5]$$

The rate of methylation with DMC is much faster than that with methanol. The methylation with DMC proceeded at 523 K over NaY, while the methylation with methanol over NaY did not proceed even at 623 K, though a 9.4% yield was obtained over CsX. This indicates that the rate of reaction [5] is much faster than that of reaction [4]. DMC is much more effective than methanol as the methylating agent.

CONCLUSIONS

PAN can be effectively monomethylated with methanol or DMC. With methanol a 27% yield of MPAN was obtained at 623 K over CsX. With DMC, a 72% yield of MPAN was obtained at 533 K over NaY. DMC is thus a much more effective methylating agent than methanol. The results indicate that methylation of the active methylene compound can be performed with solid base catalysts by using methanol or DMC. We have shown that the selective methylations of aniline and phenol proceed in combinations of alkali ion-exchanged zeolites as catalysts and DMC as the methylating agent (18, 19). These examples indicate the potentialities of DMC as a methylating agent for versatile methylation reactions over heterogeneous catalysts.

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