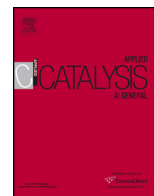




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Hydrogenation of ketones over bifunctional Pt-heteropoly acid catalyst in the gas phase

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ABSTRACT

Gas-phase hydrogenation of a wide range of ketones to alkanes, including hydrogenation of aliphatic ketones and acetophenone, was investigated using bifunctional metal–acid catalysis. The catalysts were comprised of a metal (Pt, Ru, Ni, and Cu) supported on acidic caesium salt of tungstophosphoric heteropoly acid $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW). The reaction occurred via a sequence of steps involving hydrogenation of ketone to alcohol on metal sites followed by dehydration of alcohol to alkene on acid sites and finally hydrogenation of alkene to alkane on metal sites. Catalyst activity decreased in the order: Pt > Ru > Ni > Cu. Pt/CsPW showed the highest catalytic activity, giving almost 100% alkane yield at 100 °C and 1 bar pressure. Evidence is provided that the reaction with Pt/CsPW at 100 °C is limited by ketone-to-alcohol hydrogenation, whereas at lower temperatures (≤ 60 °C) by alcohol dehydration yielding alcohol as the main product. The catalyst comprised of a physical mixture of Pt/C + CsPW was found to be highly efficient as well, which indicates that the reaction is not limited by migration of intermediates between metal and acid sites in the bifunctional catalyst.

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1. Introduction

Oxygen-containing organic compounds such as ketones, carboxylic acids, alcohols, and phenols, etc., readily available from natural resources, are attractive as renewable raw materials for the production of value-added chemicals and biofuels [1,2]. For fuel applications, they require reduction in oxygen content to increase their caloric value. Much current research is focussed on deoxygenation of organic oxygenates using heterogeneous catalysis, in particular for the upgrading of biomass-derived oxygenates obtained from fermentation, hydrolysis, and fast pyrolysis of biomass [3–7].

Biomass-derived ketones can be further upgraded by aldol condensation and hydrogenation to produce alkanes that fall in the gasoline/diesel range. The hydrogenation of ketones on supported metal catalysts (e.g., Pt/C and Pd/C) to form alcohols is feasible and well documented [8]; however, further hydrogenation to alkanes is rather difficult to achieve on such catalysts [9,10]. The ketone-to-alkane hydrogenation can be achieved much easier using bifunctional metal–acid catalysts ([9–11] and references therein). This process occurs via a sequence of steps involving hydrogenation of ketone to alcohol on metal sites followed by dehydration of

secondary alcohol to alkene on acid sites and finally hydrogenation of alkene to alkane on metal sites (Scheme 1).

Previously, this group have reported that platinum on acidic supports, namely Pt on zeolite HZSM-5 [9] and acidic caesium salt of tungstophosphoric heteropoly acid $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW) [10], is active bifunctional catalyst for hydrogenation of methyl isobutyl ketone (MIBK) to the corresponding alkane 2-methylpentane (MP) in the gas phase. 0.5%Pt/CsPW, possessing very strong Brønsted acidity in addition to Pt metal sites, has been found to be particularly efficient catalyst giving 100% yield of MP at 100 °C and 1 bar pressure without alkane isomerisation [10]. Recently, Mizuno et al. [11] have applied this catalyst for hydrogenation of ketones, phenols, and ethers in the liquid phase at 120 °C and 5 bar H_2 pressure.

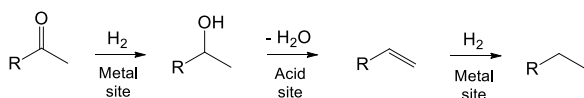
Here, we investigate the hydrogenation (hydrodeoxygenation) of a variety of ketones including aliphatic ketones and acetophenone in the gas phase using bifunctional metal–acid catalysts comprising Pt, Ru, Ni, and Cu supported on CsPW. It is demonstrated that 0.5%Pt/CsPW is a highly efficient and versatile catalyst for the ketone-to-alkane hydrogenation, and an insight into reaction mechanism is gained.

2. Experimental

2.1. Chemicals and catalysts

MIBK (99%), diisobutyl ketone (80%), acetophenone ($\geq 98\%$), 2-octanone (98%), cyclohexanone ($\geq 99\%$), 3-pentanone ($\geq 99\%$), and

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Scheme 1. Ketone hydrogenation via bifunctional metal–acid catalysis.

inorganic chemicals used for catalysts preparation were purchased from Aldrich and 2-butanone (99%) and 2-hexanone (98%) from Acros Organics. Carbon-supported platinum 10%Pt/C (7.1% Pt from ICP analysis) was from Johnson Matthey. H₂ and N₂ gases (>99%) were supplied by the British Oxygen Company.

Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsPW) was prepared according to the literature procedure [12] by adding dropwise an aqueous solution of Cs₂CO₃ (0.47 M) to an aqueous solution of H₃PW₁₂O₄₀ (0.75 M) at 40 °C with continuous stirring. The precipitate obtained was aged in aqueous slurry for 24 h at room temperature. The slurry was then slowly evaporated to dryness in a rotary evaporator at 45 °C to afford the CsPW as a white powder. The catalyst was calcined under vacuum at 150 °C/10^{−3} kPa for 1.5 h.

Bifunctional metal–acid catalysts were prepared by wet impregnation of CsPW with an appropriate metal precursor (Pt(acac)₂, H₂PtCl₆, RuCl₃, Ni(NO₃)₂, and Cu(NO₃)₂) followed by reduction of metal ion to metal with H₂. The metal loadings quoted were confirmed by the ICP–AES elemental analysis; these were in good agreement with the preparation stoichiometries since the preparations did not involve operations such as filtration and washing which could cause metal loss.

0.5%Pt/CsPW was prepared by stirring CsPW powder with 0.02 M Pt(acac)₂ solution in benzene at room temperature for 1 h, followed by slow evaporation of benzene in a rotary evaporator at room temperature [13]. The catalyst was calcined under vacuum at 150 °C/10^{−3} kPa and then reduced in an oven by a hydrogen flow at 250 °C for 2 h. Two other modifications of this catalyst were prepared by impregnation of CsPW with an aqueous solution of H₂PtCl₆, followed by drying in a rotary evaporator at 45 °C and the same calcination and reduction procedures. One, designated as 0.5%Pt/CsPW-I, was prepared by direct wet impregnation of CsPW powder with 0.1 M aqueous solution of H₂PtCl₆ involving stirring the aqueous slurry for 24 h at room temperature, followed by the workup procedure. The other, designated as 0.5%Pt/CsPW-A, was prepared by adding 0.1 M aqueous solution of H₂PtCl₆ to the freshly precipitated aqueous CsPW slurry and ageing the mixture at room temperature with stirring for 24 h, followed by the workup.

The physical mixture of 10%Pt/C and CsPW containing 0.5% of Pt was prepared by grinding a 1:20 w/w mixture of the two components.

Two modifications of 5%Ru/CsPW, designated as 5%Ru/CsPW-I and 5%Ru/CsPW-A, were prepared by impregnation of CsPW with 0.1 M aqueous solution of RuCl₃ similar to the preparation of 0.5%Pt/CsPW-I and 0.5%Pt/CsPW-A.

10%Cu/CsPW catalyst, designated as 10%Cu/CsPW-I, was prepared as described elsewhere [13] by stirring CsPW powder with an aqueous solution of Cu(NO₃)₂·6H₂O for 24 h at room temperature, followed by drying in a rotary evaporator at 65 °C and calcination at 150 °C/10^{−3} kPa for 1.5 h. Finally, the sample was reduced in H₂ flow at 400 °C for 2 h. Another modification of this catalyst, designated as 10%Cu/CsPW-A, was prepared by adding an aqueous solution of Cu(NO₃)₂·6H₂O to the freshly precipitated aqueous CsPW slurry and ageing the mixture at room temperature with stirring for 24 h, followed by the same workup.

Two modifications of 10%Ni/CsPW catalyst, designated as 10%Ni/CsPW-I and 10%Ni/CsPW-A, were prepared similarly to the corresponding 10%Cu/CsPW catalysts using Ni(NO₃)₂·6H₂O as a precursor.

2.2. Techniques

The BET surface area and porosity of catalysts were determined from nitrogen physisorption measured on a Micromeritics ASAP 2010 instrument at −196 °C. Before measurement, the samples were evacuated at 250 °C for 2 h. Powder X-ray diffraction (XRD) spectra of catalysts were recorded on a PANalytical Xpert diffractometer with a CuKα radiation (λ = 1.542 Å). XRD patterns were attributed using the JCPDS database. ICP–AES elemental analysis was carried out on a Spectro Ciros emission spectrometer.

Metal dispersion of Pt and Ru in the catalysts was measured in a flow system by hydrogen chemisorption using the hydrogen–oxygen titration pulse method described previously [14]. A catalyst sample (50 mg) reduced by hydrogen was pre-exposed to air at room temperature for 1 h then placed in a glass sample tube connected to a Micromeritics TPD/TPR 2900 instrument and stabilised at a specified temperature under nitrogen flow. The hydrogen–oxygen titration was carried out at room temperature for Pt catalysts and at 100 °C for Ru catalysts. Fifty microliter pulses of pure H₂ were injected in the N₂ flow in 3 min intervals until the catalyst was saturated with hydrogen. The metal dispersion, *D*, defined as the fraction of metal (*M*) at the surface, $D = M_s/M_{\text{total}}$, was calculated assuming the stoichiometry of H₂ adsorption: $M_sO + 1.5 H_2 \rightarrow M_sH + H_2O$ [15,16]. The average diameter of metal particles, *d*, was obtained from the empirical equation $d \text{ (nm)} = 0.9/D$ [16]. For the commercial 10%Pt/C catalyst, Pt dispersion was also determined by pulse chemisorption of CO in He flow at 50 °C (20 mg catalyst sample, 50 μL pulses of pure CO, adsorption stoichiometry Pt₅:CO = 1). For Cu catalysts, the metal particle size was determined by XRD using the Scherrer equation, with line broadening assessed as the full width at half maximum intensity (FWHM). The dispersion of Cu particles, *D*, was calculated from the equation $d \text{ (nm)} = 1.1/D$ [17].

2.3. Catalyst testing

The hydrogenation of ketones was carried out in the gas phase in flowing H₂. The catalysts were tested at 60–100 °C under atmospheric pressure in a Pyrex fixed-bed down-flow reactor (9 mm internal diameter) fitted with an on-line gas chromatograph (Varian Star 3400 CX instrument with a 30 m × 0.25 mm HP INNOWAX capillary column and a flame ionisation detector). The temperature in the reactor was controlled by a Eurotherm controller using a thermocouple placed at the top of the catalyst bed. The gas feed contained a variable amount ketone in H₂ as a carrier gas. The ketone was fed by passing H₂ carrier gas flow controlled by a Brooks mass flow controller through a stainless steel saturator, which held the liquid ketone at appropriate temperature to maintain the chosen reactant partial pressure. The downstream gas lines and valves were heated to 180 °C to prevent substrate and product condensation. The gas feed entered the reactor at the top at a flow rate of 20–100 mL min^{−1}. The reactor was packed with 0.2 g catalyst powder of 45–180 μm particle size. In some cases, to reduce conversion, a smaller amount of catalyst was used as a homogeneous mixture with silica of a total weight of 0.2 g. Prior to reaction, the catalysts were pre-treated in H₂ for 1 h at the reaction temperature unless stated otherwise. The dehydration of 2-methyl-4-pentanol was studied similarly, except using N₂ as a carrier gas instead of H₂. Once reaction started, the downstream gas flow was analysed by the on-line GC to obtain reactant conversion and product selectivity. The selectivity was defined as moles of product formed per one mole of reactant converted and quoted in mole per cent. The mean absolute percentage error in conversion and selectivity was ≤10% and the carbon balance was maintained within 95%.

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