

Fries rearrangement of phenyl acetate catalysed by platinum-doped heteropoly salt: Catalyst regeneration and reuse

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Abstract

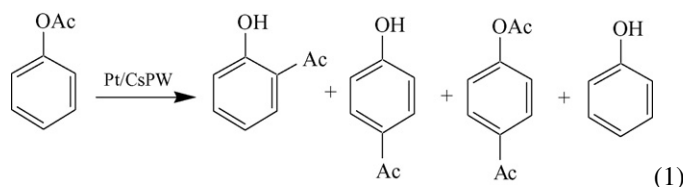
The acidic cesium heteropoly salt $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW) is an active solid acid catalyst for the liquid-phase Fries rearrangement of phenyl acetate, which, similar to other solid acid catalysts, suffers from deactivation due to coke deposition. Coke burning cannot effectively regenerate CsPW because of its relatively low thermal stability. Doping CsPW with Pt metal (0.3 wt%) allows full regeneration of catalyst activity and selectivity by the aerobic oxidation of coke at 350 °C and ambient pressure, which occurs without any structural damage to the catalyst. Pt doping practically does not affect the activity and selectivity of CsPW. As a coke-burning catalyst, Pt is much more efficient than Pd; the latter requires almost ten times higher a metal loading. The Pt/CsPW catalyst is characterised by XRD, TGA/TPO, FTIR and H_2 chemisorption. © 2006 Elsevier B.V. All rights reserved.

Keywords: Fries reaction; Heteropoly acid; Catalyst regeneration; Platinum doping

1. Introduction

Fries rearrangement of aryl esters, a special case of Friedel–Crafts acylation, provides an important route for the synthesis of aromatic hydroxyketones that are intermediates in manufacturing fine and speciality chemicals as well as pharmaceuticals [1–4]. Present practice requires a prohibitively large amount of a Lewis or Brønsted acid (e.g., AlCl_3 or H_2SO_4) as a homogeneous catalyst, which results in substantial amount of waste and strong corrosion [1,2]. To overcome this problem, much effort has been put into developing solid acid catalysts for Fries rearrangement [1–4]. Keggin-type heteropoly acids (HPAs), e.g., $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW), and acidic heteropoly salts such as $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW) have been found to be highly active solid acid catalysts for Fries reaction [5–7]. These catalysts are much more active than zeolites (H-beta) and H_2SO_4 . PW and CsPW can be separated and reused, although with reduced activity due to catalyst coking. Regeneration of HPA catalysts is difficult because of a relatively low thermal stability of HPA, which does not allow burning coke off the catalysts directly, like in the case of, e.g., zeolites [8,9]. Modification of solid acid catalysts by platinum group metals, e.g., Pt or Pd, to enhance their regeneration is well known [10,11].

Previously, we have shown that doping HPA catalysts with palladium (2.1 wt%) reduces the temperature of coke burning down to 350 °C compared to 550 °C for the undoped catalysts. This allowed sustainable regeneration of HPA catalysts in Fries rearrangement by air calcination at 350 °C without loss in their activity and selectivity [7], although the Pd loading was relatively high. Here we report on the effect of Pt doping on the regeneration and reuse of solid HPA catalysts in liquid-phase Fries rearrangement of phenyl acetate (PhOAc) (Eq. (1)). It is demonstrated that the Pt doping is much more efficient for this purpose than Pd doping. Previously, Pt-doped HPA catalysts have been studied in alkane isomerisation [12 and references therein]:



2. Experimental

2.1. Catalyst preparation

The acidic salt $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW) was prepared by the literature method [13]. Platinum-doped CsPW catalysts con-

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Table 1
Catalyst characterisation

Catalyst ^a	S_{BET} (m ² /g)	Pore size (Å)	Pore volume (cm ³ /g)	H ₂ O ^b (wt%)	W (wt%)	D^c	d^d (nm)
CsPW	126	35	0.107	1.1	65.7		
1.0% Pt/CsPW	108	38	0.104	1.5	65.3	0.45	2.0
0.3% Pt/CsPW	94	40	0.086	1.8	65.3	0.50	1.8

^a Catalysts pretreated at 150 °C/0.5 Torr for 1.5 h; W and Pt content in anhydrous catalysts from ICP analysis.

^b From TGA as a weight loss in the range of 30–300 °C.

^c Platinum dispersion from H₂ chemisorption.

^d Platinum particle size: $d = 0.9/D$.

taining 0.3 and 1.0 wt% Pt were prepared by impregnating a CsPW powder (4 g) with the required amount of 0.03 mol/L aqueous solution of H₂PtCl₆ which was added dropwise with stirring to the aqueous suspension of CsPW at room temperature. The resulting pale yellow suspension was kept overnight at room temperature. Then water was evaporated at 45 °C using a rotary evaporator to yield a yellow powder, which was dried at 150 °C/0.5 Torr for 1.5 h. The reduction of Pt(IV) to Pt(0) was carried out by a hydrogen flow at 250 °C for 2 h to yield a black catalyst powder. Unless stated otherwise, all the catalysts were calcined at 150 °C/0.5 Torr for 1.5 h and stored in a desiccator over P₂O₅. Catalyst characterisation is given in Table 1.

2.2. Techniques

Surface area and porosity of catalysts were measured by nitrogen physisorption on a Micromeritics ASAP 2000 instrument. Thermogravimetric analyses (TGA) were performed using a Perkin-Elmer TGA 7 instrument under nitrogen flow. The same instrument was used for temperature-programmed oxidation (TPO) of coked catalysts under air flow [14]. Powder X-ray diffraction (XRD) spectra of catalysts were recorded on a Stoe Stadi-P diffractometer with a monochromatic Cu K α radiation from a germanium monochromator in the angular range $15^\circ \leq 2\theta \leq 90^\circ$, with a step width of 0.04° and count-time of 5 s per step. Diffuse reflectance IR spectra were recorded on a Nicolet NEXUS FTIR instrument using powder mixtures of catalysts with KBr. Tungsten and platinum content in the catalysts was measured by inductively coupled plasma (ICP) atomic emission spectroscopy on a Spectra Ciros CCD spectrometer. Hydrogen chemisorption on Pt/CsPW catalysts was measured by the pulse technique using a Micromeritics TPD/TPR 2900 instrument. A catalyst sample (0.5 g) pre-exposed to air for several days at room temperature was placed in a glass sample tube connected to the instrument and stabilised at $30 \pm 1^\circ\text{C}$ under nitrogen flow of 70 mL/min. Pulses of pure H₂ (50 μL) were injected in the flow in 3 min intervals until the catalyst was saturated with hydrogen. The dispersion of platinum in the catalysts, D , defined as the fraction of platinum at the surface, $D = \text{Pt}_s/\text{Pt}_{\text{total}}$, was calculated assuming the stoichiometry of H₂ adsorption: $\text{Pt}_s\text{O} + 1.5\text{H}_2 \rightarrow \text{Pt}_s\text{H} + \text{H}_2\text{O}$ [15]. The average size of Pt particles, d , was obtained from the empirical equation d (nm) = $0.9/D$ [16]. It should be noted that H₂ did not adsorb on CsPW under the experimental conditions.

2.3. Fries rearrangement

The rearrangement of phenyl acetate was carried out in nitrobenzene at 130 °C under nitrogen atmosphere in a glass reactor equipped with a condenser and a magnetic stirrer. Typically, the total weight of reaction mixture (PhOAc + PhNO₂) was 7.0 g and the ratio PhOAc/PhNO₂ = 25:75 wt%. Dodecane (1 wt%) was added as a gas chromatography (GC) internal standard. To monitor the reaction, 0.1 mL samples of the reaction mixture were taken periodically, diluted to 1 mL with 1,2-dichloroethane (DCE) and analysed by GC using a Varian 3380 chromatograph with autosampler equipped with a 30 m \times 0.25 mm BP1 capillary column. Reaction products were identified by GC and GC-MS using authentic samples. Catalyst regeneration and reuse studies were carried out on a scale of 50 g of the initial reaction mixture, using the procedure previously employed for Pd/CsPW [7]. After each run, the catalyst was filtered off and, prior to reuse, washed with DCE at room temperature, calcined at 350 °C for 2 h under air flow of 20 mL/min, followed by steaming with wet air at 200 °C for 1 h and drying at 150 °C/0.5 Torr/1.5 h. The treatment with DCE and calcination were applied for removing coke from the catalyst. The post-calcination steaming was intended to restore the proton sites that might have been destroyed during the calcination. A part of the catalyst was taken for analysing carbon and tungsten content. As a result, in successive runs the reaction was gradually scaling down to ca. 5–7 g reaction mixture.

3. Results and discussion

The rearrangement of aryl esters using PW/SiO₂ and CsPW as the catalysts has been reported previously [5–7]. With PW/SiO₂, the reaction is homogeneous in aryl esters (without solvent) and PhNO₂ but heterogeneous in non-polar solvents, e.g., decane. With CsPW, that is insoluble in common solvents, the reaction is heterogeneous in all these media, which makes the CsPW a better catalyst for this reaction. The rearrangement of PhOAc yields 2- and 4-hydroxyacetophenones (2HAP and 4HAP) and 4-acetoxyacetophenone (4AAP) together with phenol (Eq. (1)) [5–7]. 2HAP, 4AAP and phenol are considered to be the primary products, 2HAP being formed by the intramolecular rearrangement of PhOAc whereas 4AAP and PhOH by the self-acylation: $2\text{PhOAc} \rightarrow 4\text{AAP} + \text{PhOH}$. In contrast, 4HAP appears to be the secondary product formed by the intermolecular acylation of phenol with PhOAc [3]. Usually, the yield of phenol is greater than that of 4AAP, as part of PhOH results

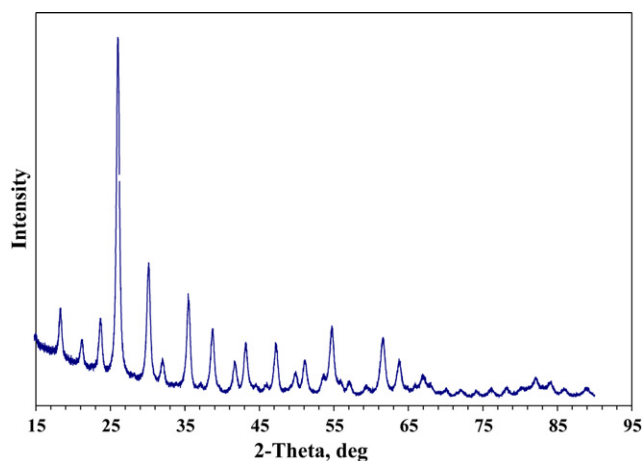


Fig. 1. XRD pattern of the fresh 1% Pt/CsPW catalyst (Cu K α radiation).

from the decomposition and/or hydrolysis of PhOAc that also produce ketene, acetic acid and acetic anhydride. Solvent plays a significant role in Fries reaction, polar solvents such as PhNO₂ favour the formation of the *para*-acylation products [3].

This study aims at improving the regeneration and reuse of CsPW in Fries reaction by doping the catalyst with Pt (0.3–1.0%) in order to enhance coke burning. The regeneration protocol previously developed and proved successful for Pd/CsPW [7] is used here for Pt/CsPW. The Pt/CsPW catalysts possessed a texture similar to that of the previously studied Pd/CsPW and their elemental composition was in agreement with that expected from the preparation method (Table 1). From H₂ chemisorption, the dispersion of the Pt particles was 0.45–0.50 corresponding to an average particle size of 1.8–2.0 nm. Powder XRD of Pt/CsPW (Fig. 1) shows the well-known pattern of crystalline CsPW [17]. It should be noted that the XRD of Pt/CsPW, both fresh and used, did not show any pattern of Pt metal. Thus the most intense 1 1 1 diffraction peak of Pt phase at $2\theta = 39.8^\circ$ is not seen in Fig. 1. This indicates a fine dispersion of Pt in the catalysts in agreement with the hydrogen chemisorption measurements.

Table 2 shows the results for PhOAc rearrangement catalysed by CsPW and Pt/CsPW in nitrobenzene. As found previously [7],

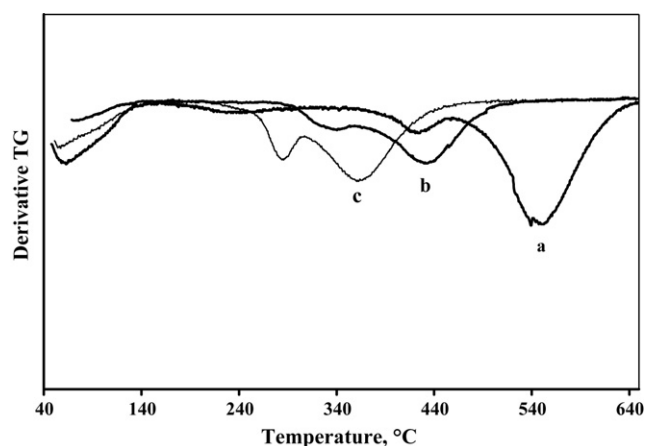


Fig. 2. TGA/TPO in air for coked catalysts after use for rearrangement of PhOAc: (a) CsPW; (b) 0.3% Pt/CsPW; (c) 1% Pt/CsPW.

the CsPW reuse with a mild workup by washing the catalyst with DCE results in a sharp decline of catalyst activity and selectivity to acylated products, which indicates a loss of catalyst acidity. Also a large increase in side product formation was observed in successive runs. A more forcing workup by air calcination at 350 °C followed by steaming has been found to improve the catalyst reuse, although the decline of catalyst activity remained significant [7].

Temperature-programmed oxidation (TGA/TPO) in air for the coked CsPW and Pt/CsPW catalysts (carbon content 2.4–3.5%) is shown in Fig. 2. In each case two peaks are observed, which can be attributed to 'hard' coke (major peak at higher temperature) and 'soft' coke (lower temperature) [14]. For the undoped CsPW these peaks are centred at 556 and 424 °C, respectively, for 0.3% Pt/CsPW at 437 and 334 °C and for 1% Pt/CsPW at 359 and 284 °C. Similar results have been obtained for other supported Pt catalysts, e.g., Pt/Al₂O₃ [10]. Therefore, the TGA/TPO results show that coke on the Pt/CsPW burns at significantly lower temperatures than on the CsPW, hence the Pt doping could enhance catalyst regeneration.

Pt doping (0.3–1%) of CsPW indeed greatly improved the catalyst reuse (Table 2, Fig. 3). Oxidative treatment of the used

Table 2

Catalyst reuse in Fries rearrangement of PhOAc in nitrobenzene (PhOAc/PhNO₂ = 25:75 wt%, 130 °C, 2 h, 2.3 wt% catalyst)

Catalyst	Conversion (%)	Selectivity (%)					C ^a wt%	W ^a wt%
		PhOH	2HAP	4HAP	4AAP	Other		
CsPW	22	51.3	4.5	14.0	27.9	2.3	2.4 ^b	
0.3% Pt/CsPW ^c	24	52.4	4.4	10.8	28.2	4.2	0	65
0.3% Pt/CsPW ^c	22	51.0	4.5	11.7	28.6	4.2	0	64
0.3% Pt/CsPW ^c	22	50.7	4.0	9.9	28.9	6.5	0	63
0.3% Pt/CsPW ^c	22	51.8	4.2	10.3	29.5	4.2	0	63
1% Pt/CsPW ^c	24	55.6	4.3	12.3	23.5	4.3	0	65
1% Pt/CsPW ^c	22	60.2	4.2	10.7	20.7	4.2	0	66
1% Pt/CsPW ^c	24	55.9	4.8	11.5	22.5	5.3	0	65
1% Pt/CsPW ^c	23	60.6	4.1	10.1	20.9	4.3	0	63

^a The carbon content from elemental analysis and tungsten content from ICP in used anhydrous catalysts after regeneration.

^b The carbon content was measured after washing the catalyst with DCE.

^c Successive runs; after each run the catalyst was separated by filtration, washed with DCE at room temperature, calcined in air at 350 °C/2 h, followed by steaming at 200 °C/1 h and drying at 150 °C/0.5 Torr/1.5 h.

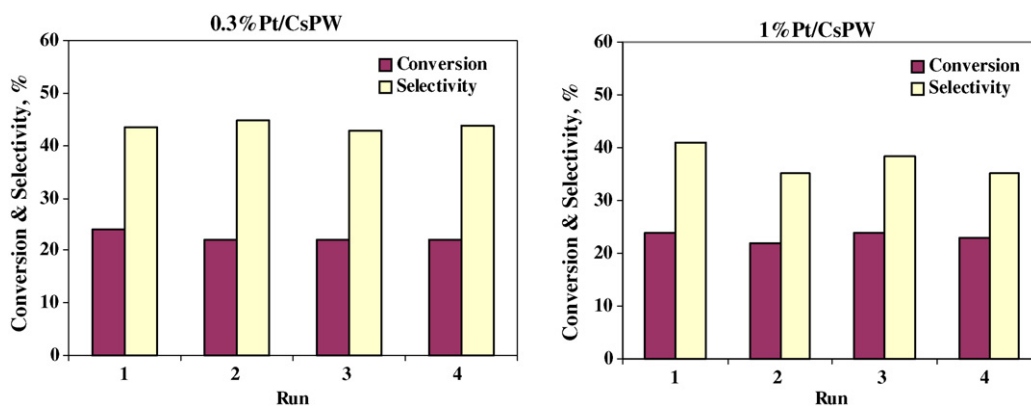


Fig. 3. Catalyst reuse in Fries rearrangement of PhOAc: conversion and total acylation selectivity (2HAP + 4HAP + 4AAP) in successive runs.

catalysts by air at 350 °C followed by steaming at 200 °C allowed full recovery of their activity and selectivity over four successive runs. The above regeneration completely removed coke from the Pt/CsPW catalysts after use (Table 2, Fig. 4). The reaction with Pt/CsPW was truly heterogeneous because CsPW is insoluble in PhNO₂. Tungsten did not leach from the catalyst, as can be seen from the constant W content in the catalyst throughout all successive runs (Table 2). Comparing the performance of CsPW and Pt/CsPW, one can conclude that the Pt doping has little effect on the catalyst activity and selectivity. Nevertheless, 0.3% Pt/CsPW showed a better performance in catalyst reuse than 1% Pt/CsPW, providing a higher and steadier activity as well as a higher total acylation selectivity (Fig. 3). This may indicate that the Pt in the latter catalyst interfered with the active acid sites. As a coke-burning catalyst, Pt is much more efficient than the previously studied Pd. Thus 0.3% Pt doping is sufficient for sustainable catalyst regeneration, whereas in the case of Pd it requires 2.1% metal loading [7].

The oxidative regeneration at 350 °C does not cause any visible damage to the catalysts structure. FTIR spectra of the catalyst before and after use (Fig. 5) show that the Keggin structure of CsPW, exhibiting four characteristic IR bands in the range 750–1100 cm⁻¹ [18], remained unchanged during four successive reaction runs.

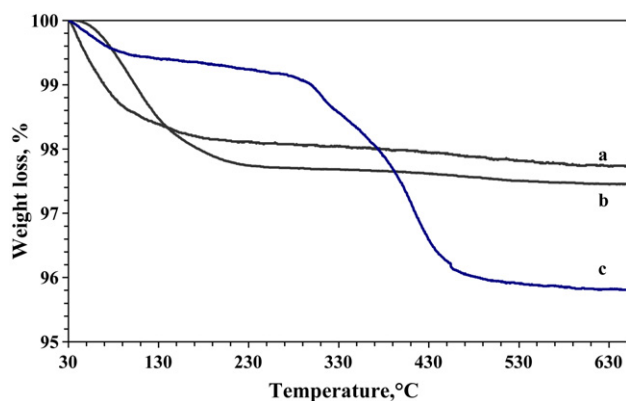


Fig. 4. TGA/TPO in air for 0.3% Pt/CsPW: (a) fresh catalyst; (b) used catalyst after air calcination at 350 °C/2 h followed by steaming at 200 °C/1 h, (c) coked catalyst after use.

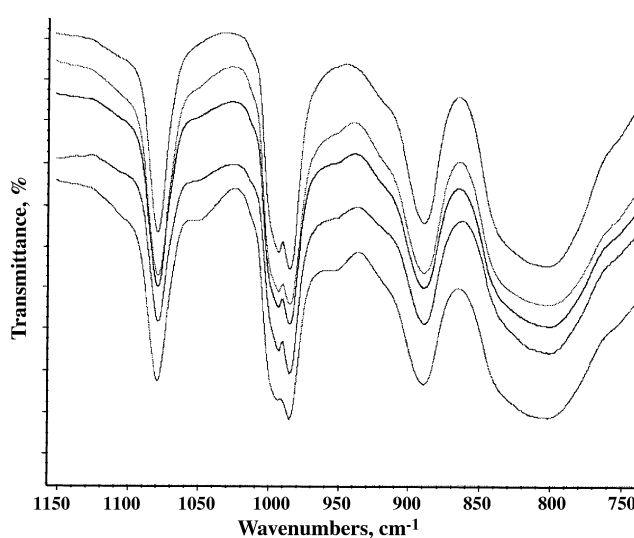


Fig. 5. FTIR spectra of 0.3% Pt/CsPW. From bottom to top: prior to use and after use and regeneration in four successive runs in PhOAc rearrangement (Table 2).

4. Conclusion

Pt-doped (0.3 wt%) acidic heteropoly salt Cs_{2.5}H_{0.5}PW₁₂O₄₀ (Pt/CsPW) is active and reusable solid acid catalyst for the Fries rearrangement of phenyl acetate in heterogeneous liquid-phase systems. The catalyst can be easily separated by filtration and, after its regeneration by the aerobic burning of coke at 350 °C, reused without loss in activity and selectivity. This regeneration causes no structural damage to the Pt/CsPW catalyst. As a coke-burning catalyst, Pt is much more efficient than the previously studied Pd; the latter requires almost ten times higher a metal loading [7]. The Pt doping may be effective for sustainable catalyst regeneration in other liquid- and gas-phase processes catalysed by solid heteropoly acids.

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