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SYNTHESIS OF ACETONITRILE AND RELATED COMPOUNDS FROM CO-H_2-NH_3 OVER Mo/SiO_2

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In the reaction of CO-H_2-NH_3 on Mo/SiO_2 catalysts, HCN is formed and is considered to be the principal intermediate for the formation of CH_3CN. At low temperature methylamine is also formed.

Much of the work in C_1 chemistry has centered on CO-H_2 reactions to yield hydrocarbons and alcohols. However, it would be highly desirable to synthesize organo-nitrogen compounds directly from CO-H_2-NH_3 mixture. Several processes have been patented that convert CO-H_3-NH_3 to amines [1,2] and amides [3]. Monsanto patented preparation of CH_3CN from CO-H_2-NH_3 in the presence of molybdenum catalysts [4]. This method is particularly interesting since the C_2 compound is directly produced from CO as the carbon source. It is very difficult to obtain selectively C_2 compounds such as C_2H_6, ethanol and acetaldehyde from CO-H_2 although C_1 compounds like CH_4 and methanol can be produced in almost 100% selectivity [5]. We have investigated in detail the CH_3CN formation reaction over molybdenum catalysts. We now report that HCN is formed from CO-H_2-NH_3 and is considered to be the principal intermediate for the formation of CH_3CN.

The catalysts were prepared by impregnating silica gel with an aqueous solution of $(NH_4)_6Mo_7O_{24}4H_2O$. The impregnates were dried overnight at 120 °C, treated under a stream of He at 400 °C and then reduced by H_2 at 500 °C. Reactions were carried out under atmospheric pressure in a tubular flow reactor containing 1 g of catalyst.

It has been reported that silica-supported Mo catalysts produce CH_3CN, hydrocarbon and CO_2 from CO-H_2-NH_3 [4]. We have found that HCN and methylamines are also produced. Alcohols obtained for the reaction of CO-H_2 [6] were no longer formed. As can be seen in fig. 1, the distribution of products was

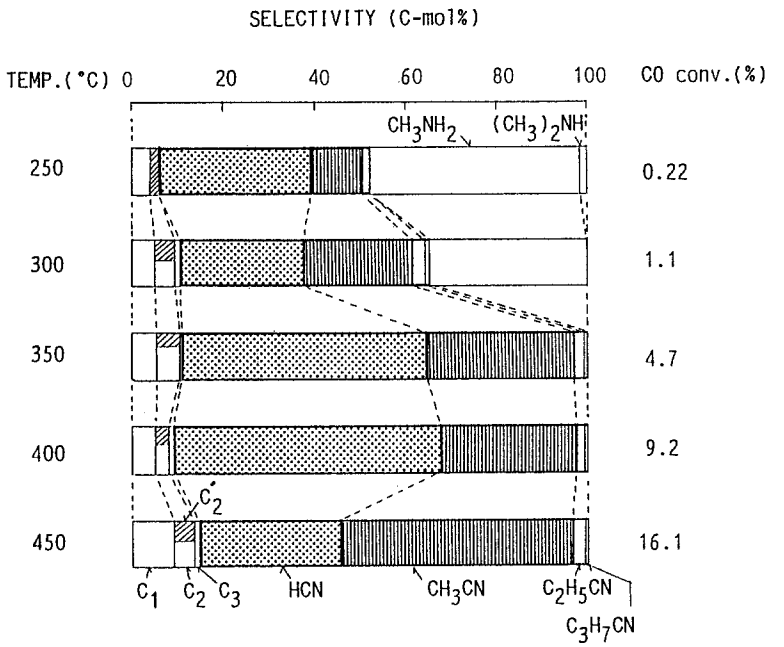

Fig. 1. Effect of temperature on distribution of product from CO-H_2-NH_3.

greatly dependent on reaction temperature. With increasing reaction temperature from 250 to 350 °C, the selectivity and the yield of both HCN and CH_3CN were increased at the expense of those of amines. The yield of CH_3CN attained a maximum at 450 °C. According to Henrich-Olive and Olive, methylamine can be converted into CH_3CN over silica-supported molybdenum [7]. Reaction mechanism suggested by them involves reductive elimination of NH_3 from methylamine, generating a carbene ligand, which inserts into the C-H bond of HCN formed by dehydrogenation of methylamine, finally giving CH_3CN. Our experiments have revealed that HCN is formed in excess, compared to methylamine, at 250–300 °C, whereas the formation of HCN from methylamine is thermodynamically unfavorable at this temperature range; the equilibrium constant is 2.2×10^{-5} and 4.2×10^{-4} at 250 and 300 °C, respectively. Hence the formation of HCN apparently precedes that of methylamine.

The catalytic carbonyaltion of NH_3 to $HCONH_2$ in the presence of H_2 has been described [8]. Dehydration of $HCONH_2$ is a well-known method for preparing HCN. Formation of $HCONH_2$ was not observed under our reaction conditions; the $HCONH_2$ level was estimated to be very low in this range of temperature and pressure. However, formamides such as *N*-methylformamide and *N*, *N*-dimethylformamide was obtained at 1.6 MPa of $CO/H_2/NH_3 = 3/3/2$. Thus it is conceivable that HCN was formed by way of $HCONH_2$.

Figure 2 shows the influence of time factor (W/F, g-cat h mol^{-1}) on the selectivity for HCN and CH_3CN. With decreasing contact time, the selectivity for

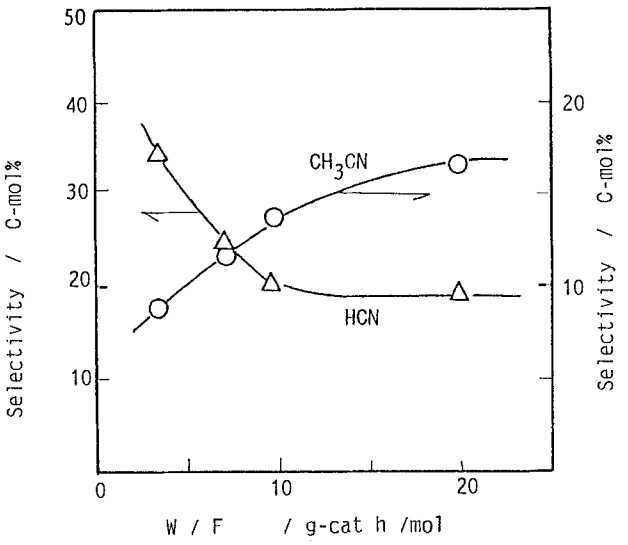

Fig. 2. Change in selectivity for HCN and CH_3CN with time factor.

HCN was increased, while the selectivity for CH_3CN was decreased. This suggests that HCN be the intermediate for CH_3CN; the contribution of the methylamine transformation to CH_3CN synthesis seems to be relatively unimportant. To confirm the mechanism of CH_3CN synthesis, the effect of addition of HCN and methylamine to CO-H_2 has been investigated (table 1). The yield of acetonitrile was increased on addition of HCN. On the other hand, the addition of methylamine resulted in the decrease in the yield of CH_3CN. No dehydrogenation of methylamine to HCN occurred at 250–300 °C. These findings suggest that the major path to CH_3CN from CO-H_2-NH_3 is the reaction of HCN with

Table 1
Effect of additives to synthesis gas on space time yields

Temp. (°C)	Feed gas	CO Conv. (%)	Yield (g-product/kg-cat./h)		
			CH_3CN	HCN	CH_3NH_2
250	CO-H_2-NH_3	0.22	0.078	0.31	0.50
	CO-H_2-HCN	0.30	0.21	–	0.20
	CO-H_2-CH_3NH_2	0.15	0.051	0.0	–
	CO-H_2-$C_2H_5NH_2$	1.1	2.3	0.0	0.10
300	CO-H_2-NH_3	1.1	0.91	1.3	2.0
	CO-H_2-HCN	0.64	1.8	–	1.2
	CO-H_2-CH_3NH_2	1.9	0.80	0.0	–
	CO-H_2-$C_2H_5NH_2$	3.7	29.3	0.0	0.44

Catalyst: Mo(10 wt%)/SiO_2, reaction conditions: $W/F = 10$ g-cat·h/mol, $NH_3 = 19.7\%$, HCN = 0.57%, $CH_3NH_2 = 1.6\%$, $C_2H_5NH_2 = 2.7\%$.

carbene species which could be formed from $CO\text{-}H_2$. The hydrogenation of CO to hydrocarbons is considered to occur by way of carbene formation. In view of the lowering of CO conversion by addition of NH_3 or HCN (table 1), the concentration of surface CH_2 should be higher in the $CO\text{-}H_2$ reaction than in the $CO\text{-}H_2\text{-}NH_3$ or HCN reaction. We have examined transient response to switching the reactant gas from $CO\text{-}H_2$ to $CO\text{-}H_2$-HCN. The formation rate right after the switching proved 5–6 times higher than that in the steady-state, consistent with the higher concentration of surface CH_2 in the $CO\text{-}H_2$ reaction above postulated. We propose that this unique reaction of HCN with surface CH_2 be the reason for the selective formation of the C_2 compound. The formation of small amounts of propionitrile and butyronitrile (fig. 1) could be similarly explained by the reaction of ethylene or propylene with HCN.

One might consider that CH_3CN was formed by way of dehydrogenation of ethylamine [9], which could be formed by the reaction of ethylene (from $CO\text{-}H_2$) with NH_3. As shown in table 1, the dehydrogenation of ethylamine to acetonitrile occurred under our reaction conditions. However, the yield of ethylamine was negligible in the temperature range studied. Moreover, on addition of K to Mo/SiO_2 catalysts, the yield of CH_3CN from $CO\text{-}H_2\text{-}NH_3$ decreased whereas the yield of ethylene was increased, ruling out the intermediacy of ethylamine.

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