CHEMISTRY LETTERS, pp. 1345-1346, 1979.

CATALYTIC ACTIVITY OF VARIOUS 12-MOLYBDOPHOSPHATES FOR METHACROLEIN OXIDATION

Koichi EGUCHI, Isao ASO, Noboru YAMAZOE, and Tetsuro SEIYAMA
Department of Materials Science and Technology,
Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

12-Molybdophosphoric acid and its salts were examined as catalysts for methacrolein oxidation. The catalytic activity was strongly dependent on the kind of counter ion, the highest activity being attained by Co(II) salt. The effect of counter ion was well expressed in terms of ionic potential.

Heteropoly acids and their salts, some of which have strong acidity and/or oxidizing power, find many uses in catalysis. Especially 12-molybdophosphoric acid and its salts are noteworthy of their activity for methacrolein (MA) oxidation to methacrylic acid (MAA). Although 12-molybdophosphate catalysts containing various kinds of counter ions are found in patents, the effects of the counter ions have not been studied satisfactorily. This paper deals with the effects of counter ions on the catalytic activity for the methacrolein oxidation.

12-Molybdophosphoric acid ($H_3PMo_{12}O_{40}$) was prepared from MoO_3 and H_3PO_4,1) and its salts were from $H_3PMo_{12}O_{40}$ and corresponding metal carbonates. The structure and thermal stability of them were examined by using X-ray diffraction, differential thermal analysis (DTA), and thermal gravimetry (TG). Catalysts were calcined at 320°C for 2 h before use. Surface area was measured by BET method after evacuating further at 200°C for 30 min. The oxidation of MA was carried out in a flow system at 320°C. A gaseous mixture of 3.3 % MA, 5 % oxygen, and balance (nitrogen) was fed and products were analysed by gas chromatography. Data were taken when a steady state was attained. The conversion levels of MA were less than 10 %.

The results of the oxidation of MA over various 12-molybdophosphates are summarized in Table 1. All molybdophosphates were more or less active for the oxidation giving mainly MAA, CO, and CO_2. Since MoO_3 itself was inactive for MAA formation, it is evident that the polyanion structure contributes to the MAA formation activity of these catalysts. However, selectivity to MAA was unexpectedly low being less than 50 % in every case. The highest MAA selectivity (46 %) was obtained by Tl^+ salt, while the lowest one (12 %) was by Cs^+ salt.

Since the surface area was largely different depending on catalyst, their catalytic activities for the MA oxidation are compared per unit surface area in the table. The highest activity was shown by Co(II) salt. Generally speaking, the salts of transition metals or Group IIa metals were more active than the other catalysts. Although these salts decomposed thermally at 400-500°C, their X-ray diffraction patterns were unchanged before and after the reaction. On the other hand, the salts of mono-valent cations were generally less active than the above salts. Of these, Tl^+, Cs^+, and K^+ salts were prepared in fine particles, and thermally stable up to the melting points (650-700°C).[2] It is remarkable that $H_3PMo_{12}O_{40}$ was only moderately active. This suggests that the Brönsted acidity of the catalyst is not so important for the MAA formation, although patents often assume the acidity very important.[3]

The variation of catalytic activity just mentioned should be considered as reflecting the effect of the counter cations of 12-molybdophosphates. The effect, however, could not be well explained in terms of the heat of oxide formation (ΔH_f°) or electronegativity of counter cations. After various attempts, we found that the ionic potential (Z/r) of counter cation could be a good parameter for this case. The correlation between Z/r and the rate of MAA formation over 12-molybdophosphates is shown in Fig. 1. The meaning of the correlation, however, remains to be clarified by further studies. Considering that the parameter Z/r deeply affects the coulombic interactions between ions in the crystalline lattice, the observed correlation of Fig. 1 may be associated with the stability of ionic lattice or crystal perfection of the heteropoly compounds.

Table 1 Oxidation of methacrolein over 12-molybdophosphates, $M_3^{n+}(PMo_{12}O_{40})_n$. ($W/F = 0.5\ g\cdot s/cm^3$, $T = 320°C$)

Counter Cation M^{n+}	Surface Area (m^2/g)	Specific Activity*	Selectivity to MAA (%)	CO (%)	CO_2 (%)
H^+	19.3	0.8	31	33	36
NH_4^+	26.9	0.2	45	25	29
Na^+	3.3	0.8	34	19	45
K^+	20.9	0.3	37	19	44
Cs^+	22.9	0.3	12	28	60
Ca^{2+}	1.3	4.7	38	19	43
Ba^{2+}	1.9	3.5	42	20	38
Tl^+	82.9	0.3	46	29	25
Cu^{2+}	2.2	5.6	23	48	29
Ag^+	4.4	1.2	19	22	58
Mn^{2+}	3.1	3.1	38	24	37
Co^{2+}	1.4	6.5	42	26	32
Ni^{2+}	2.7	4.7	43	21	36
La^{3+}	2.7	3.1	41	27	32
MoO_3	2.6	0.7	0	37	62
V_2O_5	3.0	6.5	32	24	44

* Rate of MA oxidation per m^2. ($10^{-8} mol/s\cdot m^2$)

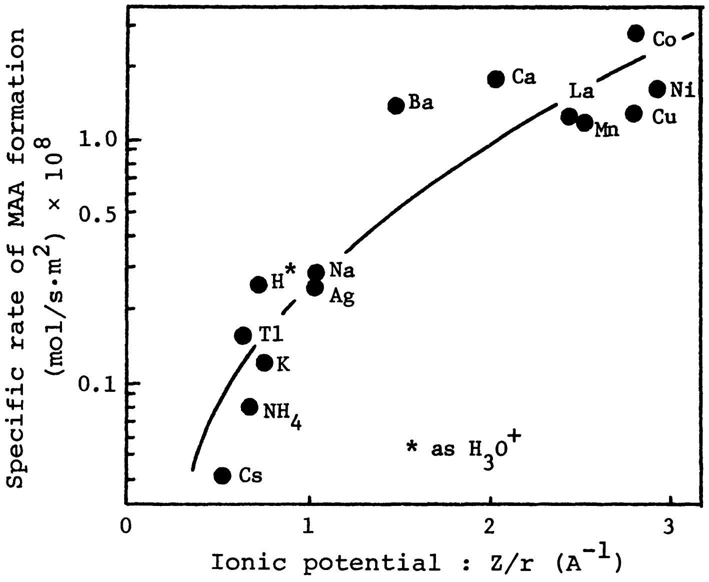

Fig.1 Correlation between activity of MA oxidation and ionic potential.

REFERENCES

1. G.A.Tsigdinos, IEC.Prod.Res. Develop., 13, 267 (1974).
2. W.P.Thistlethwaite, J.Inorg.Nucl. Chem., 28, 2143 (1966).
3. e.g., Patent (Japan), 50-23013.

(Received August 27, 1979)