



Heterogeneous acid catalysis by heteropoly acids: Approaches to catalyst deactivation[☆]

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ABSTRACT

Heterogeneous acid catalysis by heteropoly acids (HPAs) has the potential of great economic rewards and green benefits. Its application, however, has been limited to some extent because of a relatively low thermal stability of HPAs, hence difficulty of catalyst regeneration (decoking). The aim of this paper is to discuss approaches to the problem of catalyst deactivation that could be instrumental to achieve sustainable performance of solid HPA catalysts. These approaches include: developing new 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

Catalysis by heteropoly acids (HPAs) is at the forefront of fundamental and applied catalysis [1–12]. Systematic mechanistic studies of HPA catalysis at the molecular level have led to a series of large-scale industrial applications of these catalysts in organic synthesis [1,7]. HPAs possess unique physicochemical properties, with their structural mobility and multifunctionality being the most important for catalysis [1–7]. Unlike metal oxides and zeolites, HPAs have discrete and mobile ionic structure. On the one hand, HPAs possess very strong Brønsted acidity, and on the other, appropriate redox properties. Both the acid and redox properties can be tuned by varying the chemical composition of HPA. Consequently, acid catalysis and selective oxidation are the major areas of catalytic applications of HPAs.

There are many structural types of heteropoly compounds (polyoxometalates), which have been reviewed in detail elsewhere [13,14]. The majority of catalytic applications use the most stable and easily available Keggin 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 the addendum atom (Mo^{6+} , W^{6+} , etc.). The structure of the heteropoly anion is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedra MO_6 . Fig. 1 shows the Keggin structure in polyhedral representation. Most typical Keggin HPAs such as $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ are commercially available.

HPA catalysts are currently used in several industrial processes (Table 1) [7]. The top two processes in the table are heterogeneously catalysed selective oxidations in the gas phase—the oxidation of methacrolein to methacrylic acid and ethene to acetic acid. All other processes are acid-catalysed reactions. These include homogeneous liquid-phase hydration of olefins, propene and butenes, to yield alcohols, and biphasic polymerisation of tetrahydrofuran to poly(tetramethylene glycole). More recently, synthesis of ethyl acetate by direct addition of acetic acid to ethene in the gas phase over HPA catalyst has been commercialised by Showa Denko in Japan [9] and BP in the UK (the Avada process) [15].

Heterogeneous acid catalysis by HPAs has attracted much interest because of its potential of great economic rewards and green benefits [1–12]. HPAs possess stronger (Brønsted) acidity than conventional solid acid catalysts such as acidic oxides and zeolites. The acid strength of Keggin HPAs decreases in the order: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiMo_{12}O_{40}$ [1,5–7]. The acid sites in HPA are more uniform and easier to control than those in other solid acid catalysts. Usually, tungsten HPAs are the catalysts of choice because of their stronger acidity, higher thermal stability and lower oxidation potential compared to molybdenum acids [1–7].

Being stronger acids, HPAs are generally more active catalysts than the conventional solid acid catalysts, which allows efficient operation under milder conditions.

A serious problem to HPA catalysts is their low thermal stability, hence limited reaction temperature and, especially, difficulty of regeneration of solid HPA catalysts (decoking) [7,12]. The temperature at which Keggin HPAs lose all acidic protons decreases in the order: $H_3PW_{12}O_{40}$ (465 °C) $>$ $H_4SiW_{12}O_{40}$ (445 °C) $>$ $H_3PMo_{12}O_{40}$ (375 °C) $>$ $H_4SiMo_{12}O_{40}$ (350 °C), the strongest acid $H_3PW_{12}O_{40}$

[☆] In memory of Eric Derouane.

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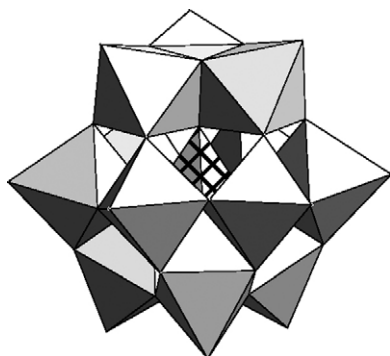


Fig. 1. Structure of Keggin heteropoly anion $[\alpha\text{-XM}_{12}\text{O}_{40}]^{n-}$ [13].

being the most stable [7]. Complete decomposition of Keggin structure to the constituent oxides occurs at higher temperatures, but follows the same order: 610, 540, 495 and 375 °C, respectively [6].

The TGA profile for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ hydrate exhibits three main peaks [5,7,16]: (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 100–280 °C centred at about 200 °C, accounted for the loss of ca. 6 H_2O molecules per Keggin unit, corresponding to the dehydration of a relatively stable hexahydrate $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$, in which the waters are hydrogen-bonded to the acidic protons to form the $[\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{O}\text{H}_2]$ ions; and (3) a broad peak in the range 370–550 °C centred at about 450 °C, which is due to the loss of 1.5 H_2O molecules of constitutional water from the anhydrous $\text{H}_3\text{PW}_{12}\text{O}_{40}$, corresponding to the loss of all acidic protons to form an anhydride phase $\text{PW}_{12}\text{O}_{38.5}$, which admittedly comprises Keggin-type species with oxygen vacancy. The decomposition is complete at about 600–610 °C to form the constituent oxides P_2O_5 and WO_3 , which exhibits an exotherm in DTA and DSC [5–7]. The course of thermal decomposition of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ hydrate is shown in Scheme 1 [7].

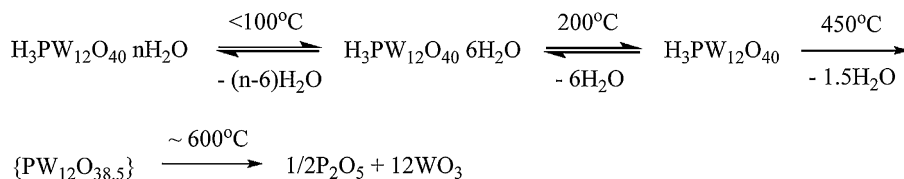
Various aspects of catalyst deactivation and regeneration are well covered in the literature [17,18]. Coke formation is the most frequent cause of catalyst deactivation in heterogeneous acid-catalysed organic reactions [18–21]. Much research has been carried out into coke formation on the catalysts for petrochemical processes such as catalytic cracking, reforming and hydrotreatment. The most studied catalysts include amorphous silica-alumina, zeolites and alumina, and also those doped with metals such

as palladium, platinum and nickel [18–21]. Catalyst regeneration (decoking) is usually carried out by coke combustion in oxygen-containing atmosphere at 450–550 °C [18–21]. For the oxide and zeolite catalysts possessing sufficient thermal stability, combustion of coke is an effective method to recover catalyst activity.

Solid HPA catalysts in organic reactions suffer from deactivation by coking, similar to the conventional solid acid catalysts. Although little information is available about coke formation on HPA catalysts, there is plenty of evidence that tungsten HPA catalysts deactivated by coke fail to recover their activity by the standard combustion of coke. This is the result of the low thermal stability of HPAs.

It has been suggested [7,12] that the activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is already lost irreversibly after its deprotonation with the loss of 1.5 H_2O molecules of constitutional water to form $\text{PW}_{12}\text{O}_{38.5}$ (Scheme 1). This is backed by TPD and XRD studies of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ dehydration (Moffat et al. [5] and references therein). It has been demonstrated that water desorbed from $\text{H}_3\text{PW}_{12}\text{O}_{40}$ hydrate by outgassing at 190 or 320 °C (i.e. before HPA deprotonation started) can be replaced by exposing the HPA to water vapour at 25 °C for 16 h. But outgassing at 450 °C for 1.5 h, leading to the formation of $\text{PW}_{12}\text{O}_{38.5}$, destroyed the ability of HPA to restore the initial amount of hydration water. The XRD pattern for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ showed pronounced line broadening on heating between 190 and 320 °C in air for 1.5 h. Re-exposure of the HPA, pre-treated at 320 °C, to water vapour at 25 °C for 16 h reproduced the XRD pattern observed after pre-treatment at 190 °C, albeit with a lower intensity. Heating at 500 °C for 1.5 h caused decomposition of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ to its constituent oxides WO_3 and P_2O_5 (the WO_3 was detected by XRD). Similar results have been obtained for $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ [5]. On the contrary, according to Essayem et al. [22], $\text{H}_3\text{PW}_{12}\text{O}_{40}$ hydrate, partially deprotonated at 400 °C to an approximately equimolar mixture of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{PW}_{12}\text{O}_{38.5}$, restored its acid sites on treatment with a nitrogen flow containing 3% D_2O at 200 °C for 3 h. This, however, does not prove that reprotonation of the pure $\text{PW}_{12}\text{O}_{38.5}$ phase can be done this way. The presence of significant amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the mixture could greatly enhance the process of rehydration by acid catalysis.

All the data considered, the standard catalyst decoking, that is carried out at ca. 500 °C for several hours, in most cases will irreversibly decompose HPA catalysts to their constituent oxides. It should be pointed out that there is no evidence that tungsten HPAs ($\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$), once decomposed, could reconstruct upon hydrothermal treatment (steaming) of the constituent oxides; nor can these HPAs be synthesised from oxides



Scheme 1. Thermal decomposition of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ hydrate.

Table 1

Industrial processes catalysed by heteropoly acids [7].

Reaction	Catalyst	Type ^a	Start
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO} + \text{O}_2 \rightarrow \text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$	Mo-V-P-HPA	het	1982
$\text{CH}_2=\text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{COOH}$	Pd- $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$	het	1997
$\text{CH}_2=\text{CHCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	hom	1972
$\text{CH}_2=\text{C}(\text{CH}_3)_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH}$	$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	hom	1984
$\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$	$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	hom	1989
$n\text{THF} + \text{H}_2\text{O} \rightarrow \text{HO}-(\text{CH}_2)_4-\text{O}-\text{H}$	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	bip	1985
$\text{CH}_2=\text{CH}_2 + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{CH}_2\text{OOCCH}_3$	$\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$	het	2001

^a hom, homogeneous; het, heterogeneous; bip, biphasic.

under hydrothermal conditions. In contrast, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ is known to reconstruct Keggin anions on exposure of its constituent oxides to moist air [5].

The difficulty in HPA regeneration makes coking the most serious problem for heterogeneous acid catalysis by HPAs [7,12]. Other possible causes of HPA deactivation, such as poisoning, aggregation, dehydration and decomposition of HPA, could also play a role but not as critical as coking, at least at the moderate reaction temperatures that are typical of acid catalysis by HPAs (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, namely developing 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 [12].

2. Development of HPA catalysts possessing high thermal stability

In recent years, there has been considerable activity in this direction, focusing mainly on oxide composites comprising tungsten(VI) polyoxometalates and Nb(V), Zr(IV) or Ti(IV) oxides as an oxide matrix [23–31]. These composites are usually prepared by wet chemical synthesis, followed by calcination at 500–750 °C, i.e. at temperatures considerably higher than the temperature of HPA decomposition. The materials thus made contain HPA precursors or HPA decomposition products, possessing Brønsted and Lewis acid sites of moderate strength. These materials have been found active in a range of Friedel–Crafts reactions, often with good catalyst recycling. However, their activity is considerably lower than that of the standard solid HPA catalysts. For example, the $\text{H}_3\text{PO}_4\text{-WO}_3\text{-Nb}_2\text{O}_5$ (9:55:36 wt%) composite with a surface area of 58 m²/g has been prepared by interaction of $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$, Nb(V) oxalate and H_3PO_4 in aqueous solution, followed by evaporation and calcination at 500 °C [23]. It has been tested in the alkylation of anisole by benzyl alcohol to yield 94% of the alkylation product. The catalyst is reported to be recyclable many times without loss of its activity. However, it is less active than the $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Nb}_2\text{O}_5$ catalyst prepared by the usual impregnation of niobium(V) oxide with $\text{H}_3\text{PW}_{12}\text{O}_{40}$, but the latter is not recyclable. Another composite has been obtained by impregnation of 15% $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ on zirconium(IV) oxide and calcination at 700 °C [25]. From Raman spectra, it contains ZrO_2 -anchored mono-oxotungstate and possesses Brønsted and Lewis acid sites. This solid acid material is active in the acylation of veratrole by benzoic anhydride, with no leaching and good catalyst recycling after regeneration by coke combustion at 500 °C. However, this catalyst is less active than HY zeolite per gram of catalyst, whereas the standard solid HPA catalysts, e.g. $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$, are usually much more active than the HY.

The composite materials based on W(VI) polyoxometalates and Nb(V), Zr(IV) or Ti(IV) oxides may have advantage over zeolite acid catalysts in the case of reactions involving large organic molecules that will not fit into zeolite pores. Future work on thermally stable HPA composites should be aimed at obtaining materials possessing stronger acid sites.

3. Modification of HPA catalysts to enhance coke combustion

Doping of solid acid catalysts with platinum group metals (PGM) such as Pd and Pt to enhance catalyst regeneration by coke combustion is well documented [18,19]. Typical examples are zeo-

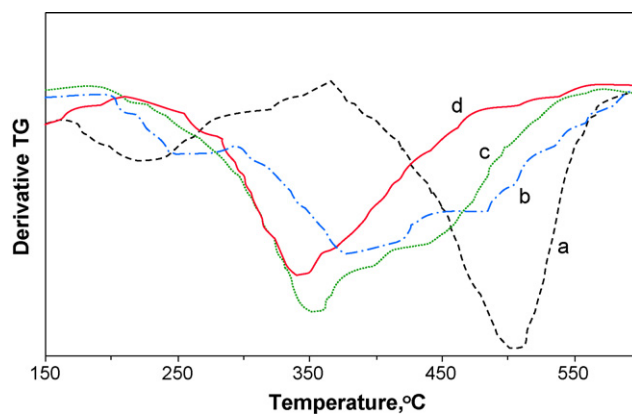


Fig. 2. TGA/TPO in air for Pd-doped 20% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ coked by propene in a fixed-bed flow reactor at 200 °C: (a) no Pd doping, (b) 1.6% Pd, (c) 2.0% Pd and (d) 2.5% Pd [32,33].

lite and alumina doped with PGM employed as the catalysts for alkane isomerisation and cracking [18,19]. The metal additives promote bifunctional metal–acid mechanism of alkane conversion and enhance catalyst stability to coking. Regarding the catalyst decoking, the role of metal sites is twofold: on the one hand, they catalyse coke combustion, and on the other, change the nature of coke depositing on the catalyst making it more aliphatic and hence easier combustible [19]. PGM-doped HPAs have been reported as catalysts for alkane isomerisation (Section 6).

PGM doping has been found effective for enhancing regeneration of HPA catalysts for propene oligomerisation [32,33]. The effect of Pd doping on coke combustion can be seen from the TGA/TPO for the coked catalyst 20% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ (Fig. 2) [32,33]. The catalyst has been 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 catalyst, this temperature decreases; the higher the Pd loading the lower is the temperature of coke combustion. With 2% Pd doping, coke burns at 350 °C, which is well below the decomposition temperature for $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

Fig. 3.

Using XPS and ³¹P MAS NMR, it has been shown that coking does not affect the structure of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [33]. From XPS, the oxidation state of tungsten is 6+ in both the fresh and coked catalyst. The ³¹P chemical shift is the same for the as-made, Pd-doped and coked catalysts (about –15 ppm versus 85% H_3PO_4 , as expected for $\text{H}_3\text{PW}_{12}\text{O}_{40}$), which indicates that the Keggin structure remains

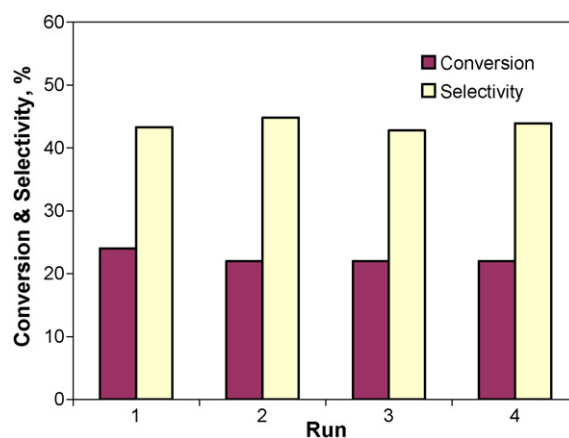


Fig. 3. Catalyst reuse in Fries rearrangement of PhOAc: conversion and total acylation selectivity in successive runs (0.3%Pt/CsPW (2.3 wt%), in nitrobenzene, 130 °C, 2 h) [35].

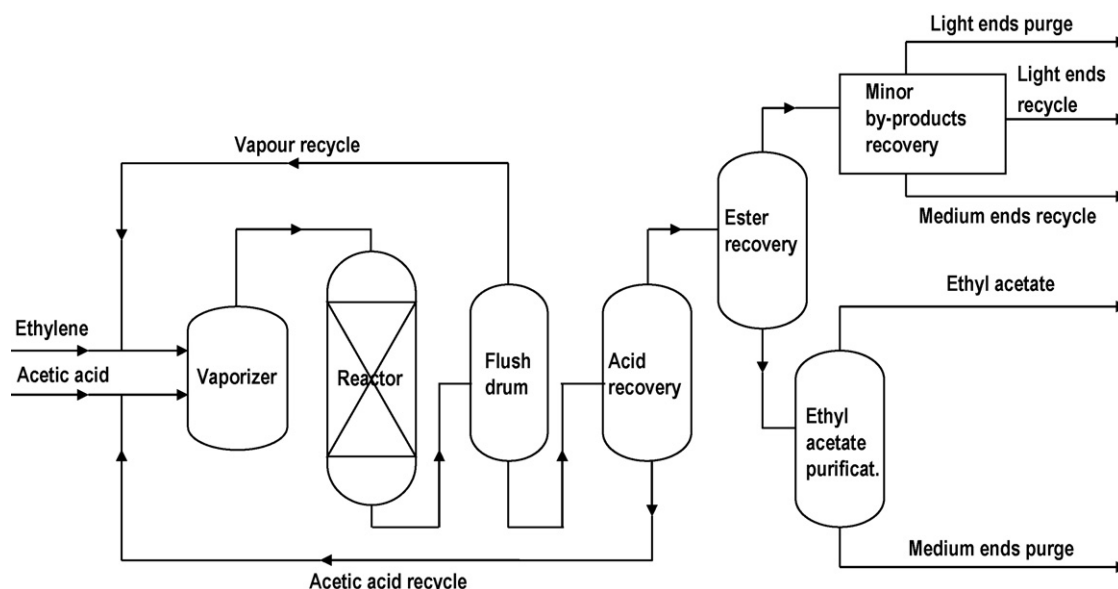


Fig. 4. Flowchart for the BP's Avada process [15].

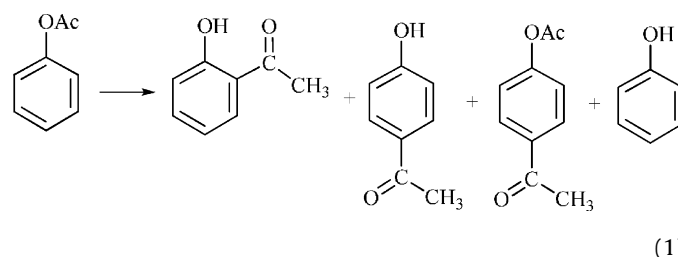
intact. As shown by ^{13}C CP/MAS NMR for the coked $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts, Pd doping does affect the nature of coke depositing on the catalyst [32]. On the undoped catalyst, both aliphatic (soft) and polyaromatic (hard) coke are formed. In contrast, the Pd-doped catalyst builds only aliphatic coke which will burn off more easily. From these results, the effect of palladium in HPA catalyst appears to be the same as in alumina or zeolite, i.e. Pd catalyses the combustion of coke and inhibits the formation of hard polyaromatic coke, which is more difficult to burn off [32,33].

Palladium doping has been found effective to enhance in-situ regeneration of silica-supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst for the gas-phase oligomerisation of propene [33]. The reaction has been carried out in a fixed-bed flow reactor, yielding C_{12} to C_{18} oligomers as major products. The undoped and Pd-doped $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts both have high initial activity, but suffer from fast deactivation due to coking. As expected from the TPO studies, the Pd-doped catalyst can be regenerated to regain its activity fully by combustion of coke at 350°C in air flow, followed by treatment with H_2 to reduce Pd(II) to Pd(0). In contrast, the undoped catalyst fails to recover its activity under such conditions.

Doping with palladium and platinum has also proved effective for regeneration and recycling of HPA catalysts for Friedel–Crafts acylation in liquid-phase batch processes [34–37]. This is illustrated by studies of Fries rearrangement of phenyl acetate, yielding acylated phenols (Eq. (1)) [36,37]. HPAs are very efficient solid acid catalysts for this reaction, much more active than H_2SO_4 and acidic zeolites. The bulk acidic salt $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW), which is insoluble hence easily recyclable, is especially good catalyst for this reaction. However, CsPW is deactivated by carbonaceous deposit and requires regeneration. The TGA/TPO analysis of the coked CsPW after its use for the Fries rearrangement of PhOAc shows, that coke combustion is complete at about 550°C . This temperature, however, is too high for the catalyst to retain its integrity. In the case of

Pd-doped CsPW (2 wt% Pd), coke is already gone at 350°C , indicating that catalyst regeneration may be possible at this temperature [34].

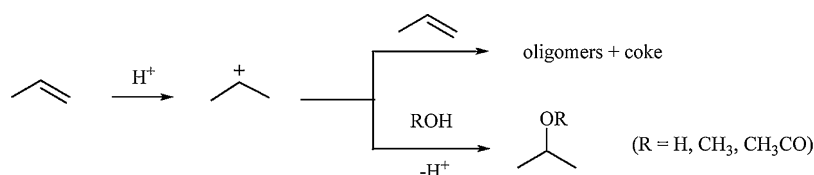
Platinum doping has been found to be even more effective, enhancing coke combustion at a Pt loading as low as 0.3 wt% [35]. Fig. 4 shows excellent recycling of the 0.3%Pt/CsPW catalyst in the Fries rearrangement of PhOAc. After each run the catalyst has been separated and regenerated by air calcination at 350°C , followed by steaming at 200°C to restore the acid sites. As evidenced by FTIR, the Keggin structure of the CsPW remains unchanged after multiple catalyst regeneration and reuse [35].



It should be noted, however, that PGM doping could initiate side reactions, thus impairing the selectivity. Although no such effect has been observed in Friedel–Crafts acylation [34,35], it may be the case in other reactions; therefore, care must be taken regarding possible effect of PGM on reaction selectivity.

4. Inhibition of coke formation on HPA catalysts

Catalyst regeneration is an expensive procedure. Obviously, it would be preferable to prevent the catalyst from coking in the first place to avoid its regeneration. Coke inhibition on HPA catalysts has been studied using propene oligomerisation as a model



Scheme 2. Acid-catalysed oligomerisation of propene.

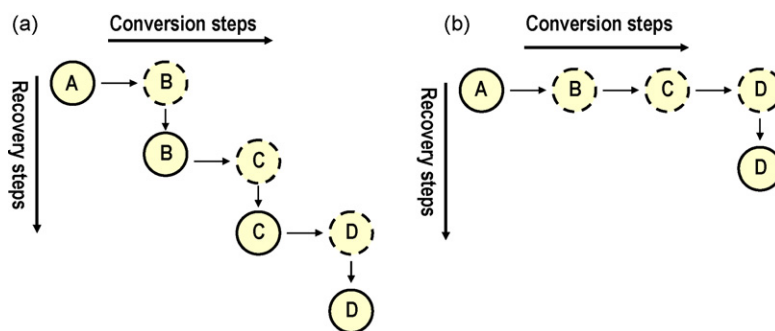
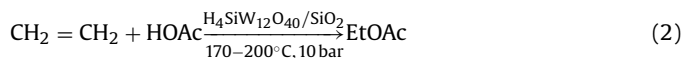


Fig. 5. Conventional step-by-step process with recovery after each conversion step (a) and cascade process without intermediate recovery steps (b) [48].

reaction [32,33]. The reaction occurs via the carbenium ion mechanism yielding propene oligomers and coke (Scheme 2). The oligomers may be considered as coke precursors. Addition of nucleophilic molecules, such as water, methanol and acetic acid, has been found to affect greatly the reaction selectivity by reacting with carbenium ion intermediates to yield oxygenates at the expense of the oligomers and coke (Scheme 2). Water has been found to be the most effective coke inhibitor, with the amount of coke decreased sevenfold compared with the background (Table 2) [33].

On industrial scale, addition of water to the reactor feed has been proved effective to prolong catalyst lifetime in the BP's Avada process for the synthesis of ethyl acetate [15,38]. In this process, ethyl acetate is produced by interaction of acetic acid with ethene in the gas phase in the presence of tungstosilicic acid supported on silica as the catalyst (Eq. (2)).



In 2001 this process was commercialised on a scale of 220,000 ton/year at Hull in the UK. This is the largest ethyl acetate plant in the world. Fig. 5 shows a schematic flowchart for the Avada process. Ethene and acetic acid are fed through evaporator to the adiabatic fixed-bed reactor containing the catalyst $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$. In order to achieve sustained catalyst performance, steam (3–8 mol%) is added to the reactor. The addition of water leads to reversible formation of ethanol and diethyl ether as byproducts, which are recycled back to the reactor. The product ethyl acetate is obtained in several separation and purification steps. Table 3 compares the performance of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ with other solid acid catalysts, illustrating that the HPA is a highly active catalyst for the synthesis of ethyl acetate [38]. Addition of water is essential for the stable performance of HPA catalyst. Without water, the catalyst deactivates quickly due to extensive formation of coke. The effect of water on the catalyst in this process is probably manifold. In addition to coke inhibition, water stabilises HPA by preventing it from dehydration. This simple remedy has allowed BP to achieve economically viable lifetime of their HPA catalyst [15,38]. It should be pointed out, however, that the addition of water is not a universal cure. Although effective in the water-tolerant ethyl acetate process, it is unlikely to work in other reactions that are incompatible with water such as Friedel–Crafts acylation and alkane isomerisation.

Table 2
Effect of additives (7 vol%) to propene flow on coke formation on 40% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ at 150 °C [33].

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

5. Reactions in supercritical fluids

Heterogeneous catalysis in supercritical fluids offers considerable benefits (for a review, see [39]). Use of supercritical fluids can greatly intensify mass and heat transfer, thus enhancing the reaction rate and selectivity and also product separation. On top of that, supercritical methodology can facilitate catalyst regeneration and increase catalyst lifetime. Supercritical fluids possess unique solvent properties which have long been utilized in separation technologies such as extraction and chromatography and are now gaining increasing interest for application in catalytic synthesis. Supercritical fluids are miscible with gases and can dissolve solids and liquids. Usually, the supercritical methodology is applied in the region near the critical point, $(1.0-1.2) \times T_c$ and $(1-2) \times P_c$, where T_c and P_c are the critical temperature and pressure of the fluid. In this region, densities are close to or above the critical density of the fluid, and the dissolution power of the fluid is at its maximum. Supercritical fluids exhibit considerably higher solubilities than the corresponding gases for heavy organic compounds which may deactivate catalysts and promote coking. Changing process conditions from gas phase to dense supercritical medium can suppress this deactivation. Furthermore, enhanced diffusivity in supercritical system can accelerate the transfer of coke precursors from the catalyst surface hence reduce the amount of coke formed.

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 [40–46]. The isomerisation of n-butane has been studied in the supercritical n-butane in a fixed-bed flow reactor using 20% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$, 20% $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ (260 °C, 110 bar), sulfated zirconia (215 °C, 61 bar) and H-mordenite (300 °C, 138 bar) as the catalysts [41,42]. Gas-phase isomerisation on these catalysts suffers from rapid deactivation due to catalyst coking. In contrast, the supercritical system shows 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 can be regenerated in the supercritical system at n-butane density close to its critical value to regain almost fully their initial activity. The isomerisation on HPA/ TiO_2 and sulfated zirconia in supercritical n-butane provides 80% selectivity to isobutane at 20–25% conversion. H-mordenite gives <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% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$, 20% $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$, sulfated zirconia, 15% WO_3/TiO_2 and 0.5%Pt/ $\gamma\text{-Al}_2\text{O}_3\text{-Cl}$ [43]. In the supercritical system (140–165 °C, 40–45 bar), both reactions are fast, with a steady catalytic activity. In contrast, in the liquid phase and particularly in

Table 3
Solid acid catalysts for the synthesis of ethyl acetate from ethene and acetic acid [38].

Catalyst	C ₂ H ₄ /AcOH (mol/mol)	Temp. (°C)	Pressure (bar)	Contact time (s)	H ₂ O 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 ₄ SiW ₁₂ O ₄₀ /SiO ₂	12/1	180	10	2	6	380

the gas phase the reactions occur slower, and rapid catalyst deactivation has been observed.

The alkylation of cresols with tert-butanol over H₃PW₁₂O₄₀ supported on MCM-41 mesoporous silicate in supercritical CO₂ has been found to exhibit less catalyst deactivation compared to other reaction media such as hexane as solvent and without solvent. The catalyst is recyclable without significant loss of catalytic activity and retains mesoporous structure after three recycles [44].

It should be noted, however, that the benefits gained from the supercritical 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 [39].

6. Cascade reactions using multifunctional HPA catalysts

Development of cascade (tandem) processes without intermediate separation steps using multifunctional catalysts is an important strategy to carry out sustainable organic synthesis with high atom and energy efficiency [47,48]. Multifunctional catalysts contain two or more catalytic functions (acid, base, metal, etc.) acting synergistically to carry out a multistep cascade reaction. Fig. 5 illustrates the difference between a conventional step-by-step process with recovery after each conversion step and a cascade (one-pot) process without intermediate recovery steps. In addition to reduction of the number of separation steps, cascade processing can overcome thermodynamic limitations by combining thermodynamically unfavourable reaction steps with favourable steps, driving the cascade process forward [47,48].

HPAs are inherently multifunctional compounds [1–7]. Their acid and redox properties can be tuned by varying the HPA composition. Solid HPAs allow for considerable alteration of their texture and can be modified to introduce another chemical function, e.g. metal function [1–7]. Solid Keggin HPAs such as H₃PW₁₂O₄₀ doped with Pd and Pt have been reported as bifunctional catalysts for alkane isomerisation [49–52]. There is evidence that combination of HPA acid catalysis and redox catalysis in heterogeneous cascade process can lead to efficient processing, less sensitive to deactivation by coking compared with conventional HPA catalysis [53]. This approach is illustrated below on recent examples including synthesis of methyl isobutyl ketone (MIBK) and synthesis of (–)-menthol from (+)-citranellal using multifunctional HPA catalysts.

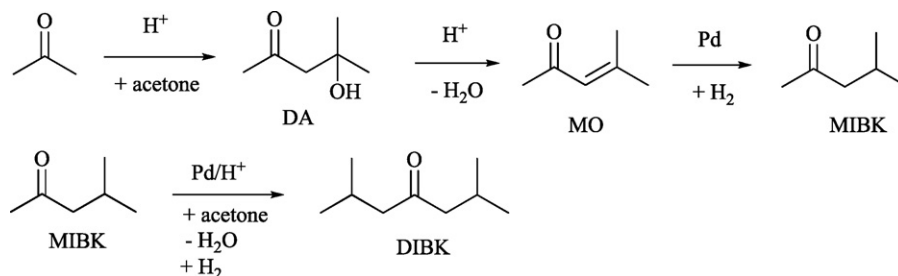
MIBK is one of the most widely used aliphatic ketones and is mainly employed as a solvent for paint and extraction [54].

Diisobutyl ketone (DIBK), a byproduct in the synthesis of MIBK, is a good solvent for a variety of natural and synthetic resins. Traditionally, MIBK is manufactured via a three-step process involving base-catalysed aldol condensation of acetone to diacetone alcohol (DA), acid-catalysed dehydration of DA to mesityl oxide (MO) and metal-catalysed hydrogenation of MO to MIBK [55]. One-step synthesis of MIBK in liquid and gas phase has been developed. This process uses bifunctional acid/redox catalysts comprising acidic resins, zeolites or zirconium phosphate with addition of platinum group metals, usually palladium ([53] and references therein). The proposed mechanism of the one-step synthesis of MIBK on a bifunctional catalyst Pd/{H⁺} is shown in Scheme 3 [56]. MIBK forms in three steps: acid-catalysed condensation of acetone to DA, acid-catalysed dehydration of DA to MO and selective hydrogenation of the C=C bond in MO on Pd sites to yield MIBK. The first step is limited by unfavourable equilibrium, the other two are thermodynamically favourable, making the overall process exothermic ($\Delta H = -117$ kJ/mol) [55]. DIBK forms in subsequent reactions of MIBK.

The Pd-doped acidic heteropoly salt Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsPW) has been found to be a very efficient bifunctional catalyst for the one-step conversion of acetone to MIBK in the gas and liquid phase [53]. CsPW is well known as a water-insoluble strong Brønsted acid and a versatile solid acid catalyst possessing considerable thermal stability (≥ 500 °C) [1,7].

In the liquid-phase batch process, Pd/CsPW catalyst gives 92% MIBK selectivity and 95% total MIBK + DIBK at 140–160 °C and a very low H₂ pressure of only 5–7 bar (usually 20 bar or higher) [53]. Doping the Pd/CsPW catalyst with Cu leads to further increase in selectivity up to 95% MIBK and 98% MIBK + DIBK. The Cu-Pd/CsPW catalyst could be reused after washing it with acetone, albeit with reduced activity.

In the gas-phase process in a fixed-bed flow reactor, the Pd/CsPW catalyst gives 83% MIBK selectivity, with 91% total selectivity to MIBK + DIBK [53]. The reaction occurs at remarkable low temperatures of 80–100 °C (usually above 140 °C, e.g. with Pd/zeolite catalyst). This may be explained by the strong acidity of CsPW enhancing the first two steps of the process (Scheme 3). The reaction clearly requires both acid and redox catalyses which are provided by CsPW and Pd, respectively. When CsPW is used alone in the absence of palladium, MIBK is not observed, with MO being the major product. In the gas-phase reaction, Pd/CsPW exhibits very good durability. Catalyst deactivation is not observed after 25 h of continuous operation (Fig. 6). Only a small amount of coke ($\leq 1\%$)



Scheme 3. Synthesis of MIBK and DIBK over bifunctional Pd/acid catalyst.

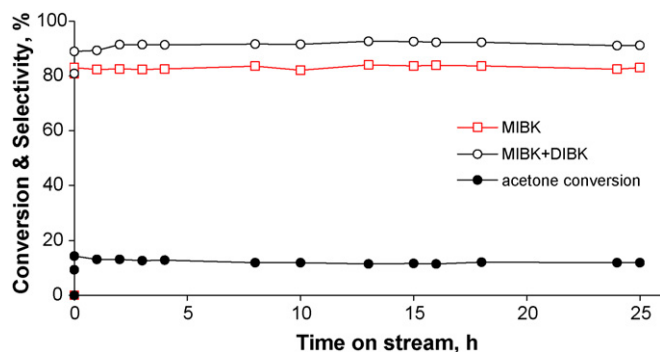
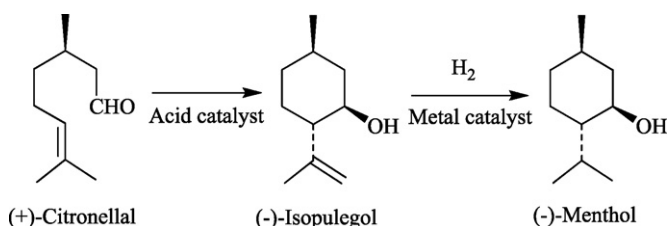


Fig. 6. Gas-phase acetone conversion and product selectivities vs. time on stream (fixed-bed flow reactor, 0.20 g 0.5%Pd/CsPW catalyst, 7.5 mL/min H₂ flow, [acetone]/[H₂] = 2:1, 100 °C) [53].



Scheme 4. Synthesis of menthol from citronellal.

is formed in the reaction, which does not affect the catalyst performance. Such a minor coking may be due to the efficient removal of coke precursors by in-situ hydrogenation on Pd. It should be noted that in the absence of H₂ the catalyst loses its activity in about 4 h, with MO being the main reaction product. Therefore, in this heterogeneous cascade process, combination of HPA acid catalysis with Pd-catalysed hydrogenation is effective to protect the catalyst from deactivation by coking.

Menthol is important ingredient of various cosmetic, pharmaceutical and other specialty products, hence its synthesis is of considerable interest [57,58]. Amongst eight isomers of menthol, only (–)-menthol is the desired product, which possesses a characteristic odor and produces a physiological cooling effect. One of the major synthetic routes to (–)-menthol is the Takasago process involving acid-catalysed cyclisation of (+)-citronellal to (–)-isopulegol in the presence of aqueous ZnBr₂ followed by Ni-catalysed hydrogenation (Scheme 4) [58]. Besides (–)-isopulegol, the cyclisation may produce three stereoisomers together with other byproducts. The present industrial practice of citronellal cyclisation requires large quantities of ZnBr₂ as a homogeneous catalyst, which causes environmental problems due to the formation of large amount of waste upon catalyst separation. The use of heterogeneous catalysis for this reaction, therefore, would be a much cleaner option.

Recently, one-pot synthesis of menthol from citronellal, with simultaneous cyclisation and hydrogenation over a bifunctional acid/hydrogenation catalyst, has attracted interest. Catalysts such as Ru-ZnBr₂/SiO₂ [59], Cu/SiO₂ [60] and Ir/H-Beta zeolite [61] have been used. Although simpler, the one-pot syntheses are lengthy procedures or require a high catalyst/substrate ratio, often with a relatively low (–)-menthol yield. Thus with 3%Ir/H-Beta, a 75% yield of (–)-menthol in 30-hour reaction at 80 °C has been obtained [61]. The 10%Ru-ZnBr₂/SiO₂ catalyst gives 85% (–)-menthol yield, with less than 1 g substrate converted per gram of catalyst [59]. In the one-pot synthesis via Scheme 4, the cyclisation must be fast to avoid hydrogenation of citronellal. The reported procedures [59–61], however, have used the catalysts with relatively weak acid sites. As a result, the cyclisation is slow, and only moderately active

hydrogenation catalysts can be used to prevent hydrogenation of citronellal. Therefore, for process intensification, it would be beneficial to apply a bifunctional catalyst with stronger acid sites as well as more active metal sites such as palladium.

Silica-supported heteropoly acid H₃PW₁₂O₄₀ has been reported as an efficient solid acid catalyst for the cyclisation of (+)-citronellal to (–)-isopulegol [62]. More recently, silica-supported H₃PW₁₂O₄₀ doped with 5 wt% palladium has been reported as an active catalyst for the one-pot transformation of (+)-citronellal to menthol via acid-catalysed cyclisation followed by Pd-catalysed hydrogenation, with a 92% yield of menthol at 100% citronellal conversion and 85% stereoselectivity for the desired (–)-menthol [63]. The reaction occurs in cyclohexane at 70 °C and 35 bar H₂ pressure. This result is on the level with or better than those reported so far [59–61]. It is important that no products of citronellal hydrogenation have been found. This indicates that in this system citronellal cyclisation occurs much faster than the hydrogenation of isopulegol. The reaction appears to be truly heterogeneous. No HPA leaching from the catalyst into cyclohexane solution has been observed. The catalyst could be easily separated and, after washing with the solvent, recycled several times, albeit with gradually decreasing activity. Catalyst regeneration by combustion of coke, as applied for Fries reaction [35] (Sect. 3), would probably improve catalyst reuse in this reaction.

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 HPA catalysis, making regeneration (decoking) of solid HPA catalysts difficult. Several approaches can be instrumental in overcoming deactivation of HPA catalysts to achieve sustainable catalyst performance. One of these could be the development of new HPA materials possessing high thermal stability. Recent studies have provided some new solid acid catalysts, for example oxide composites comprising tungsten(VI) polyoxometalates and niobium(V), zirconium(IV) or titanium(IV) oxides, exhibiting good regeneration and reuse. However, these catalysts have relatively weak acid sites hence a lower catalytic activity compared with the standard solid HPA catalysts. Work should be continued to obtain thermally stable HPA materials possessing stronger acid sites. Another approach is the modification of HPA catalysts by platinum group metals to enhance coke combustion. This method has proved effective for catalyst regeneration by combustion of coke without destroying the structure of HPA. For acid-catalysed processes that tolerate the presence of water, addition of water to the reactor feed can effectively inhibit coke formation and prolong catalyst lifetime (BP's Avada process). The life of HPA catalyst can also be longer when the reaction is carried out in supercritical system. However, the high cost of supercritical process technology should be taken into account. Finally, HPAs can be used with high efficiency and better stability toward deactivation within heterogeneous multifunctional catalysts for cascade processes involving acid and redox catalyses.

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