Sustainable heterogeneous acid catalysis by heteropoly acids

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Abstract

Heterogeneous acid catalysis by heteropoly acids (HPAs) has the potential of substantial economic and green benefits. Its application, however, has been limited because of the difficulty of catalyst regeneration due to a relatively low thermal stability of HPAs. The aim of this paper is to discuss the perspectives of acid catalysis by solid HPAs, in particular focusing on several approaches that could help overcome the deactivation of HPA catalysts to achieve sustainable catalyst performance. These approaches include: developing novel HPA catalysts possessing high thermal stability, modification of HPA catalysts to enhance coke combustion, inhibition of coke formation on HPA catalysts during operation, reactions in supercritical fluids and cascade reactions using multifunctional HPA catalysis.
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1. Introduction

Today, catalysis by heteropoly acids (HPAs) is a well-established area [1–5]. Arguably, it is one of the most successful areas in contemporary catalysis, where systematic studies of HPA catalysts at the molecular level have led to a string of large-scale industrial applications [4]. HPAs possess unique physicochemical properties, with their structural mobility and multifunctionality the most important for catalysis [1–4]. HPAs, unlike metal oxides and zeolites, have discrete and mobile ionic structure. They possess, on one hand, a very strong Brønsted acidity and, on the other hand, appropriate redox properties, which can be tuned by varying the chemical composition of HPA. Consequently, acid catalysis and catalytic oxidation are the two major areas of catalysis by HPAs.

Although there are many structural types of HPAs [1,4,6], the majority of the catalytic applications use the most common Keggin type HPAs, especially for acid catalysis. The Keggin HPAs comprise heteropoly anions of the formula $[XM_{12}O_{40}]^{n-}$ (α-isomer), where X is the heteroatom (P^{5+}, Si^{4+}, etc.) and M is the addenda atom (Mo^{6+}, W^{6+}, etc.). The structure of the Keggin anion is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedra MO_6 (Fig. 1). Most typical HPAs, such as $H_3PW_{12}O_{40}$, H_4 $SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$, are commercially available.

Presently, HPAs are used as catalysts in several industrial processes [4], the most important shown in Table 1. The top two are heterogeneously catalysed selective oxidations in gas phase: the oxidation of methacrolein to methacrylic acid and ethylene to acetic acid. The rest are acid-catalysed reactions including the homogeneous liquid-phase hydration of olefins, the biphasic polymerisation of THF to poly(tetramethylene glycole) and the gas-phase synthesis of ethyl acetate from ethylene and acetic acid (BP's AVADA process).

Heterogeneous acid catalysis by HPAs has the potential of a great economic reward and green benefits—hence much interest in it [1–5]. The acidity of HPAs is stronger than that of the conventional solid acid catalysts (e.g., acidic oxides and zeolites), decreasing in the order: $H_3PW_{12}O_{40} > H_4$ $SiW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiMo_{12}O_{40}$ [1,2,4]. The acid sites in HPA are more uniform and easier to control than those in other solid acid catalysts. Being stronger acids, HPA are generally more active catalysts than the conventional solid acid catalysts, which allows efficient operating under milder conditions. However, there is a serious problem to HPA catalysts—their low thermal stability, hence limited reaction temperature and, especially, difficulty of regeneration of solid HPA catalysts (decoking) [2,4]. The thermal stability of Keggin HPAs, defined as the temperature at which all acidic protons are lost, decreases in the order: $H_3PW_{12}O_{40}$ (465 °C) > H_4 $SiW_{12}O_{40}$ (445 °C) > $H_3PMo_{12}O_{40}$ (375 °C) > $H_4SiMo_{12}O_{40}$

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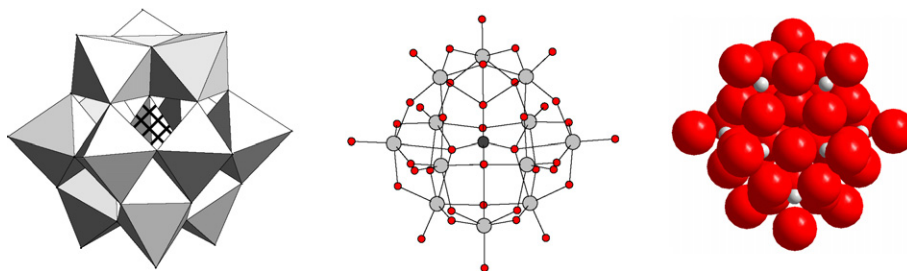*E-mail address:* kozhev@liverpool.ac.uk.

Fig. 1. The structure of the Keggin heteropoly anion $[\alpha\text{-XM}_{12}O_{40}]^{n-}$ in polyhedral (left), ball-and-stick (middle) and space-filling (right) representations [6].

Table 1
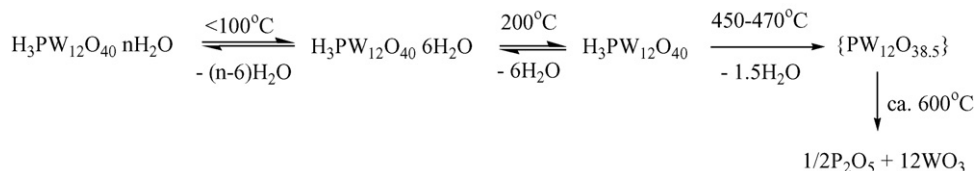Industrial processes catalysed by heteropoly acids [4]

Reaction	Catalyst	Type	Start
$CH_2\text{-}C(CH_3)CHO + YO_2 Yr YCH_2\text{-}C(CH_3)COOH$	Mo–V–P–HPA	het	1982
$CH_2\text{-}CH_2 Y + YO_2 Yr YCH_3COOH$	$Pd\text{-}H_4SiW_{12}O_{40}/SiO_2$	het	1997
$CH_2\text{-}CHCH_3 Y + YH_2O Yr YCH_3CH(OH)CH_3$	$H_4SiW_{12}O_{40}$	hom	1972
$CH_2\text{-}C(CH_3)_2 Y + YH_2O Yr Y(CH_3)_3COH$	$H_3PMo_{12}O_{40}$	hom	1984
$CH_3CH\text{-}CHCH_3 Y + YH_2O Yr YCH_3CH(OH)CH_2CH_3$	$H_3PMo_{12}O_{40}$	hom	1989
$n THF Y + YH_2O Yr YHO\text{-}[\text{-}(CH_2)_4\text{-}O\text{-}]_n\text{-}H$	$H_3PW_{12}O_{40}$	bip	1985
$CH_2\text{-}CH_2 Y + YCH_3COOH Yr YCH_3CH_2O_2CCH_3$	$H_4SiW_{12}O_{40}/SiO_2$	het	2001

hom = homogeneous, het = heterogeneous and bip = biphasic.

(350 °C), the strongest acid $H_3PW_{12}O_{40}$ being the most stable [2,4].

Fig. 2 shows the TGA profile for $H_3PW_{12}O_{40}$ hydrate [4]. Three main peaks can be observed: (1) a peak at a temperature below 100 °C corresponding to the loss of physisorbed water (a variable amount depending on the number of hydration waters in the sample); (2) a peak in the temperature range of

of 370–600 °C centred at 450–470 °C due to the loss of $1.5H_2O$ molecules corresponding to the loss of all acidic protons and the beginning of decomposition of the Keggin structure. For tungsten HPAs, the latter loss is practically irreversible, which causes irreversible loss of catalytic activity. The decomposition is complete at about 610 °C to form P_2O_5 and WO_3, which is shown by an exotherm in DTA and DSC [4,7]. Therefore, the thermal decomposition of $H_3PW_{12}O_{40}$ follows the course:

$$H_3PW_{12}O_{40}\, nH_2O \underset{-(n-6)H_2O}{\overset{<100^{\circ}C}{\rightleftharpoons}} H_3PW_{12}O_{40}\, 6H_2O \underset{-6H_2O}{\overset{200^{\circ}C}{\rightleftharpoons}} H_3PW_{12}O_{40} \underset{-1.5H_2O}{\overset{450\text{-}470^{\circ}C}{\longrightarrow}} \{PW_{12}O_{38.5}\}$$

$$\downarrow ca.\ 600^{\circ}C$$

$$1/2P_2O_5 + 12WO_3$$

100–280 °C centred at about 200 °C accounted for the loss of ca. $6H_2O$ molecules per Keggin unit, corresponding to the dehydration of a relatively stable hexahydrate $H_3PW_{12}O_{40}\cdot 6H_2O$, in which the waters are hydrogen-bonded to the acidic protons to form the $[H_2O\cdots H^+ \cdots OH_2]$ ions; and (3) a peak in the range
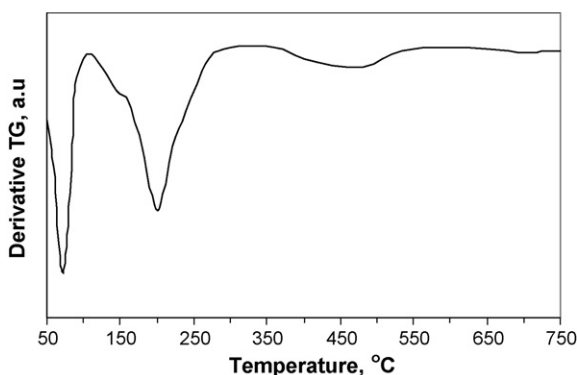

Fig. 2. TGA for $H_3PW_{12}O_{40}$ hydrate [4].

Coke formation is the most frequent cause of catalyst deactivation in heterogeneous acid-catalysed organic reactions [8–11]. Therefore, much research has been carried out on coke formation on the catalysts for petrochemical processes (cracking, reforming, hydrotreatment, etc.). The most studied catalysts include amorphous silica–alumina, zeolites and acidic alumina, as well as those doped with metals such as palladium, platinum and nickel [8–11]. Catalyst regeneration (decoking) is usually carried out by coke combustion at 450–550 °C [8–11]. For the oxide and zeolite catalysts possessing sufficient thermal stability, the combustion is an effective method to recover catalyst activity. Solid HPA catalysts in organic reactions, like the conventional solid acid catalysts, suffer from deactivation by coking. Little information is available about coke formation on HPA catalysts though. For the coked HPA catalysts, the problem is that the standard catalyst regeneration by coke combustion is not applicable due to the low thermal stability of HPAs, which makes coking the most serious problem for heterogeneous acid catalysis by HPAs [2,4]. Other possible causes of HPA deactivation, such as poisoning, aggregation, dehydration and decomposition

of HPA, could also play a role, but these are not as crucial as the coking, at least at moderate reaction temperatures 100–300 °C.

The question is how to overcome the problem of coking and make heterogeneous acid catalysis by HPA sustainable? Several directions that may be instrumental to achieve this goal will be discussed here. These are: developing novel HPA catalysts possessing high thermal stability; modification of HPA catalysts to enhance coke combustion; inhibition of coke formation on HPA catalysts during operation; reactions in supercritical fluids; and cascade reactions using multifunctional HPA catalysis.

2. Development of novel HPA catalysts possessing high thermal stability

There has been considerable activity in this direction recently, with the main focus on oxide composites comprising W(VI) polyoxometalates and niobia or zirconia ([12,13] and references therein). The composites are usually prepared by wet chemical synthesis, followed by calcination at 500–750 °C, i.e., at temperatures higher than the temperature of HPA decomposition. The materials thus made contained HPA precursors or HPA decomposition products, possessing Brønsted and Lewis acid sites of moderate strength. These materials have been found active in Friedel–Crafts reactions, with good catalyst recycling. However, their activity is considerably lower than that of the standard HPA catalysts. For example, the H_3PO_4–WO_3–Nb_2O_5 (9:55:36 wt.%) composite with a surface area of $58 \, m^2/g$ was prepared by interaction of $(NH_4)_{10}W_{12}O_{41}$, Nb(V) oxalate and H_3PO_4 in aqueous solution, followed by evaporation and calcination at 500 °C [12]. It was tested in the alkylation of anisole by benzyl alcohol (Eq. (1)) to yield 94% of the alkylation product. The catalyst was recyclable many times without loss of its activity. This catalyst, however, was less active than the $H_3PW_{12}O_{40}/Nb_2O_5$ catalyst prepared by the usual impregnation of niobia with $H_3PW_{12}O_{40}$, but the latter was not recyclable

(1)
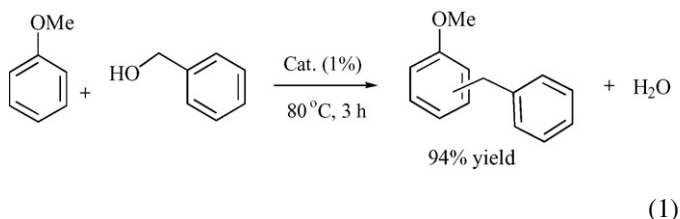
Another composite was obtained by impregnation of 15% $H_4SiW_{12}O_{40}$ on zirconia and calcination at 700 °C [13]. From Raman spectra, it contained ZrO_2-anchored mono-oxotungstate and possessed Brønsted and Lewis acid sites. This solid acid was active in the acylation of veratrole by benzoic anhydride (Eq. (2)), with no leaching and good catalyst recycling after regeneration by coke combustion at 500 °C. However, this catalyst was less active than HY zeolite per 1 g catalyst, whereas the standard HPA catalysts are about 10 times more active than the HY. Therefore, the above-mentioned composite materials based on niobia and zirconia possess relatively weak acid sites and as solid acid catalysts have practically no advantage over the acidic

zeolites. Work should continue to obtain the HPA materials possessing stronger acid sites

(2)
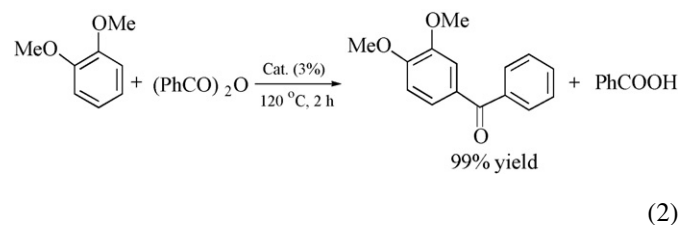
3. Modification of HPA catalysts to enhance coke combustion

Doping of solid acid catalysts with platinum group metals (PGM) such as Pd and Pt is well known to enhance catalyst regeneration by coke combustion. For example, this method has been used for zeolite and alumina catalysts for alkane isomerisation and cracking [8,9]. We have found that the PGM doping is also effective for enhancing the regeneration of solid HPA catalysts [14–17].

The effect of Pd doping on coke combustion is apparent from the TGA/TPO for the coked 20% $H_3PW_{12}O_{40}/SiO_2$ (Fig. 3) [14,15]. The catalyst was coked by propene in a fixed bed flow reactor at 200 °C. In the absence of Pd, coke burns at about 500 °C. In the case of Pd-doped catalysts, this temperature decreases, the higher the Pd loading the lower the temperature of coke combustion. With 2% Pd doping, coke burns at 350 °C, which is well below the temperature of $H_3PW_{12}O_{40}$ decomposition.

XPS and ^{31}P MAS NMR showed that coking does not affect the structure of $H_3PW_{12}O_{40}$ [15]. From XPS, the oxidation state of tungsten was 6+ in both the fresh and coked catalyst. The ^{31}P chemical shift was the same for the as-made, Pd-doped and coked catalyst (ca. −15 ppm versus 85% H_3PO_4, as expected for $H_3PW_{12}O_{40}$), which indicates that the Keggin structure remains intact. ^{13}C CP/MAS NMR for coked $H_3PW_{12}O_{40}$ catalysts showed that Pd doping does affect the nature of coke depositing on the catalyst [14]. On the undoped catalyst, both aliphatic (soft) and polyaromatic (hard) coke formed. In contrast, the Pd-
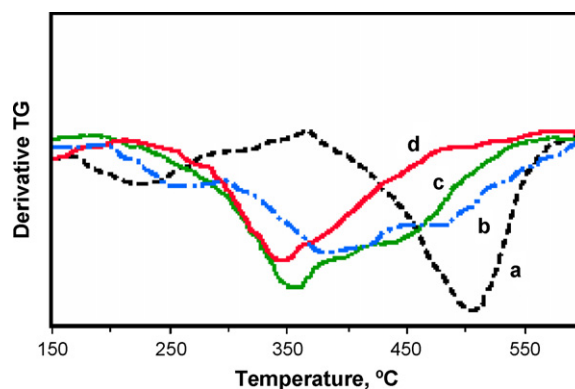

Fig. 3. TGA/TPO in air for Pd-doped 20% $H_3PW_{12}O_{40}/SiO_2$ coked by propene in a fixed bed flow reactor at 200 °C: (a) no Pd doping, (b) 1.6% Pd, (c) 2.0% Pd and (d) 2.5% Pd [14,15].
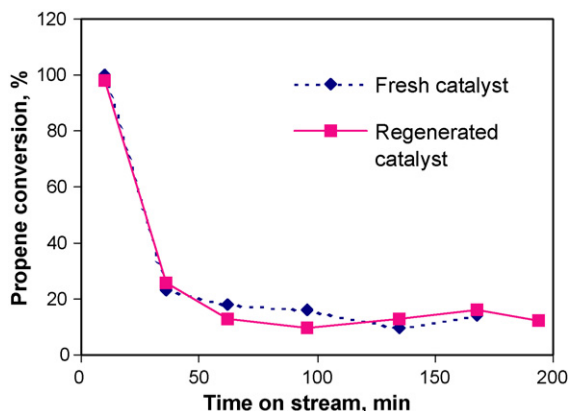
Fig. 4. The performance of fresh and regenerated 2.5% Pd/20% $H_3PW_{12}O_{40}$/SiO$_2$ catalysts in the gas-phase propene oligomerisation (fixed bed flow reactor, 200 °C, 2% C_3H_6 in N_2, GHSV = 6000 h^{-1}; in situ regeneration by air calcination at 350 °C/2 h followed by reduction with H_2 at 225 °C/2 h) [15].

doped catalyst built only the aliphatic coke which would burn off easier. From these results, the effect of Pd appears to be two-fold. On one hand, the Pd can catalyse the combustion of coke. On the other, it inhibits the formation of hard polyaromatic coke, which is more difficult to burn off [14,15].

The Pd doping was found effective to enhance the regeneration of silica-supported $H_3PW_{12}O_{40}$ catalyst for the gas-phase oligomerisation of propene [15]. The reaction was carried out in a fixed bed flow reactor, yielding C_{12} to C_{18} oligomers as the major products. The undoped and Pd-doped $H_3PW_{12}O_{40}$ catalysts both had a high initial activity, but suffered from fast deactivation due to coking. As expected from the TPO studies, the Pd doping allowed for the catalyst to be regenerated in situ by the combustion of coke at 350 °C to fully regain its activity (Fig. 4). In contrast, the undoped $H_3PW_{12}O_{40}$ catalyst was impossible to regenerate under such conditions.

Doping with Pd and Pt also proved effective for regeneration and recycling of HPA catalysts for Friedel–Crafts acylation in liquid-phase batch processes [16,17]. This is illustrated by our studies of Fries rearrangement of phenyl acetate, a practically important reaction yielding acylated phenols (Eq. (3)). Solid HPAs are very efficient catalysts for this reaction, much more active than H_2SO_4 and acidic zeolites [18,19]. The bulk acidic
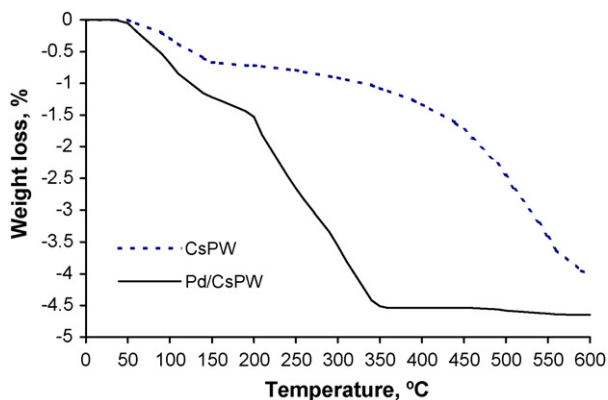

Fig. 5. TGA/TPO in air for the coked catalysts CsPW and 2.1% Pd/CsPW after use for Fries reaction of PhOAc (in nitrobenzene, 130 °C, 2 h) [16].
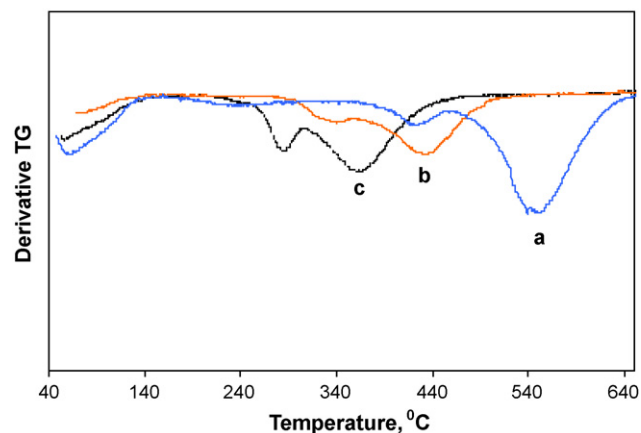

Fig. 6. TGA/TPO in air for the coked catalysts after use for Fries reaction of PhOAc (in nitrobenzene, 130 °C, 2 h): (a) CsPW, (b) 0.3% Pt/CsPW and (c) 1% Pt/CsPW [17].

salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) which is insoluble, hence easily recyclable, is especially good solid acid catalyst for this reaction. However, this catalyst is deactivated by carbonaceous deposit and requires regeneration. From the TGA/TPO (Fig. 5), coke combustion on the CsPW catalyst after its use for the Fries rearrangement of PhOAc is complete at about 550 °C. This temperature is too high for the regeneration of this catalyst. In the case of Pd-doped CsPW (2.1% Pd), coke is already gone at 350 °C [16].

Platinum doping was found to be even more effective, enhancing coke combustion at a Pt loading as low as 0.3% [17]. The TGA/TPO (Fig. 6) shows two combustion peaks at a lower and higher temperature, which can be attributed to soft aliphatic coke and hard polyaromatic coke, respectively

$$(3)$$
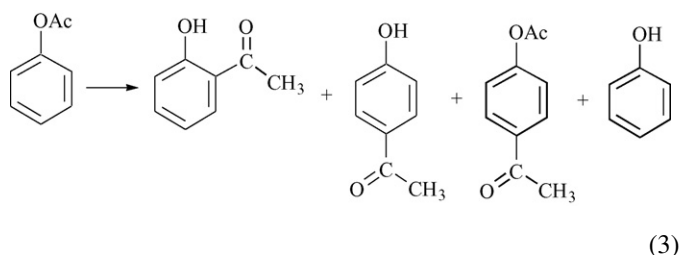
The doping with Pd and Pt allows sustainable ex situ regeneration of solid HPA catalysts for Fries reaction by coke combustion [16,17]. Fig. 7 shows excellent recycling of the 0.3% Pt/CsPW catalyst in the Fries rearrangement of PhOAc. After each run the catalyst was separated and regenerated by air calcination at 350 °C, followed by steaming at 200 °C to restore the acid sites. As evidenced by FTIR, the Keggin structure of the CsPW remained unchanged after catalyst regeneration and reuse [17]. Care must be taken regarding possible effect of PGM on reaction selectivity. Although no such effect was observed in the Fries reaction [16,17], it might be the case in other reactions.

4. Inhibition of coke formation on HPA catalysts

Obviously, it is much better to prevent the catalyst from coking to avoid its regeneration in the first place. In collaboration
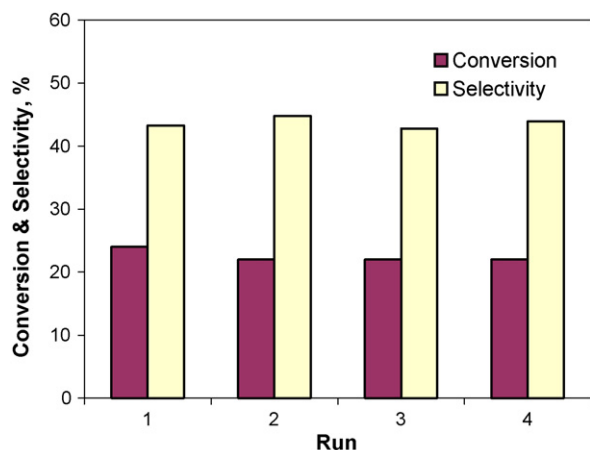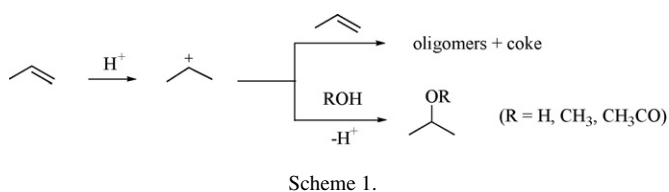
Fig. 7. Catalyst reuse in Fries rearrangement of PhOAc: conversion and total acylation selectivity in successive runs (0.3% Pt/CsPW (2.3 wt.%), in nitrobenzene, 130 °C, 2 h) [17].

Scheme 1.

with BP, we studied coke inhibition in HPA catalysed propene oligomerisation as a model reaction [14,15]. The reaction occurs via the carbenium ion mechanism yielding propene oligomers and coke (Scheme 1). The oligomers may be considered as coke precursors. Addition of nucleophilic molecules, such as water, methanol and acetic acid, was found to greatly affect the reaction selectivity by reacting with carbenium ion intermediates to yield oxygenates at the expense of the oligomers and coke (Scheme 1). The nucleophilic additives also help remove coke precursors from the catalyst surface. Water was found to be the most effective coke inhibitor, with the amount of coke decreased to about 1/7 of the background (Table 2) [15].

The addition of water to the feed has been used by BP in order to prolong catalyst lifetime in the vapour-phase synthesis of ethyl acetate over $H_4SiW_{12}O_{40}/SiO_2$ catalyst (Table 1) [20,21]. In 2001, this process was commercialised on a scale of 220,000 t/year in England. Table 3 illustrates the high catalytic activity of HPA in comparison with other solid acid catalysts in terms of the space–time yield [20]. Co-feeding water is essential for the stable performance of the HPA catalyst. Without water, the catalyst deactivates quickly due to coking. The addition of water causes the formation of ethanol and diethyl ether as

Table 2
Effect of additives (7 vol.%) to propene flow on coke formation on the 40% $H_3PW_{12}O_{40}/SiO_2$ catalyst at 150 °C [15]

Additive	Time on stream (h)	Amount of coke (%)
None	3.0	3.6
H_2O	3.0	0.5
Methanol	3.0	1.7
Acetic acid	3.0	2.6

by-products, which are recycled back to the reactor. The effect of water is probably manifold. Besides the coke inhibition, the water should stabilise the catalyst by preventing it from dehydration. Therefore, for the ethyl acetate process, which tolerates the presence of some water, the inhibition of coke formation by water proved to be a success, which ensured economically viable lifetime of HPA catalyst [20,21]. It should be pointed out, however, that this is not a universal recipe. It would hardly work out for the reactions incompatible with water such as Friedel–Crafts acylation and alkane isomerisation.

5. Reactions in supercritical fluids

Heterogeneous catalysis in supercritical fluids (SCFs) offers considerable benefits (for a review, see [22]). Use of SCFs in heterogeneous catalysis can enhance the reaction rate, selectivity control and product separation, intensify mass and heat transfer, facilitate catalyst regeneration and increase catalyst lifetime. SCFs possess unique solvent properties which have long been utilized in separation technology (extraction and chromatography) and are now gaining increasing interest for application in catalytic synthesis. SCFs are miscible with gases and can dissolve solids and liquids. Usually, the SCF methodology is applied in the region near the critical point, $(1.0–1.2)T_c$ and $(1–2)P_c$, where densities are close to, or above, the critical density of the fluid, and the dissolution power of the fluid is at its maximum. SCFs exhibit considerably higher solubilities than corresponding gases for heavy organic compounds which may deactivate catalysts and promote coking. Changing process conditions from gas phase to dense supercritical medium may suppress this deactivation. Furthermore, enhanced diffusivity in supercritical system can accelerate the transfer of coke precursors from the catalyst surface.

It has been reported that the lifetime of solid HPA catalysts can be significantly longer in supercritical systems than in conventional gas or liquid systems, and regeneration of HPA catalysts deactivated by coking can be accomplished in supercritical systems by extracting the carbonaceous deposits from the catalyst surface [23–26]. The isomerisation of *n*-butane has been studied in the supercritical *n*-butane in a flow reactor using 20% $H_3PW_{12}O_{40}/TiO_2$, 20% $H_4SiW_{12}O_{40}/TiO_2$ (260 °C, 110 bar), sulfated zirconia (215 °C, 61 bar) and H-mordenite (300 °C, 138 bar) as the catalysts [24,25]. The gas-phase isomerisation on these catalysts exhibited rapid deactivation due to catalyst coking. The supercritical system showed a stable activity without catalyst deactivation, for more than 5 h on stream in the case of HPA/TiO_2. The catalysts coked in the gas-phase isomerisation could be regenerated in the supercritical system at the *n*-butane density close to its critical value to almost fully regain their initial activity. On the HPA/TiO_2 and sulfated zirconia in supercritical *n*-butane, the selectivity to isobutane reached 80% at 20–25% conversion. H-mordenite gave <40% selectivity at 25% conversion, with *n*-butane cracking dominating.

The alkylation of isobutane with butenes competing with butene oligomerisation has been studied in supercritical and conventional gas–liquid systems over a range of solid acid catalysts such as 20% $H_3PW_{12}O_{40}/TiO_2$, 20% $H_4SiW_{12}O_{40}/TiO_2$, sul-

Table 3
Solid acid catalysts for the synthesis of ethyl acetate from ethylene and acetic acid [20]

Catalyst	C_2H_4/AcOH (mol/mol)	Temperature (°C)	Pressure (bar)	Contact time (s)	H_2O in feed (mol%)	STY (g/L h)
H-montmorillonite	5/1	200	50	4	0	144
XE386 resin	5/1	155	50	4	0	120
Nafion-H	5/1	170	50	4	0	102
H-Zeolite Y	5/1	200	50	4	0	2
$H_4SiW_{12}O_{40}$/SiO_2	12/1	180	10	2	6	380

fated zirconia, 15% WO_3/TiO_2 and 0.5% Pt/γ-Al_2O_3–Cl [26]. In the supercritical system (140–165 °C, 40–45 bar), both reactions were fast, with a steady catalytic activity. In contrast, in the liquid phase and particularly in the gas phase the reactions occurred slower, and rapid catalyst deactivation was observed.

It should be noted, however, that the benefits gained from the SCF methodology must be carefully weighed against the higher costs of supercritical process technology. Typically reactions at supercritical conditions require high pressures, and the potential danger of such conditions should never be ignored [22].

6. Cascade reactions using multifunctional HPA catalysts

The development of one-pot cascade processes without intermediate separation steps using multifunctional catalysts is an important strategy to carry out sustainable organic synthesis with a high atom and energy efficiency [27,28]. Multifunctional catalysts contain two or more catalytic functions (acid, base, metal, etc.) acting synergistically to carry out a cascade reaction. There is evidence that a combination of HPA acid catalysis and a redox catalysis in a heterogeneous cascade process may lead to efficient processing, less sensitive to deactivation by coking compared to the conventional HPA catalysis [29].

This approach can be illustrated by our study of the bifunctional Pd-HPA catalyst for the one-step conversion of acetone to methyl isobutyl ketone (MIBK) [29]. This is a cascade reaction involving the acid-catalysed condensation of acetone to diacetone alcohol (DA) and its dehydration to mesityl oxide (MO), followed by hydrogenation of MO to MIBK on Pd metal sites (Scheme 2). The MIBK can react further in the same way to give diisobutyl ketone (DIBK). All these steps occur simultaneously on a bifunctional Pd-acid catalyst in gas or liquid phase. Both MIBK and DIBK are good solvents for paint and produced on a large scale.
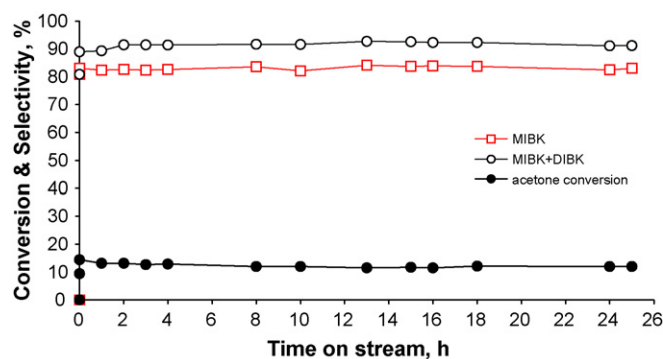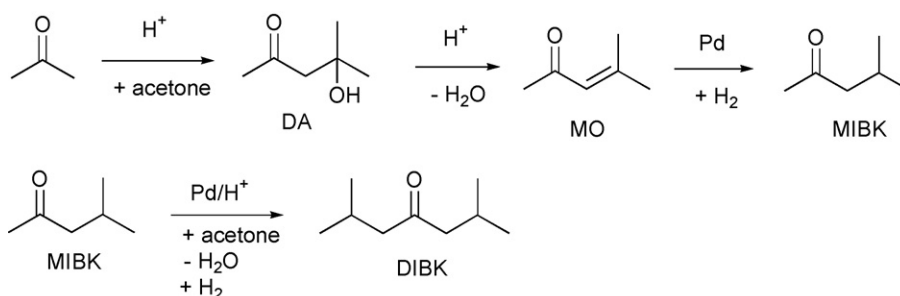

Fig. 8. Gas-phase acetone conversion and product selectivities vs. time on stream (fixed bed flow reactor, 0.20 g 0.5% Pd/CsPW, 7.5 mL/min H_2 flow, [acetone]/[H_2] = 2:1, 100 °C) [24].

The Pd-doped CsPW catalyst was found to be on a level with the best catalysts for this reaction [29]. In the continuous gas-phase process, it gives 83% MIBK selectivity, with 91% total selectivity to MIBK + DIBK. The reaction occurs at 100 °C, whereas the usual temperature is above 140 °C (e.g., with Pd–zeolite). This may be explained by the stronger acidity of HPA compared to the zeolite. In the liquid-phase batch process, 95% MIBK and 98% total MIBK + DIBK was obtained at an unprecedented low H_2 pressure of only 5–7 bar (usually 20 bar or higher). In the gas-phase reaction, the HPA catalyst showed excellent durability: no deactivation was observed during 25-h operation (Fig. 8). It should be noted that in the absence of H_2 the catalyst lost its activity in about 4 h (in this case, MO was the main reaction product). Only a small amount of coke (ca. 1%) was formed in the reaction, which did not affect the catalyst performance. Such a minor coking may be due to the efficient coke removal by in situ hydrogenation. Therefore the combination of the HPA acid catalysis with Pd-catalysed hydrogenation in heterogeneous cascade process is effective to avoid catalyst deactivation by coking.

Scheme 2.

Similarly, a combination of HPA acid catalysis with catalytic oxidation may be effective to reduce catalyst coking. However, in such a case it may be more difficult to make the acid and oxidation steps compatible.

7. Conclusions

Heterogeneous acid catalysis by heteropoly acids offers substantial economic and environmental benefits. However, the relatively low thermal stability of HPAs is a serious problem to the HPA catalysis due to the difficulty of regeneration of solid HPA catalysts (decoking). Several approaches can be instrumental in overcoming the deactivation of HPA catalysts to achieve sustainable catalyst performance. One of these may be the development of novel HPA materials possessing high thermal stability. Recent studies have provided some new solid acid catalysts, e.g., those comprising W(VI) polyoxometalates on ZrO_2 and Nb_2O_5, exhibiting good regeneration and reuse. However, these catalysts have weak acid sites and low catalytic activity compared to the standard HPA catalysts. Another approach is the modification of HPA catalysts by Pt and Pd to enhance coke combustion. This method has proved effective for in situ and ex situ catalyst regeneration by the combustion of coke at 350 °C without destroying the structure of HPA. For acid-catalysed processes tolerating the presence of water, co-feeding water can effectively inhibit coke formation and prolong catalyst lifetime (BP's AVADA process). The lifetime of HPA catalyst can be prolonged when the reaction is carried out in supercritical system. However, high cost of supercritical process technology should be taken into account. Finally, HPAs have the potential to be used effectively within heterogeneous multifunctional catalysts for cascade processes involving acid and redox catalysis. Such processes can have high efficiency and greater stability towards HPA deactivation.

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