Direct Oxidation of Isobutane into Methacrylic Acid and Methacrolein over $Cs_{2.5}Ni_{0.08}$-substituted $H_3PMo_{12}O_{40}$

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Cs^+, and Ni^{2+}, Mn^{2+} or Fe^{3+} substitution for H^+ in $H_3PMo_{12}O_{40}$ greatly enhanced the catalytic activity for the title reaction and among the catalysts tested $Cs_{2.5}Ni_{0.08}H_{0.34}PMo_{12}O_{40}$ gave the highest yield of methacrylic acid and methacrolein.

Selective oxidation of alkanes by molecular oxygen is of great interest and growing importance but little is known about this reaction.[1] We have recently expanded our fundamental knowledge of the metal-catalysed O_2-based oxidation of cyclohexane and other alkanes by using heteropoly compounds.[2] Efforts continue to focus on the selective oxidation of isobutane to yield methacrylic acid.

Methacrylic acid is used for the synthesis of methyl methacrylate, an important monomer for resin production. It has traditionally been manufactured by the reaction of acetone with the hazardous hydrogen cyanide,[3–5] in a process that overproduces solid ammonium hydrogen sulfate. Alternative methods, the methylation of propionaldehyde or the oxidation of isobutene, have recently been developed,[3–5] but these require high-price feedstocks and consist of two-step reactions.[3–6] It would be advantageous to use a cheaper feedstock, isobutane, and to produce methacrylic acid directly from isobutane and molecular oxygen.[3,4] We now report the catalytic activity of the Cs- and Ni-substituted $H_3PMo_{12}O_{40}$ for this reaction.

The catalysts were prepared by the method in ref. 7. An aqueous solution of the metal nitrate (0.08 mol dm^{-3}) was added dropwise to an aqueous solution of $H_3PMo_{12}O_{40}$ (0.06 mol dm^{-3}), followed by the addition of an aqueous solution of Cs_2CO_3 (0.08 mol dm^{-3}) at 50 °C. The resulting suspension was evaporated to dryness at 50 °C.

The reactions were performed in a flow reactor (Pyrex tube, 12 mm internal diameter) at an applied temperature of 300–360 °C under atmospheric pressure. The feed gas consisted of 17% (*v*/*v*) of isobutane, 0.33% (*v*/*v*) of O_2, and N_2 balance unless otherwise stated. Total flow rates were *ca.* 30 cm^3 min^{-1}. It was confirmed for $Cs_{2.5}Ni_{0.08}H_{0.34}PMo_{12}O_{40}$ that the conversion and selectivity were little changed by mixing with SiC (1.5 g) to prevent an undesirable temperature rise. Prior to the reaction, 1 g of each catalyst was treated in an O_2 stream (60 cm^3 min^{-1}) for 1 h at 300 °C. The outlet gases were withdrawn intermittently with the aid of a sampler directly connected to the system and analysed by a FID and TCD gas chromatography with FFAP, Porapack Q and Molecular Sieve 5A columns. The conversion and the selectivity were determined after 2–5 h of reaction, when nearly steady state conversion and selectivity were obtained for each catalyst. The carbon balance was in the range of 95–100%.

The results for $Cs_xH_{3-x}PMo_{12}O_{40}$ (Cs_xPMo_{12}) catalysts are shown in Table 1. The conversions were 7, 6, 11, 16, 17 and 8% for $x = 0, 1, 2, 2.5, 2.85$ and 3, respectively and the highest conversion was observed around $x = 2.5$–2.85. The products observed were methacrylic acid (MAA), methacrolein (MAL), acetic acid, acetone, CO and CO_2. The yields of MAA on $Cs_xH_{3-x}PMo_{12}O_{40}$ were 0.3, 1.4, 3.7, 3.9, 0.8 and 0% for x = 0, 1, 2, 2.5, 2.85 and 3, respectively. Thus, the substitution of Cs^+ for H^+ in $H_3PMo_{12}O_{40}$ resulted in a great enhancement of the MAA production and the yield reached a maximum around $x = 2.5$. The sum of the yields of MAA and MAL on $Cs_{2.5}PMo_{12}$ reached 5.1%, the highest among $Cs_xH_{3-x}PMo_{12}O_{40}$ catalysts. It has been reported that $(VO)_2P_2O_7$ shows high catalytic activity for the oxidation of *n*-butane and *n*-pentane[6] and that $H_3PMo_{12}O_{40}$ is more active than $(VO)_2P_2O_7$ for the oxidation of isobutane.[8] $Cs_{2.5}PMo_{12}$ is known to have high oxidizing ability among $Cs_xH_{3-x}PMo_{12}O_{40}$ catalysts[9] and to contain a large proportion of surface protons.[10] The high catalytic performance of $Cs_{2.5}PMo_{12}$ may result from such oxidation and acidic properties.

Table 1 Oxidation of isobutane over $Cs_xH_{3-x}PMo_{12}O_{40}$ at 340 °C[a]

		Selectivity[b] (%)					
x	Conv. (%)	MAA	MAL	AcOH	CO	CO_2	Sum of yields of MAA + MAL (%)
0	7	4	18	8	44	26	1.5
1	6	23	17	10	32	18	2.4
2	11	34	10	7	29	21	4.8
2.5	16	24	7	7	41	21	5.1
2.85	17	5	10	5	44	37	2.4
3[c]	8	0	10	6	32	35	0.8

[a] Isobutane, 17% (*v*/*v*); O_2, 33% (*v*/*v*); N_2, balance; catalyst, 1.0 g; total flow rate, *ca.* 30 cm^3 min^{-1}. [b] Calculated on the basis of C_4 (isobutane). [c] The selectivity to acetone was 17%.

Table 2 Effect of transition metal ions on oxidation of isobutane over $M^{n+}{}_{0.08}Cs_{2.5}H_{0.5-0.08n}PMo_{12}O_{40}$ at 340 °C[a]

		Selectivity[b] (%)					
M^{n+}	Conv. (%)	MAA	MAL	AcOH	CO	CO_2	Sum of yields of MAA + MAL (%)
H^+	16	24	7	7	41	21	5.1
Ni^{2+}[c]	24	27	6	7	36	23	8.0
Mn^{2+}	21	20	11	9	44	16	6.5
Fe^{3+}	14	35	11	7	27	26	6.3
Cu^{2+}	12	12	10	7	37	34	2.6
Co^{2+}	7	11	15	6	48	20	1.9

[a,b] See Table 1. [c] A small amount of acetone was observed.

The catalytic properties of $Cs_{2.5}PMo_{12}$ were changed by the addition of transition metal ions. Table 2 shows the effect of additives. The addition of Ni, Mn or Fe increased the yields of MAA and MAL, Ni being the most effective with increases in the yields of MAA and MAL to 6.5 and 1.5%, respectively.[11] In contrast, Co and Cu decreased the yields.†

In order to confirm the structure of $Cs_{2.5}Ni_{0.08}H_{0.34}PMo_{12}O_{40}$ during the reaction, IR spectra were measured before and after the reaction. The sample showed the intense 1063, 966 (with a shoulder at 970 cm^{-1}) and 866 cm^{-1} bands and the very broad 800 cm^{-1} band which are assigned to ν(P–O), ν(Mo=O), corner-sharing ν(Mo–O–Mo), and edge-sharing ν(Mo–O–Mo) of the Keggin structure, respectively, by analogy with the assignment for $PMo_{12}O_{40}^{3-}$ Keggin anion.[12] No changes in the IR spectra were observed after the reaction, showing that the structure of the Keggin anion was retained during the reaction in the temperature range 300–360 °C.

Thus, the results show that Cs and Ni are an excellent combination for the oxidation of isobutane into MAA and MAL over modified $PMo_{12}O_{40}^{3-}$ heteropolyanions.

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Footnote

† The effectiveness of the additives and the extent of MAA formation depended significantly on the reaction conditions; under oxygen-poor condition [isobutane, 33% (*v/v*); O_2, 13% (*v/v*); N_2, 54% (*v/v*); total flow rates, *ca.* 15 cm^3 min^{-1}; $Cs_{2.5}PMo_{12}$, 1 g; react. temp., 340 °C], no MAA was produced and Cu^{2+} was the most efficient additive to increase the yield of MAL on $Cs_{2.5}PMo_{12}$: M. Tateishi, N. Mizuno and M. Iwamoto, experiments in progress.

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