Kinetics and Catalysis, Vol. 42, No. 2, 2001, pp. 212–216. Translated from Kinetika i Kataliz, Vol. 42, No. 2, 2001, pp. 237–241.
Original Russian Text Copyright © 2001 by Stytsenko, W. Lee, J. Lee.

Catalyst Design for Methacrolein Oxidation to Methacrylic Acid[1]

V. D. Stytsenko*, W. H. Lee, and J. W. Lee****
** Gubkin Russian State University of Oil and Gas, Moscow, 117917 Russia*
*** LG Chemical Ltd., Research Park, Korea*

Received July 20, 2000

Abstract—Heteropoly compounds (HPCs) with the general formula $CsMHPVMo_{11}O_{40}$ are prepared and tested as catalysts. The influence of elements entering the formula on the catalyst properties is studied: Cs defines the acidity and specific area, V controls the selectivity, and the transition metal M defines the mobility of oxygen in the bulk and the catalyst activity. The mechanism of methacrolein oxidation over HPCs is investigated. Using the response method and mass spectrometry of the reaction mixture, it is shown that only the catalyst oxygen atoms take part in the formation of methacrylic acid and that the transport of active oxygen to adsorbed methacrolein plays a key role in the oxidation process. A correlation between the HPC activity and the redox ability of the metal cation $M^{n+} \longleftrightarrow M^{n+i}$ ($i = 1$ or 2) is found. New catalysts for methacrolein oxidation to methacrylic acid are developed on the basis of this correlation. These are the salts of PVMo-poly acid with Cs, Cu, and the transition metal M as cations. These catalysts are more active (a conversion of up to 91%) and selective (up to 98%) compared to conventional catalysts for methacrolein oxidation to methacrylic acid.

INTRODUCTION

Methacrylates are large-scale products used in polymer manufacturing. A key step of the current commercial production of methacrylic acid is methacrolein (MA) oxidation to methacrylic acid, and heteropoly compounds are good catalysts for this process [1].

It is known that HPCs belong to the family of polyoxometallates, of which twelfth-series compounds are the most abundant and important. They have the general formula $K_xEA_{12}O_{40} \cdot nH_2O$ and a highly organized three-level structure. The primary structure is a Keggin unit (KU) with a central atom E (P, Si, Al, etc.) having a coordination number of 4 and forming an EO_4 tetrahedron surrounded with twelve AO_6 octahedra with common vertices and edges (A = Mo, W, V); where K is a counter-cation (proton, Group I and II metals, and transition metals) [2].

For catalytic methacrolein oxidation over heteropoly compounds, a consecutive scheme was proposed:

$$\mathrm{RCHO} \underset{1}{\overset{\mathrm{Cat(H^+)}}{\rightleftarrows}} \mathrm{RCH(OM)_2} \xrightarrow[2]{\mathrm{Cat(O)}} \cdots \mathrm{RCOOH}$$

$$(\mathrm{Cat} = \mathrm{HPC}),$$

where the first step catalyzed by acid function is fast, and the dehydrogenation of an acetal intermediate (step 2) is the rate-determining step [3]. Therefore, the catalyst for methacrolein oxidation should provide these two functions and a redox ability is the main property that affects the catalyst activity [4]. This property is also important for the structural stability of HPC [5] because, after reaching a considerable extent of reduction, it decomposes into a mixture of catalytically low-active oxides [5, 6].

Heteropoly compounds are a system with mutually related chemical properties. For instance, the partial substitution of protons by cesium in a cation sublattice both affects the acidity and sharply increases the specific surface area of a heteropoly compound [7]. The substitution of Mo by V atoms in a polyanion leads to a decrease in the acidity of HPC [2] and the weakening of the oxygen–metal bond. In turn, with a decrease in the acidity, the redox ability of HPC lowers [8].

In our analysis of published data and preliminary tests, we chose the system $CsM_xH_{3-x}PVMo_{11}O_{40}$, where the acidic and redox properties could readily be controlled.

The aim of this work was to investigate the effect of substitution elements, Cs and V, and the nature of transition metal M on both the catalytic and redox properties of HPCs, and to develop on this basis a scientific method to the catalyst design for methacrolein oxidation.

EXPERIMENTAL

Catalysts having various concentrations of Cs, V, and transition metals M were prepared by the same procedure of the coprecipitation [9] of an aqueous solution of ammonium molybdate, ammonium metavanadate, and phosphoric acid with a solution of the nitrates of Cs, transition metal, and nitric acid. Some HPCs were prepared from chemically pure PMo_{12} and $PVMo_{11}$ heteropoly acids (Aldrich) by exchange reaction. The precipitate of the HPCs was dried in air and calcined at

---

[1] Proceedings of the II All-Russian Workshop on Highly Organized Catalytic Systems.

0023-1584/01/4202-0212$25.00 © 2001 MAIK “Nauka / Interperiodica”

Table 1. Methacrolein oxidation over HPC $Cs_xM_yH_{4-x-y}PV_zMo_{12-z}O_{40}$ ([MA] = 2.9%; $[O_2]$ = 8.7%; τ = 3.3 s; V_0 = 1100 h^{-1})

HPC	x	y	z	Selectivity to MAA, %	$[MAA]^{***}_{max}$, %
1	1.0	0	1.0	75	55 (310)
2	0.9	0.1 Cu	1.0	94	67 (330)
3*	1.0	0.2 Cu	1.0	91	77 (330)
4	1.0	0.2 Cu	1.0	92	77 (320)
5	1.0	0.3 Cu	1.0	93	84 (310)
6	1.3	0.3 Cu	1.0	85	43 (330)
7	1.5	0.2 Cu	1.0	82	67 (310)
8	1.0	0.3 Ag	1.0	~50	11 (330)
9**	1.3	0.1 Cu	0	72	33 (320)
10	1.3	0.1 Cu	0	73	34 (320)
11	1.0	0.3 Cu	1.3	96	37 (330)

* Prepared from $H_4PVMo_{12}O_{40}$.
** Prepared from $H_3PMo_{11}O_{40}$.
*** Temperature is indicated in parenthesis (°C).

230–360°C for 6 h. The thermal stability of the HPCs was evaluated by thermogravimetry using a DTA Perkin–Elmer instrument. The surface area of the HPCs was measured by the BET method.

Catalysts (1–2 g) were tested in a quartz flow reactor. A reaction mixture contained Ar, H_2O, O_2, and MA with a $H_2O : O_2$: MA ratio of 3.6 : 3 : 1; its volume hourly space velocity (VHSV) was 1100 h^{-1}. Analysis of the reaction mixture leaving the reactor was performed by with a 5890 Series gas chromatograph and a VG Quadrupoles mass spectrometer. Methacrylic acid (MAA), acetic acid (usually <5%), and carbon oxides were found in the reaction products. The data presented in the tables characterized the steady state of catalysts, which were kept for at least 6 h, or for more than 50 h for the best catalysts, after specific oxidative treatment.

RESULTS AND DISCUSSION

The applicability of the procedure chosen for the synthesis of HPCs was demonstrated by comparing the properties (thermal stability, specific surface area, and catalytic activity) of compounds obtained from the mixture of reagents and synthesized by direct exchange from heteropoly acid reagents (Table 1, samples 4, 10 and 3, 9; Table 2, samples with 0.3 mol Cu/KU). The samples of these two types were identical. All samples of HPCs were stable up to at least 400°C and their surface areas were 2–3 m^2/g.

At the first stage of investigation, it was necessary to find the basic composition of catalysts, which was stable and selective in MA transformation into MAA. In this set of experiments, heteropoly compounds $Cs_xM_yH_{4-x-y}PV_zMo_{12-z}O_{40}$ having various concentrations of Cs (x = 0.9–1.5 mol), Cu (y = 0–0.5 mol), and V (z = 0–1.3 mol) in KU were tested. Table 1 presents the results of the tests.

It is evident from Table 1 that copper is an essential component of HPCs providing the high activity and selectivity of methacrolein oxidation where its concentration is ≥0.2 mol/KU. The optimal concentrations of Cs and V in the system are close to unity: with an increase in the cesium and vanadium concentrations to 1.3 mol/KU, the activity drops sharply, but the elimination of vanadium also leads to a decreases in the catalyst selectivity to methacrylic acid. Thus, the basic composition of the catalyst should correspond to the formula $CsCu_{0.2}H_{2.8}PVMo_{11}O_{40}$.

Generally, the redox properties of heteropoly compounds depend on the nature of transition metal cations in HPCs that also serve as centers for reagent activating [10]. To substantiate the choice of these transition metals, the mechanism should be refined using the activity response on a change in the gas composition. The typical curves of the catalytic activity response for HPCs are shown in Fig. 1.

It is evident from Fig. 1 that, if methacrolein is excluded from the catalytic mixture, the product formation will not be observed (curves *2* and *6*), but this oxidative treatment improves the catalyst activity (curves *3* and *7*). Therefore, chemisorbed methacrolein is absent from the catalyst surface under a steady state. On the contrary, when methacrolein is fed to the catalyst in the absence of oxygen, the formation of methacrylic acid is observed (curve *4*), essentially with the same rate as in catalysis. Therefore, the concentration

Table 2. Effect of transition metal additives on the properties of basic catalyst $Cs_xM_yH_{4-x-y}PV_zMo_{12-z}O_{40}$ ([MA] = 2.9%; $[O_2]$ = 8.7%; τ = 3.3 s)

Metal concentration, mol/KU	Selectivity to MAA, %	MAA yield*, %	Ref.
0.2Cu; $z = 1$	92	77 (320)	This work
0.1Cu + 0.1Mn; $z = 1$	97	60 (320)	″
0.2Cu + 0.1Mn; $z = 1$	94	81 (330)	″
0.2Cu + 0.1Ce; $z = 1$	95	73 (330)	″
0.2Cu + 0.1Co; $z = 1$	99	25 (330)	″
0.2Cu + 0.1Fe; $z = 1$	95	60 (330)	″
0.2Cu + 0.1Pb; $z = 1$	93	83 (330)	″
0.2Cu + 0.1Sn; $z = 1$	89	41 (330)	″
0.3Cu; $z = 1$	93	84 (310)	″
0.3Cu**; $z = 1$	95	82 (320)	″
0.2Cu + 0.2Bi; $z = 1$	98	76 (330)	″
0.2Cu + 0.1Ag; $z = 1$	96	65 (330)	″
0.2Cu + 0.1Bi; $z = 1$	97	76 (320)	″
$z = 0.5$; Cs : Cu : NH_4 = 1 : 0.1 : 0.2	83.8	70.4 (285)	[1]
$x = 2$; $y = 0$; $z = 0$	90	59 (320)	[8]
$y = 3$***; $z = 0$	75.3	63.4 (310)****	[11]
$z = 0$; Cs : Pb : Cr = 2 : 0.2 : 1	72.3	21.2 (310)	[13]

* Temperature is indicated in parenthesis (°C).
** Prepared from acid $H_4PVMo_{11}O_{40}$.
*** Residual amount of ammonia ions not indicated.
**** The contact time was 5.3 s.

of active oxygen on the surface is rather high. The rate of product formation significantly decreases with time after the removal of about 25% of oxygen[2] and this process also continues in catalysis (curve *5*).

In the experiment on varying the reagent concentrations, we found that the reaction order with respect to MA is close to unity, but the oxygen concentration has no effect on the rate of catalytic reaction. Similar regularities were observed earlier with the ammonium salt of a heteropoly acid as a catalyst [11].

It follows from these data that

(a) The catalytic activity of HPCs is attributed to oxygen ions, and methacrylic acid is formed due to the interaction between gaseous aldehyde (or aldehyde weakly bound to the surface) and the active oxygen of the catalyst;

(b) The mobility of oxygen ions in the bulk of HPCs is responsible for the formation of methacrylic acid at a constant rate even in the absence of gaseous oxygen;

(c) When the catalyst is reduced to about 25%, its activity decreases because oxygen diffusion does not compensate for the loss of active oxygen on the surface, but the activities of all vanadium-containing catalysts significantly increase after oxidative treatment (O_2, 300°C).

Thus, the transition metal was chosen from metals that can be reduced and reoxidized at $T \sim 300$°C, namely Ag, Bi, Ce, Co, Cu, Fe, Mn, Pb, and Sn. These metals were added to the basic catalyst in amounts of 0.1 mol/KU so that the variation of catalytic properties would reflect the influence of the redox ability of transition metals. The results obtained are presented in Table 2 showing that these Group II–VII transition metals with various redox properties have a strong effect on the activity and selectivity of the basic catalyst.

---

[2] The quantity of [O] removed from catalyst ZO was calculated from the quantity of methacrylic acid formed after feeding MA (without O_2) to the catalyst, the reaction $C_3H_5CHO + ZO_x \longrightarrow C_3H_5COOH + ZO_{x-1}$; $(x - 1)/x \le 25\%$.

The proximity of the rates of catalysis and that of the reduction of HPC points to the existence of a correlation between the catalytic activity and the reduction ability of HPC. We chose the heat effect of the reduction of transition metal oxides under standard conditions as a measure of their redox ability. To calculate the values of the heat effect, the standard enthalpies of formation of corresponding transition metal oxides [12] were used taking into account the stoichiometry of the reduction process. As a measure of catalytic activity, we used the conversion of methacrolein over the steady-state catalyst at 310 and 320°C.

The results obtained are presented in Table 3 and Fig. 2. It can be seen in Fig. 2 that the catalytic activity as a function of the heat effect of the reduction (ΔH_r^{298}) of transition metal oxides has a maximum around 73 kJ/mol, which corresponds to copper ions; the additives of Mn, Pb, and Bi ions are rather effective as well. As shown in Table 2, catalysts including these additives have improved activity and selectivity (up to 98%) and provide a better yield of MAA (76–84%) compared to the conventional catalysts for methacrolein oxidation [1, 8, 11, 13], for which the yield of MAA does not exceed 71%.

Based on the correlation that we found, it can be deduced that the HPC having the composition $CsCu_{0.3}H_{2.7}PVMo_{11}O_{40}$ is the optimal catalyst for methacrolein oxidation to methacrylic acid. After the partial substitution of Cu (0.1 mol/KU) by metals (Mn, Pb, or Ag) whose oxides are stronger oxidants than CuO, the catalyst activity and selectivity decrease, whereas the addition of weaker oxidants than CuO (oxides of Bi, Ce, Fe, Mn, and Sn) leads to a decrease in the activity and an increase in the selectivity to MAA.

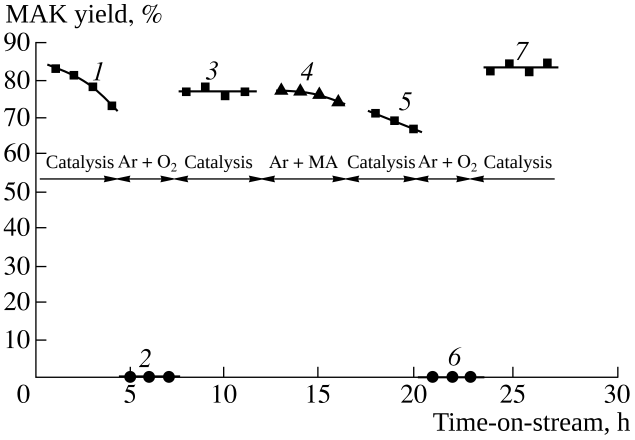

Fig. 1. Effect of the redox treatment of $CsCu_{0.2}HPVMo_{11}O_{40}$ on the yield of methacrylic acid at 573K and O_2/MA = 3 : 1. (*1*, *3*, *5*, *7*) catalysis; (*2*, *6*) response to the absence of MA in the mixture; and (*4*) response to the absence of O_2 in the mixture.

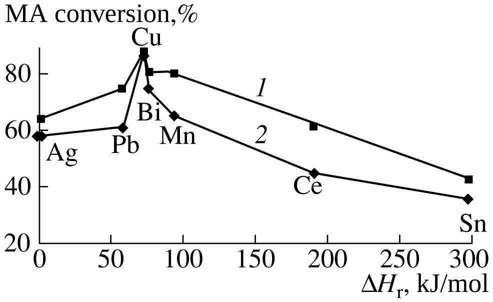

Fig. 2. Correlation between the catalytic activity of $CsM_{0.1}Cu_{0.2}HPVMo_{11}O_{40}$ and the heat effect of reduction of transition metal oxides. M = Ag, Pb, Cu, Bi, Mn, Ce, and Sn: (*1*) 320°C and (*2*) 310°C.

Thus, the correlation between the HPC activity and the redox ability of metal cation $M^{n+} \longleftrightarrow M^{n+i}$ (i = 1 or 2) was found. On this basis, new catalysts for producing methacrylic acid were developed, which are the salts of PVMo-heteropoly acid comprising Cs, Cu, and the transition metal M as cations.

Table 3. Catalytic activity of $CsCu_{0.2}M_{0.1}H_{2.7}PVMo_{11}O_{40}$ in methacrolein oxidation and redox properties of transition metal (M) oxides

Redox process	Enthalpy of oxide formation $-\Delta H_f^{298}$, kJ/mol		Enthalpy of reduction ΔH_r^{298}, kJ/g-at. M	MA conversion, %	
	lower	higher		310°C	320°C
$Ag_2O_2 \longleftrightarrow Ag_2O$	31.1	24.3	–3.4	58	64
$Bi_2O_3 \longleftrightarrow 2BiO$	210.7	573.9	76.2	75	81
$2CeO_2 \longleftrightarrow Ce_2O_3$	1796.2	1088.7	190.6	45	62
$2CuO \longleftrightarrow Cu_2O$	168.6	157.3	73.0	88	87
$Fe_2O_3 \longleftrightarrow 2FeO$	272.0	824.0	140.0	32	49
$Mn_2O_3 \longleftrightarrow 2MnO$	1387.8	959.0	94.3	65	80
$PbO_2 \longleftrightarrow PbO$	219.0	277.4	58.4	61	75
$SnO_2 \longleftrightarrow SnO$	280.7	577.6	296.9	36	43

ACKNOWLEDGMENTS

Authors thank the directors of LG Chemical Ltd. for financial support of this study.

REFERENCES

1. Eur. Patent Appl. 418657 and 442517, 1991.
2. Maksimov, G.M., *Usp. Khim.*, 1995, vol. 64, no. 5, p. 485.
3. Konishi, Y., Sakata, K., Misono, M., and Yoneda, Y., *J. Catal.*, 1982, vol. 77, p. 169.
4. Misono, M., Okuhara, T., and Mizuno, N., *Successful Design of Catalysts*, Inui, T., Ed., Amsterdam: Elsevier, 1988, p. 267.
5. Misono, M., Mizuno, N., and Komaya, T., *Proc. 8th Int. Congr. on Catalysis*, Berlin: Chemie–Dechema, 1984, vol. 5, p. 487.
6. Taouk, B., Ghoussoub, D., Bennani, A., *et al.*, *J. Chim. Phys.*, 1992, vol. 89, p. 435.
7. Tatematsu, S., Hibi, H., Okuhara, T., and Misono, M., *Chem. Lett.*, 1979, p. 31.
8. Okuhara, T., Mizuno, N., and Misono, M., *Adv. Catal.*, 1996, vol. 41, p. 113.
9. Misono, M., Komaya, T., Sekiguchi, H., and Yoneda, Y., *Chem. Lett.*, 1982, p. 53.
10. Kim, H.C., Moon, S.H., and Lee, W.Y., *Chem. Lett.*, 1991, p. 447.
11. Korchak, V.N., Kutyrev, M.Yu., and Staroverova, I.N., *Kinet. Katal.*, 1990, vol. 31, no. 6, p. 1424.
12. *CRC Handbook of Chemistry and Physics*, Ride, D.R., Ed., New York: CRC, 1981, Table D-45.
13. Zhiznevskii, V.M., Shipailo, V.Ya., Grimalyuk, B.T., and Bazhan, L.V., *Ukr. Khim. Zh.*, 1996, vol. 62, no. 11, p. 22.