Isomerisation of n-hexane over bifunctional Pt-heteropoly acid catalyst: Enhancing effect of gold

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**Abstract**

Isomerisation of n-hexane was studied in the presence of acid and bifunctional metal-acid catalysts based on Keggin-type heteropoly acids (HPA), in particular focusing on Cs2.5H0.5PW12O40 (CsPW) and Pt/CsPW as the catalysts, using a fixed-bed microreactor under differential conditions (n-hexane conversion ≤ 10%) at 180-220 oC, ambient pressure and a ratio of n-hexane and H2 partial pressures of 0.06-0.24. The turnover rate of HPA-catalysed isomerisation was found to correlate with the acid strength of HPA (initial enthalpy of ammonia adsorption). Bifunctional Pt-HPA catalysts were more efficient than monofunctional HPA catalysts. In the isomerisation over Pt/CsPW bifunctional catalyst, n-hexane dehydrogenation step was found to equilibrate at a molar ratio of Pt and H+ surface sites Pts/H+ ≥ 0.8, corresponding to a Pt loading ≥ 6%. Bimetallic PtAu/CsPW catalyst showed higher activity in n-hexane isomerisation than Pt/CsPW, although the Au alone without Pt was inert. In the presence of Au, the turnover rate at Pt sites increased more than twofold. The effect of Au is attributed to PtAu alloying. Scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM-EDX) and X-ray diffraction (XRD) analyses of PtAu/CsPW indicated the presence of bimetallic PtAu nanoparticles with a wide range of Pt/Au atomic ratios.

*Keywords*: Isomerisation; n-Hexane; Bifunctional catalysis; Platinum; Gold; Heteropoly acid.

1. **Introduction**

Isomerisation of linear C5–C6 alkanes, which are relatively stable toward cracking, is used in industry to produce high octane gasoline. For example, n-hexane isomerisation to 2-methylpentane (2MP) and 3-methylpentane (3MP) increases the research octane number (RON) from 25 to 74. Further branching to 2,2- and 2,3-dimethylbutane isomers (22DMB and 23DMB) increases RON to 96 and 105, respectively [1].



**Scheme 1.** Acid-catalysed pathway for n-hexane isomerisation via monomolecular mechanism.

Alkane isomerisation can occur via an acid-catalysed pathway on strong Lewis and Brønsted acid sites [2,3] (Scheme 1). With Lewis acids, a linear alkane, e.g., n-hexane, can be isomerised through a monomolecular carbenium-ion chain mechanism including carbenium ions produced by H- abstraction on Lewis acid sites. The carbenium ions then form a protonated cyclopropane intermediate, which undergoes β-migration of methyl group followed by H- transfer from an n-hexane molecule to give mono-branched 2MP and 3MP as the primary isomerisation products together with the carbenium ions continuing the chain process (not shown in Scheme 1). Subsequent isomerisation of 2MP and 3MP can lead to formation of 23DMB and 22DMB. On strong Brønsted acid sites, carbonium ions are formed by protonation of a C-H bond. The carbonium ions then undergo H2 elimination to give the carbenium ions leading to the formation of 2MP and 3MP. Proton elimination from the carbenium ions could give alkenes. The latter form oligomers and coke, which cause catalyst deactivation (Scheme 1). In addition, C6- hydrocarbons can be formed by cracking of hexane isomers. Also C6- and C6+ products can be produced by disproportionation of C12 cation intermediates formed from the C6 carbenium ions and an alkene (bimolecular mechanism) [2,3].

Industrial isomerisation of linear alkanes is carried out using bifunctional metal-acid catalysts, usually platinum supported on chlorinated alumina or acidic zeolites (e.g., mordenite) in the presence of hydrogen (hydroisomerisation) [1]. The reaction is suggested to proceed in accordance with Scheme 2 involving alkane dehydrogenation on Pt sites followed by isomerisation of the alkene formed on acid sites of support [4]. The alkene isomer is then hydrogenated on the platinum to give the branched alkane. The bifunctional pathway (Scheme 2) is much more efficient than the acid-catalysed pathway (Scheme 1). Platinum in the bifunctional catalyst is important not only in enhancing the isomerisation process, but also in reducing the steady state alkene concentration. The latter increases reaction selectivity due to diminishing the contribution of the bimolecular mechanism [5] and reduces coke formation, thus improving catalyst lifetime [1].



**Scheme 2.** Bifunctional catalysed pathway for n-hexane isomerisation (hydroisomerisation).

Heteropoly acids (HPAs) possessing very strong Brønsted acidity have attracted much interest as acid catalysts, in particular tungsten HPAs with Keggin structure such as H3PW12O40 (HPW) and H4SiW12O40 (HSiW) [6-8]. In recent years, Pt-HPA bifunctional catalysis for alkane isomerisation has been studied extensively to show its high efficiency in this reaction ([9-12] and references therein).

Here, we investigate the Pt-HPA bifunctional catalysis in the isomerisation of n-hexane, focussing on the use of Cs2.5H0.5PW12O40 (CsPW) as the acid component. CsPW is an insoluble acidic salt of 12-tungstophosphoric acid, which has important advantages over the parent HPW in possessing much larger surface area (hence larger surface acidity) and higher thermal stability, while having the Brønsted acid sites almost as strong as in HPW [6,7]. Also, we report here an enhancing effect of Au on n-hexane isomerisation over Pt/CsPW. It is demonstrated that modification of the Pt/CsPW catalyst with gold increases the reaction turnover rate at Pt surface sites more than twofold, although the gold alone without Pt is practically inactive in this reaction. It is suggested that the enhancement is caused by PtAu alloying. STEM-EDX and XRD analysis of the PtAu/CsPW catalysts indicates the presence of bimetallic PtAu nanoparticles with a wide range of Pt/Au atomic ratios.

**2. Experimental**

*2.1. Chemicals and catalysts*

n-Hexane (>99%), H2PtCl6 hydrate, HAuCl4·3H2O, H3PW12O40 (HPW, 99%) and H4SiW12O40 (HSiW, 99.9%) hydrates were all purchased from Sigma-Aldrich. Catalyst supports P25 titania (anatase/rutile = 3:1) and Aerosil 300 silica were from Degussa. H2 gas cylinders (>99%) were supplied by the British Oxygen Company.

Cesium tungstophosphate Cs2.5H0.5PW12O40 (CsPW) was prepared according to the literature procedure [13,14] by adding drop-wise the required amount of aqueous solution of cesium carbonate to aqueous solution of H3PW12O40 to afford CsPW as a white precipitate. The material was isolated, vacuum dried at 150 oC/10-3 kPa for 1.5 h. A similar procedure was used for the preparation of Cs2.25H0.75PW12O40 (Cs2.25PW). Silica- and titania-supported HPW and HSiW catalysts were prepared by wet impregnation of HPA onto support as described elsewhere [14] and dried at 150 oC/10-3 kPa for 1.5 h. Information about these solid acid catalysts and supports is given in Table 1; it includes their texture, proton site density and acid strength represented by the initial enthalpy of ammonia adsorption [14].

CsPW-supported bifunctional metal-acid catalysts, Pt/CsPW and Au/CsPW, were prepared as described previously [15] by wet impregnation of CsPW powder with aqueous solutions of H2PtCl6 or HAuCl4.This involved stirring the aqueous slurry at 50 oC for 2 h followed by rotoevaporation to dryness and reduction with H2 flow at 250 oC for 2 h. The bimetallic PtAu/CsPW catalysts were prepared similarly by co-impregnation of CsPW with H2PtCl6 and HAuCl4 with reduction by H2 as above. Metal content in these catalysts was determined by ICP-AES analysis (see below). Physical mixtures of bifunctional catalysts and SiO2 with a specified Pt and Au loading were prepared by grinding the catalysts with Aerosil 300 silica. Properties of the bifunctional catalysts are shown in Table 2.

*2.2. Techniques*

The surface area and porosity of catalysts were determined from nitrogen physisorption measured on a Micromeritics ASAP 2010 instrument at −196 oC. Before measurement, the samples were evacuated at 250 oC for 2 h. Powder X-ray diffraction (XRD) patterns of catalysts were recorded on a PANalytical Xpert diffractometer with CuKα radiation (*λ* = 1.542 Å) and attributed using the JCPDS database. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) elemental analysis was carried out on a Spectro Ciros optical emission spectrometer. Thermo Flash EA 1112 analyser was used to determine carbon content in spent catalysts by combustion chemical analysis.

Scanning transmission electron microscopy (STEM) imaging and energy dispersive X-ray spectroscopy (EDX) analysis of catalysts was carried out on an aberration-corrected JEOL JEM 2100FCs instrument operated at 200 kV, equipped with an EDAX Octane T Optima 60 windowless silicon drift detector. For STEM analysis, the samples were prepared by scooping up the catalyst powder by a TEM grid (holey carbon film on 300 Ni mesh, Agar Scientific) followed by shaking to remove excess material from the grid.

Platinum dispersion in the catalysts was measured on a Micromeritics TPD/TPR 2900 instrument using the hydrogen-oxygen titration pulse method in a flow system at room temperature as described previously [15,16].The Pt dispersion, *D*, defined as the Pt fraction at the surface, *D* = Pts/Pttotal, was calculated assuming the stoichiometry of H2 adsorption: PtsO + 1.5 H2 → PtsH + H2O [17,18]. Adsorption of H2 observed on the PtAu catalysts was attributed entirely to platinum as Au/CsPW did not adsorb any hydrogen under such conditions [15].The average diameter of Pt particles, *d*, was obtained from the empirical equation *d* (nm) = 0.9/*D* [18].For some PtAu/CsPW catalysts, the metal particle size was also estimated by XRD using the Scherrer equation, with line broadening assessed as the full width at half maximum intensity (FWHM).

*2.3. Catalyst testing*

Isomerisation of n-hexane was carried out at the gas-solid interface in flowing H2 at 180-220 oC. The catalysts were tested under atmospheric pressure at a ratio of n-hexane and H2 partial pressures of 0.06-0.24 in a Pyrex fixed-bed down-flow microreactor (9 mm internal diameter) fitted with an on-line gas chromatograph (Varian Star 3400 CX instrument with a 30 m x 0.25 mm HP INNOWAX capillary column and a flame ionisation detector). For more accurate off-line GC analysis of C6- hydrocarbon products, a 60 m x 0.32 mm GS-GasPro capillary column was used. The temperature in the reactor was controlled by a Eurotherm controller (±0.5 oC) using a thermocouple placed at the top of the catalyst bed. n-Hexane was fed by passing H2 flow controlled by a Brooks mass flow controller through a stainless steel saturator, which held n-hexane at 0 oC (ice bath) to maintain the chosen reactant partial pressure of 5.78 kPa (5.8 mol% concentration of n-hexane in H2 flow) unless stated otherwise. The downstream gas lines and valves were heated to 150 oC to prevent substrate and product condensation. The gas feed entered the reactor from the top at a flow rate of 20 mL min-1. The reactor was packed with 0.20 g catalyst powder of 45-180 μm particle size. Unless stated otherwise, the reaction was carried out at a space time *W/F* = 69.2 g h mol-1, where *W* is the catalyst weight (in grams) and *F* is the inlet molar flow rate of n-hexane (in mol h-1). Prior to reaction, the catalysts were pre-treated in situ for 1 h at the reaction temperature. Once reaction started, the downstream gas flow was analysed by the on-line GC to obtain reactant conversion and product composition. Product selectivity was defined as moles of product formed per one mole of n-hexane converted and quoted in mole per cent. The mean absolute percentage error in conversion and selectivity was ≤ 5% and the carbon balance was maintained within 95%. Reaction rates (*R*) were determined as *R = XF/W* (in mol gcat-1h-1), where *X* is the fractional conversion of n-hexane. In most cases, the reaction was carried out at differential conditions (*X* ≤ 0.1), where *X* is directly proportional to the reaction rate. In some cases, the catalysts were diluted with silica in order to achieve low conversion.

1. **Results and discussion**

*3.1. Acid-catalysed isomerisation of n-hexane*

Bulk and supported heteropoly acids HSiW and HPW were found to have small activity in n-hexane isomerisation. Bulk acidic Cs salts of HPW, i.e. CsPW and Cs2.25PW, showed better activities in this reaction (Table 3) despite their weaker acidity compared to the bulk HPW (Table 1). This can be attributed to the larger surface area hence larger proton site density of the Cs salts (Table 1). 2MP and 3MP were the main reaction products, which formed with 65-67% and 29-31% selectivity, respectively, together with 3-5% of cracking products (mainly C3-C5 hydrocarbons). Double-branched 23DMB isomer was formed in less than 1% selectivity. Strong catalyst deactivation was observed, which can be assigned to coke deposition. Initially white, CsPW catalyst turned black after reaction, with a carbon content of 0.6 wt% as determined by combustion chemical analysis for the reaction at 180 oC after 6 h time on stream (Table S1 in the Supporting Information). As seen from the time course of reaction with CsPW at 200 oC (Fig. 1), n-hexane conversion is strongly affected by catalyst deactivation, however without changing reaction selectivity. Practically the same results were obtained when using N2 instead of H2 as the carrier gas.

The rates of acid-catalysed isomerisation of n-hexane (*R*) and turnover frequencies (TOFH) per surface proton site were calculated using the values of n-hexane conversion for 1 h time on stream (Table 3). The required densities of surface proton sites are given in Table 1; these were estimated as described elsewhere [14]. For supported HPA catalysts, which contained HPW or HSiW at a sub-monolayer loading of 15%, all HPA protons were assumed to be equally available for reaction. For bulk HPW, HSiW and Cs salts of HPW, the number of surface proton sites was calculated using a Keggin unit cross section of 144 Å2 [6,7] and the catalyst surface areas from Table 1.

The TOFH values obtained ranged from 0.1 h-1 for 15%HPW/TiO2 to 5.2 h-1 for bulk HPW (Table 3) indicating a strong effect of catalyst acid strength on the reaction turnover rate. Fig. 2 shows the relationship between the activity of catalysts in n-hexane isomerisation, ln (TOFH), and their acid strength represented by the initial enthalpy of ammonia adsorption, Δ*H*NH3 (Table 1). Although there is considerable scatter of points, which is probably caused by catalyst deactivation, this relationship clearly indicates that Brønsted acid sites play important role in n-hexane isomerisation over heteropoly acid catalysts as can be anticipated from the reaction mechanism shown in Scheme 1.

*3.2. Bifunctional metal-acid catalysed isomerisation of n-hexane*

As expected, Pt/CsPW bifunctional catalysts in the presence of H2 were more efficient in n-hexane isomerisation than the acid catalyst CsPW. The Pt/CsPW catalysts showed higher catalytic activity and displayed much less catalyst deactivation compared to CsPW (Fig. 3). The amount of coke in spent Pt/CsPW catalysts was below the detection limit after reaction at 180 oC (6 h on stream) (Table S1). When using N2 as the carrier gas in the absence of H2, the activity of Pt/CsPW was much lower and strong catalyst deactivation was observed (Fig. S1). The activity of Pt/CsPW increased with increasing Pt loading (Table 4, entries 1-3, 5 and 6). Thus 5.78%Pt/CsPW gave a tenfold higher n-hexane conversion than CsPW at 200 oC (entries 2 and 6). The reaction products included 2MP (64-69% selectivity), 3MP (30-32%) and 23DMB (0.8-1.2%) together with 2-5% of cracking products (mainly C3-C5 hydrocarbons) at n-hexane conversion of 4-22%. Similar product selectivity was observed with CsPW without Pt (Table 4, entries 1 and 2). This indicates that Pt does not affect β-migration of methyl group in the protonated cyclopropane intermediate (Scheme 1 and 2). The low 23DMB selectivity can be explained by the low n-hexane conversion under the chosen differential reaction conditions. It should be noted that the conversions and selectivities observed were far from equilibrium values. The equilibrium C6 alkane isomer mixture at 200 oC contains n-hexane (14%), 2MP (31%), 3MP (20%), 22DMB (26%) and 23DMB (9%), which corresponds to 86% n-hexane conversion [19]. It should be noted that there was no C6+ hydrocarbons observed among the reaction products. This indicates the reaction occurring via the monomolecular mechanism (Scheme 2) in agreement with the literature [5].

Kinetics of alkane isomerisation over Pt-acid bifunctional catalysts based on zeolites and heteropoly acids has been addressed in previous reports [10,20,21]. n-Hexane is relatively stable towards cracking, therefore the rate of isomerisation could be approximated by the rate of n-hexane conversion [21]. When the dehydrogenation reaction step is equilibrated and the isomerisation step is rate limiting (Scheme 2) and also the hydrocarbon concentrations inside catalyst pores are in equilibrium with the gas phase, the overall rate of isomerisation *R* is given by equation (1), where *Kd* is the equilibrium constant of dehydrogenation, *Kp* is the equilibrium constant of protonation, *ki* is the rate constant of isomerisation, *PC­6* is the partial pressure of n-hexane, *PH2* is the partial pressure of hydrogen and *α* is the order of reaction (*α* ≤ 1) [20,21].

 (1)

The rate limiting step is determined by the balance between metal and acid functionalities in bifunctional catalyst, i.e., the ratio of accessible surface metal and acid sites Pts/H+ [4,10,20-22]. In the case of catalysts based on zeolites (e.g., H-MOR, H-BEA, H-USY, etc.), the dehydrogenation step is usually equilibrated at Pts/H+ < 0.1, and the isomerisation step becomes rate limiting [20,22]. For Pt-HPA catalysts based on HPW possessing significantly stronger proton sites compared to zeolites [14], a much higher Pts/H+ ratio may be required to equilibrate the dehydrogenation step [10].

Fig. 4 shows the plot of n-hexane conversion over Pt/CsPW catalyst as a function of Pt loading. As seen, the conversion increases with increasing the Pt loading, levelling off at ≥ 6% Pt loading. Fig. 5 shows the same results represented as turnover frequencies TOFH and TOFPt versus the Pts/H+ ratio, where the TOFH and TOFPt were calculated per surface H+ and Pts site, respectively, using conversion data at 200 oC and the Pt dispersion from Table 2. It was also assumed that the proton site density of CsPW (0.076 mmol g-1, Table 1) was not affected by Pt loading. The contribution of CsPW (Table 4, entry 2) was subtracted from the total conversion when calculating the TOFPt. As expected from Scheme 2, TOFH increases and TOFPt decreases with increasing the Pts/H+ ratio, levelling off as the dehydrogenation step reaches quasi-equilibrium (Fig. 5). These results demonstrate that under the chosen reaction conditions (200 oC, *P*C6/*P*H2 *=* 0.061), n-hexane dehydrogenation step is equilibrated over Pt/CsPW catalyst at Pts/H+ ≥ 0.8, which corresponds to a Pt loading of ~6%. This Pts/H+ value is predictably higher than that usually found for Pt/zeolite catalysts, which can be attributed to the stronger acidity of CsPW compared to the conventional zeolites.

The apparent activation energy, *Ea*, for n-hexane isomerisation over 5.78%Pt/CsPW was found to be 79 kJ mol-1 in the temperature range of 180-220 oC. The Arrhenius plot is shown in Fig. 6; in this plot, the differential conversion of n-hexane *X* which is directly proportional to the reaction rate is used. The high *Ea* value obtained indicates no diffusion limitations in the isomerisation reaction over Pt/CsPW.

The isomerisation reaction is first order in Pt/CsPW catalyst (Fig. 7). The order in n-hexane was found to be 0.90 in agreement with eq. (1) (Fig. 8, where *PC6* is varied at practically constant *PH2*). Also in accordance with eq. (1), the reaction rate increases with increasing the partial pressure ratio *P*C6/*P*H2; 4-fold increase in *P*C6/*P*H2 caused a factor of 1.5-1.8 increase in reaction rate for Pt/CsPW catalysts at 180 oC (Table 5). Overall, these kinetic results are in good agreement with eq. (1), taking into account that in these reaction systems n-hexane dehydrogenation step was not always fully equilibrated.

*3.3. Effect of gold*

It has been well documented that bimetallic PtAu and PdAu catalysts frequently have an enhanced performance in comparison to monometallic Pt and Pd catalysts ([15,23-32] and references therein), for example in hydrogenation [32], hydrodeoxygenation [15,24], hydrodesulphurisation [30,31], oxidation [25-27] and other reactions (for review, see [23,28,29]). The enhancement of catalyst performance by addition of gold can be attributed to geometric (ensemble) and electronic (ligand) effects of the constituent elements in PtAu and PdAu bimetallic species [28,29].

A wide range of bimetallic catalysts have been studied in alkane and cycloalkane reactions such as hydrogenolysis, isomerisation, cyclisation, ring enlargement, etc., dating back to the 1970s [33-40]; these include both supported and alloy film PtAu and PdAu catalysts [33,36,37,39,40]. A short communication by Fraissard et al. [40] has reported the use of PtAu nanoparticles supported on zeolites (HY and HZSM-5) for hydroisomerisation of n-hexane. It has been found that 1%Pt/0.2%Au/HY and 1%Pt/HY have the same activity and selectivity in this reaction without any Au enhancement; 1%Pt/0.2%Au/HZSM-5 shows good performance stability, but has not been tested against its Pt-only analogue.

Here we looked at the effect of Au additives on the performance of Pt/CsPW catalysts in the isomerisation of n-hexane. In this work, supported bimetallic catalysts PtAu/CsPW were prepared by co-impregnation of platinum and gold precursors onto CsPW followed by reduction of solid pre-catalysts with H2 at 250 oC. This method would favour the formation of supported PtAu nanoparticles of a random composition together with various Pt and Au nanoparticles, rather than more uniform bimetallics that can be prepared in solution [29].Information about the PtAu/CsPW catalysts studied (catalyst texture and metal dispersion) is given in Table 2.

STEM-EDX analysis indicated the presence of bimetallic nanoparticles in the PtAu/CsPW catalysts. The high-angle annular dark field (HAADF) STEM images of 5.78%Pt/CsPW, 2.62%Au/CsPW and 5.57%Pt/4.25%Au/CsPW catalysts are shown in Fig. 9, with metal nanoparticles indicated as bright spots on the darker background. These STEM images are difficult to analyse due to W, Pt and Au having similar large atomic numbers *Z* (74, 78, and 79, respectively). CsPW containing 70 wt% of W displays a strong background which makes it difficult to distinguish smaller Pt and Au particles from the *Z*-contrast HAADF images and determine accurately metal particle size distribution. Nevertheless, in Fig. 9a (5.78%Pt/CsPW catalyst), one can see platinum particles of ≤ 12 nm in size. The image of 2.62%Au/CsPW (Fig 9b) shows oval shaped gold particles sized up 4 to 25 nm, with an average gold particle size ≤ 10 nm. Particles of a similar size and shape can be also seen in Fig. 9c (5.57%Pt/4.25%Au/CsPW), which indicates a PtAu alloying on the catalyst surface (see EDX analysis below).

The EDX analysis of a large number of metal nanoparticles in the 5.57%Pt/4.25%Au/CsPW catalyst showed that all these particles contained both Pt and Au in Pt/Au atomic ratios varying from 0.5 to 7.7 (Fig. S4 and Fig. S5). EDX elemental mapping (Fig. S6) shows that Pt and Au maps cover the same areas of PtAu/CsPW catalyst particles, indicating formation of a non-uniform PtAu particles (alloys), with local variations in Pt/Au atomic ratio.

Fig. 10a shows the XRD patterns of 5.57%Pt/4.25%Au/CsPW and 5.78%Pt/CsPW catalysts, in which the bcc pattern of crystalline CsPW [41] is dominated. Also clearly seen is the fcc pattern of Pt (39.8o [111] and 46.2o [200]) and Au (38.2o [111] and 44.4o [200]) metal nanoparticles. This confirms coexistence of Pt and Au particles in the PtAu/CsPW catalyst. In addition, PtAu bimetallic particles may be present with diffraction pattern falling in between the corresponding diffractions of the pure metals [29], which is obscured by the intense pattern of CsPW. Indeed, the close-up normalized difference XRD (Fig. 10b) shows a broad diffraction peak in the range of 38-40o and possibly a weaker [200] peak in the range 44-46o between the diffractions of pure Pt and Au, which could be attributed to PtAu alloys. In Fig. 10a, the Pt peaks appear notably broader than the Au peaks, indicating higher dispersion of Pt particles. Although accurate analysis of metal particle size is difficult due to the prevailing CsPW pattern, rough estimate from the [111] peaks using the Scherrer equation gave 60 and 30 nm volume-average particle size for Au and Pt, respectively. This estimate, however, may be biased towards larger metal particles.

Representative results of PtAu/CsPW catalyst testing are shown in Table 4. Addition of gold to the Pt/CsPW catalysts was found to increase n-hexane conversion by a factor of 1.3 to 1.7 (Table 4, cf. entry 3 with 7 and 5 with 8), although the Au alone without Pt was inert (cf. entries 9 and 10 with 1). The effect of gold cannot be attributed to any change in Pt dispersion because Au additives practically did not change the dispersion of Pt in these catalysts (Table 2).

As seen from Table 4, gold additives, while increasing the conversion, did not affect reaction selectivity. This indicates that the effect of gold is pertinent to the Pt-catalysed dehydrogenation reaction step and does not affect subsequent reactions of carbenium ions (Scheme 2). It is important that the scale of Au effect on catalyst activity depended on the Pt loading, i.e., on the degree of equilibration of the dehydrogenation reaction step. Subtracting the contribution of CsPW (entry 1) from the conversion values in entries 3, 5, 7 and 8 gives the Au enhancement scale of a factor of 2.0 at a low Pt loading (~0.3%) and only a factor of 1.3 at a higher loading (~6%). This implies that the effect of Au is the strongest when alkane dehydrogenation is the rate-limiting step and decreases as alkane dehydrogenation approaches equilibrium.

Fig. 11 and 12 show comparative time courses for PtAu/CsPW versus Pt/CsPW and Au/CsPW versus CsPW, respectively, with n-hexane conversion and product selectivity as a function of the time on stream. Practically no coke was found in spent PtAu/CsPW catalysts, although a small amount of coke (0.3% C) was formed in Au/CsPW catalyst (Table S1). Nevertheless, the amount of coke in the Au/CsPW was less than that in CsPW (0.6%). This might explain a better performance stability of Au/CsPW compared to CsPW which can be seen in Fig. 12.

Kinetically, the reaction with PtAu/CsPW catalyst was found to be very similar to that with the monometallic Pt/CsPW described above. For PtAu/CsPW, the apparent activation energy was found to be 86 kJ mol-1 at 180-220 oC (cf. 79 kJ mol-1 for Pt/CsPW). As seen from the Arrhenius plot (Fig. 6), n-hexane conversion for the PtAu catalyst is higher than that for the Pt catalyst with very close Pt loading, thus conforming the Au enhancement in the whole temperature range. Similar to Pt/CsPW, the reaction with PtAu/CsPW is first order in the catalyst (Fig. S2) and 0.90 order in n-hexane (Fig. S3). Table 5 compares the effect of the *PC6/PH2* ratio for the reaction with Pt/CsPW and PtAu/CsPW catalysts. In both cases, the reaction rate increases with increasing the *PC6/PH2* ratio (a factor of 1.8-1.9 for PtAu/CsPW and 1.5-1.8 for Pt/CsPW when the *PC6/PH2* ratio was increased from 0.061 to 0.24); this is in agreement with rate equation (1). These results show that the reaction with both catalysts fits well with this equation.

The values of TOFPt in Table 5 give a more accurate estimate of the scale of gold effect. As seen, the gold enhancement of TOFPt is a factor of 2.2-2.3 for the 0.28-0.32% Pt loading and 1.4-1.7 for the 5.57-5.78% Pt loading. Thus the enhancing effect of gold decreases with increasing the Pt loading as n-hexane dehydrogenation step approaches quasi-equilibrium. It can therefore be anticipated that when the dehydrogenation step is fully equilibrated, the effect of gold will be close to zero.

Therefore, the results obtained demonstrate that gold additives can increase the activity of Pt/CsPW bifunctional catalyst in hydroisomerisation of n-hexane, although the gold alone is not active. More specifically, gold increases the catalytic activity of Pt sites in alkane dehydrogenation step. When alkane dehydrogenation is the rate-limiting step, the enhancing effect on the isomerisation reaction is at its maximum. At such conditions the enhancement of the turnover rate at the Pt surface sites amounts to a factor of ≥ 2 as can be seen from the TOFPt values in Table 5. Conversely, the effect of gold decreases as the dehydrogenation step approaches quasi-equilibrium. As shown above, in n-hexane isomerisation over Pt/CsPW, the dehydrogenation step is equilibrated at a molar ratio of Pt and H+ surface sites Pts/H+ ≥ 0.8, corresponding to a Pt loading ≥ 6%. As a result, the gold enhancement is observable at Pts/H+ < 0.8 in this system. In the case of Pt-zeolite catalysts, the dehydrogenation step is equilibrated at Pts/H+ < 0.1 [20,22], which is due to the weaker acid strength of zeolites compared to HPA. In this regard, the lack of gold enhancement in n-hexane isomerisation over 1%Pt/0.2%Au/HY as compared to 1%Pt/HY reported by Fraissard et al. [40] can be explained by equilibration of n-hexane dehydrogenation step in this system.

The nature of gold enhancement may be attributed to the previously documented electronic (ligand) and geometric (ensemble) effects in bimetallic PtAu species [28,29]. Our STEM-EDX analysis clearly indicates the presence of bimetallic PtAu nanoparticles in the PtAu/CsPW catalyst. The interaction between Pt and Au in these nanoparticles can lead to the superior catalyst performance in n-hexane isomerisation. Thorough structural characterisation of PtAu/CsPW catalyst complemented by computational studies may provide further insights into the gold effect in this system.

**4. Conclusions**

The isomerisation of n-hexane was carried out using acid and bifunctional metal-acid catalysts based on Keggin-type heteropoly acids at a gas-solid interface at 180-220 oC and ambient pressure in a fixed-bed microreactor. The bifunctional catalysts studied comprised Pt as the metal component and Cs2.5H0.5PW12O40 (CsPW), an acidic Cs salt of heteropoly acid H3PW12O40, as the acid component. Addition of gold to the Pt/CsPW catalyst was found to increase the catalytic activity, although the Au alone without Pt was inert. The enhancement of catalyst performance is suggested to be caused by PtAu alloying. The STEM-EDX and XRD analyses of the PtAu/CsPW catalysts indicate the presence of bimetallic PtAu nanoparticles with a wide range of Pt/Au atomic ratios.

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**Table 1**

Information about acid catalysts [14].

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Catalysts | *S*BETa  m2g-1 | Pore volumeb  cm3g-1 | Pore sizec  Å | H+ sitesd  mmol g-1 | Δ*H*NH3e  kJ mol-1 |
| TiO2 (P25 Degussa) | 44 | 0.10 | 90 |  |  |
| SiO2 (Aerosil 300) | 300f |  |  |  |  |
| H3PW12O40 (HPW) | 5.6 | 0.04 | 81 | 0.019 | -197 |
| H4SiW12O40 (HSiW) | 9.0 | 0.02 | 71 | 0.042 | -171 |
| Cs2.5H0.5PW12O40 (CsPW) | 132 | 0.10 | 29 | 0.076 | -164 |
| Cs2.25H0.75PW12O40 | 128 | 0.07 | 22 | 0.110 | -162 |
| 15%HPW/SiO2 | 202 | 1.00 | 169 | 0.156 | -154 |
| 15%HSiW/SiO2 | 221 | 1.02 | 185 | 0.208 | -154 |
| 15%HPW/TiO2 | 45 | 0.20 | 174 | 0.156 | -143 |

aBET surface area. bSingle point total pore volume at *P/Po* = 0.97. cAverage BET pore diameter. dProton site density (see the text for its calculation). eInitial enthalpy of NH3 adsorption at 150 oC (±3 kJ mol-1).  fManufacturer’s value.

**Table 2**

Information about bifunctional catalysts.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Catalysta | *S*BETb  m2g-1 | Pore volumec  cm3g-1 | Pore sized  Å | *D*e | *D*f  nm |
| CsPW | 132 | 0.10 | 29 |  |  |
| 0.11%Pt/CsPW | 125 | 0.101 | 30 | 0.85 | 1.1 |
| 0.23%Pt/CsPW | 121 | 0.090 | 30 | 0.76 | 1.2 |
| 0.32%Pt/CsPW | 124 | 0.095 | 31 | 0.61 | 1.5 |
| 0.71%Pt/CsPW | 112 | 0.088 | 32 | 0.55 | 1.6 |
| 2.45%Pt/CsPW | 110 | 0.085 | 31 | 0.29 | 3.1 |
| 3.56%Pt/CsPW | 102 | 0.072 | 28 | 0.13 | 6.9 |
| 3.76%Pt/CsPW | 108 | 0.078 | 29 | 0.26 | 3.5 |
| 5.78%Pt/CsPW | 93 | 0.076 | 33 | 0.19 | 4.7 |
| 5.87%Pt/CsPW | 102 | 0.067 | 26 | 0.22 | 4.1 |
| 11.5%Pt/CsPW | 70 | 0.069 | 40 | 0.15 | 6.0 |
| 0.28%Pt/0.35%Au/CsPW | 122 | 0.107 | 35 | 0.55 | 1.6 |
| 5.57%Pt/4.25%Au/CsPW | 91 | 0.082 | 36 | 0.17 | 5.3 |
| 2.62%Au/CsPWg | 103 | 0.090 | 35 |  | ≤10 |

aMetal loading obtained from ICP-AES analysis. bBET surface area. cSingle point total pore volume at *P/Po* = 0.97. dAverage BET pore diameter. ePt dispersion determined from H2/O2 titration; for PtAu catalysts assuming negligible H­2 adsorption on gold. fMetal particle diameter: for Pt from the equation *d* (nm) = 0.9/*D*, for Au from STEM. gNo H2 adsorption observed.

**Table 3**

Acid-catalysed isomerisation of n-hexane.a

|  |  |  |  |
| --- | --- | --- | --- |
| Catalyst | Conversionb  % | 103 *R*c  mol g-1h-1 | TOFHd  h-1 |
| CsPW | 2.7 | 0.38 | 5.1 |
| Cs2.25H0.75PW12O40 (Cs2.25PW) | 2.8 | 0.41 | 3.7 |
| HPW | 0.7 | 0.10 | 5.2 |
| HSiW | 1.0 | 0.15 | 3.6 |
| 15%HPW/SiO2 | 0.34 | 0.049 | 0.32 |
| 15%HPW/TiO2 | 0.14 | 0.020 | 0.13 |
| 15%HSiW/SiO2 | 0.16 | 0.023 | 0.11 |

a200 oC, 0.20 g catalyst, 5.78 kPa n-hexane partial pressure in H2 flow (20 mL min-1). bn-Hexane conversion at 1 h time on stream (mean of two parallel runs). cReaction rate calculated from *R = XF/W*, where *X* is the fractional conversion of n-hexane, *W* is the catalyst weight (0.20 g) and *F* is the molar flow rate of n-hexane (*W/F* = 69.2 g h mol-1). dTurnover frequency per surface proton site; proton site densities are given in Table 1.

**Table 4**

n-Hexane isomerisation over bifunctional metal-acid catalysts.a

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Catalyst | Temperature  (oC) | Conversionb  (%) | Selectivityc (%) | | |
| 2MP+23DMBd | 3MP | Othere |
| (1) CsPW | 180 | 1.5 (4) | 68.6 | 31.1 | 0.3 |
| (2) CsPW | 200 | 2.2 (4) | 66.9 | 30.4 | 2.7 |
| (3) 0.32%Pt/CsPW | 180 | 3.9 (6) | 65.9 | 31.6 | 2.5 |
| (4) 5.78%Pt/CsPW | 150 | 1.5 (2) |  |  |  |
| (5) 5.78%Pt/CsPW | 180 | 8.0 (6) | 65.8 | 32.0 | 2.2 |
| (6) 5.78%Pt/CsPW | 200 | 22.3 (4) | 64.0 | 31.9 | 4.1 |
| (7) 0.28%Pt/0.35%Au/CsPW | 180 | 6.6 (6) | 66.8 | 30.7 | 2.5 |
| (8) 5.57%Pt/4.25%Au/CsPW | 180 | 10.2 (6) | 64.1 | 34.9 | 1.0 |
| (9) 2.62%Au/CsPW | 180 | 1.4 (4) | 65.1 | 30.4 | 4.6 |
| (10) 2.62%Au/CsPW | 180 | 1.3 (6) | 65.1 | 30.4 | 4.6 |

a0.20 g catalyst, 5.78 kPa n-hexane partial pressure in H2 flow (20 mL min-1). b,cAverage n-hexane conversion and product selectivity over the time on stream given in square brackets. d2,3-Dimethylbutane (23DMB) selectivity 0.8-1.2%. eC6- cracking products, mainly C3-C5; no C6+ hydrocarbons observed.

**Table 5**

Effect of *P*C6/*P*H2 partial pressure ratio.a

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalyst | *PC6/PH2* | Conversionb  % | 103 *R*c  mol g-1h-1 | TOFPtd  h-1 |
| 0.32%Pt/CsPW | 0.061 | 3.89 | 0.39 | 24 |
| 0.32%Pt/CsPW | 0.24 | 2.50 | 0.72 | 44 |
| 5.78%Pt/CsPW | 0.061 | 7.95 | 0.98 | 3.3 |
| 5.78%Pt/CsPW | 0.24 | 4.11 | 1.5 | 5.1 |
| 0.28%Pt/0.35%Au/CsPW | 0.061 | 6.55 | 0.77 | 54 |
| 0.28%Pt/0.35%Au/CsPW | 0.24 | 3.86 | 1.4 | 96 |
| 5.57%Pt/4.25%Au/CsPW | 0.061 | 10.2 | 1.3 | 4.6 |
| 5.57%Pt/4.25%Au/CsPW | 0.24 | 7.11 | 2.5 | 8.6 |

a180 oC, 0.20 g catalyst, 20 mL min-1 flow rate. bAverage conversion over 6 h time on stream (mean of two parallel runs). cReaction rate calculated from *R = XF/W*, where *X* is the fractional conversion of n-hexane with the contribution of CsPW (0.012 and 0.010 at *PC6/PH2* = 0.061 and 0.24, respectively) subtracted, *W* is the catalyst weight (0.20 g) and *F* is the molar flow rate of n-hexane (*W/F* = 20.8 and 69.2 g h mol-1 at *PC6/PH2* = 0.24 and 0.061, respectively). dTurnover frequency per surface Pts site with CsPW contribution subtracted.

**Figure captions**

**Fig. 1.** Isomerisation of n-hexane catalysed by CsPW (0.20 g) at 200 oC, 5.78 kPa n-hexane partial pressure in H2 flow (20 mL min-1).

**Fig. 2.** Plot of ln(TOF) (TOF in h-1) versus Δ*H*NH3 for n-hexane isomerisation catalysed by HPA catalysts (0.20 g catalyst, 200 oC, 5.78 kPa n-hexane partial pressure, 20 mL min-1 H2 flow rate): 15%HPW/TiO2 (1), 15%HSiW/SiO2 (2), 15%HPW/SiO2 (3), Cs2.25PW (4), CsPW (5), HSiW (6), HPW (7).

**Fig. 3.** Isomerisation of n-hexane catalysed by 0.32%Pt/CsPW (0.20 g) at 180 oC, 5.78 kPa n-hexane partial pressure in H2 flow (20 mL min-1). Open circles show n-hexane conversion with CsPW catalyst at the same conditions; reaction selectivities are similar in both cases.

**Fig. 4.** Plot of n-hexane conversion versus Pt loading: Pt/CsPW (0.20 g), 200 oC, 5.78 kPa n-hexane partial pressure in H2 flow (20 mL min-1), 5 h time on stream.

**Fig 5.** Plot of TOFPt (a) and TOFH (b) for n-hexane isomerisation over Pt/CsPW (0.20 g) versus atomic ratio of Pts and H+ surface sites: 200 oC, 5.78 kPa n-hexane partial pressure in H2 flow (20 mL min-1), 5 h time on stream.

**Fig. 6.** Arrhenius plot for n-hexane isomerisation: (a) 5.78%Pt/CsPW (0.04 g) + SiO2 (0.16 g) (*Ea* = 79 kJ mol-1); (b) 5.57%Pt/4.25%Au/CsPW (0.04 g) + SiO2 (0.16 g) (*Ea* = 86 kJ mol-1); 5.78 kPa n-hexane partial pressure in H2 flow (20 mL min-1), 6 h time on stream.

**Fig. 7.** Plot of n-hexane conversion versus catalyst weight: 5.87%Pt/CsPW diluted with SiO2 to 0.20 g, 200 oC, 5.78 kPa n-hexane partial pressure in H2 flow (20 mL min-1), 6 h time on stream.

**Fig. 8.** Plot of reaction rate versus n-hexane partial pressure: 5.87%Pt/CsPW (0.04 g) + SiO2 (0.16 g), 200 oC, 20 mL min-1 flow rate, 6 h time on stream, *PH2* = 94-98 kPa (reaction order in n-hexane 0.90).

**Fig. 9.** HAADF-STEM images of (a) 5.78%Pt/CsPW, (b) 2.62%Au/CsPW and (c) 5.57%Pt/4.25%Au/CsPW catalysts, showing noble metal nanoparticles as bright spots.

**Fig. 10.** Powder XRD patterns: (a) 5.78%Pt/CsPW (1) and 5.57%Pt/4.25%Au/CsPW (2); (b) normalized difference (2)-(1) XRD pattern showing a broad [111] fcc PtAu alloy peak in the range 38-40o and possibly a weaker [200] PtAu alloy peak in the range 44-46o.

**Fig. 11.** n-Hexane isomerisation catalysed by 0.28%Pt/0.35%Au/CsPW (0.20 g) at 180 oC, 5.78 kPa n-hexane partial pressure in H2 flow (20 mL min-1). Open circles show n-hexane conversion with 0.32%Pt/CsPW catalyst at the same conditions; reaction selectivities are practically the same in both cases.

**Fig. 12.** n-Hexane isomerisation catalysed by 2.62%Au/CsPW (0.20 g) at 180 oC, 5.78 kPa n-hexane partial pressure, 20 mL min-1 H2 flow rate. Open circles show n-hexane conversion with CsPW catalyst at the same conditions; reaction selectivities are practically the same in both cases.

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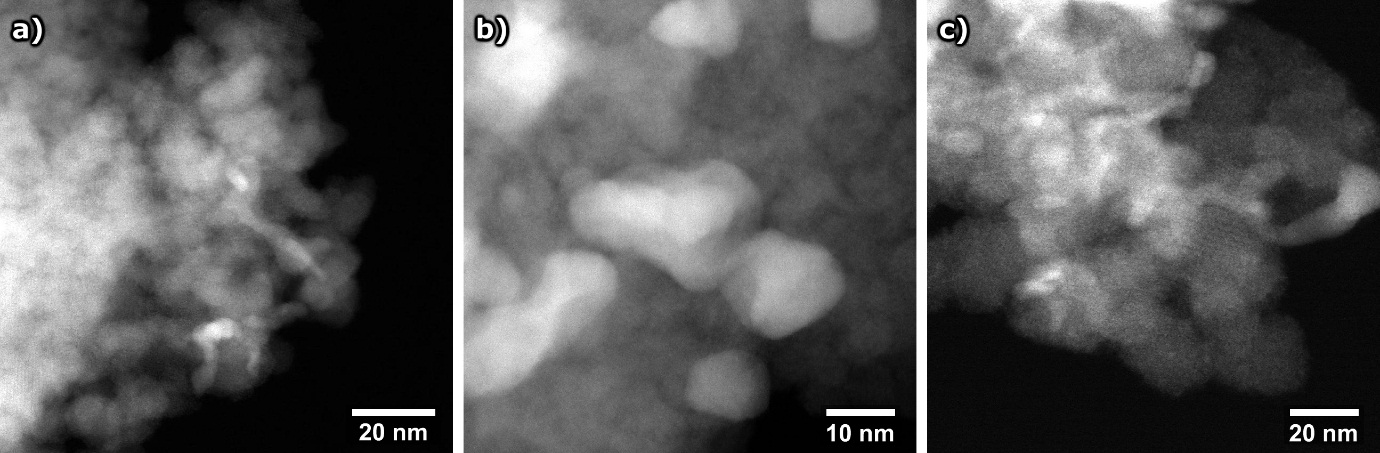
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