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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 $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) and Pt/CsPW as the catalysts, using a fixed-bed microreactor under differential conditions (*n*-hexane conversion ≤ 10%) at 180–220 °C, ambient pressure and a ratio of *n*-hexane and H_2 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 $Pt_s/H^+ \geq 0.8$, 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.

1. Introduction

Isomerisation of linear C_5–C_6 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].

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 H_2 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, C_{6-} hydrocarbons can be formed by cracking of hexane isomers. Also C_{6-} and C_{6+} products can be produced by disproportionation of C_{12} cation intermediates formed from the C_6 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 con-

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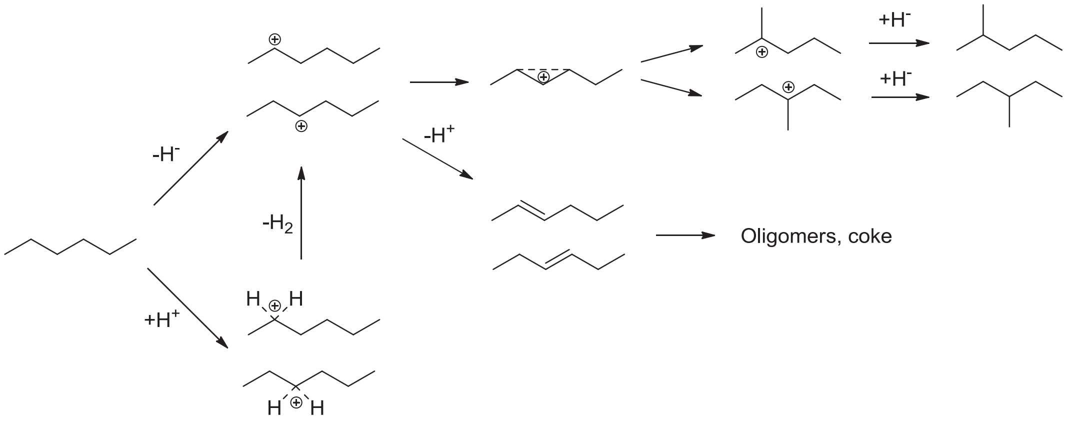
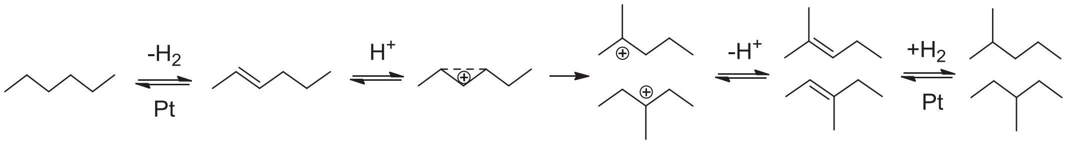


Scheme 1. Acid-catalysed pathway for *n*-hexane isomerisation via monomolecular mechanism.



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

tribution of the bimolecular mechanism [5] and reduces coke formation, thus improving catalyst lifetime [1].

Heteropoly acids (HPAs) possessing very strong Brønsted acidity have attracted much interest as acid catalysts, in particular tungsten HPAs with Keggin structure such as $H_3PW_{12}O_{40}$ (HPW) and $H_4SiW_{12}O_{40}$ (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 $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (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%), H_2PtCl_6 hydrate, $HAuCl_4{\cdot}3H_2O$, $H_3PW_{12}O_{40}$ (HPW, 99%) and $H_4SiW_{12}O_{40}$ (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. H_2 gas cylinders (>99%) were supplied by the British Oxygen Company.

Cesium tungstophosphate $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (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 $H_3PW_{12}O_{40}$ to afford CsPW as a white precipitate. The material was isolated, vacuum dried at 150 °C/10^{-3} kPa for 1.5 h. A similar procedure was used for the preparation of $Cs_{2.25}H_{0.75}PW_{12}O_{40}$ ($Cs_{2.25}$PW). 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 °C/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 H_2PtCl_6 or $HAuCl_4$. This involved stirring the aqueous slurry at 50 °C for 2 h followed by rotoevaporation to dryness and reduction with H_2 flow at 250 °C for 2 h. The bimetallic PtAu/CsPW catalysts were prepared similarly by co-impregnation of CsPW with H_2PtCl_6 and $HAuCl_4$ with reduction by H_2 as above. Metal content in these catalysts was determined by ICP-AES analysis (see below). Physical mixtures of bifunctional catalysts and SiO_2 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 °C. Before measurement, the samples were evacuated at 250 °C 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