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Research of the Activity of Catalysts on the Base of $H_3PW_{12}O_{40}$ in Partial Oxidative Conversion of C_3–C_4 alkanes

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Abstract Catalysts from heteropoly acid $H_3PW_{12}O_{40}$ and its Cs, Na, Ba, Pb, Ca, Cd, Cr, Mn, V, La salts supported on clinoptilolite, alumosilicate are highly active in oxidative conversion of propane–butane (OCPB) mixture and formation of C_2–C_4 olefins, oxygen-containing compounds at temperatures $T = 100$–800 °C. Optimum yields of ethylene and propylene are achieved on heteropoly acid its Cs and Cr salts. The processes of oxidative dehydrogenation (ODPB) and cracking are concurrent in formation of olefins. High activity is caused by dispersity of supported catalysts (XRD, IRS) both formation of crystal hydrates and an amorphous phase of heteropoly acid in a condition of interaction with the carrier.

Keywords Propane–butane mixture · Oxidative conversion · Ethylene · Propylene · Butylenes · $H_3PW_{12}O_{40}$ · Heteropoly compound · Clinoptilolite · Alumosilicate

1 Introduction

W and Mo heteropoly compounds (HPC) supported on carriers are widely investigated as catalysts for reactions of selective oxidative conversion of C_1–C_4 alkanes. Special interest to them is caused by a unique combination of the acid–basic and redox active centers inside complex molecules [1–4]. Catalytic reactions of the oxidative type which has been carried out at $T = 320$–400 °C in conditions of their stability in liquid-phase and vapour-phase processes on HPC in solutions, on films, solid oxides are more investigated owing to low heat stability of compact heteropoly acids (HPA, 350–500 °C) [1–7]. In case of compact HPC their use in oxidative processes for synthesis of oxygen-containing compounds from C_3, C_4 alkanes, mainly carbon acids, aldehydes, ketones, (meth)acrylic acids, (meth)acrolein, acetic, propionic acids and others are more widely known [5–7]. About 12 series HPA: $H_3PMo_{12}O_{40}$ modified by Ce, V, Sb, Cs, Fe, Cu, W, Bi, Cr in the form of acid-forming elements or counter-cations were used as catalysts [1–3, 5, 7–13]. The investigations on influence of the nature of carrier including zeolites on process are well-known [14–17]. The investigations of catalytic activity in reaction of oxidative conversion of C_3–C_4 alkanes into oxygen-containing compounds (alcohols, aldehydes, acids, ketones), C_2–C_4 olefins and H_2 over W-, Mo-HPC with P and Si as central atoms supported on Si-containing oxide carriers are developed. The investigations were carried out at high-temperature 300–800 °C, $P = 1$ atm [16–25].

The parallel investigation of the activity of supported catalysts (W, Mo), its physical and chemical characteristics, structural transformation of HPC in city at oxidative conversion of C_1–C_3, C_4 alkanes under the action of temperature and reaction components (H_2, alkane, O_2, water vapor, hydrocarbon + $O_2 \pm H_2O$, $O_2 + H_2O$) permit to find the main factors which determine the increase of activity and thermal stability at long processing in comparison with compact HPC: using of low-percentage (1–15%) catalysts from HPC over carriers; existence in catalysts of Keggin type HPC in the form of finely divided crystallites and amorphous phases in a position of powerful interaction with carrier; using of water as additive and soft additional oxidant (isotope method) of reaction.

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Special functions of water (super heated water vapor ± O_2) consist in realization of reversible "regeneration" of HPC structure from fragments of thermal destruction in city ($T_{regen.} = 650–800$ °C). The last promotes steady catalytic action of supported HPC in oxidation of alkanes at high-temperature processes (up to 800–850 °C ≥100 h) [20, 23, 24, 26].

2 Experimental

Supported catalysts on the base of $H_3PW_{12}O_{40}$ HPA and its salts (Na, Cs, Ca, Ba, Cu, Pb, Cd, etc.) were prepared by impregnation with following drying on air at 110 °C during 4 h. About 15% mas. is the content of HPC over carrier. Synthetic aluminosilicate ($Si/Al = 10$, $S = 320\ m^2/g$) and clinoptilolite—natural Sary-Ozek sorbent ($Si/Al = 5$, $S = 9.8\ m^2/g$) processed by 10% HCl and washed by distilled water up to pH 6, 7 were used as carriers. Clinoptilolite has zeolites-like structure according to XRD, IRS and element analysis. XRD data indicate on presence the crystallites of HPC ($2\theta = 8–11°$), amorphous phase "HPC-clinoptilolite" ($2\theta = 3.14–4.45°$), in the composition of supported catalyst [18].

Experiments were carried out in a flow unit with fixed layer of catalyst with cooling system for reaction products. Gas mixture (C_3H_8-30 vol.%, n- and i-C_4H_{10}-70 vol.%), and oxygen of air at different ratios were used for experiments. The water vapor was added in ratio $HC:H_2O = 1:0.21$ mol. Initial reaction mixture and products were analyzed by chromatographic method.

3 Results

Regardless of catalytic composition and reaction conditions the oxygen-containing products (aldehydes, alcohols, and acids), olefins (ethylene, propylene, n- and i-butylenes) and other products (hydrogen, methane, and carbon dioxide) were obtained in the process of oxidative conversion of alkanes (Fig. 1). They form next series according to maximum formation temperatures, °C: C_3H_7OH-2, C_4H_9OH-2 (200–500) < CH_2O, C_2H_4O, HCOOH (500–700) < C_2H_4, C_3H_6, C_4H_8 (600–800) < CH_4, H_2, CO_2 (800). Thus, the products of dehydrogenation and cracking are formed at temperatures above 600 °C, and oxygen-containing products—at more low temperatures.

The results of oxidative conversion of propane–butane mixture over 15%$H_3PW_{12}O_{40}$/clinoptilolite are presented in Table 1. It was shown that oxygenates (alcohols and aldehydes) were condensed into liquid-phase at $T_{reac.} = 400–700$ °C. Yields of oxygenates (%) at $T = 600$ °C: 1.23-CH_2O, 0.79-C_3H_7OH-2, 0.26, 0.93-C_4H_9OH-1, -2 and 0.21-*i*-C_4H_9OH. Formation of acetic aldehyde was recorded.

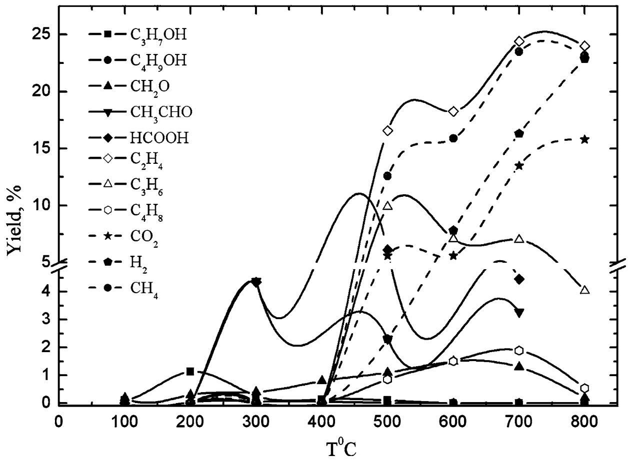

Fig. 1 Influence of the reaction temperature on yield of products of OCPB. Conditions: catalyst 15%$H_3PW_{12}O_{40}$/alumosilicate, $C_3–C_4:O_2:N_2 = 1:1:4$, $HC:H_2O = 1:0.21$ mol., $\tau = 0.29$ s, $W = 12{,}400\ h^{-1}$

Formation of $C_2–C_4$ olefins is determined by reaction temperature too. Maximums for formation ($C_3–C_4:O_2 = 3:1$) of butylenes—18.6% at 600 °C, propylene—10.6% at 700 °C, ethylene—21.9% at 800 °C were observed at increase of temperature from 300 to 800 °C. Olefins are formed at high reaction temperature together with cracking products (methane, hydrogen, carbon dioxide) due to excess of hydrocarbons relatively of oxygen in reaction mixture and total consumption of oxygen to 500–600 °C.

Influence the contact time (τ) of catalyst with reaction medium at 500–800 °C on the process was investigated in above-mentioned conditions, Fig. 2. $\tau = 0.29$ and 0.4 s are more optimal for production of C_2H_4 and C_3H_6, C_4H_8 from C_3, C_4 alkanes.

It was detected the influence of alkane:oxygen ratio in reaction mixture on yield of main products. Optimal yields of C_2H_4 observed at 1:1 ratio, C_3H_6-2:1 and C_4H_8-3:1 during variation of $C_3–C_4:O_2$ ratio from 1:2 to 3:1, Fig. 3, Table 1.

Influence of the nature of counter cation for $H_3PW_{12}O_{40}$ HPC on direction of oxidative conversion of $C_3–C_4$ alkanes at $T = 300–800$ °C and $P = 1$ atm was investigated over 15%$Me_xPW_{12}O_{40}$/clinoptilolite (alumosilicate) catalysts where Me = Cs, Na, Ba, Ca, Cd, Pb, Mn, Cr, V, La. It was installed formation of the product of oxidative dehydrogenation—C_2H_4, C_3H_6, C_4H_8, $C_3–C_4$ alcohols, acetaldehyde, formic acid, CO_2, CH_4, H_2. The yield of products was different depending on cation type.

It was installed that yields of olefins, CO_2, CH_4, H_2 are increased with raising of reaction temperature over 15%$Cr_xPW_{12}O_{40}$/clinoptilolite, Table 2. Formation of

Table 1 Influence of reaction temperature on yield of the products of partial oxidation of C_3–C_4 hydrocarbons over 15% $H_3PW_{12}O_{40}$/clinoptilolite catalyst

T, °C	Conversion C_3–C_4, %	Yield, %										
		C_3H_7OH-2	C_4H_9OH-2	C_4H_9OH-1	i-C_4H_9OH	CH_2O[a]	C_2H_4	C_3H_6	C_4H_8	CH_4	CO_2	H_2
C_3–C_4:O_2 = 3:1												
300	5.40	0.27	0.11	0.00	0.00	1.13	0.00	0.44	0.00	0.00	0.1	0.00
400	16.4	0.42	0.26	0.00	0.00	1.20	0.54	1.78	13.3	0.19	0.1	0.00
500	55.5	0.63	0.56	0.22	0.19	1.23	4.47	5.41	14.3	3.11	6.4	1.50
600	81.1	0.79	0.93	0.26	0.21	1.23	7.31	9.78	18.6	4.47	7.7	5.70
700	83.0	0.39	0.52	0.11	0.09	1.18	11.78	10.67	15.5	5.83	9.1	10.7
800	90.2	0.17	0.19	0.00	0.00	1.10	21.94	7.56	6.20	11.2	10.5	16.6
C_3–C_4:O_2 = 2:1												
500	68.0	1.1	1.5	0.4	0.2	1.57	14.2	20.0	12.5	1.9	0.2	3.8
700	70.0	0.4	0.4	0.0	0.0	1.60	16.4	19.8	1.1	3.0	4.6	18.9
800	96.0	0.0	0.0	0.0	0.0	1.27	23.3	8.5	0.0	5.5	8.1	25.5
C_3–C_4:O_2 = 1:1												
500	100	0.78	0.58	0.46	0.17	2.68	31.8	9.7	11.6	9.2	5.2	30.7
700	100	0.39	0.31	0.09	0.00	1.48	35.2	12.1	7.7	10.1	8.90	32.0
800	100	0.00	0.00	0.00	0.00	1.28	34.0	4.9	1.0	13.0	10.6	40.0

C_3–C_4:O_2:N_2 = (1–3):1:4 $P = 1$ atm, $\tau = 0.29$ s, HC:H_2O = 1:0.21 mol

[a] Acetaldehyde is formed too

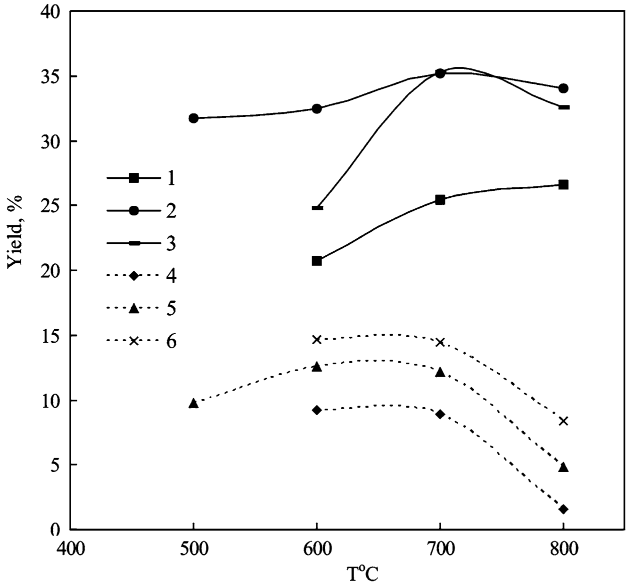

Fig. 2 Influence of *T* and contact time—τ (s) on yield of C_2H_4: 1–0.20; 2–0.29; 3–0.40; C_3H_6: 4–0.20; 5–0.29; 6–0.40. Conditions: catalyst 15%$H_3PW_{12}O_{40}$/clinoptilolite, C_3–C_4:O_2:N_2: = 1:1:4; HC:H_2O = 1:0.21 mol., $\tau = 0.29$ s; $W = 12{,}400\ h^{-1}$

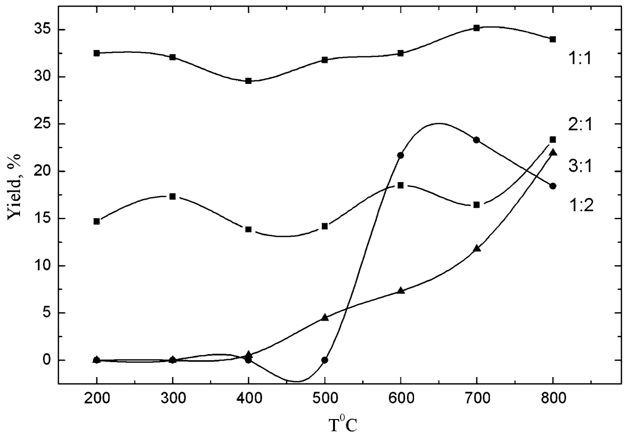

Fig. 3 Influence of C_3–C_4:O_2 ratio in reaction mixture on yield of C_2H_4. Catalyst 15%$H_3PW_{12}O_{40}$/clinoptilolite, HC:H_2O = 1:0.21 mol., $\tau = 0.29$ s

olefins at temperatures ≤300 °C is absent. Yield of ethylene is optimal at $T = 700$–800 °C, butylenes and propylene at 500–600 °C. Optimal yield of ethylene—27.1%–30.7% at 77.8%–80.9% conversion of C_3–C_4 alkanes, propylene—22.5%–27.0%, butylenes—2.7%–2.8% at 68.1%–73.3% conversion. Formation of CH_4 and H_2 is optimal at 700–800 °C—7.0%–10.0% and 22.0%–30.0%, accordingly. It was installed the parallel formation of acetaldehyde—2.7%–7.8%, formic acid—4.7%–10.7%, C_3H_7OH-1, 2—up to 1.4%, C_4H_9OH-1, 2—0.1%–0.8%, and traces of formaldehyde.

Similar laws on influence of reaction temperature on yield of C_2H_4 and C_3H_6 in OCPB process observed for other catalysts supported on a clinoptilolite from tungsten HPC, Fig. 4a. From the sum of the results presented in

Table 2 Influence of reaction temperature on oxidative conversion of C_3–C_4 alkanes mixture into C_2–C_4 olefins and CO_2, CH_4, H_2 over 15%$Cr_xPW_{12}O_{40}$/clinoptilolite catalyst

T, °C	C, %	Yield of products, %									
		C_3H_7OH-1,2	C_4H_9OH-1,2	CH_3CHO	HCOOH[a]	C_2H_4	C_3H_6	C_4H_8	CO_2	H_2	CH_4
300	34.7	1.4	0.1	2.7	4.7	0.0	0.0	0.0	1.0	9.1	0.0
400	39.9	–	–	–	–	17.7	11.7	0.0	2.2	10.0	1.9
500	68.1	1.1	0.1	3.6	3.5	19.3	22.5	2.8	3.0	13.1	2.4
600	73.3	–	–	–	–	23.0	27.0	2.7	5.1	15.0	5.3
700	77.8	0.9	0.8	7.8	10.7	27.1	15.1	2.3	6.2	22.0	7.0
800	80.9	0.0	0.0	0.0	0.0	30.7	10.5	1.2	9.3	30.0	10.0

$P = 1$ atm, $\tau = 0.29$ s, C_3H_8:C_4H_{10}:O_2:N_2 = 1:2.3:3.3:13.2 vol.; HC:H_2O = 1:0.21 mol

[a] CH_2O traces

Table 2 and Fig. 4a etc., follows that modifying cations in $Me_nPW_{12}O_{40}$/clinoptilolite catalysts on a degree of the influence on yield (%) of C_2–C_4 olefins in ODPB can be arranged in series:

C_2H_4–Ba(14.9) < Ca(21.4) < Mn(21.7) < La(29.9) < Cd, Pb(30.4) < Cr(30.7) < V(32.7) < Na(33.1) < HPA(34.0) < Cs(40.0) at 800 °C;
C_3H_6–Pb(4.9) < Mn(6.0) < Ba(8.2) < La(9.0) < Ca(9.8) < V(10.3) < HPA(12.1) < Cd(12.6) < Na(13.6) < Cs (16.6) < Cr(27.0) at 600 °C;
C_4H_8–Pb, Ba, Na, Mn, V, Ca(traces) < Cd(1.2) < Cs(2.0) < Cr(2.7) < La(3.2) < HPA(14.7) at 600 °C.

The catalyst from 15% $H_3PW_{12}O_{40}$/clinoptilolite has the highest activity in synthesis of C_4H_8 from C_3–C_4 alkanes. Thus modification of PW_{12} acid by Cs cation (ethylene) and Cr (propylene) is possible. Process productivity by C_2H_4 is 1,758 l/kg Cat h or 11,723 l/kg HPA h, by C_3H_6 771 l/kg Cat h or 5,140 l/kg HPA h, and by C_4H_8 217 l/kg Cat h or 1,449 l/kg HPA h. Supporting of HPC on other carrier—aluminosilicate decrease the optimum temperature of the synthesis of ethylene up to 725 °C and results in decrease of the yield of ethylene and propylene in compared conditions on 10–20%. Formation of butylenes is not found, Fig. 4b.

Oxidative conversion of individual C_3H_8 and C_4H_{10} into C_2–C_3 olefins on 15%$Me_xPW_{12}O_{40}$/support catalysts does not change optimum reaction temperature (700 °C), but causes either decrease (C_3H_8), or increase (C_4H_{10}) yield of olefins concerning their formation from mixture of C_3–C_4 alkanes in similar conditions.

According to results of IRS, XRD, TPR, and DTA researches it is supposed, that steady activity of the low-percentage supported catalysts from 12 series W (P, Si) HPC (1–15% HPC) in reactions of oxidative dehydrogenation of propane–butane mixture and other alkanes (C_1, C_2) under the action of high-temperature and reaction media is caused by:

- finely divided distribution of HPC on the carrier mainly with formation of amorphous phases of traces crystallites too ($2\,\theta = 6$–$8°$), 15% HPA;
- preservation of W HPC clusters under the action of components of the reaction media (O_2 + water vapor) up to 650 °C (SiW), 750 °C (PW), and occurrence not phase oxide-like compounds from HPC of unstated stoichiometry (WO_{3-x}, WO_{2+x} type) (800–900 °C) together with preservation of absorption bands (IRS) from some functional groups of HPC (W–O–W, Si(P)–O–W) at their displacement in area of absorption bands SiO_2-fragments of the carrier (650–900 °C). It indicates on expressed mutual influence in system the HPC-carrier, probably, interaction;
- finely divided distribution on carriers which stabilizes W HPC (H, Cs, Cr, Ca-counter ion) clusters, thermal destruction of which on component oxides on air and steam–air mixture it is not observed up to 1,000 °C (DTA); or 800–900 °C (TPR, IRS, XRD), accordingly;
- finely divided distribution of W HPC on carriers (1%–15%HPC) with the phenomena of interaction which leads to hardening of W–O communication in structural fragments (shift of TPR peaks into high-temperature area in comparison with compact HPC);

Hardening of W–O bond and easy "regeneration" of HPC structure in situ at high-temperature oxidation of alkanes (600–800 °C) under the action of the components of reaction media, especially O_2 and super heated water vapor mixture too, probably, causes stable productivity of catalysts on olefins and thermal stability at long operation [16, 18, 19, 22–24, 26].

4 Conclusion

From the results of oxidative conversion of C_3–C_4 alkanes on catalysts from 15% $H_3PW_{12}O_{40}$/clinoptilolite and its

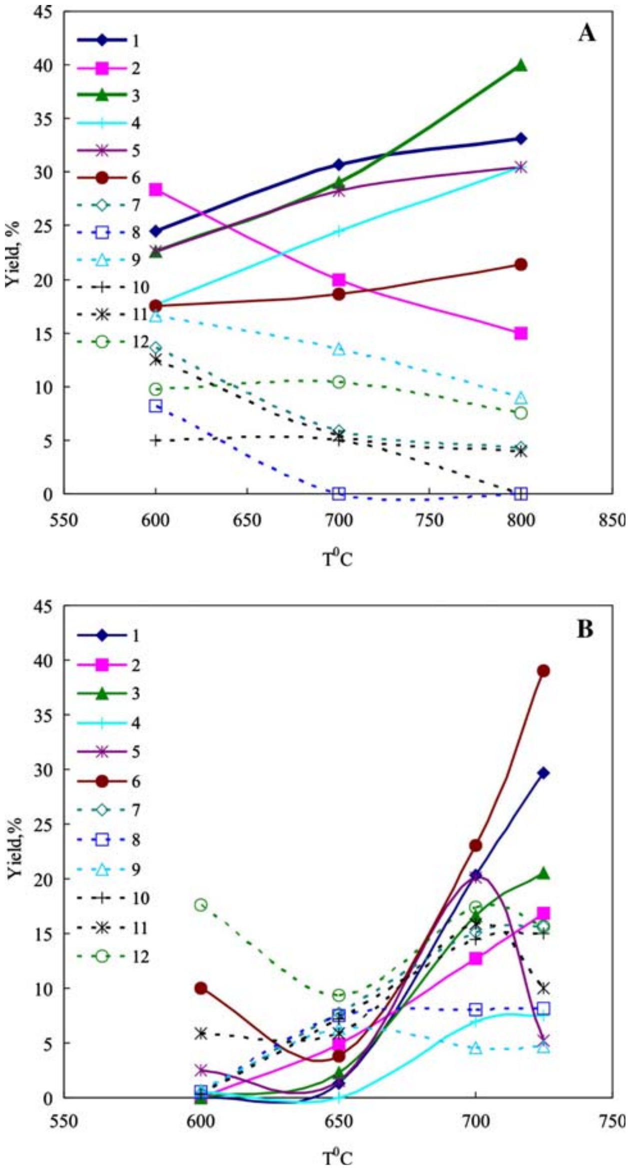

Fig. 4 Oxidative dehydrogenation of propane–butane mixture over 15% $Me_xPW_{12}O_{40}$ supported on **a** clinoptilolite and **b** aluminosilicate. Yield of C_2H_4: 1-Na; 2-Ba; 3-Cs; 4-Pb; 5-Cd; 6-Ca and C_3H_6: 7-Na; 8-Ba; 9-Cs; 10-Pb; 11-Cd; 12-Ca

salts follows, that the greatest yields of oxygen-containing products are observed at $T = 500$–600 °C, and olefins from 400 to 800 °C. Ratio of 1:1 is the optimum C_3–C_4:O_2 ratio for synthesis of C_2H_4, 2:1—C_3H_6 and 3:1—C_4H_8. Productivity of process by C_2H_4 is 1,758 l/kg Cat h or 11,723 l/kg HPA h, by C_3H_6 771 l/kg Cat h or 5,140 l/kg HPA h, and by C_4H_8 217 l/kg Cat h or 1,449 l/kg HPA h.

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