SELECTIVE SYNTHESIS OF LIGHT OLEFINS FROM DIMETHYL ETHER OVER ACIDIC SALTS OF H₃PW₁₂O₄₀ WITH 1,3,5-TRIAZINE

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Formation of acidic salts of $H_3 PW_{12}O_{40}$ with 1,3,5-triazine suppressed effectively hydrogen transfer step, producing olefin-rich hydrocarbons in the conversion of dimethyl ether without losing the catalytic activity.

Recently, heteropolyacids, e.g., $H_3 PW_{12}O_{40}$ (abbreviated as PW_{12}) have been reported to catalyze the conversion of methanol to hydrocarbons.²⁾ However, the selectivity to light olefins was not high. The selectivity was much improved by the use of 1,4-diazine salt of PW_{12} (abbreviated as

DA-PW₁₂), but the catalytic activity decreased to a low level.³⁾

1,4-diazine



1,3,5-triazine

We wish to report here that the acidic salts of PW_{12} with 1,3,5-triazine (TA- PW_{12}) produced

selectively light olefins from dimethyl ether with a considerably high activity. The salt was prepared by adding dropwise the aqueous solution of the organic base to the aqueous solution of PW_{12} (molar ratio of $base/PW_{12} = 1$). The catalyst was obtained by drying the solid overnight in an evacuated desiccator. The dried catalyst powder was placed in a glass tubular reactor (5.5 mm of inside diameter) and pretreated at 290°C in flowing helium. The reaction was carried out in a continuous flow system at 290°C under 1 atm. Dimethyl ether (0.2 atm in helium) was fed at the rate of 1.6×10^{-3} mole h^{-1} . The products were analyzed by gas chromatography in the same way as described previously.³

The reaction reached a steady state after 2 h over TA-PW₁₂ and PW₁₂. The products were only hydrocarbons. Their compositions at the steady state (at about 10% conversion) are summarized in Table 1. In the case of the DA-PW₁₂, the rate increased gradually accompanying a decrease in selectivity, so that data at a similar conversion level are given in the table. The selectivity to light olefins was much higher for the two organic salts than for the acidic form: C_2-C_5 olefins were formed with 70 - 76% selectivity, while the selectivity was only 47% for PW₁₂. As for the catalytic activity, TA-PW₁₂ and PW₁₂ were much more active than DA-PW₁₂. Thus, TA-PW₁₂ shows a high selectivity as DA-PW₁₂, without losing the catalytic activity of PW₁₂. It is remarkable that the olefin/paraffin ratio of $C_2 - C_5$ hydrocarbons reached 5.4 for TA-PW₁₂, while it was only 1.1 for PW₁₂ (note that these two catalysts were very similar both in the activity and in the distribution of carbon number). This result indicates that the salt formation with 1,3,5-triazine little affects the condensation step, but effectively suppresses the

hydrogen transfer step which yields paraffins. Besides the products in the gas phase as given in the table, a few percents of heavier hydrocarbons were collected at the outlet of the reactor. They consisted mainly of hexamethylbenzene as identified by GC-MS, IR and NMR.

Figure 1 shows the relationships between the selectivity and the conversion. The selectivity decreased gradually with the increase in conversion over these catalysts, but the superior selectivity of the salts was maintained even at higher conversions. When methanol (0.3 atm in helium) was used as a reactant instead of dimethyl ether, the selectivity of TA-PW₁₂ decreased slightly (57%), but was still greater than that of PW₁₂. Since methanol and dimethyl ether are readily absorbed by PW₁₂⁴ and its salts, the present reaction presumably proceeds in the bulk of the catalysts. The specific selectivity of these salts is probably related to the characteristics of "pseudo-liquid phase".^{4,5)}

Table 1. Composition of Hydrocarbons Obtained from the Conversion of Dimethyl Ether at 290°C

Catalyst	^{PW} 12	DA-PW12	TA-PW ₁₂
W/F (g.h.mole ⁻¹)	226	1500	126
Conversion(%)	13.2	7.7	8.1
$C_2 - C_5$ olefin (%)	46.9	69.9	76.3
Product	Distrib	outions (wt%)
Methane	4.5	10.2	5.5
Ethylene	13.5	22.7	15.2
Ethane	0.4	0.4	0.4
Propene	18.1	32.5	23.3
Propane	9.6	4.1	2.7
Butenes	11.2	10.9	25.5
Butanes	20.8	9.0	7.2
Pentenes	4.1	3.8	12.3
Pentanes	12.2	4.0	3.9
с ₆	5.6	2.4	4.0
$C_2 - C_5$ olefins	 _	4.0	
$C_2 - C_5$ paraffins	1.1	4.0	5.4



Fig. 1. Dependence of the Selectivity of C₂-C₅ Olefins on Conversion (290°C)

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(Received May 24, 1982)