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# Performance of potassium 12-tungstophosphoric salts as catalysts for isobutane/butene alkylation in subcritical and supercritical phases

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## Abstract

Potassium salts of $H_3PW_{12}O_{40}$ heteropolyacid have been synthesised with different K contents and studied for their acid and catalytic properties in liquid phase isobutane alkylation by but-2-ene or but-1-ene. Subcritical and supercritical conditions have been chosen for comparison in a batch reactor.

The influence of the protonic site density has been studied. High acid density was observed to be detrimental for akylation reaction which was explained by increased olefin dimerisation, the main side reaction responsible of catalyst poisoning. A $K_{2.6}H_{0.4}P$ sample was tested in a batch reactor in liquid subcritical, near supercritical and in low and high density supercritical isobutane/butene mixture (418 K, $P = 4$–9 MPa). An increase in the quality of the alkylate with the density of the supercritical phase was observed which almost counterbalanced the negative effect of the high temperature necessary to reach supercritical isobutane conditions.

In the presence of porous alkaline salts of 12-tungstophosphoric acid, alkylation to oligomerisation ratio is significantly improved over solids with a low density of strong Brønsted sites and by the use of high density supercritical isobutane conditions, the latter preserving hydride transfer and trimethyl pentane (TMP) formation.

*Keywords:* 12-tungstophosphoric salts; Isobutane alkylation; Butene alkylation; Subcritical/supercritical conditions

## 1. Introduction

The alkylation of isobutane with $C_4$ olefins has been used in commercial operation since 1940s. The alkylate produced has been used to create high quality, high octane index, and clean burning gasolines. The two current commercial processes use highly corrosive, toxic and hazardous liquid sulphuric and hydrofluoric acids. These processes raise safety, corrosion and environmental issues.

The environmental issues raised by the use of these liquid acids are at the origin of an intensive research on alternative solid acid catalysts. However, the major problem, using solid catalysts, is their rapid deactivation, due to the deposit of butene oligomers [1,2]. Several processes have been proposed, the majority of them dealing with strong acids such as triflic, sulphuric acids, $BF_3$, etc. supported on inert materials like silica. None of them are commercial yet, although the solid liquid phase (SLP) process using triflic acid on silica

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in the 5–31°C temperature range [3,4], developed by Haldor Topsoe A/S, may well be in the future while UOP has also announced a new solid acid process and RIPP (Beijing) developed at pilot plant scale a process using heteropolyacid (HPA) catalyst in supercritical and continuous flow bed conditions at 418 K (see the paper from his plenary lecture by M. He in this issue).

Heteropolyacids appear as excellent candidates for the isobutane alkylation reaction because of their unique molecularity and their strong acid properties [5–7]. Furthermore, it is clear that both acidic properties and acid site accessibility by the reactants are critical for alkylation, and it is thus interesting to study catalyst acidity modification and the use of supercritical isobutane to enhance the formation of trimethylpentanes (TMP) and to minimize the rate of catalyst deactivation. Supercritical fluids [8–10] have the properties of both liquids and gases, variable density, good mass transfer properties and zero surface tension reducing diffusional constraints and increasing solubility. The latter is expected to be beneficial by eliminating deposits and, hopefully, enhancing catalyst life time as already demonstrated successfully for several heterogeneous catalysis reactions [11–16].

Unfortunately to reach supercritical isobutane conditions, high temperatures (e.g. 418 K) are needed, which is unfavourable to the alkylation reaction as it is known to enhance secondary reactions, e.g. butene oligomerisation and cracking.

The objective of this work was to compare the catalytic properties and lifetime of different potassium salts of heteropolyacids with the Keggin structure, either in a flow or in a batch microreactor, operating in liquid phase and in none or near supercritical conditions.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

Acidic potassium salts of $H_3PW_{12}O_{40}$ were prepared according to a method described previously by adding KCl to an aqueous solution of the parent acid [6]. Five 12-tunsgstophosphoric potassium salts ($K_xH_{3-x}PW_{12}O_{40}nH_2O$) were synthesised by precipitation with increasing potassium contents in the synthesis medium corresponding to stoichiometries of: 1.0, 1.5, 2.0, 2.5 and 2.7 per Keggin unit, respectively. The precipitates were washed in distilled water and freeze-dried. The samples were characterized by $N_2$ adsorption (porosity, surface area), DTA (phase changes), TGA (content in water molecules and protons), FTIR (lattice vibration and acidic features) and XRD (crystalline structure). Their chemical composition were determined by chemical analysis of K and W elements.

### 2.2. Liquid phase alkylation in a continuous flow fixed bed reactor

The continuous fixed bed microreactor was connected to a six multiports valve enabling analyses at short time on stream. Usual conditions were: $m_{\text{cat}} = 1\,\text{g}$, catalyst particle with size $ø < 0.125\,\text{mm}$ diluted in 0.5 g SiC ($ø < 0.045\,\text{mm}$), molar ratio $\text{i-C}_4/\text{C}_4^{=} = 60$, WHSV referred to but-2-ene $0.31\,\text{h}^{-1}$, total flow rate $0.5\,\text{cm}^3\,\text{min}^{-1}$, $T_{\text{pret}} = 573\,\text{K}$ under dry He flow and $T_{\text{reaction}} = 313\,\text{K}$. The tubular reactor was carefully loaded to get a compact catalyst bed in order to prevent by pass and minimize pressure drop. The internal diameter of the reactor and the total liquid flow rate were adjusted to ensure good hydrodynamic conditions and to prevent interparticle diffusion. Internal diffusion was minimised by small particle size ($ø < 0.125\,\text{mm}$). Catalytic activity was checked to be measured under kinetic control regime, i.e. butene conversion was observed to decrease by half when using half the catalyst amount while the alkylate selectivity remained unchanged. The selectivity to alkylate (Se $C_5^+$, wt.%) is defined as the total of $C_5^+$ alkylate divided by the amount of butene converted. For $\text{i-C}_4/\text{C}_4^{=}$ alkylation only, the theoretical value is 204 wt.%. The selectivity in a given $C_n$ fraction (Se $C_n$, wt.%) is defined as total $C_n$ divided by the total alkylate ($C_5^+$, wt.%).

### 2.3. Liquid subcritical and supercritical alkylation in a batch reactor

Supercritical constants are $T_C = 407.8$, 419.6, 435.6 and 428.6 K, and $P_C = 3.63$, 4.02, 4.20 and 3.99 MPa, for isobutane, but-1-ene, *cis*-but-2-ene and *trans*-but-2-ene, respectively, i.e. $T_C = 408.4\,\text{K}$ and $P_C = 3.65\,\text{MPa}$ for $\text{i-C}_4/\text{C}_4^{=} = 20$, $T_C$ and $P_C$

Table 1
Physicochemical features of the $K_xH_{3-x}PW_{12}O_{40}$ samples

| Synthesis (K/P ratio) | True (K/P ratio)[a] | H/P (TGA) | $S_{BET}$ ($m^2\,g^{-1}$) | $H^+$ density ($10^{-6}$ mol $H^+\,m^{-2}$) |
|---|---|---|---|---|
| 2.7 | $K_{2.60}P$ | 0.40 | 156 | 0.9 |
| 2.5 | $K_{2.45}P$ | 0.55 | 150 | 1.2 |
| 2.0 | $K_{2.31}P$ | 0.69 | 95 | 2.6 |
| 1.5 | $K_{2.28}P$ | 0.72 | 61 | 3.5 |
| 1.0 | $K_{2.21}P$ | 0.79 | 50 | 3.5 |

[a] Deduced from TGA analysis of H content [6] and from chemical analysis of K and W.

being the critical temperature and pressure for the i-$C_4$/but-1-ene mixture.

Experiments in subcritical and supercritical conditions were performed in a batch reactor (160 $cm^3$) equipped with on line GC analysis, over $K_{2.6}H_{0.4}PW_{12}O_{40}$ sample (3 g). The catalyst was pretreated in situ at 573 K under dry $N_2$ flow (40 $cm^3\,h^{-1}$). Supercritical conditions were attained by introducing an initial volume of isobutane ($V_i$ i-$C_4$) at the necessary temperature and pressure ($T > 408.4$ K and $P > 3.7$ MPa). The i-$C_4/C_4^=$ mixture was then introduced under vigorous stirring (2000 rpm) to reach a final molar ratio i-$C_4/C_4^=$ of 20 or 60. Such a procedure prevents catalyst poisoning by butene oligomerisation when reaction begins.

## 3. Experimental results and discussion

### 3.1. Catalysts characterization by physical chemical techniques

As for acidic Cs salts, the increase in K/P ratio in the synthesis medium leads to samples with higher chemical K/P ratios than expected from the synthesis stoichiometries and high surface area values (Table 1). However, at variance with the Cs case [17], pore size distributions were almost unchanged over a large range of compositions. All samples were microporous irregardless of the $K^+$ content, thus ensuring that similar diffusion constraints were prevalent.

The Brønsted acid site densities given in Table 1 were calculated from the surface area and the total number of protons per Keggin unit, assuming that the acidic potassium salts corresponded to the $H_3P$ phase dispersed on the neutral $K_3P$ salt and that each heteropolyanion occupied 1.44 $nm^2$. When $H_3P$ content exceeds monolayer coverage, as in the case of $K_{2.28}P$ and $K_{2.21}P$ samples. the protonic density is taken equal to that of the bulk acid.

### 3.2. Effect of the protonic density of the heteropolycompounds on the liquid phase i-$C_4/C_4^=$ alkylation performed in the continuous flow reactor

All experiments were conducted under the conditions reported in the experimental section. All samples showed a maximum in conversion after ca. 10 min on stream. This initial induction period can be tentatively explained by the conditioning of the catalyst surface by the reactants or by a progressive saturation of the protonic sites by but-2-ene as proposed for zeolitic materials [18].

The initial alkylate selectivity was quite similar for all $K_xH_{3-x}P$ catalysts, with a value much higher than 204%, which indicates that alkylation is the main catalytic pathway and that self alkylation of isobutane also occurred in the early stages of the reaction. The thermodynamically favoured 224 TMP was the major isomer, which is also consistent with a self alkylation pathway. For all catalysts, a decrease of the alkylate selectivity with time on stream was observed. The alkylate selectivity decreased faster when the protonic density increases, the product distribution being initially similar for all samples (Fig. 1). However, catalyst stability depends on protonic density, e.g. during the first 80 min, the $K_{2.60}P$ and $K_{2.45}P$ samples exhibited little variations, saturated $C_8$ hydrocarbon being the main components (TMP Se = 60%, dimethylhexanes Se = 20%), cracked products ($C_5$–$C_7$) reaching 15%, and $C_8$ olefins only 2%, while for the $K_{2.31}P$ sample, the decrease of TMP and cracked products (respectively from 56 and 23% down to 35 and 4% after 45 min) was counterbalanced by an increased yield in dimethyl-

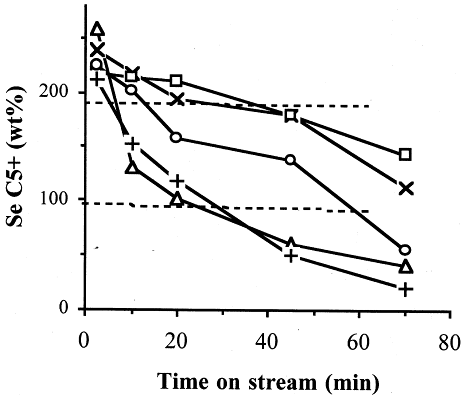

Fig. 1. Variations of the selectivity in $C_5{}^+$ product in wt.% against time on stream in a flow microreactor at 313 K, total flow rate $0.5\,\mathrm{cm}^3\,\mathrm{min}^{-1}$, $\text{i-C}_4/\text{C}_4{}^{2-} = 60$, $P = 2\,\mathrm{MPa}$, $m_{\mathrm{cata}} = 1\,\mathrm{g}$ for five samples pretreated under He flow at 573 K for 2 h. (×): $K_{2.60}P$; (□): $K_{2.45}P$; (○): $K_{2.31}P$; (△): $K_{2.28}P$; (+): $K_{2.21}P$.

hexanes and olefins (respectively from 15 and 0% up to 34 and 21%). The *n*-butane formation which reflects the hydride transfer between the *sec*-butylcarbenium ion (formed through protonation of butene) and isobutane, decreases from 4.4 to 0%. Similar and larger effects were observed for the $K_{2.28}P$ and $K_{2.21}P$ samples. On deactivated samples, $C_8$ hydrocarbons are desorbed from the surface as olefins, giving back a hydrogen to the catalyst.

These results demonstrate the influence of the Brønsted acid site density on the deactivation mechanism over heteropolycompounds. It is generally believed that high alkylate production is favoured if hydride transfer from isobutane to the *sec*-butylcarbenium ion is faster than the addition of a second olefin to the former *sec*-butylcarbenium ion. Since both pathways are bimolecular reactions, the negative influence of a high protonic density on the catalyst stability suggests that hydride transfer between isobutane and the *sec*-butylcarbenium ion requires isolated acidic sites while the addition of a second olefin to the *sec*-butylcarbenium ion may involve more acidic sites acting concomitantly. This proposal is of course only valid if acid strength is not influenced by the protonic density. Note that a similar conclusion on the positive role of acid density on $\text{i-C}_4/\text{C}_4{}^{=}$ alkylation was reported recently [19] for La–Y zeolite modified by alkali and alkaline-earth cations.

### *3.3. Comparison of* $\text{i-C}_4/\text{C}_4{}^{=}$ *alkylation properties under subcritical and supercritical conditions over the* $K_{2.6}H_{0.4}P$ *sample in a batch reactor*

Comparison of the performances of the $K_{2.6}P$ sample was carried out in liquid subcritical and supercritical phases conditions within the Peng–Robinson equation diagram shown in Fig. 2, the different phases being abbreviated as follows: LTL = low temperature liquid phase, HTL = high temperature liquid phase, SC = supercritical, LDSC = low density supercritical fluid and HDSC = high density supercritical fluid, as indicated in Fig. 2.

As usually observed in liquid phase, activity and selectivity of the alkylation reaction are strongly dependent on reaction conditions. This holds particularly true for the influence of the $\text{i-C}_4/\text{C}_4{}^{=}$ ratio, reaction temperature, etc. For example, in LTL phase, a $\text{i-C}_4/\text{C}_4{}^{=}$ ratio increase from 20 to 60 raised the $C_8$ formation from 79.1 up to 88.7%, the olefin formation being suppressed (Table 2). Under all conditions, a temperature increase led mainly to an increase in the amount of the cracked products ($C_5$–$C_7$) at the expense of the alkylated compounds, even in supercritical phase, and in the $C_8$ fraction, to an increase of the DMHs fraction at the expense of TMP. It appears that the temperature increase favours the addition of a second olefin to *sec*-butyl carbenium ion rather than the

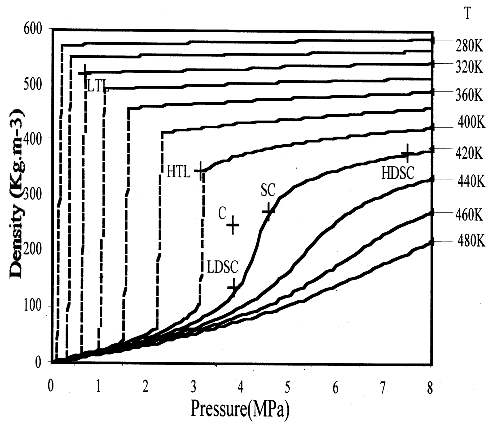

Fig. 2. Correlation curves between density and pressure for isobutane at different temperatures using the Peng–Robinson equation of state for isobutane. Symbols are defined in the text, C being the critical point for isobutane.

Table 2
Catalytic data for $K_{2.6}H_{0.4}P$ sample in isobutane alkylation in liquid, subcritical and supercritical phases after 80 min[a]

| | Experimental phases | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | A | | | B | | | C | | |
| | LTL | HTL | SC | LTL | HTL | SC | LTL | HTL | SC |
| $T$ (K) | 313 | 403 | 418 | 313 | 403 | 418 | 313 | 403 | 418 |
| $V_i$ i-$C_4$ ($cm^3$) | 58.5 | 58.5 | 58.5 | 113 | 113 | 113 | 58.5 | 58.5 | 58.5 |
| i-$C_4/C_4^=$ ratio | 19.8 | 19.8 | 19.9 | 20.2 | 19.9 | 19.9 | 59.9 | 60.4 | 60.7 |
| Density ($g\,cm^{-3}$) | 0.52 | 0.36 | 0.11–0.33[b] | 0.52 | 0.36 | 0.29–0.33[b] | 0.52 | 0.36 | 0.11–0.33[b] |
| $C_4^=$ conv. (wt.%) | 56 | 64 | 61 | 93 | 80 | 88 | 100 | 100 | 100 |
| $C_5^+$ (wt.%) | | | | | | | | | |
| $C_5$–$C_7$ | 1.4 | 17.5 | 29.1 | 0 | 9.1 | 9.1 | 0 | 11.9 | 16.8 |
| $C_8$ | 79.1 | 73.1 | 62.9 | 81.3 | 82.2 | 77.5 | 88.7 | 78.9 | 60.8 |
| $C_9^+$ | 19.5 | 9.4 | 8.0 | 18.6 | 8.7 | 13.4 | 11.3 | 9.2 | 22.4 |
| $C_8$ (wt.%) | | | | | | | | | |
| TMPs | 69.1 | 42.4 | 50.6 | 82.0 | 59.1 | 57.0 | 81.8 | 67.1 | 47.3 |
| DMHs | 18.4 | 35.3 | 41.4 | 18.0 | 31.5 | 36.0 | 18.2 | 32.9 | 50.0 |
| $C_8^=$ | 12.5 | 22.3 | 8.0 | 0 | 9.4 | 7.0 | 0 | 0 | 2.3 |

[a] Influence of the i-$C_4/C_4^=$ ratio and of the initial volume of i-$C_4$ ($V_i$ i-$C_4$) used to wet the catalyst (see text).
[b] Density value after the addition of i-$C_4/C_4^=$ mixture.

hydride transfer from isobutane to the former cation, even in supercritical conditions.

The *initial* amount of i-$C_4$ ($V_i$ i-$C_4$) introduced, before the i-$C_4/C_4^{2-}$ mixture was added, was observed to strongly influence the catalyst behaviour, e.g. when a large initial volume of i-$C_4$ was used, $C_8$ compounds (particularly TMP) were observed to increase at the expense of $C_8$ olefins and cracked products (Table 2, parts A and B).

As it is known that the properties of supercritical fluids are dependent on their nature and on their density, experiments were performed along the isotherm curve at 418 K in Fig. 2. Catalytic data show that, compared to the reference experiments near SC, the use of a LDSC or HDSC resulted in different levels of butene conversion and distinct selectivities (Table 3). The increase of the density led to a total conversion of butene, an increased yield of $C_8$, particularly the TMPs, and lower amounts of heavy compounds ($C_9^+$). In addition, in HDSC conditions the formation of olefins was suppressed, which proves that hydride transfer capacity was preserved in presence of a dense fluid.

The higher activity of the catalyst for alkylation in high density supercritical conditions can thus be related to the higher solvation ability of dense isobutane and higher diffusion properties. It is proposed that in such conditions consecutive reactions such as polyalkylation and cracking are minimized and that

Table 3
Catalytic data for $K_{2.6}H_{0.4}P$ sample for alkylation in liquid subcritical and supercritical phases after 80 min. Influence of the supercritical phase density[a]

| Phases | $T_{reac}$ (K) | $P$ (MPa) | Density ($g\,cm^{-3}$) | $C_4^=$ conv. (%) | $C_5^+$ distribution (wt.%) | | | $C_8$ distribution (wt.%) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $C_5$–$C_7$ | $C_8$ | $C_9^+$ | TMP | DMH | $C_8^=$ |
| LDSC | 418 | 3.9–4.0[b] | 0.11–0.13[b] | 77 | 12.4 | 60.2 | 27.3 | 41.2 | 40.4 | 18.3 |
| Near SC | 418 | 4.7–6.2[b] | 0.29–0.33[b] | 88 | 9.1 | 77.5 | 13.4 | 57.0 | 36 | 7.0 |
| HDSC | 418 | 7.7–9.0[b] | 0.36–0.38[b] | 100 | 3.2 | 89.2 | 7.6 | 61.2 | 38.7 | 0 |

[a] Conditions: final i-$C_4/C_4^=$ ratio = 20.
[b] Density and pressure values after addition of i-$C_4/C_4^=$ mixture.

more efficient extraction of heavy carbonaceous compounds takes place.

## 4. Conclusion

The influence of the protonic site density has been studied and was observed to be crucial in akylation reaction and detrimental for high values. The latter point can be explained by preferential olefin oligomerisation, the main side reaction responsible of catalyst poisoning if catalysts of high protonic density are used.

Over a $K_{2.6}H_{0.4}P$ sample in batch conditions a decrease in the quality of the alkylate with temperature was observed, whatever using subcritical or supercritical conditions. However, the increase of the density of the supercritical phase, in isothermal conditions, resulted in the improvement of the alkylate quality, almost withstanding the negative effect of the high temperature necessary to reach the supercritical conditions.

We conclude that in the presence of porous alkaline salts of 12-tungstophosphoric acid, the alkylation to oligomerisation ratio is significantly improved over solids having a low density of strong Brønsted sites and by the use of high density supercritical isobutane conditions, the latter favouring hydride transfer and TMPs formation. However, the catalytic performances at supercritical conditions in a batch reactor does not appear to match the performance of the current industrial practice.

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