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12-TUNGSTOPHOSPHATES AS DEHYDROGENATION CATALYSTS
DEHYDROGENATION OF MONOMETHYLAMINE TO HYDROGENCYANIDE

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Monomethylamine is dehydrogenated to yield hydrogencyanide by the catalysis of 12-tungstophosphates at temperature range of 400-500 °C. Simultaneous hydrogenolysis to yield methane and ammonia was also observed. Typical solid acid catalysts, such as Al_2O_3 or SiO_2-Al_2O_3 have no activity for the reaction. Catalytic activity for the dehydrogenation might be ascribed to the affinity of polyanion to hydrogen atoms.

Catalysis of heteropoly compounds hitherto reported were mainly for acidic and oxidative reactions. To our knowledge, no published data has been found as to dehydrogenation activity of the compounds. Some indirect suggestions concerning about the affinity of the polyanion to hydrogen atoms, however, are available. We have studied reduction of 12-molybdophosphates with hydrogen.[1] Some of the dissociated hydrogen atoms reduced the polyanion, but considerable fraction of hydrogen atoms were restored in the solid lattice. Izumi et al. reported hydrogenation activity of $PdSO_4$/$H_3PW_{12}O_{40}$ system.[2] $PdSO_4$ is to dissociate hydrogen molecules and polyanion keeps hydrogen atoms to its neighbor and hydrogenates substrates. These results suggest potential applications of the compounds to dehydrogenation catalysts. We wish to report here that 12-tungstophosphates have catalytic activities for the dehydrogenation of methylamine to yield HCN. Dual functional catalysis consisting of acidic and dehydrogenating activity allows to yield HCN directly from methanol and ammonia.

The reaction was carried out by using closed gas circulation apparatus, volume of which was 544 cm^3. Gas composition was monitored by means of IR spectrometer which was located on line of gas circulation loop. Formation of H_2, which is inactive to IR beams, was confirmed by mass spectroscopy and by volumetric measurements. Catalysts were $H_3PW_{12}O_{40}$ and its salts, which were prepared by the methods reported previously.[1,3] Monomethylamine (MMA) was obtained from was turned black, characteristics of carbon formation, and because CO_2 was produced when oxygen was contacted with used (and treated in vacuo at 400 °C) catalyst.

Activity test of MMA decomposition was repeated three times. Between each run, reactor was evacuated at 400 °C for 10 min. Rate of absorption and rate of formation of CH_4, NH_3, and HCN decreased with the number of runs, however selectivity to HCN increased. For example, HCN was the predominant product in the third run. Infrared spectroscopic examination revealed that the Keggin structure was not destroyed after the reaction.

Figure 2 shows effects of reaction temperature on MMA decomposition. HCN formation becomes predominant and material balance approached to 100 % at higher temperatures. In Figs. 1 and 2, CH_4 and NH_3 formation occurs in a similar fashion while HCN formation differs from the two.

Figure 3 shows TPD profile of MMA. Adsorption and/or absorption of MMA was done at room temperature and equilibrated at 4.8 molecules /Keggin unit. At a lower temperature than 300 °C, NH_3 was the sole product, indicating disproportionation of MMA.

$$2\,CH_3NH_2 \longrightarrow (CH_3)_2NH + NH_3$$

Hence DMA has stronger basicity than NH_3, it may not be found in the gas phase. At higher temperatures than 300 °C, formation of CH_4, NH_3, and HCN were simultaneously occurred. It was rather surprising that neither DMA nor TMA was found in the gas phase.

When MMA was contacted with Al_2O_3 or SiO_2-Al_2O_3, as examples of typical solid acid catalysts, no formation of HCN and CH_4 was observed. In stead, DMA and TMA as well as NH_3 were produced. Accordingly, formation of HCN and NH_3 were related not with acidic properties but with hydrogenation and dehydrogenation activities, which might be ascribed to the polyanion.

Figure 4 shows one step synthesis of HCN from methanol and ammonia. Since methylamine formation occurs on solid acid catalysts,[4)] HCN formation seems to proceed in a consecutive manner;

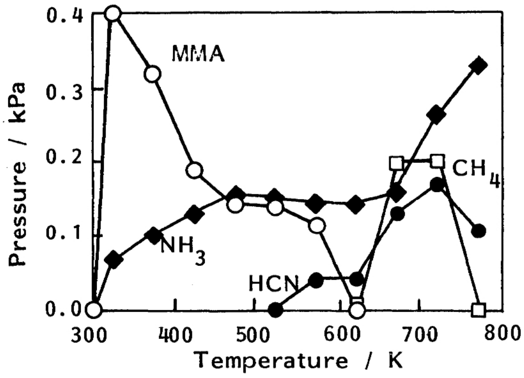

Fig.3. TPD profile of MMA.
Catalyst; $H_2Fe_{1/3}PW_{12}O_{40}$ 0.5 g.

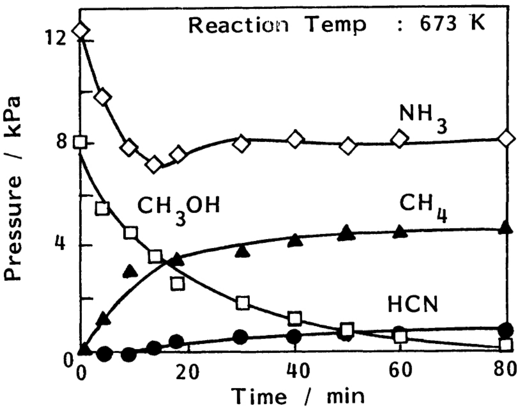

Fig.4. Direct synthesis of HCN from CH_3OH and NH_3.
Catalyst : $H_2Fe_{1/3}PW_{12}O_{40}$ 2 g,
reactant : CH_3OH 8.1 kPa, NH_3 12.6 kPa.

commercialy available aqueous solution of MMA. The solution was treated with KOH in order to remove most of the water and resultant gas was purified by several freeze-thaw cycles.

Figure 1 shows typical results of MMA decomposition. In any of catalysts employed, products found in the gas phase were HCN, CH_4, and NH_3. Any other products such as dimethylamine (DMA) or trimethylamine (TMA) were not detected, however, it does not exclude the possibility of their formation in the solid lattice of the catalyst ("Pseudo-liquid phase").[5)] Because of high affinity of the catalyst to polar substances, they may not desorb even if they are produced. In the cases of $H_3PW_{12}O_{40}$ and $H_2Fe_{1/3}$-salt, absorption of MMA rapidly completed and the three products appeared upon the contact. On the other hand, the absorption was slower in the case of Na_3-salt, and HCN formation seems to have an "induction period". Apparently, material balance was not established. Table 1 shows carbon-, nitrogen-, and hydrogen-balance based upon gas phase analysis after the reaction. A part of this insufficient material balance is due to absorption of methylamines (including ammonia). Irreversible carbon formation should also be taken into consideration, because the color of the used catalyst

Table 1. Material balances based on the gas phase analysis after 40 min of the reaction

Atoms	Before the reaction	Gaseous products				In the catalyst
	MMA (100 parts)	NH_3	CH_4	HCN	H_2	
N	100	48.3		21.8		29.9
C	100		22.3	21.8		55.9
H	500	145	89.1	21.8	114	130

Catalyst : $H_2Fe_{1/3}PW_{12}O_{40}$, data corresponds to Fig. 1-b.

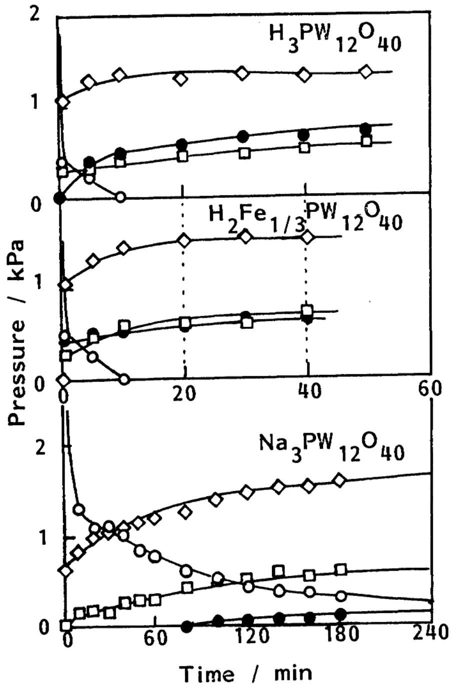

Fig. 1. Decomposition of MMA. initial pressure of MMA: 2.9 kPa reaction temperature: 673 K
(○): MMA . (◇): NH_3
(●): HCN . (□): CH_4

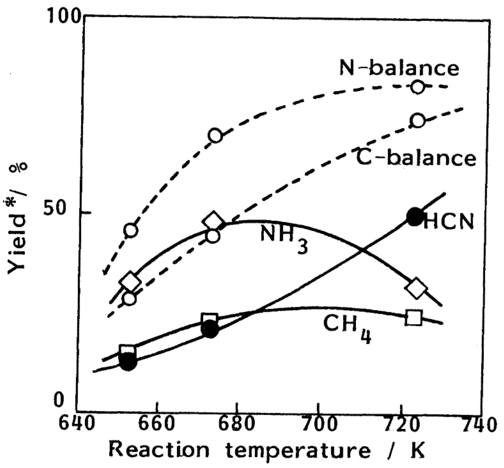

Fig. 2. The effect of reaction temperature.
catalyst : $H_2Fe_{1/3}PW_{12}O_{40}$ 0.5 g
* After 60 min of reaction

intermolecular dehydration of methanol and ammonia catalysed by acidic properties and dehydrogenation by polyanion.

Dehydrogenation of other substances than MMA also proceeds on the catalyst. Tested reactions were, butenes to butadiene, cyclohexene to benzene and cyclohexane to benzene. In all cases, the formation of H_2 was confirmed showing that the reaction is not a stoichiometric oxidation in which lattic e oxygen was consumed. Dehydrogenation of butane to butene or butadiene was also tried but unsuccessful. Reaction mechanisms of dehydrogenation will be studied in near future. We do believe that dehydrogenation activity of heteropoly compounds stimulate new ideas for catlaysis design of the compounds.

References

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