CHEMISTRY LETTERS, pp. 209-212, 1993.

An Unusual Suppression of Trimethylamine Formation in the High Temperature Alkylation of Ammonia with Methanol over $(NH_4)_3PW_{12}O_{40}$

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A synthesis of methylamines from ammonia and methanol was studied by using mainly the title heteropoly catalyst. Although at low temperatures below ca. 750 K the three methylamines (MMA, DMA, and TMA) were formed as usual, at higher temperatures the formation of TMA was completely suppressed. This unusual product selectivity was explained by the strong adsoption of TMA to the catalyst.

Methylamines [mono-(MMA), di-(DMA), and trimethylamine(TMA)] are commercially prepared by the alkylation of ammonia with methanol at high temperatures over a solid acid catalyst such as silica-alumina, alumina, etc.[1)] Basically, the alkylation proceeds toward equilibrium favoring the formation of TMA; therefore, in such a commercial process, a considerable amount of TMA is formed together with DMA and MMA even when the reaction is operated at a low feed ratio of CH_3OH/NH_3, e.g.1/3. This has been a problem with such conventional catalysts, because the current market demand is oriented to MMA and DMA, especially to DMA.[2)] Furthermore, TMA, when mixed with the other amines, forms an azeotropic mixture, which causes a difficult separation problem. Therefore, it has been an important subject to develop a new effective catalyst which can preferably be used for selective synthesis of MMA and DMA from ammonia and methanol with depressing the formation of TMA.

Mochida et al. have shown that zeolites having smaller pore sizes tend to give a better selectivity to MMA and DMA in this alkylation.[3)] Segawa at al. have reported that a reduction in the aperture size of a mordenite results in a drastic improvement in the selectivity to MMA and DMA with suppressing the formation of TMA almost completely.[4)]

Besides, Niiyama et al. have implied in their studies on the decomposition of methylamines over heteropoly compounds, such as $H_3PW_{12}O_{40}$, $H_2FePW_{12}O_{40}$, etc., that some of such heteropoly compounds may be effective for the synthesis of methylamines from ammonia and methanol.5)

Thus, we examined the alkylation of ammonia with methanol over a variety of salts of a heteropoly acid[$X_3PW_{12}O_{40}$, X=Cs, Ca, Fe, $N(n\text{-}Bu)_4$ or NH_4], and found that they were effective for this reaction and that, if the reaction was conducted at high temperatures above 750 K, the formation of TMA was completely suppressed, which resulted in an increase in the total yield of MMA and DMA. In this letter, since the ammonium salt(referred to NH_4PW) was the most active and exhibited the most drastic temperature effect, we mainly describe the catalytic features of NH_4PW in this alkylation.

The NH_4PW catalyst was prepared according to Moffat's method.6) The reaction was carried out in a pyrex tube reactor(i.d.= ca.8 mm) at different temperatures by flowing a mixed gas of ammonia(42 kPa), methanol(21 kPa), and helium(36 kPa; balance) at a constant feed rate(F=10-60 cm^3/min) through a fixed bed of the catalyst(W=0.5-3 g) which was preteated in the reactor at 673 K for 1h in a He flow before the reaction. The reaction products were analyzed mainly by gas chromatography.

Figure 1 shows a typical result of the ammonia-methanol reaction over the NH_4PW catalyst at different temperatures. As Fig.1 shows, at temperatures below ca.750 K, all of the methylamines were observed and TMA was predominant. This is an ordinary product distribution as commonly observed at high conversions with conventional catalysts, such as alumina, etc.. However, at higher temperatures, an abnormal product distribution was observed with the NH_4PW catalyst. That is, at temperatures above ca.680 K, the yield of TMA decreased with an increase in the temperature and suddenly became zero around 750 K, while the formation of MMA and DMA was still significant and the yield of MMA increased even above 750 K, although the formation of N_2 as well as CH_4 became significant.

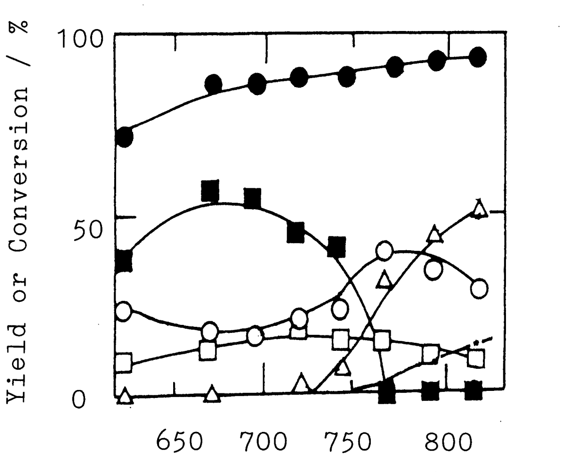

Fig.1. Effect of reaction temperature on the conversion of methanol (●) and yield of MMA(○), DMA(□), TMA(■), CH_4(△) and N_2(•). Catalyst : NH_4PW . W/F= 0.3 g-cat min cm^{-3}.

One may consider from Fig.1 that the decrease in the yield of TMA is associated with its consecutive decomposition to N_2 and CH_4; however, even so, the yield of N_2 as well as that of CH_4 is so small that the complete disappearance of TMA can not be explained only by such a consecutive decomposition. Of course, it is not due to the thermodynamical limitation, because TMA is thermodynamically the most stable among the three methyl amines even at such high temperatures (equilibrium ratios of MMA/DMA/TMA = 1.7/2.8/14 at 800 K and at methanol conversion = 90%).

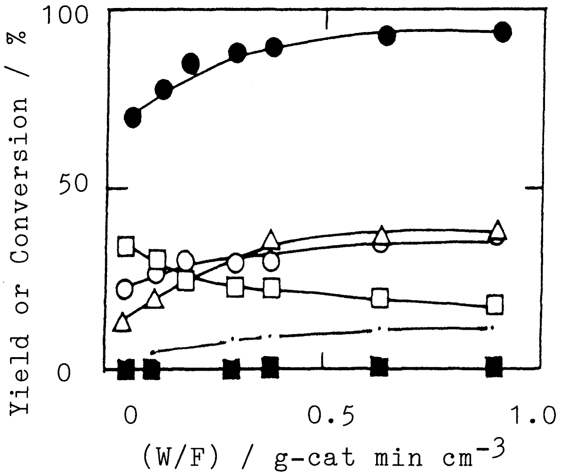

Fig.2. Effect of W/F on the conversion of methanol and yield of methylamines, CH_4 and N_2. Reaction temp. : 773 K. Keys : see Fig.1.

In order to confirm this unusual product distribution, we run the reaction at 773 K but at different contact times, W/F. The results appear in Fig. 2. As shown in Fig.2, no TMA was formed throughout in the wide W/F range even at such a low W/F at which the formation of either N_2 or CH_4 is low enough. Figure 2 also implies that CH_4 is formed by the hydrogenolysis of DMA and methanol with H_2 formed from NH_3 ($2NH_3 \rightarrow N_2+3H_2$; $DMA+H_2 \rightarrow MMA+CH_4$; $CH_3OH+H_2 \rightarrow CH_4+H_2O$). In fact, a reasonable amount of H_2 was detected in the products.

Since the complete absence of TMA can not be well explained by such consecutive reactions, we examined behaviors in the desorption and surface reactions of each methylamine preadsorbed on the NH_4PW catalyst by means of TPD experiments as follow. Each methylamine, namely MMA, DMA, or TMA, was adsorbed at 323 K for 30 min in a helium flow (carrier gas 20 cm^3 min^{-1}) to the catalyst(1 g) which was preheated at 673 K for 1 h in helium flow, and then the temperature was raised at a constant rate of 10 K/min in the carrier gas(20cm^3/min), while the total TPD response being measured by using a TCD detector and, for the deconvolution of the TPD peaks, the composition of the desorbed species being monitored periodically by mass spectroscopy and also by gas chromatography. The resulting TPD spectra of the TMA- and DMA-preadsorbed

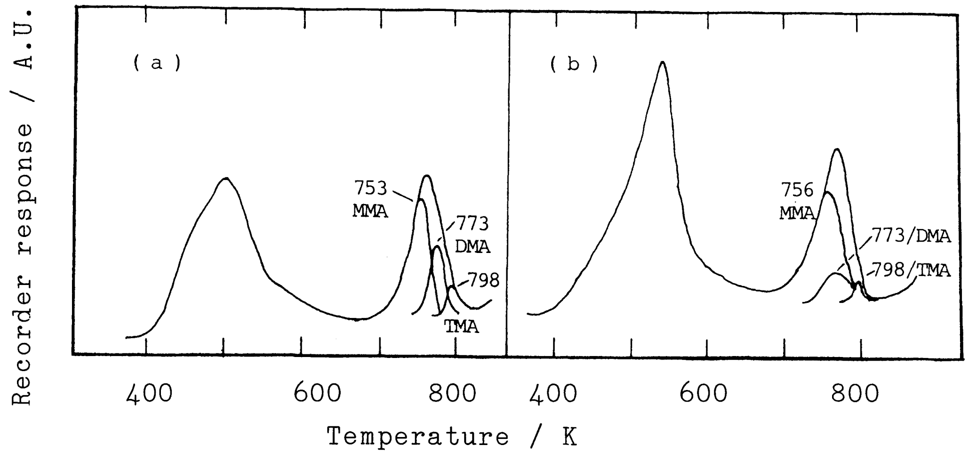

Fig.3. TPD curve of (a)TMA- and (b)DMA-preadsorbed catalysts.

catalysts are shown in Fig.3, (a) and (b), respectively (since a similar result was obtained with the MMA-preadsorbed one, its data is omitted here).

From these TPD spectra, we can point out the following points. (1) Every amine-preadsorbed catalyst gives two TPD peaks which appear around 500 and 750 K, respectively, indicating that each amine is adsorbed on the catalyst in two distinctly different manners. (2) Every amine preadsorbed and strongly adsorbed is desorbed always as the three amines (MMA, DMA, and TMA) and stepwise in this order around 750 K. This suggests that the conversions of one amine to the other amines on the surface easily occur before the desorption and that the degree of their adsorption strength increases in that order, MMA<DMA<TMA.[7] Besides, we also found that the TPD curve of an NH_3-preadsorbed catalyst comprises three significant peaks of NH_3 around 500, 750 and 950 K, respectively. Thus we suggests that the facile interconversions among the strongly adsorbed amines proceed by different reactions, including the reactions of TMA or DMA with the strongly adsorbed NH_3 or NH_4^+ and the transalkylations among the three amines.

The unusual suppression of the TMA formation in the high temperature alkylation of ammonia with methanol described above can also be well explained with a similar mechanism, namely the desorption-control mechanism (Eq.1). That is, at such high temperatures, it is expected that TMA is adsorbed more strongly than the other two amines and that the interconversions among these three methylamines adsorbed on the surface are fast; therefore, TMA does not desorb as such but does as the other amines.

$$\begin{tikzcd} \text{MMA} & \text{DMA} & \text{TMA} & \text{gas phase} \\ \text{MMA}_{ads} \arrow[u, Rightarrow, "\text{fast}"'] \arrow[r, Leftrightarrow, "\text{fast}"'] & \text{DMA}_{ads} \arrow[u, Rightarrow, "\text{fast}"'] \arrow[r, Leftrightarrow, "\text{fast}"'] & \text{TMA}_{ads} \arrow[u, Rightarrow, "\times"', "\text{very slow}"] & \text{on the surface} \end{tikzcd} \qquad (1)$$

We can currently suggest such a desorption-control mechanism (Eq.1) as a probable mechanism for the unusual product selectivity observed with NH_4PW or the other salts of $H_3PW_{12}O_{40}$ as described above. More detail studies on the reaction mechanisms, including the difference of the active sites for the high and low temperature reactions are now in progress.

References

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6) H.Hayashi and J.B Moffat, J.Catal., 83, 192(1983).
7) It is known that even alkali salts of $H_3PW_{12}O_{40}$ have acidic characters, and that NH_4PW exhibits a strong acidity as high as its acid forms, especially used at higher temperatures. Besides, the sequence of the basicity of methylamines in the gas phase is known to be TMA>DMA>MMA.

(Received September 24, 1992)