Isomerization of Cyclohexane over Bifunctional Pt-, Au- and PtAu-Heteropoly Acid Catalysts

Abdulrahman Alazman, Domagoj Belic, Abdullah Alotaibi, Elena F. Kozhevnikova, Ivan V. Kozhevnikov[[1]](#footnote-1)

*University of Liverpool, Department of Chemistry, Liverpool L69 7ZD, UK*

**Abstract**

Isomerization of cyclohexane was investigated in the presence of monofunctional acid and bifunctional metal-acid catalysts based on Keggin-type heteropoly acid H3PW12O40 and Pt and Au as the metal components using a differential fixed-bed microreactor at 180-300 oC, ambient pressure and a C6H12/H2 partial pressure ratio of 0.04-0.14. Particular emphasis was placed on the acidic Cs salt, Cs2.5H0.5PW12O40 (CsPW) as the acid catalyst and Pt/CsPW, Au/CsPW and PtAu/CsPW as the bifunctional catalysts. Pt/CsPW and Au/CsPW were more efficient than the monofunctional acid catalyst CsPW, and Pt/CsPW more active than Au/CsPW, both giving >99% selectivity to methylcyclopentane. It was found that with Pt/CsPW, cyclohexane dehydrogenation step equilibrated at a molar ratio of Pt and H+ surface sites Pt/H+ ≥ 0.7, which is much higher than for Pt/zeolite. PtAu/CsPW bimetallic catalyst exhibited a 2-fold higher activity in cyclohexane isomerization and a 3.5-fold higher activity in the accompanying dehydrogenation of cyclohexane to benzene than the mixture of Pt/CsPW and Au/CsPW with the same metal loading. The enhancing effect of gold is assigneg to PtAu bimetallic particles, which had a higher Pt dispersion than the Pt in Pt/CsPW. Scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM-EDX) revealed bimetallic PtAu particles in PtAu/CsPW with a wide range of Pt/Au atomic ratios. No enhancing effect of gold was found in the case of carbon-supported catalyst PtAu/C physically mixed with CsPW, and the STEM-EDX analysis revealed no modification of Pt sites by Au in this catalyst.

*Keywords*: Isomerization; Cyclohexane; Bifunctional catalysis; Platinum; Gold; Heteropoly acid.

1. **Introduction**

Skeletal isomerization of alkanes is the basis for several important industrial processes. Isomerization of linear C5–C6 alkanes is used in industry for the production of high octane gasoline, whereas longer-chain alkane isomerization is important for lowering pour point of lubricants and jet and diesel fuels [1,2]. Isomerization of cycloalkanes is of interest for the reduction of toxic aromatics, especially benzene, in gasoline to protect the environment [2]. Benzene, while possessing high octane number (research octane number, RON, 100), is carcinogenic to humans. Reduction of benzene in gasoline may be achieved practically without a loss in gasoline octane rating by hydrogenation of benzene to cyclohexane (RON 84) followed by isomerization to methylcyclopentane (RON 96) [3,4].

The isomerization of cyclohexane can proceed via an acid catalysed route on strong Lewis and Brønsted acid sites (Scheme 1) or via bifunctional metal-acid catalysis (Scheme 2). The acid catalysed isomerization of alkanes can occur via a monomolecular carbenium-ion chain mechanism [2,5]. With Lewis acids, cyclohexyl carbenium ion is produced by H- abstraction on a Lewis acid site. This ion then undergoes methyl group migration through a protonated cyclopropane intermediate, which is followed by H- transfer from a cyclohexane molecule to give methylcyclopentane (MCP) isomerization product together with cyclohexyl carbenium ion continuing the chain process. On strong Brønsted acid sites, a carbonium ion is initially formed by C-H bond protonation in cyclohexane. This ion eliminates H2 to form the cyclohexyl carbenium ion and further MCP. Proton elimination from intermediate carbenium ions produces alkenes, which can build coke, causing deactivation of catalyst (Scheme 1). Besides, C6- hydrocarbons can be produced by cracking of C6 isomers. In addition, C6- and C6+ hydrocarbons can be formed via disproportionation of C12 cations originated from alkenes and C6 carbenium ions (bimolecular mechanism) [2,5].



**Scheme 1.** Acid-catalysed isomerization of cyclohexane via monomolecular mechanism.

With bifunctional metal-acid catalysts, typically containing platinum on acidic supports, for example, Pt/zeolite, alkane isomerization proceeds in the presence of hydrogen (often referred to as hydroisomerization) [1]. The reaction can be assumed to occur via Scheme 2 involving cyclohexane dehydrogenation on metal sites followed by isomerization of cyclohexene formed to methylcyclopentene on acid sites of support [6]. The latter is hydrogenated on the metal sites to give MCP. In general, the bifunctional route is more efficient than the acid catalysed route. In the bifunctional catalyst, Pt not only enhances the isomerization process, but also reduces the steady state alkene concentration. This increases reaction selectivity due to suppressing the bimolecular mechanism [5] and diminishes coke formation [1].



**Scheme 2.** Isomerization of cyclohexane via bifunctional route.

Keggin-type heteropoly acids (HPAs), in particular tungsten HPAs possessing very strong Brønsted acidity, have attracted much interest as acid catalysts. These include primarily HPAs such as H3PW12O40 and H4SiW12O40 as well as their acidic Cs salts such as Cs2.5H0.5PW12O40 (CsPW) [7-9]. Pt–HPA bifunctional catalysis has been extensively studied in alkane isomerization, and its effectiveness has been demonstrated ([4,10-17] and references therein). Pt–HPA catalysts have been reported for the isomerization of cycloalkanes such as cyclohexane [4] and methylcyclohexane [16].

Alkane isomerization via bifunctional metal-acid catalysis can be further enhanced using bimetallic PtAu catalysts. This has been reported for methylcyclopentane isomerization over PtAu/HY and PdAu/HY by Fraissard et al. [18] and more recently for n-hexane isomerization over PtAu/CsPW by ourselves [17].

In this work, we investigate the metal–HPA bifunctional catalysis for the isomerization of cyclohexane, focussing on CsPW as the acid component and Pt and Au as the metal components. Insoluble acidic salt CsPW has important advantages over the parent H3PW12O40 (HPW). It has a higher thermal stability and much larger surface area (therefore larger surface site density), with the proton sites almost as strong as those in HPW [7,8]. We also investigate the enhancing effect of Au on cyclohexane isomerization and on the accompanying dehydrogenation of cyclohexane to benzene over Pt/CsPW. It is shown that the addition of gold to Pt/CsPW gives a significant increase in catalytic activity. The gold enhancement is attributed to PtAu bimetallic particles, which is supported by STEM-EDX.

**2. Experimental**

*2.1. Chemicals and catalysts*

Cyclohexane (>99%), H2PtCl6 hydrate, HAuCl4·3H2O, H3PW12O40 hydrate (HPW, 99%) and activated carbon Darco KB-B (150 µm particle size) were purchased from Sigma-Aldrich. Aerosil 300 silica (surface area *S*BET = 300 m2g-1) was from Degussa; it was wetted and calcined at 400 oC prior to use. H2 gas cylinders (>99%) were supplied by the British Oxygen Company.

CsPW was prepared according to the literature procedure [19,20] and vacuum dried at 150 oC/10-3 kPa for 1.5 h. Bifunctional catalysts Pt/CsPW and Au/CsPW were prepared by wet impregnation of CsPW with aqueous solutions of H2PtCl6 or HAuCl4, as described previously [21].The preparation involved stirring the aqueous slurry at 50 oC for 2 h, rotary evaporation to dryness and reduction with H2 flow at 250 oC for 2 h. PtAu/CsPW bimetallic catalysts were prepared similarly via co-impregnation of CsPW with H2PtCl6 and HAuCl4 from aqueous solution with reduction by H2 as above. Another Pt/CsPW catalyst, hereafter referred to as Pt/CsPW-b, was prepared using a water- and chloride-free procedure by impregnating Pt(acac)2 onto CsPW from benzene solution. This was done by stirring CsPW with 0.02 M Pt(acac)2 benzene solution at room temperature for 1 h, followed by rotoevaporation of benzene at room temperature, drying under vacuum at 150 oC/10-3 kPa and reduction by hydrogen as above. Pt and Au loading in these catalysts was determined by ICP-AES. Physical mixtures of bifunctional catalysts with CsPW and SiO2 were prepared by grinding the catalysts with CsPW and Aerosil 300 silica.

Pt/C and Au/C catalysts were prepared by impregnating Darco KB-B activated carbon with aqueous solutions of H2PtCl6 and HAuCl4 at 50 oC for 2 h followed by rotoevaporation to dryness and reduction with H2 as above [21]. PtAu/C bimetallic catalysts were prepared similarly by co-impregnating the carbon support with H2PtCl6 and HAuCl4. Physically mixed bifunctional catalysts Pt/C + CsPW, Au/C + CsPW and PtAu/C + CsPW were prepared by grinding a mixture of the corresponding components. Information about the catalysts prepared is given in Table 1.

**Table 1.** Information about catalysts.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Catalysta | *S*BETb  m2g-1 | Pore volumec  cm3g-1 | Pore sized  Å | *D*e | *d*f  nm |
| H3PW12O40 (HPW) | 7.8 | 0.012 | 63 |  |  |
| Cs2.5H0.5PW12O40 (CsPW) | 139 | 0.079 | 23 |  |  |
| 6.0%Pt/CsPW | 84 | 0.052 | 25 | 0.17h | 4.7i |
| 5.6%Pt/CsPW-bg | 105 | 0.068 | 26 | 0.15h | 6.0i |
| 5.9%Pt/4.4%Au/CsPW | 62 | 0.065 | 42 | 0.27h | 5.3i |
| 4.7%Au/CsPWj | 103 | 0.048 | 33 | ≥0.09i | ≤10k |
| Darco KB-B activated carbon | 977 | 0.89 | 35 |  |  |
| 5.0%Au/C | 1207 | 1.00 | 33 | 0.094i | 9.6k |
| 6.2%Pt/C | 1224 | 1.04 | 34 | 0.26i | 3.5k; 3.0l |
| 6.7%Pt/5.0%Au/C | 1177 | 0.98 | 33 | 0.21i  0.02i | 4.2 Ptl  54 Aul |

aMetal catalysts prepared by impregnating H2PtCl6 and HAuCl4 onto CsPW or activated carbon from aqueous medium; metal loading determined from ICP-AES analysis. bBET surface area. cSingle point total pore volume at *P/Po* = 0.97. dAverage BET pore diameter. eMetal dispersion. fMetal particle size. gThe catalyst prepared by impregnating Pt(acac)2 onto CsPW from benzene solution. hPt dispersion from H2/O2 titration; for PtAu catalysts, assumed negligible H­2 adsorption on gold. iCalculated from the equation *d* (nm) = 0.9/*D*. jNo H2 adsorption observed on the Au/CsPW catalyst. kMetal particle diameter from TEM and STEM. lMetal particle diameter from powder XRD (Scherrer equation).

*2.2. Techniques*

The texture of catalysts was characterised by nitrogen physisorption measured on a Micromeritics ASAP 2010 instrument at −196 oC. Prior to measurement, the samples were pre-treated at 250 oC in vacuum for 2 h. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out on a Spectro Ciros optical emission spectrometer. 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. Combustion chemical analysis (Thermo Flash EA 1112 instrument) was used to determine carbon content in spent catalysts.

Transmission electron microscopy (TEM) imaging of catalysts was carried out on FEI Tecnai Spirit BioTWIN instrument at 120 kV operation. 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 TEM and STEM analysis, the samples were prepared by scooping up the catalyst powder by a TEM grid (holey carbon film on 300 Ni or Cu mesh, Agar Scientific) followed by shaking to remove excess material from the grid.

Pt dispersion in the catalysts was determined on a Micromeritics TPD/TPR 2900 instrument equipped with a thermal conductivity detector (TCD) using the H2/O2 titration pulse method in a flow system at room temperature as described elsewhere [22] using 50-75 mg catalyst samples in N2 flow (50 mL min-1). After completion of H2/O2 titration, H2-TPD was measured by increasing the temperature from room temperature to 250 oC at a rate of 10 oC per minute. The H2/O2 titration and H2-TPD procedure is illustrated in Fig. S1 in the Supporting Information. The Pt dispersion (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 [23,24]. H2 adsorption observed on the PtAu catalysts was attributed to platinum as Au/CsPW did not adsorb any hydrogen under such conditions [21].The average diameter of Pt particles, *d*, was calculated from the empirical equation *d* (nm) = 0.9/*D* [24]. For Pt/C and Au/C, the metal particle size was determined by TEM and for Au/CsPW by STEM (Supporting Information, Fig. S2 and S3).For PtAu/C catalyst, the Pt and Au particle size was determined by XRD using the Scherrer equation.

*2.3. Catalyst testing*

The isomerization of cyclohexane was carried out in a H2 flow at 180-300 oC. The catalysts were tested under ambient pressure at a ratio of cyclohexane and H2 partial pressures of 0.04-0.14 in a Pyrex fixed-bed down-flow microreactor (9 mm internal diameter) fitted with an on-line gas chromatograph (Varian 3800 instrument with a 30 m x 0.25 mm x 0.5 µm HP INNOWAX capillary column and a flame ionisation detector). 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. Cyclohexane was fed by passing H2 flow controlled by a Brooks mass flow controller through a stainless steel saturator, which held cyclohexane at 0 oC (ice bath) to maintain the chosen reactant partial pressure of 3.4 kPa (3.4 mol% concentration of cyclohexane in H2 flow). The concentration of cyclohexane was varied by diluting the gas flow with H2. 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. Prior to reaction, the catalysts were pre-treated in situ for 1 h at the reaction temperature in H2 flow. The reaction was carried out at a space time *W/F* = 24 – 118 g h mol-1, where *W* is the catalyst weight and *F* is the inlet molar flow rate of cyclohexane. Product selectivity was defined as moles of product formed per one mole of cyclohexane 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 cyclohexane. Generally, the reaction was carried out at differential conditions (*X* ≤ 0.1), where *X* is directly proportional to the reaction rate. Whenever required, the catalysts were diluted with silica in order to achieve a low conversion. Pt/CsPW and Au/CsPW catalysts showed stable performance in cyclohexane isomerization, reaching steady state within 30 – 70 min time on stream (TOS). Generally, their deactivation did not exceed 10-15% of the initial conversion rate over 12 h TOS (Fig. 1). For calculating the reaction rates, initial conversion values *X* at 70 – 100 min TOS were used.

1. **Results and discussion**

*3.1. Acid-catalysed isomerization of cyclohexane over CsPW*

Bulk heteropoly acid HPW had small activity in cyclohexane isomerization (Table 2) despite its very strong Brønsted acidity [25]. This can be explained by the low surface area of HPW (7.8 m2g) (Table 1), hence low density of surface proton sites in the catalyst. In contrast, CsPW, despite its somewhat weaker acidity compared to the bulk HPW [25], showed relatively high initial activity in this reaction, although suffered from strong deactivation, as seen in Fig. 1. The higher activity of CsPW can be attributed to its larger surface area (139 m2g), hence larger (about 3-fold) density of surface proton sites, as compared to HPW. Similar results have been reported for the isomerization of n-hexane [17]. The strong catalyst deactivation can be attributed to coke deposition originated from alkene oligomerisation (Scheme 1). CsPW, initially white, turned black after reaction (200 oC, 18 h on stream, Fig. 1). From combustion chemical analysis, the spent catalyst contained 0.76 wt% of carbon. Methylcyclopentane (MCP) was the main product of cyclohexane isomerization: 98% selectivity, with 2% of cracking products (mainly C3-C4 hydrocarbons). C6+ hydrocarbons were not observed in reaction products, which indicates the monomolecular mechanism of cyclohexane isomerization over CsPW (Scheme 1). It should be noted that the selectivity did not change over entire range of the time on stream despite strong catalyst deactivation. Besides, the results practically did not change when using N2 instead of H2 as the carrier gas.

*3.2. Isomerization of cyclohexane over bifunctional metal-acid catalysts*

CsPW-supported and physically mixed bifunctional metal-acid catalysts in the presence of H2 were much more efficient in cyclohexane isomerization than CsPW alone. All bifunctional catalysts showed similar initial deactivation profiles – a sharp initial drop in cyclohexane conversion (probably due to deactivation of the strongest proton sites in CsPW) followed by steady-state course. As expected, Pt/CsPW (prepared from H2PtCl6 in aqueous medium) showed much higher catalytic activity than CsPW (Table 2) and a very good performance stability during 12 h on stream (Fig. 1). Pt/CsPW-b catalyst prepared from Pt(acac)2 in benzene with similar Pt loading and dispersion (Table 1) was twice as active as Pt/CsPW (Table 2) and showed stable performance during 20 h on stream (Fig. 1). The higher activity of Pt/CsPW-b may be explained by stronger acidity of the CsPW support due to the water-free preparation procedure. At about 6% Pt loading, cyclohexane dehydrogenation step is likely to be equilibrated (see below), and the isomerization of cyclohexyl carbenium ion becomes the rate-limiting step (Scheme 2). Consequently, the rate of the isomerization step should increase with increasing catalyst acid strength, leading to an increase in the overall reaction rate as observed in the case of Pt/CsPW-b in comparison to Pt/CsPW. The amount of coke in spent Pt/CsPW and Pt/CsPW-b catalysts was below detection limit. However, in the absence of H2 when using N2 as the carrier gas, Pt/CsPW and Pt/CsPW-b catalysts predictably suffered strong deactivation just as CsPW alone did. Unexpectedly, Au/CsPW showed a relatively high activity (Table 2) and excellent performance stability during 20 h on stream (Fig. 1). This is different from n-hexane isomerization, where Au/CsPW was virtually inactive [17].

**Table 2.** Isomerization of cyclohexane over acid and bifunctional metal-acid catalysts.a

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Catalyst | T (oC) | TOSb (h) | Conv.c (%) | Select.c (%) | |
| C6H6 | MCP |
| HPW | 200 | 2.5 | 0.5 | 0 | >99 |
| CsPW | 200 | 6.0 | 3.0 | 0 | 98 |
| 6.0%Pt/CsPW | 200 | 6.0 | 15 | 0 | >99 |
| 5.6%Pt/CsPW-b | 200 | 6.0 | 27 | 0 | >99 |
| 4.7%Au/CsPW | 200 | 6.0 | 7.1 | 0 | >99 |
| 6.2%Pt/C+CsPW (1:5 w/w, 1.0%Pt)d | 200 | 4.0 | 12 | 0 | >99 |
| 6.2%Pt/C+CsPW (1:5 w/w, 1.0%Pt)d | 250 | 4.0 | 26 | 15 | 85 |
| 6.2%Pt/C+CsPW (1:5 w/w, 1.0%Pt)d | 300 | 4.0 | 55 | 62 | 38 |

a0.20 g catalyst, 3.4 kPa cyclohexane partial pressure, 20 mL min-1H2 flow, 200 oC, *W/F* = 118 g h mol-1, catalyst pretreatment at 200oC/1h in H2 flow. bTime on stream. cCyclohexane conversion and methylcyclopentane selectivity at the TOS given; C3-C4 cracking by-products also formed, but no C6+ hydrocarbons observed. dPhysical mixture of 6.2%Pt/C and CsPW (0.20 g in total).

**Fig. 1.** Time course for cyclohexane isomerization in the presence of CsPW, 4.7%Au/CsPW, 6.0%Pt/CsPW and 5.6%PtCsPW-b catalysts (0.20 g) at 200 oC, 3.4 kPa cyclohexane pressure, 20 mL min-1 H2 flow rate, *W/F* = 118 g h mol-1. For all catalysts, MCP selectivity ≥99% over entire range of TOS.

Physically mixed Pt/C + CsPW bifunctional catalysts had activities comparable to those of the CsPW-supported catalysts Pt/CsPW (Table 2). This suggests that the reaction is not limited by migration of alkene intermediates between the metal and acid sites in bifunctional catalysts since in the mixed catalysts their H+ and Pt surface sites are far apart compared to the supported Pt/CsPW catalysts (micrometer versus nanometer distance).

Both Pt and Au bifunctional catalysts had very high selectivity to MCP (>99%) at least up to 27% cyclohexane conversion at 200 oC (Table 2). It should be pointed out that under the chosen reaction conditions, cyclohexane-to-MCP isomerization was far from equilibrium and occurred under kinetic control. The equilibrium conversion of cyclohexane to MCP at 200 oC was calculated to be 70% (Supporting Information), in agreement with the literature [4]. The absence of C6+ hydrocarbons in reaction products suggests the reaction occurring via the monomolecular mechanism as shown in Scheme 2. At higher temperatures, 250-300 oC, benzene was also formed at the expense of MCP by dehydrogenation of cyclohexane on Pt sites. As expected, the selectivity to benzene increased with increasing the temperature, reaching 62% at 300 oC (Table 2).

Kinetics of alkane isomerization in the presence of bifunctional Pt-acid catalysts based on heteropoly acids and zeolites has been discussed previously [15,16,26,27]. Since cyclohexane is stable toward cracking (Table 2), the rate of its isomerization can be approximated by the rate of cyclohexane conversion (in the absence of benzene formation). It has been shown that when the dehydrogenation step is at equilibrium and the isomerization step is rate limiting (Scheme 2), the overall isomerization rate *R* obeys equation (1), where *Kd* is the equilibrium constant of dehydrogenation, *Kp* is the equilibrium constant of protonation, *ki* is the isomerization rate constant, *PC­6* is the cyclohexane partial pressure, *PH2* is the hydrogen partial pressure and *α* is the reaction order (*α* ≤ 1) [26,27].

 (1)

It has been shown that the rate limiting step is determined by the molar ratio of surface metal and acid sites Pts/H+ [4,15,17,26-28]. In the case of Pt−zeolite catalysts, including H-MOR, H-BEA, H-USY, etc., the alkane dehydrogenation step is typically equilibrated at Pts/H+ < 0.1, so that the isomerization step becomes rate limiting [26,28]. In the case of Pt-HPA catalysts having stronger proton sites than those in zeolites [29], a higher Pts/H+ molar ratio is required for the dehydrogenation step to attain equilibrium [15,17]. In the isomerization of n-hexane over Pt/CsPW, the dehydrogenation step has been found to equilibrate at Pts/H+ ≥ 0.8 [17].

**Fig. 2.** Plot of cyclohexane conversion versus Pt loading (A) and plot of TOFPt versus molar ratio of Pts and H+ surface sites (B) for cyclohexane isomerization over 6.0%Pt/CsPW: varied amount of 6.0%Pt/CsPW diluted by CsPW to 0.20 g, 200 oC, 3.4 kPa cyclohexane partial pressure, 20 mL min-1 H2 flow rate.

Fig. 2A shows a plot of cyclohexane conversion over Pt/CsPW versus Pt loading. It can be seen that the conversion increases with the Pt loading, plateauing out at about 6% Pt loading. The same data are presented in Fig. 2B as turnover frequency TOFPt versus the Pts/H+ ratio; the TOFPt values were calculated per surface Pt atom using the cyclohexane conversion data at 200 oC and Pt dispersion from Table 1. When calculating TOFPt, the minor contribution of CsPW was subtracted from the total conversion. The density of surface proton sites in CsPW was calculated using a cross section of 144 Å2 for the Keggin heteropoly anion [7,8] and the CsPW surface area of 139 m2g-1 (Table 1) supposing that the number of accessible protons was 0.5 per Keggin unit at the surface; this gave a proton site density of 0.080 mmol g-1. Also it was suggested that the H+ surface density was not affected by Pt. As anticipated from Scheme 2, TOFPt diminishes as the Pts/H+ ratio increases, reaching a plateau as the dehydrogenation step attains quasi-equilibrium (Fig. 2B). This demonstrates that over Pt/CsPW catalyst, cyclohexane dehydrogenation step is equilibrated at Pts/H+ ≥ 0.7, corresponding to a Pt loading ≥ 6%. As expected, this Pts/H+ value is higher than that for Pt/zeolite catalysts due to the stronger acidity of CsPW in comparison to zeolites. Similar results were also obtained for the Pt/CsPW-b prepared using the chloride-free anhydrous procedure (Fig. S4).

**Fig. 3.** Arrhenius plot for cyclohexane isomerization: 6.0%Pt/CsPW (0.04 g) + SiO2 (0.16 g) (*Ea* = 131 kJ mol-1); 5.6%Pt/CsPW-b (0.04 g) + SiO2 (0.16 g) (*Ea* = 120 kJ mol-1); 5.9%Pt/4.4%Au/CsPW (0.04 g) + SiO2 (0.16 g) (*Ea* = 34 kJ mol-1); 3.4 kPa cyclohexane partial pressure, 20 mL min-1 H2 flow rate; *X* is the differential fractional conversion.

The apparent activation energy, *Ea*, for cyclohexane isomerization over 6.0%Pt/CsPW and 5.6%Pt/CsPW-b was found 131 and 120 kJ mol-1, respectively, in 180-220 oC temperature range. The corresponding Arrhenius plots are shown in Fig. 3 (these plots use the differential conversion of cyclohexane *X*, which is directly proportional to the reaction rate). These high *Ea* values indicate no diffusion limitations in cyclohexane isomerization over these catalysts.

**Fig. 4.** Plot of cyclohexane conversion (differential data) versus catalyst weight: 6%Pt/CsPW (diamonds), 5.6%Pt/CsPW-b (circles), 5.9%Pt/4.4%Au/CsPW (triangles); varied amount of catalysts diluted with SiO2 to 0.20 g; 200 oC, 3.4 kPa cyclohexane partial pressure, 20 mL min-1 H2 flow rate.

The isomerization reaction order in Pt/CsPW and Pt/CsPW-b catalysts was close to 1 (Fig. 4). The order in cyclohexane was found to be 0.49 and 0.55 for Pt/CsPW and Pt/CsPW-b, respectively (Fig. 5, where *PC6* is varied at practically constant *PH2*). These results comply with eq. (1). Also in agreement with eq. (1), the initial rate of reaction over Pt/CsPW increased with decreasing the hydrogen pressure *P*H2 (Table 3); simultaneously increased the rate of catalyst deactivation, as seen from the reaction course at longer times on stream (Fig. S5). Therefore, the kinetics is in fairly good agreement with the rate equation (1), considering that cyclohexane dehydrogenation step was not always at equilibrium in these reaction systems.

**Fig. 5.** Plot of reaction rate versus cyclohexane partial pressure: 5.9%Pt/4.4%Au/CsPW (0.04 g) + SiO2 (0.16 g) (triangles, order in cyclohexane 0.59), 5.6%Pt/CsPW-b (0.04 g) + SiO2 (0.16 g) (circles, order in cyclohexane 0.55), 6.0%Pt/CsPW (0.04 g) + SiO2 (0.16 g) (diamonds, order in cyclohexane 0.49); 200 oC, 20 mL min-1 flow rate, *PH2* = 96–99 kPa.

**Table 3.**  Effect of hydrogen pressure on the rate of cyclohexane isomerization.a

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| H2 pressure (kPa) | 97 | 73 | 48 | 24 |
| Initial conversion (%) | 3.9 | 5.5 | 4.4 | 4.0 |
| 103 Initial rate (mol g-1h-1)b | 1.6 | 2.3 | 1.9 | 1.7 |

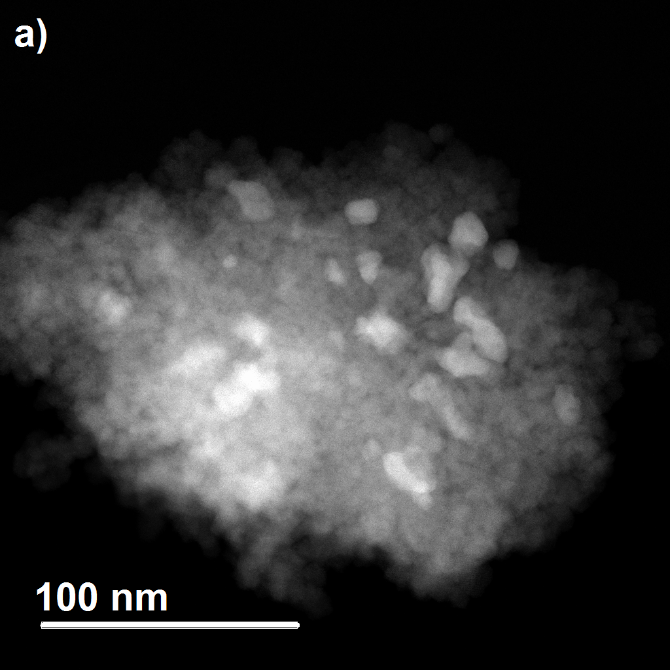
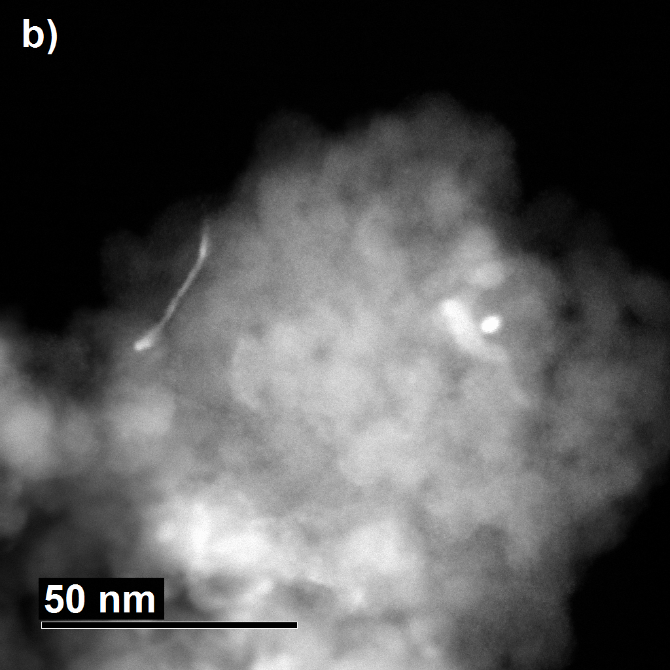
a Catalyst 6.0%Pt/CsPW (0.04 g) + SiO2 (0.16 g), 3.4 kPa cyclohexane partial pressure, 200 oC, 20 mL min-1 rate of H2 + N2 flow at different H2/N2 volume ratios. bReaction rate calculated from *R = XF/W*, where *X* is the initial fractional conversion of cyclohexane and the space time *W/F =* 24 mol g-1h-1.

*3.3. Effect of gold*

There has been a continued interest in bimetallic catalysis since the discovery of superior properties of PtSn, PtIr and PtRe catalysts in petrochemistry and petroleum reforming in the 1960s ([30,31] and references therein). Bimetallic catalysts often exhibit higher catalytic activity than either of their components due to a better stability to deactivation. Typically, hydrogenolysis of C-C bond is suppressed in favour of reactions such as hydrogenation, dehydrogenation and isomerization, leading to an increase in reaction selectivity. It is suggested that the enhanced performance of bimetallic catalysts is mainly determined by the geometric ensemble size effect, and an electronic ligand effect may also take place [30,31].

PtAu and PdAu bimetallic catalysts often exhibit an enhanced activity in comparison to monometallic Pt and Pd catalysts ([17,21,30-52]), for example in hydrogenation [44], hydrodeoxygenation [21,36], hydrodesulfurisation [42,43], oxidation [37-39] and other reactions ([30,31,35,40,41]). PdAu/HY and PtAu/HY have been used for isomerization of methylcyclopentane [34] and n-hexane [52]. For the methylcyclopentane isomerization, the PdAu/HY and PtAu/HY catalysts exhibited an increase in activity and selectivity in comparison with the corresponding Pd/HY and Pt/HY catalysts. No such effect has been observed for the n-hexane isomerization, though. Previously, we have reported an Au enhancement for the isomerization of n-hexane catalysed by PtAu/CsPW and attributed it to PtAu bimetallics [17].

In this work, we examined the effect of gold on the activity and selectivity of Pt/CsPW and Pt/C + CsPW physically mixed catalysts in the isomerization of cyclohexane as well as in the accompanying dehydrogenation of cyclohexane to benzene and attempted to assess the effect of gold on the turnover reaction rate at Pt sites. The supported bimetallic catalysts 5.9%Pt/4.4%Au/CsPW and 6.7%Pt/5.0%Au/C were prepared by co-impregnation of H2PtCl6 and HAuCl4 precursors onto CsPW and activated carbon, respectively, from aqueous medium followed by reduction with H2 at 250 oC. This preparation is likely to give supported bimetallic PtAu particles of a random composition together with monometallic Pt and Au particles, rather than relatively uniform bimetallics that can be obtained by size-controlled synthesis in solution [41].Table 1 presents the texture and metal dispersion for these catalysts. Notably, the addition of Au to Pt/CsPW catalyst increased the Pt dispersion from 0.17±0.02 to 0.27±0.02% (average values from four H2/O2 titrations); in contrast, Au addition to Pt/C virtually did not alter Pt dispersion.

**Fig. 6.** HAADF-STEM images of (a) 5.0%Au/CsPW and (b) 5.6%Pt/4.3%Au/CsPW catalysts, displaying noble metal particles as bright spots. Elongated PtAu nanostructures can be seen in image (b).

Previously, PtAu/CsPW, Pt/CsPW and Au/CsPW catalyst have been characterised by STEM-EDX and powder XRD [17,21]. These catalysts consist of 10-20 nm CsPW particles (*bcc* crystal structure with a lattice constant of 12 Å) and contain noble metal particles from ~20 nm down to metal atoms. Au/CsPW has larger Au particles up to ~20 nm, whereas Pt/CsPW has smaller particles, less than 5 nm. The bimetallic PtAu/CsPW catalyst shows a similar content and, in addition to monometallic Pt and Au particles, contains non-uniform bimetallic PtAu particles with a Pt/Au atomic ratio varying from 0.5 to 7.7 (Fig. S6). The appearance of the PtAu nanostructures is frequently more elongated than those in Au/CsPW, as can be seen in Fig. 6 and Fig. S6. It should be noted that the STEM images of PtAu/CsPW are difficult to examine because W, Pt and Au have similar large atomic numbers *Z* (74, 78, and 79, respectively). Besides, CsPW containing ca. 70 wt% of tungsten exhibits a strong background which obscures smaller Pt and Au particles in the *Z*-contrast high-angle annular dark field (HAADF) images which makes it difficult to determine precisely metal particle size distribution. XRD analysis of metal particle size is also difficult due to the dominated pattern of the crystalline CsPW.

Representative results of catalyst testing at 200 oC and 6 h TOS are shown in Table 4. These include two sets of testing of Pt/CsPW, Au/CsPW, Pt/CsPW + Au/CsPW and PtAu/CsPW catalysts with the same Pt and Au content in each set: 0.59-0.60% Pt and 0.44-0.47% Au in the first set and 1.2% Pt and 0.88-0.94% Au in the second. The content of CsPW was also kept constant in each set. The full reaction time courses (12-14 h TOS) for the first set are shown in Fig. 7. The time courses for the second set were similar, but with higher conversion rates, as expected. These reactions notably exhibit a stronger catalyst deactivation than the reactions shown in Fig. 1 because of the lower metal content. Under such conditions, Au and CsPW made very small contributions to the cyclohexane conversion. As seen in Table 4, the bimetallic PtAu/CsPW catalyst is more active than the either of Pt/CsPW and Au/CsPW catalysts and the two of them together (cf. entry 4 with 5 and 9 with 10). With PtAu/CsPW catalyst, cyclohexane conversion increased by a factor of 2.2 at 0.6% Pt content and by a factor of 1.7 at 1.2% Pt content in comparison with the combined activity of Pt/CsPW + Au/CsPW at 200 oC (note that the compared catalysts in entries 4 and 5 as well as 9 and 10 have the same Pt, Au and CsPW content). Evidently, the scale of gold effect on catalyst activity depends on the Pt content, that is on the extent of equilibration of cyclohexane dehydrogenation step (Scheme 2). The effect of gold is stronger when the dehydrogenation step is the rate-limiting one and decreases as this step approaches equilibrium.

**Table 4.** Effect of gold on isomerization of cyclohexane over Pt/CsPW bifunctional catalysts.a

|  |  |
| --- | --- |
| Catalystb | Conv.c (%) |
| 1) CsPW + SiO2 (2:8 w/w) | 0.5 |
| 2) 4.7%Au/CsPW + CsPW + SiO2 (1:1:8 w/w, 0.47%Au) | 0.9 |
| 3) 6.0%Pt/CsPW + CsPW + SiO2 (1:1:8 w/w, 0.60%Pt) | 3.3 |
| 4) 5.9%Pt/4.4%Au/CsPW + CsPW + SiO2 (1:1:8 w/w, 0.59%Pt, 0.44%Au) | 7.4 |
| 5) 6.0%Pt/CsPW + 4.7%Au/CsPW + SiO2 (1:1:8 w/w, 0.60%Pt, 0.47%Au) | 3.3 |
| 6) CsPW + SiO2 (2:3 w/w) | 0.8 |
| 7) 4.7%Au/CsPW + CsPW + SiO2 (1:1:3 w/w, 0.94%Au) | 1.1 |
| 8) 6.0%Pt/CsPW + CsPW + SiO2 (1:1:3 w/w, 1.2%Pt) | 6.1 |
| 9) 5.9%Pt/4.4%Au/CsPW + CsPW + SiO2 (1:1:3 w/w, 1.2%Pt, 0.88%Au) | 11 |
| 10) 6.0%Pt/CsPW + 4.7%Au/CsPW + SiO2 (1:1:3 w/w, 1.2%Pt, 0.94%Au) | 6.8 |

a 200 oC, 3.4 kPa cyclohexane partial pressure, 20 mL min-1 H2 flow rate, 6 h time on stream, *W/F* = 24 g h mol-1 (entries 1-5) and 47 g h mol-1 (entries 6-10),catalyst pretreatment at 200oC/1h in H2 flow. bCatalysts (0.20 g) were physical mixtures prepared by grinding all components together. cCyclohexane conversion at 6 h TOS; MCP selectivity >98% with C3-C4 cracking by-products formed; no C6+ hydrocarbons observed.

While enhancing cyclohexane conversion, gold additives did not influence reaction selectivity. This suggests that the gold affects the metal-catalysed dehydrogenation reaction step, not the subsequent transformations of carbenium ions (Scheme 2). Although Au shows some activity, it is most likely that it is the Pt that plays a major role [17]. The effect of gold on the turnover rate at a surface Pt site was estimated by subtracting the contribution of CsPW (entries 1 and 6) and using the Pt dispersion for PtAu/CsPW (*D* = 0.27) and Pt/CsPW (*D* = 0.17) (Table 1). This gave a 1.6-fold increase in the turnover rate at Pt sites at 0.6% Pt content and a tiny (1.1-fold) increase for the PtAu/CsPW catalyst at 1.2% Pt content. Since, the turnover rate at Pt sites is only moderately affected by gold additives, the Au enhancement observed can be attributed primarily to the geometric effect due to the increase in the Pt dispersion in the bimetallic PtAu/CsPW catalyst.

**Fig. 7.** Time course for cyclohexane isomerization in the presence of CsPW-supported bifunctional catalysts physically mixed with CsPW and SiO2 (0.20 g total weight) with comparable metal and CsPW content. From top to bottom: (a) 5.9%Pt/4.4%Au/CsPW (0.02 g) + CsPW (0.02 g) + SiO2 (0.16 g); (b) 6.0%Pt/CsPW (0.02 g) + CsPW (0.02 g) + SiO2 (0.16); (c) 6.0%Pt/CsPW (0.02 g) + 4.7%Au/CsPW (0.02 g) + SiO2 (0.16 g); (d) 4.7%Au/CsPW (0.02 g) + CsPW (0.02 g) + SiO2 (0.16 g); (e) CsPW (0.04 g) + SiO2 (0.16 g); 200 oC, 3.4 kPa cyclohexane pressure, 20 mL min-1 H2 flow rate, *W/F* = 24 g h mol-1, catalyst pre-treatment at 200oC/1h in H2 flow.

The electronic state of Pt in PtAu/CsPW is probably unaffected by the gold as evidenced by H2-TPD (Fig. 8). It can be seen that H2 desorption occurs at the same temperature, ca. 90 oC, for both Pt/CsPW and PtAu/CsPW catalysts, with suggests the lack of ligand effect of gold on Pt sites.

**Fig. 8.** H2-TPD for 6.0%Pt/CsPW (64 mg) and 5.9%Pt/4.4%Au/CsPW (75 mg) at 10 oC min-1 temperature ramp rate and 50 mL min-1 N2 flow rate.

Reaction kinetics with PtAu/CsPW was found similar to that with monometallic Pt/CsPW. It was first order in the catalyst (Fig. 4) and 0.59 order in cyclohexane (Fig. 5), in agreement with the rate equation (1). Important difference is that the reaction with PtAu/CsPW occurred with much lower activation energy of 34 kJ mol-1 than with Pt/CsPW (131 kJ mol-1). It should be noted that for n-hexane isomerization these activation energies have been found quite close [17]. This may be rationalised considering the different geometry of cyclohexane and n-hexane adsorption on platinum. Cyclohexane will probably require a larger surface Pt ensemble (e.g., Balandin’s sextet [53]), whereas there is no such requirement for n-hexane adsorption. As can be seen from the Arrhenius plot (Fig. 3), cyclohexane conversion with PtAu/CsPW is higher than with Pt/CsPW, which confirms the gold enhancement for the whole 180-220 oC temperature range.

At higher reaction temperatures (250-300 oC), cyclohexane isomerization was accompanied by cyclohexane dehydrogenation to benzene (Table 2). This dehydrogenation reaction was also found to exhibit significant Au enhancement, especially regarding the selectivity to benzene (Table 5). At 280 oC, the bimetallic PtAu/CsPW catalyst gave an initial cyclohexane conversion 1.3-fold higher and benzene selectivity 3.5-fold higher than the Pt/CsPW + Au/CsPW physical mixture. Although these reactions suffered stronger deactivation than those at 200 oC, showing a 3-fold decrease in conversion in 4 h TOS (Fig. S7 and S8), their selectivity pattern remained stable over the entire time course. The average enhancement factors (1.5- and 2.4-fold, respectively) were close to the above initial figures. The smaller Au effect on cyclohexane conversion (compared to 2.2-fold at 200 oC) is in agreement with the lower activation energy of cyclohexane isomerization with PtAu/CsPW in comparison with Pt/CsPW. Besides, at 280 oC, the reaction may be limited by the isomerization step rather than the dehydrogenation step (Scheme 2). The effect of Au on cyclohexane isomerization stems from the Au enhancement of partial dehydrogenation of cyclohexane to cyclohexene (Scheme 2). As the complete cyclohexane dehydrogenation to benzene is more thermodynamically feasible, a greater Au effect on this reaction may be expected, which indeed proved to be the case. Previously, the Au enhancement of dehydrogenation of methylcyclohexane to toluene over PtAu/Al2O3 has been reported [32].

It was interesting to examine the effect of support on the gold enhancement. In this regard, we tested carbon-supported physically mixed catalysts, namely PtAu/C + CsPW against Pt/C + CsPW. The Pt/C + CsPW catalyst showed a high activity, which was comparable to that of Pt/CsPW (Table 2). The representative results are shown in Table 6. It can be seen that Au/C has much lower activity than Pt/C based on the metal loading (cf. entry 2 and 3, with CsPW contribution to be subtracted). The values of TOFPt and TOFAu are 110 and 21 h-1 at 200 oC,respectively (calculated using the metal dispersion from Table 1). This means that the turnover activity of Au, although lower than that of Pt, is not negligible. It is due to the low dispersion of Au (Table 1, Fig. S2) that it has low activity based on the total metal weight. From the data shown in Table 6, it is evident that there is no Au enhancement in this system since the Pt/C and PtAu/C catalysts have the same activity (cf. entries 3 and 4).

**Table 5.** Effect of gold on benzene selectivity over Pt/CsPW bifunctional catalysts.a

|  |  |  |  |
| --- | --- | --- | --- |
| Catalyst | Conversion (%) | Selectivity (%) | |
| Methylcyclopentane | Benzene |
| Pt + Aub | 9.6 | 95 | 5.0 |
| PtAuc | 13 | 83 | 17 |

a 280 oC, 3.4 kPa cyclohexane partial pressure, 20 mL min-1 H2 flow rate, 18 min time on stream, *W/F* = 47 g h mol-1,catalyst pre-treatment at 280oC/1h in H2 flow. b Catalyst: 6.0%Pt/CsPW + 4.7%Au/CsPW + SiO2 (1:1:3 w/w, 1.2%Pt, 0.94%Au). c Catalyst: 5.9%Pt/4.4%Au/CsPW + CsPW + SiO2 (1:1:3 w/w, 1.2%Pt, 0.88%Au).

**Table 6.** Effect of gold on isomerization of cyclohexane over Pt/C + CsPW bifunctional catalysts.a

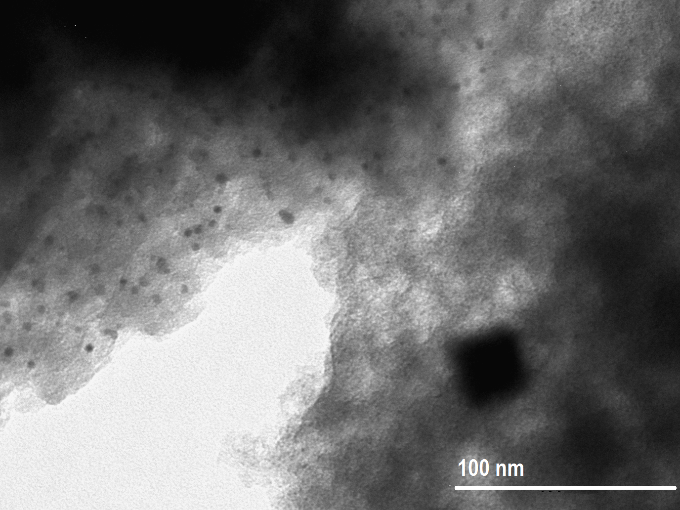
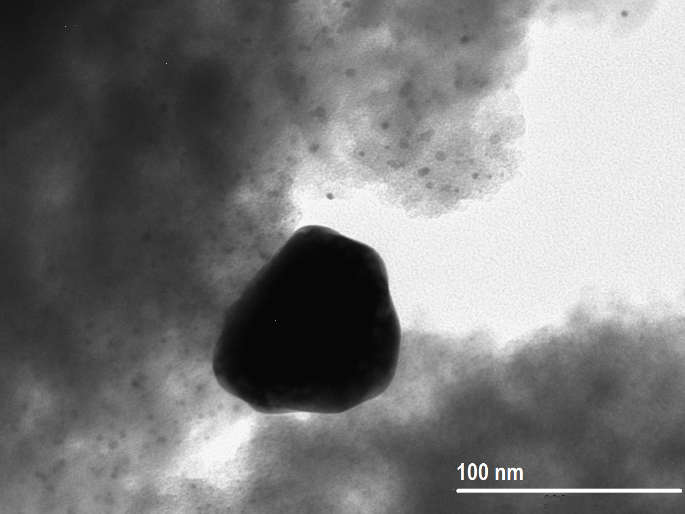
|  |  |
| --- | --- |
| Catalystb | Conversionc (%) |
| 1) CsPW | 3.0 |
| 2) 5.0%Au/C + CsPW (1:11 w/w, 0.42%Au) | 3.5 |
| 3) 6.2%Pt/C + CsPW (1:11 w/w, 0.52%Pt) | 12 |
| 4) 6.7%Pt/5.0%Au/C+CsPW (1:11 w/w, 0.56%Pt, 0.42%Au) | 12 |

a 200 oC, 3.4 kPa cyclohexane partial pressure, 20 mL min-1 H2 flow rate, 6 h time on stream, *W/F* = 118 g h mol-1, catalyst pre-treatment at 200oC/1h in H2 flow. bCatalysts (0.20 g) were physical mixtures prepared by grinding all components together. cCyclohexane conversion at 6 h TOS; MCP selectivity >98% with C3-C4 cracking by-products formed; no C6+ hydrocarbons observed.

Further, our STEM-EDX analysis of PtAu/C failed to reveal the presence of Au-reach bimetallic PtAu particles, only Pt-reach particles with atomic ratios Pt/Au ≥ 15 were found (Fig. S9). The XRD (Fig. 9) shows that Au is present on the carbon surface in the form of large particles of 50-60 nm volume average size, whereas Pt is in a highly dispersed state (4.2 nm particle size). There is hardly any PtAu alloying to be seen in these patterns. TEM images of PtAu/C (Fig. 10) show an array of finely dispersed particles (2-8 nm), presumed to be Pt, and very large Au particles of 40-80 nm in size. The large particles observed in PtAu/C samples resemble those seen in Au/C samples (9.6±3.4 nm mean size, Fig. S2), but are strikingly different in size to Pt/C (3.5±0.7 nm mean size, Fig. S3). Therefore, there is no evidence for any significant modification of Pt sites with Au on the carbon surface. This explains the lack of Au enhancement of activity of the carbon-supported Pt catalyst.

**Fig. 9.** Powder XRD patterns for 5.0%Au/C (Au particle size 62 nm from the Scherrer equation), 6.2%Pt/C (Pt particle size 3.0 nm) and 6.7%Pt/5.0%Au/C (metal particle size: Pt 4.2 nm and Au 54 nm).

The results obtained in this work demonstrate that Au additives enhance the activity of bifunctional Pt/CsPW catalyst in isomerization of cyclohexane by enhancing the alkane dehydrogenation step. The effect of Au can be accredited primarily to the increase in Pt dispersion in the bimetallic PtAu/CsPW catalyst. The Au effect on cyclohexane isomerization is at its maximum when the dehydrogenation is the rate-limiting step. The effect of Au declines as the dehydrogenation step draws nearer quasi-equilibrium. In the isomerization of cyclohexane over Pt/CsPW catalyst, the dehydrogenation step is equilibrated at a surface sites molar ratio Pts/H+ ≥ 0.7. Therefore, in this system, the Au effect is observable at Pts/H+ < 0.7. For Pt/zeolite catalysts, the dehydrogenation step approaches quasi-equilibrium at Pts/H+ < 0.1 [26,28] due to the weaker acidity of zeolites in comparison to CsPW [7,8,25]. In this case, the gold enhancement should be expected at Pts/H+ << 0.1.

**Fig. 10.** TEM images of 6.7%Pt/5.0%Au/C showing an array of relatively small (2 – 8 nm) metal particles, mostly Pt, and very large Au particles 40 – 80 nm in size.

From the data obtained, the origin of Au enhancement can be assigned to the geometric ensemble size effect in PtAu bimetallic species [30,31]. STEM-EDX and XRD indicate the presence of PtAu bimetallic particles in the PtAu/CsPW catalyst [17,21]. The geometric effect may be rationalised in terms of Balandin’s theory of catalysis [53] assuming a gold-induced geometric adjustment of the Pt sextet active site required for adsorption of cyclohexane [53]. This is supported by the increase in Pt dispersion in the PtAu/CsPW catalyst (Table 1). The gold effect appears to be dependent on the nature of support. Thus, the carbon-supported catalyst PtAu/C lacks any performance enhancement by the gold, and there is no evidence of modification of the Pt sites with Au in this catalyst. Further insights into the Au effect may be gained through in-depth structural characterisation of PtAu/CsPW catalyst supplemented by computational analysis.

**4. Conclusions**

Isomerization of cycloalkanes is of interest for the reduction of carcinogenic aromatic compounds in gasoline. The isomerization of cyclohexane was studied in the presence of metal-acid bifunctional catalysts based on Keggin heteropoly salt Cs2.5H0.5PW12O40 (CsPW) using Pt and Au as the metal components. The bifunctional pathway involves cyclohexane dehydrogenation on metal sites followed by isomerization of cyclohexene formed to methylcyclopentene on acid sites; the latter is finally hydrogenated on metal sites to produce methylcyclopentane with high selectivity (>99%). With Pt/CsPW, cyclohexane dehydrogenation step reaches quasi-equilibrium at a molar ratio of Pts and H+ surface sites Pts/H+ ≥ 0.7, which is much higher than for Pt/zeolite catalysts. PtAu/CsPW bimetallic catalyst exhibited a 2-fold higher activity in cyclohexane isomerization and a 3.5-fold higher activity in the accompanying dehydrogenation of cyclohexane to benzene than the mixture of Pt/CsPW and Au/CsPW with the same metal loading. The effect of gold is assigned to the increase in Pt dispersion in PtAu bimetallic particles. STEM-EDX revealed PtAu bimetallic particles in PtAu/CsPW with a wide range of Pt/Au atomic ratios from 0.5 to 7.7. No enhancing effect of Au was found in the case of carbon-supported Pt catalyst.

**Supporting Information**. Thermodynamic calculations, reaction time courses, H2-TPD data, STEM-ADX analysis, TEM images and particle size distribution.

**Acknowledgements**

Dr D. Belic acknowledges funding through ERC Advanced Grant “PANDORA” No. 108269.

**References**

1. Lloyd, L. *Handbook of Industrial Catalysts*, *Fundamental and Applied Catalysis*; Springer: Ney York, 2011; pp 256-258.
2. Sie, S. T. in *Handbook of Heterogeneous Catalysis*, Ertl, G, Knözinger, H., Schüth, F., Weitkamp, J., Eds.; Wiley-VCH: New York, 2008; Vol. 1, p 2809.
3. Watanabe, R.; Suzuki, T.; Okuhara, T. Skeletal Isomerization of Alkanes and Hydroisomerization of Benzene over Solid Strong Acids and Their Bifunctional Catalysts. *Catal. Today* **2001,** *66*, 123–130.
4. Miyaji, A.; Echizen, T.; Li, L.; Suzuki, T.; Yoshinaga, Y.; Okuhara, T. Selectivity and Mechanism for Skeletal Isomerization of Alkanes over Typical Solid Acids and their Pt-Promoted Catalysts. *Catal. Today* **2002,** *74*, 291–297.
5. Matsuhashi, H.; Shibata, H.; Nakamura, H.; Arata, K. Skeletal Isomerization Mechanism of Alkanes over Solid Superacid of Sulfated Zirconia. *Appl. Catal. A: General* **1999,** *187,* 99–106.
6. Weisz, P. B. in *Advances in Catalysis and Related Subjects,* Eley, D. D., Selwood, P. W., Weisz, P. B., Eds.; Academic Press: London, 1963; Vol. 13, p 157.
7. Okuhara, T.; Mizuno, N.; Misono, M. Catalytic Chemistry of Heteropoly Compounds. *Adv. Catal*. **1996,** *41*, 113-252.
8. Kozhevnikov, I. V. *Catalysis by Polyoxometalates*; Wiley & Sons: Chichester, 2002.
9. Wang, S.-S.; Yang, G.-Y. Recent Advances in Polyoxometalate-Catalyzed Reactions. *Chem. Rev.* **2015,** *115*, 4893-4962.
10. Ivanov, A. V.; Vasina, T. V.; Nissenbaum, V. D.; Kustov, L. M.; Timofeeva, M. N.; Houzvicka, J. I. Isomerization of n-Hexane on the Pt-Promoted Keggin and Dawson Tungstophosphoric Heteropoly Acids Supported on Zirconia, *Appl. Catal. A: General* **2004,** *259,* 65–72.
11. Gagea, B. C.; Lorgouilloux, Y.; Altintas, Y.; Jacobs, P. A.; Martens, J. A. Bifunctional Conversion of n-Decane over HPW Heteropoly Acid Incorporated into SBA-15 During Synthesis. *J. Catal*. **2009,** *265*, 99–108.
12. Macht, J.; Carr, R. T.; Iglesia, E. Consequences of Acid Strength for Isomerization and Elimination Catalysis on Solid Acids. *J. Am. Chem. Soc.* **2009,** *131,*6554–6565.
13. Pinto, T.; Arquillière, P.; Dufaud, V.; Lefebvre, F. Isomerization of n-Hexane over Pt-H3PW12O40/SBA-15 Bifunctional Catalysts: Effect of the Preparation Method on Catalytic Performance. *Appl. Catal. A: General* **2016,** *528*, 44–51.
14. Lefebvre, F. Acid Catalysis by Heteropolyacids: Transformations of Alkanes. *Curr. Catal.* **2017,** *6*, 77-89.
15. Knaeble, W.; Carr, R. T.; Iglesia, E. Mechanistic Interpretation of the Effects of Acid Strength on Alkane Isomerization Turnover Rates and Selectivity. *J. Catal.* **2014,** *319*, 283-296.
16. Knaeble, W.; Iglesia, E. Acid Strength and Metal-Acid Proximity Effects on Methylcyclohexane Ring Contraction Turnover Rates and Selectivities. *J. Catal*. **2016,** *344*, 817–830.
17. Alazman, A.; Belic, D.; Kozhevnikova, E. F.; Kozhevnikov, I. V. Isomerization of n-Hexane over Bifunctional Pt-Heteropoly Acid Catalyst: Enhancing Effect of Gold. *J. Catal.* **2018,** *357*, 80-89.
18. Riahi, G.; Guillemot, D.; Polisset-Thfoin, M.; Khodadadi, A. A.; Fraissard, J. Preparation, Characterization and Catalytic Activity of Gold-Based Nanoparticles on HY Zeolites. *Catal. Today* **2002,** *72*, 115-121.
19. Izumi, Y.; Ono, M.; Kitagawa, M.; Yoshida, M.; Urabe, K. Silica-Included Heteropoly Compounds as Solid Acid Catalysts. *Microporous Mater.* **1995,** *5,* 255-262.
20. Alharbi, K.; Alharbi, W.; Kozhevnikova, E. F.; Kozhevnikov, I. V. Deoxygenation of Ethers and Esters over Bifunctional Pt−Heteropoly Acid Catalyst in the Gas Phase. *ACS Catal.* **2016,** *6*, 2067–2075.
21. Poole, O.; Alharbi, K.; Belic, D.; Kozhevnikova, E. F.; Kozhevnikov, I. V. Hydrodeoxygenation of 3-Pentanone over Bifunctional Pt-Heteropoly Acid Catalyst in the Gas Phase: Enhancing Effect of Gold. *Appl. Catal. B: Environmental* **2017,** *202*, 446–453.
22. Alharbi, K.; Kozhevnikova, E. F.; Kozhevnikov, I. V. Hydrogenation of Ketones over Bifunctional Pt-Heteropoly Acidcatalyst in the Gas Phase. *Appl. Catal.* A **2015,** *504*, 457–462.
23. Benson, J. E.; Boudart, M. Hydrogen-Oxygen Titration Method for the Measurement of Supported Platinum Surface Areas. *J. Catal.* **1965,** *4*, 704-710.
24. Benson, J. E.; Hwang, H. S.; Boudart, M. Hydrogen-Oxygen Titration Method for the Measurement of Supported Palladium Surface Areas. *J. Catal.* **1973,** *30*, 146-153.
25. Okuhara, T. Water-Tolerant Solid Acid Catalysts. *Chem. Rev.* **2002,** *102*, 3641-3666.
26. Ribeiro, F.; Marcilly, C.; Guisnet, M. Hydroisomerization of n-Hexane on Platinum Zeolites: I. Kinetic Study of the Reaction on Platinum/Y-Zeolite Catalysts: Influence of the Platinum Content. *J. Catal.* **1982,** *78*, 267-274.
27. Van de Runstraat, A.; Kamp, J. A.; Stobbelaar, P. J.; Van Grondelle, J.; Krijnen, S.; Van Santen, R. A. Kinetics of Hydro-Isomerization of n-Hexane over Platinum Containing Zeolites. *J. Catal.* **1997,** *171*, 77-84.
28. Mendes, P. S. F.; Mota, F. M.; Silva, J. M.; Ribeiro, M. F.; Daudin, A.; Bouchy, C. A Systematic Study on Mixtures of Pt/Zeolite as Hydroisomerization Catalysts. [*Catal. Sci. Technol.*](http://pubs.rsc.org/en/journals/journal/cy) **2017,** *7*, 1095-1107.
29. Alharbi, W.; Kozhevnikova, E. F.; Kozhevnikov, I. V. Dehydration of Methanol to Dimethyl Ether over Heteropoly Acid Catalysts: The Relationship between Reaction Rate and Catalyst Acid Strength. *ACS Catal.* **2015,** *5*, 7186−7193.
30. Guczi, L.; Schay, Z.; Role of Bimetallic Catalysts in Catalytic Hydrogenation and Hydrogenolysis. *Stud. Surf. Sci. Catal.* **1986,** *27*, 313-336.
31. Bond, G. C. *Metal-Catalysed Reactions of Hydrocarbons*; Springer: New York, 2005.
32. Rouabah, D.; Fraissard, J. Pt-Au/Al2O3 Catalysts: Preparation, Characterization and Dehydrogenation Activity. *J. Catal.* **1993,** *144*, 30-37.
33. Chandler, B. D.; Rubinstein, L. I.; Pignolet, L. H. Alkane Dehydrogenation with Silica Supported Platinum and Platinum-Gold Catalysts Derived from Phosphine Ligated Precursors. *J. Mol. Catal*. A **1998,** *133*, 267-282.
34. Riahi, G.; Guillemot, D.; Polisset-Thfoin, M.; Khodadadi, A. A.; Fraissard, J. Preparation, Characterization and Catalytic Activity of Gold-Based Nanoparticles on HY Zeolites. *Catal. Today* **2002,** *72*, 115-121.
35. Hutchings, G. J. Nanocrystalline Gold and Gold Palladium Alloy Catalysts for Chemical Synthesis. *Chem. Commun*. **2008**, 1148–1164.
36. Sun, K.; Wilson, A. R.; Thompson, S. T.; Lamb, H. H. Catalytic Deoxygenation of Octanoic Acid over Supported Palladium: Effects of Particle Size and Alloying with Gold. *ACS Catal*. **2015,***5*, 1939−1948.
37. Han, Y. F.; Wang, J. H.; Kumar, D.; Yan, Z.; Goodman, D. W. A Kinetic Study of Vinyl Acetate Synthesis over Pd-Based Catalysts: Kinetics of Vinyl Acetate Synthesis over Pd–Au/SiO2 and Pd/SiO2 Catalysts. *J. Catal*. **2005,** *232*, 467−475.
38. Hanrieder, E. K.; Jentys, A.; Lercher, J. A. Impact of Alkali Acetate Promoters on the Dynamic Ordering of PdAu Catalysts During Vinyl Acetate Synthesis. *J. Catal*. **2016,** *333*, 71–77.
39. Xu, J.; White, T.; Li, P.; He, C.; Yu, J.; Yuan, W.; Han, Y. F. Biphasic Pd−Au Alloy Catalyst for Low-Temperature CO Oxidation. *J. Am. Chem. Soc*. **2010,** *132*, 10398−10406.
40. Coq, B.; Figueras, F. Bimetallic Palladium Catalysts: Influence of the Co-metal on the Catalyst Performance. *J. Mol. Catal. A: Chem*. **2001,** *173*, 117−134.
41. Gao, F.; Goodman, D. W. Pd–Au Bimetallic Catalysts: Understanding Alloy Effects from Planar Models and (Supported) Nanoparticles. *Chem. Soc. Rev*. **2012,** *41*, 8009−8020.
42. Venezia, A. M.; La Parola, V.; Nicoli, V.; Deganello, G. Effect of Gold on the HDS Activity of Supported Palladium Catalysts. *J. Catal.* **2002,** *212*, 56-62.
43. Venezia, A. M.; La Parola, V.; Deganello, G.; Pawelec, B.; Fierro, J. L. G. Synergetic Effect of Gold in Au/Pd Catalysts During Hydrodesulfurization Reactions of Model Compound. *J. Catal.* **2003,** *215*, 317-325.
44. Schwartz, T. J.; Lyman, S. D.; Motagamwala, A. H.; Mellmer, M. A.; Dumesic, J. A. Selective Hydrogenation of Unsaturated Carbon–Carbon Bonds in Aromatic-Containing Platform Molecule. *ACS Catal.* **2016,** *6*, 2047-2054.
45. [Van Schaik](http://www.sciencedirect.com/science/article/pii/0021951775900883#!), J. R. H.; Dessing, R. P.; Ponec, V. Reactions of Alkanes on Supported Pt-Au Alloys. *J. Catal*. **1975,** *38*, 273-282.
46. Karpinski, Z.; Clarke, J. K. A. Reactions of Alkanes on Iridium and Iridium-Gold Catalysts. *J. Chem. Soc., Faraday Trans. 1* **1975,** *71*, 2310-2318.
47. [Clarke,](http://www.sciencedirect.com/science/article/pii/0021951780904923#!) J. K. A.; [Kane,](http://www.sciencedirect.com/science/article/pii/0021951780904923#!) A. F.; Baird, T. Reaction of Alkanes and Cycloalkanes on Silica-Supported Platinum and Platinum-Gold Alloy Catalysts. *J. Catal.* **1980,** *64*, 200-212.
48. Kane, A. F.; Clarke, J. K. A. Reactions of Alkanes and Cycloalkanes on

Platinum-Gold Alloy Films. *J. Chem. Soc*., *Faraday Trans. I* **1980,** *76*,1640-1651.

1. Clarke, J. K. A.; Creaner, A. C. M.; Baird, T. Preparation of Supported Platinum-Gold Catalysts and Alkane Reactions on Selected Platinum and Platinum-Gold Supported "Clusters". *Appl. Catal*., **1984,** *9*, 85-108.
2. Karpinski, Z.; Juszczyk, W.; Stachurski, J.; Isomerization of Alkanes on Epitaxially Oriented (111) Pd-Cu and Pd-Ag Alloy Films.  *J. Chem. Soc., Faraday Trans. 1* **1985,** *81*, 1447-1454.
3. Chandler, B. D.; Schabel, A. B.; Pignolet, L. H. Preparation and Characterization of Supported Bimetallic Pt–Au and Pt–Cu Catalysts from Bimetallic Molecular Precursors. *J. Catal*. **2000,** *193*, 186–198.
4. Fraissard, J.; Gerda, V.; Patrylak, K. I.; Voloshyna, Yu. G. Isomerization of Hexane on PtAu Nanoparticles Supported on Zeolites. *Catal. Today* **2007,** *122,* 338–340.
5. Balandin, A. A. Multiplet theory of catalysis. *Russ. Chem. Rev*. **1962,** *31*, 589-614.

TOC Graphic for Manuscript



1. Corresponding author. Tel.: +44(0)1517942938

   *E-mail address:* *kozhev@liverpool.ac.uk* (I. V. Kozhevnikov) [↑](#footnote-ref-1)