Lighter Alkanes Isomerization using Heteropoly Acids

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Abstract: *The reason for deep interest in the use of heteropolyacids for catalytic application in isomerization of saturated hydrocarbons derives from their tuneable acidic and redox properties. Apart from these two major advantages, other characteristic associated with heteropolyacids is intrinsic multifunctionality. Although the restriction for using these compounds is limited due to their thermal structural stability, but these advantages are really exploitable and can be effectively used for the design of a suitable catalytic composition. This review will be useful to the researchers working in the area of improving octane number of individual model alkanes and also for naphtha.*
Keywords: *Isomerization, heteropoly acid, phosphotungstic acid, alkane*

I.   Introduction

Skeletal isomerization of alkanes is industrially important as branched chain alkanes are clean high-octane fuels. It allows to transform low octane n-paraffins, especially with five or six carbon atoms, into higher octane iso-paraffins. Weyda and Kohler in 2002 found that light naphtha streams rich in C_5 and C_6 species showed an average increase of 10–20 units in octane number due to isomerization [1]. For example, octane numbers ofn-hexane and its isomers, viz.

2-methyl pentane, 3-methyl pentane, 2,2-dimethyl butane and2,3-dimethyl butane are 31, 74, 76, 94 and 105, respectively. Similarly, octane numbers ofn-pentane and iso-pentane are 61.7 and 93.5, respectively. From a thermodynamic point of view, the formation of high octane branched isomer is favored at low temperature. Hence, the best isomerization catalysts will be strong acidic catalysts able to work at the lowest possible temperature. Variety of catalysts has been used to carry out isomerization of alkanes, owned by different licensors; however paraffin isomerization technology is dominated by UOP namely Penex[TM] (C5/C6) and Butamer[TM] (C4). Zeolites promoted by platinum, e.g. HYSOPAR® from Süd-Chemie and HS-10™ from UOP, are used in the Penex™ process [2–4]. Zeolite based catalysts have been found to be better than some other class of catalysts due to their easy handling as well as their less sensitivity to the presence of poisons, such as sulfur and water in the feedstock.

Zirconia supported catalysts is anothercategory promising for isomerization reactions, especially for alkanes at higher rates [5]. They possess super-acidity ($H_0=-15.9$) and behave as potential catalysts for n-alkanes isomerization at ambient temperature [6–11]. It was first used as hydrocarbon isomerization catalyst in 1962 by Holm and Baileys of Phillips Petroleum [12]. Sulfated zirconia, like other catalysts undergoes deactivation due to coke deposition [11], which can be avoided in the presence of super-critical conditions [13]. Deactivation can be overcome by the addition of various transition metals as promoters, such as platinum, iron, manganese [14], nickel, antimony, scandium, cobalt, zinc, chromium, vanadium, copper, cadmium, titanium, aluminum, tin, molybdenum, tungsten [15], iridium, rhodium, ruthenium, osmium and palladium. Sulfated zirconia promoted with metal ions has attracted much attention to catalyze many reactions including isomerization and hydroisomerization at low temperature. Sulfated zirconia has been used for the isomerization of n-butane even at room temperature. Despite of its advantages, sulfated zirconia is associated with major drawback of rapid deactivation.

Ledoux and coworkers observed that Mo_2-C on oxidation, gave molybdenum oxycarbide (MoO_xC_y) with selectivity for isomerization of alkanes [16]. Matsuda et al. found that MoO_3 on reduction with hydrogen at 350°C gave high surface area along with high catalytic activity and selectivity for heptane isomerization [17–18].

The activity was found to be dependent on duration and temperature of exposure to hydrogen. The catalyst was most active when Mo oxidation number was between 2.5 and 3.5. Later, they found that MoO_3 loaded with transition metals was more active than MoO_3 without metal-loading for heptane isomerization under hydrogen [19–20]. Among transition metals, Pt was most effective in enhancing the formation of H_xMoO_3 phase, which is the precursor of active MoO_xH_yphase.Industrial processes utilize these catalysts under high pressure of hydrogen (20–70 kg cm^{-2}). Chlorinated Pt/Al_2O_3 has been successfully used in petroleum processing but it requires continuous chlorination to maintain catalytic activity due to Cl$^-$ loss [21–22]. HCl is corrosive and harmful, thus requires a further purification step that increases the overall production cost.

Tungsten carbide treated with oxygen at 527°C was proved to be good catalyst for isomerization of hexanes and heptanes by Iglesia and coworkers [23]. Dehydrogenation-hydrogenation function is offered by the patches of carbide, while acidic function is offered by patches of tungsten oxide.

Although catalysts reported above have shown an yield upto 86%, they possess some major drawbacks, such as high cost, ready poisoning by impurities as sulfur and water even at concentrations as low as 10 ppm, sensitive to deactivation by coke deposition etc. This has created a need for the development of catalyst which can overcome these difficulties and give improved yield under mild conditions [24].One such category is heteropoly acids (HPAs)with discrete ionic structure [25]. It contains basic mobile units as H^+, H_5O^+, $H_5O_2^+$ etc. and polyoxometalate anions (heteropolyanions) in which metal-oxygen octahedral form basic structural units. Mobile units allow high proton acidity and corresponding heteropoly anions can stabilize cationic paraffin intermediates [26]. HPAs exist in two structures; Keggin, $H_nXM_{12}O_{40}$, and Dawson, $H_nX_2M_{18}O_{62}$ (Figure 1).
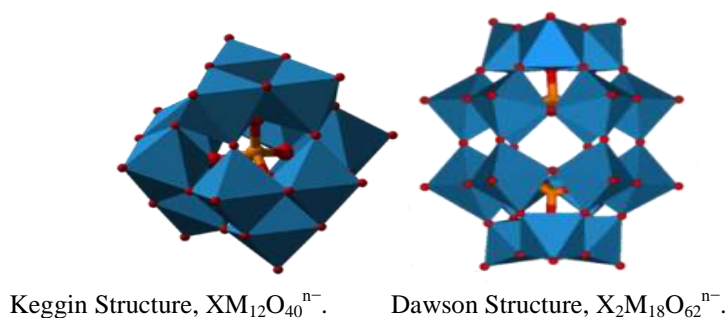

Keggin Structure, $XM_{12}O_{40}^{n-}$.   Dawson Structure, $X_2M_{18}O_{62}^{n-}$.

Fig. 1: Structures of Heteropoly Acids.

Keggin type heteropoly acids ($H_nXM_{12}O_{40}$) have been widely used as acid catalysts owing to their characteristics, such as good thermal stability, high acidity and high oxidising ability, but have limited catalytic performance due to large particle size and lower surface area. However, their efficiency can be increased in combination with other components.HPAs are comprised of three structures, viz. primary, secondary and tertiary. Primary structure consists of large heteropolyanions, i.e. metal oxide cluster molecule involving molecular nature of solid HPA. Secondary structure is a combination of primary structure, counter cations, water of crystallization and other molecules [27–29]. Tertiary structure is assembled solid HPA, which speaks about particle size, pore structure and distribution of protons in the particle and has vital influence on its catalytic activity [27, 30]. All the three structures have been illustrated in Figure 2[31–32].
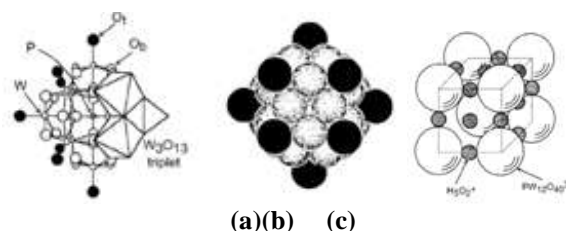

(a)(b)   (c)
Fig. 2: Structures of 12-Tungstophosphoric Acid.
(a)   Primary Structure (Keggin Structure, $PW_{12}O_{40}^{3-}$).
(b)   Secondary Structure ($H_3PW_{12}O_{40}.6H_2O$).
(c)Tertiary Structure (Particle Size, Surface Area, Pore, Uniformity of Composition).

HPAs and their salts of HPA with small cations (e.g. Na, Mg) have low surface areas (1–15 m^2/g). On the other hand, surface areas of HPA with large cations (Cs, NH_4 etc.) are much higher (50–200 m^2/g) [33]. In order to improve their catalytic activity, heteropoly acids are often used as their acidic metal-salts [34–36], or dispersed on high surface area acidic or neutral support such as silica, active carbon or acidic ion-exchange resin, but silica is most widely used [27–28, 30, 37–39].Thermal stability is very important characteristic of HPAs[30, 40]. Thermal stability of HPAs changes with heteroatom, polyatom and polyanion as: $H_3PW_{12}O_{40}$>$H_3PMo_{12}O_{40}$>$H_4SiMo_{12}O_{40}$.

Thermal stability of phosphotungstic acid is reported to be enhanced when supported on silica [41], which is due to protonated silanol groups in interaction with bridged oxygen atoms in HPA structure [42]. Keggin structure of $H_3PMo_{12}O_{40}$ is reported to be thermally stable only up to 450°C. Thermal stability of $H_3PMo_{12}O_{40}$ and its salts changes with countercations. Bi- and tetravalent metal salts are not stable. Hydrogen

form and ammonium salts decompose at 420°C and 470°C, respectively. Cesium and potassium salts are stable up to their melting points only. Thermal stability of various HPAs increases in the order: Ba^{+2}, $Co^{+2} < Cu^{+2}$, $Ni^{+2} < H^+$, $Cd^{+2} < Ca^{+2}$, $Mn^{+2} < Mg^{+2} < La^{+3}$, $Ce^{+3} < NH_4^+ < K^+$, Tl^+, Cs^+ [43].

Acid strength is one of the dominant features of isomerization catalysts. Increasing acid strength influencesisomerization reaction strongly, and rate constant of the reaction increases more sharply over stronger acid sites [44–46].Acid strength of HPAs vary in a wide range depending on polyanion structure and its constituent elements (both hetero and addenda atoms), as well as on the extent of hydration and reduction. Counter cation is also an important factor. Studies indicate that phosphotungstic acid is the strongest heteropoly acid which after dehydration becomes comparable to superacid in strength [26, 30, 47–50]. The group of Misono and Okuhara [40, 51–52] found that $H_3PW_{12}O_{40}$ gave highly acidic materials with high surface area when a part of the three protons was replaced with Cs. Thus, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was reported to be active for alkane isomerization and activity was more under hydrogen when the material was loaded with Pt [35, 52–53].

HPAs, such as $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ in solid state are pure Bronsted acids [54] and stronger acids than conventional solid acids, such as SiO_2-Al_2O_3, H_3PO_4/SiO_2 and HX and HY zeolites. Acidic properties of HPA are mainly controlled by the structure and composition of heteropolyanion itself; while the number of acid sites is influenced by counter cations and its dispersion on supports. Acid strength decreases when W is replaced by Mo and when central P atom is replaced by Si for Keggin HPAs, which are stronger acids than Dawson HPAs [55].

Heteropoly compounds provide a good basis for molecular design of mixed oxide catalysts, due to availability of information regarding its catalytic performance, chemical and physical properties, structure and method of synthesis of catalyst.Heteropoly acids also serve as the precursors for oxide catalysts. Major advantages [33] of heteropoly acids as solid acid catalysts include:

- Controllable catalyst design at atomic/molecular levels based on acidic and redox properties.
- Possibility of describing catalytic process at atomic/molecular level.
- Unique reaction field.
- Selective stabilization of reaction intermediates.

Isomerization catalysts are basically bi-functional in nature consisting of both metallic and acidic properties. Metallic sites catalyze dehydrogenation reactions while acidic sites catalyze isomerization reactions.

Mechanistic Approach of Alkane Isomerization
HPAs catalyze reactions by three different modes; viz surface type catalysis, pseudo-liquid type catalysis and bulk type catalysis [52]. Different mechanisms have been proposed for catalytic isomerizaton of alkanes, the main focus lying in the mode of formation of intermediate, acidity requirement of catalyst and role of a metallic component and hydrogen during isomerization.Acid catalyzed mechanism is an important route for isomerization reaction (Figure 3).
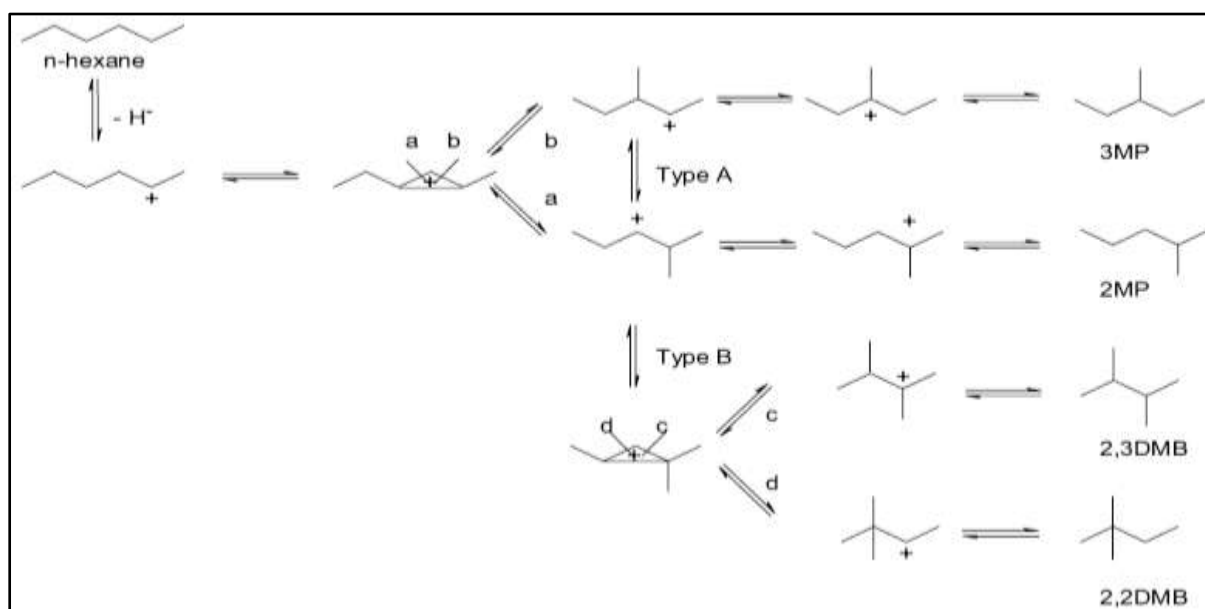

Fig. 3: Acid Catalyzed Isomerization of n-Hexane [56].

Bi-functional mechanisms another route, in which alkane is dehydrogenated to form alkene, which is protonated to give carbenium ion. Carbenium ions then turn into isomerized alkanes by hydride-transfer with reactant alkanes.
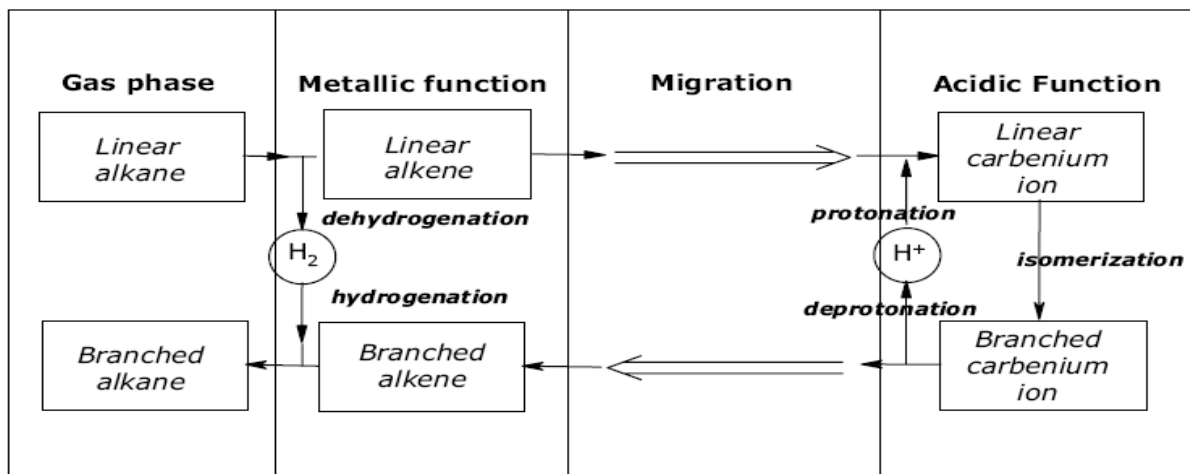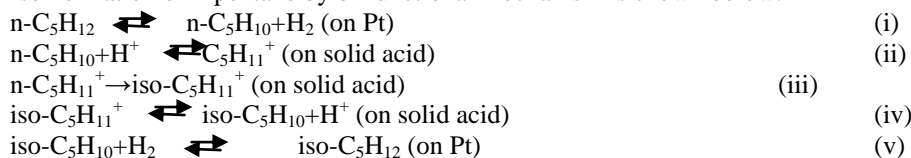

Fig. 4: Route for Bi-functional Mechanism [57].

Isomerization of n-pentane by bi-functional mechanism is shown below:

$n\text{-}C_5H_{12} \rightleftharpoons n\text{-}C_5H_{10}+H_2$ (on Pt)   (i)

$n\text{-}C_5H_{10}+H^+ \rightleftharpoons C_5H_{11}^+$ (on solid acid)   (ii)

$n\text{-}C_5H_{11}^+ \rightarrow iso\text{-}C_5H_{11}^+$ (on solid acid)   (iii)

$iso\text{-}C_5H_{11}^+ \rightleftharpoons iso\text{-}C_5H_{10}+H^+$ (on solid acid)   (iv)

$iso\text{-}C_5H_{10}+H_2 \rightleftharpoons iso\text{-}C_5H_{12}$ (on Pt)   (v)

Above mechanism suggests that activation of alkane requires a very high acidic strength which is provided by transition metal. Reaction (iii) is rate determining step for isomerization; hence dependence of this step on the acidic properties of the catalyst becomes more important. Metallocyclic mechanism does not involve carbenium ion intermediates, which are easily cracked in case of hydrocarbons with seven or more carbon atoms. Metallocyclic mechanism for isomerization of n-butane is shown in Figure 5 [58].
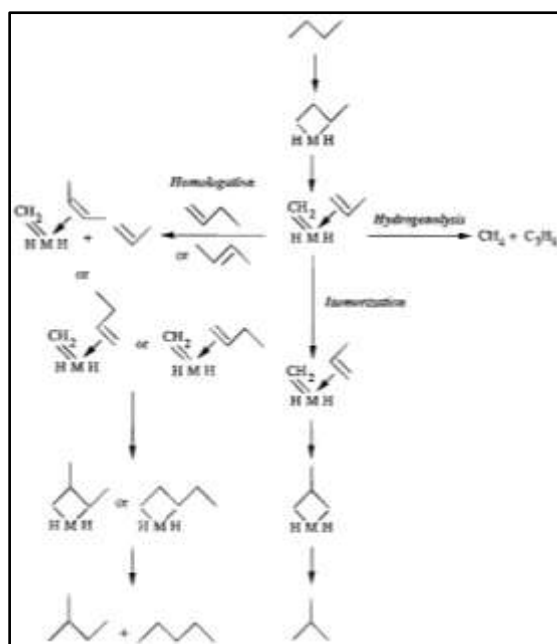

Fig. 5: Metallocyclic Mechanism for Isomerization of n-Butane [58].

THERMODYNAMICS OF ISOMERIZATION REACTIONS

Theoretical density functional theories (DFT) can also be used to investigate acid-catalyzed reactions which offer an atomic-level description of reaction mechanism, including structures and energies of adsorption and transition states (TS) [59–66]. From this, information pertinent to local electronic distribution as well as potential energy surface (PES) characterizing interactions with reactant molecules can be obtained. Thus, activation barriers can be computed from PES of the reactant and transition state relevant to the reaction. Moreover, in order to compare with experimental results directly, reaction rate constant also can be derived through transition state theory (TST). Therefore, theoretical calculations have been of great utility and allowed researchers to investigate the reaction activity with varying acid strength more directly [67]. Chu et al. studied protonation reaction of alkenes on Brønsted acid sites with varying acid strengths [68]. Ionic species are much more sensitive to acid strength than covalent species. Activation of C–H and C–C bonds are elementary steps in many hydrocarbon catalytic reactions used in petrochemical industry. Isomerization of alkanes is slightly exothermic reaction. Thus the yield of branched alkanes is thermodynamically favored by low reaction temperature [69]. Isomerization is always accompanied by consequent hydrocracking reaction resulting in small yield loss. Rates of isomerization and cracking reaction steps determine product distribution. Thus, it is essential to inhibit side reactions, such as hydro-cracking and olefin formation during isomerization in order to get higher conversion [70].

ISOMERIZATION BY HETEROPOLY ACIDS

Extent of isomerization reaction depends upon process variables, such as reactor temperature, operating pressure, weight hourly space velocity (WHSV) and H_2/hydrocarbon ratio. At lower WHSV, most of the catalysts give similar performance due to thermodynamic equilibrium limitations. Highly active catalysts normally give superior performance even at higher WHSV, therefore, allows to use more feed to process isomerization at lower catalyst volume thereby, decreases the cost also. Ideal catalyst should have proper balance between metal and acid sites, medium pore size, high dispersion of metal on surface of catalyst, mild acidity and strength distribution of acid sites [71]. HPAs serve as a good source of catalytic material for the isomerization of lighter alkanes possessing controllable acidic and redox properties.

Isomerization of n-Butane

Liu et al.used Pt-promoted $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst for the isomerization of n-butane in a fixed-bed gas-flow reactor [72]. They prepared the catalyst by two different methods, one by direct impregnation of Pt on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as support, second by using them as mechanical mixture. The hydroisomerizations of n-butane was performed in a fixed-bed quartz tubular reactor (573 K, atmospheric pressure, total flow rate 20 mL min^{-1}, catalyst amount 1 g, feed gas composition 10% n-C_4H_{10}, 10% H_2 and 80% N_2) and the products were analyzed with an on-line FID gas chromatograph equipped with Al_2O_3/KCl fused silica capillary column. The catalysts were pretreated in a flow of H_2 (60 mL min^{-1}) at 573 K for 1 h before reaction. The reactivity w.r.t. isomerization of n-butane was evaluated separately for Pt/Al_2O_3, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, Pt impregnated on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and mechanical mixture of Pt/Al_2O_3 and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Mechanical mixture of Pt/Al_2O_3 and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was reported to exhibit a higher stable conversion (64.8%) and a higher stable selectivity to isobutane (92.5%). The higher conversion to isomer with mechanical mixture as catalyst was attributed to higher surface area and uniformly distributed acid sites.In another study, n-butane was isomerized in the presence of platinum promoted phosphotungstic acid supported on silica. Reaction was performed in a flow reactor at atmospheric pressure with n-butane pressures of 2, 4 and 10 bars using 250 mg of catalyst at 373–623 K. Before reaction, catalyst was reduced at 498 K for 4 h in hydrogen (flow rate 1 ml/min) into a continuous flow reactor. Under such conditions, 97% selectivity for iso-butane has been achieved [73].

Bogdan et al.carried out isomerization of n-butane using sulfated zirconia, heteropolyacids of Keggin type $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ supported on titania and H-mordenite as catalyst [74]. Gas phase isomerization was carried out with all the catalysts in a flow type reactor at 488, 533 and 573 K and 6.1, 11.0 and 13.8 MPa, respectively. Results in supercritical state indicated stable activity with no poisoning of catalysts. Catalyst reactivation by the supercritical media was observed when n-butane density was in the vicinity of its critical value or higher and resulted in the initial value of 20–25% conversion. 80% selectivity for iso-butane was achieved on sulfated zirconia and $H_4SiW_{12}O_{40}$ supported on titania in supercritical n-butane. However in case if H-mordenite, iso-butane selectivity did not exceed 40% at 25% conversion. On zeolite catalyst, at an elevated temperature (573 K), cracking side reactions predominated yielding propane, n-pentane, iso-pentane and traces of ethane and hexane as by-product.

In 2000, Bardin and Daviscarried out skeletal isomerization of n-butane and n-pentane by phosphotungstic acid supported on silica (abbreviated as 25PW, 10PW and 5PW for 20, 10 and 5wt % $H_3PW_{12}O_{40}$ on silica, respectively) [75]. Catalytic reactions were performed in a single pass, fixed bed, quartz

tube reactor (473 K, feed flow rate 5 ml/min containing 10% n-butane and n-pentane individually). Catalyst was pretreated in situ at 473, 573 and 673 K under helium flowing at 10 ml/min. Products from reactions were analyzed by gas chromatography equipped with a flame ionization detector. Results indicated that the activity decreased as the pretreatment temperature increased, indicating that level of hydration is critical for acid catalysis. Among various catalyst samples, 10PW and 25PW were noticeably active for the isomerization reaction. Further, treatment of the catalysts with water at mild conditions recovered activity for the bulk and supported heteropolyacids for isomerization reactions.

Isomerization of n-Pentane

Essayemet al.reported that a simultaneous presence of platinum and hydrogen inhibits and suppresses the isomerization of n-pentane at 423K over HPA-based catalysts[3]. Skeletal isomerization of n-pentane has been evaluated using Pd-$H_4SiW_{12}O_{40}$/SiO_2 as catalyst [41]. The effects of the loading of $H_4SiW_{12}O_{40}$ and Pd on the catalytic activity and selectivity were systematically investigated, and the acid strength, dispersion of $H_4SiW_{12}O_{40}$, and in particular the density of acid sites on the catalyst surface was examined. Pd-free $H_4SiW_{12}O_{40}$ catalyst supported on silica ($H_4SiW_{12}O_{40}$/SiO_2) was prepared by impregnating an aqueous solution of $H_4SiW_{12}O_{40}$ on SiO_2 by incipient wetness method. Pd was incorporated to HSiW/SiO_2 by impregnation using an aqueous solution of $PdCl_2 \cdot 6H_2O$. Isomerization of n-pentane was performed in a flow reactor at 523 K under atmospheric pressure (n-pentane:H_2:He=6.1:69.4:24.5 vol. %). Pretreatment was done by exposing the catalysts to a flow of H_2 (50 cm^3min^{-1}) at 573 K for 2 h. 99.1% selectivity was reported for isopentane with 1 wt.% Pd-20 wt.% HSiW/SiO_2 as catalyst.

Soultanidiset al. [76] studied n-pentane isomerization activity and selectivity as a function of tungsten surface density, catalyst support type and calcination temperature.

Two catalysts were prepared by impregnating ammonium metatungstate, $(NH_4)_6H_2W_{12}O_{40}.5H_2O$ on amorphous zirconium hydroxide and model crystalline zirconium oxide, followed by calcination and were used to carry out isomerization of n-pentane. The catalytic studies were performed on an isothermal down-flow reactor (catalyst flow bed length 2.22 cm, 523 K, GHSV 68). Pretreatment of the catalyst was done in situ at 673 K under a continuous flow (100 cc/min) of ultrahigh purity (UHP) air for 1 h. It was observed that catalyst from zirconium hydroxide showed maximum activity at surface density of 5.2 Wnm^{-2}, in contrast to that from zirconium oxide which was found to be inactive. Further, high calcination temperature (973 K) favored the formation of Zr-WO_x clusters ranging from 0.8–1 nm without promoting their surface acidic properties.

Similar studies have been carried out for the isomerization of n-pentane by Xu et al. using platinum promoted $H_3PW_{12}O_{40}$ supported on MCM-41 and reported the optimal activity with 2% platinum and 30% tungstophosphoric acid [77]. Application of heteropoly acid supported on inert oxides for the isomerization of n-pentane and n-hexane has been patented by Masloboishchikovaet al. [78]. They prepared the catalyst by impregnating phosphotungstic acid on titania by wet incipient technique in conjunction with platinum. n-pentane isomerization was carried out in a fixed bed reactor at 0.1 MPa total pressure with a space velocity LHSV1 h^{-1}. Hydrogen: hydrocarbon ratio was 3:1 on volume basis at temperatures ranging from 190–230°C. Results indicated that with the increase in reaction temperature, conversion increased but selectivity decreased. Maximum selectivity was reported as 99% at 190°C.

Isomerization of n-Hexane

Ivanov et al. studied the activity of Pt-promoted Keggin and Dawson tungstophophoric acid (HPW) supported on zirconia for the isomerization of n-hexane [79]. Their studies established the high activity of Pt/HPW/ZrO_2 catalyst for n-hexane isomerization with the iso-hexanes yield of 80% and the selectivity of 96–98% at 463 K.n-hexane isomerization was carried out in a fixed bed reactor at 0.1 MPa total pressure with a space velocity LHSV 1 h^{-1}. Hydrogen: hydrocarbon ratio was 4:1 on volume basis at temperatures ranging from 190–210°C. Maximum selectivity was reported as 95.6% at 190°C [78]. $Cs_xH_{3-x}PW_{12}O_{40}$ catalysts with Pt metal as a promoter was used for the isomerization of n-hexane [80]. The catalyst was prepared by mixing stoichiometric ratios of $H_3PW_{12}O_{40} \cdot nH_2O$ and $Cs_3PW_{12}O_{40}$ followed by pre-treatment at different temperatures under various atmospheres of nitrogen, hydrogen and air. Pt metal was also introduced by similar means. Isomerization of n-hexane was carried out in a fixed bed micro-reactor at a total pressure of 4 bar, temperature ranging from 453–493 K, and molar hydrogen to n-hexane ratio of 10. In addition to selectivity for dibranched isomers, the overall catalytic performance was observed to be very close to that of industrial zeolite catalysts under similar reaction conditions.

Similar type of cesium salts of phosphotungstic acid supported on zirconia in combination with platinum was used by Volkovaet al.[81]. Various compositions of the substituted salts were prepared with the stoichiometric formula $Cs_xH_{3-x}PW_{12}O_{40}$ and the catalytic activity was compared with the isomerization carried out in the presence of Pt/WO_x/ZrO_2 and Pt/SO_4/ZrO_2. Isomerization of n-hexane was carried out using a flow-through reactor with a gas chromatographic analysis of gaseous and liquid products (Pressure =3 bar,

temperature 473–543 K, ratio of H_2/n-hexane =2:1). Pretreatment of the catalyst was done by reducing it in a mixture of hydrogen and helium at a temperature of 473 K for 2 h. Lowest activity was observed for Pt/WO_x/ZrO_2 (18.9% selectivity for 2,3-dimethylbutane) and highest for Pt/SO_4/ZrO_2 (23.2% selectivity for 2,3-dimethylbutane). Intermediate results were obtained for the catalyst based on heteropolyacid compound Pt/$Cs_2HPW_{12}O_{40}$ (20.6% selectivity for 2,3-dimethylbutane). Kinetic studies were also performed for the reaction. It was found that the main factor determining the activity of catalysts in the n-hexane isomerization consists in the presence of strong Lewis acidic centers (LAC) on the surface. Furthermore, it was found that the creation of novel highly efficient catalysts requires LAC concentration on the surface greater than 150 mol/g.

Liu et al.also used $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for the isomerization of n-hexane and n-heptane [82]. The catalyst was promoted by Pt/non-promoted in the presence of hydrogen at atmospheric pressure (temperature 453 and 423 K for n-hexane and n-heptane respectively, feed n-alkane 0.05 atm, H_2 0.20 atm, N_2 balance). The activity and selectivity both were observed to be increased in case of Pt promoted catalyst. It was further observed that the mechanical mixture of Pt/Al_2O_3 and $Cs_{2.5}$ salt resulted in 98.4 and 92.1% selectivities for n-hexane and n-heptane at the conversions of 58.6 and 39.4% respectively. In 2002, Kuang et al.used silica supported $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_5BW_{12}O_{40}$, promoted by Pt for isomerization of n-hexane [83]. The catalyst samples were first reduced at 498 K for 4 h in hydrogen with a flow rate of 21.8 ml/min under atmospheric pressure and then their catalytic properties were evaluated under same conditions, but hydrogen passed through a saturator containing n-hexane. The WWH (wt. of n-hexane per wt. of catalyst per hr) was 0.36 h^{-1}. Among the various catalyst systems used, 50 wt% HSiW/SiO_2 promoted by Pt/Al_2O_3 showed the best catalytic performance with a total of 61% conversion.

Similar silica-supported heteropolyacids in a mechanical mixture with reduced Ni-Ce and Pd-Ce oxides were studied by Habautet al. [84]. Silica-supported heterophosphotungstic, heterosilicotungstic and heteroborotungstic acids were prepared by wet incipient method. Ce-Ni and Ce-Pd oxides were prepared separately and before reaction both types of oxides were reduced at 498 and 553 K for 4 h in hydrogen (flow rate 21.8 ml/min) under atmospheric pressure to get Ni-Ce-O and Pd-Ce-O, respectively. Catalytic properties were evaluated after saturating n-hexane with hydrogen (WWH=0.36 h^{-1}) and the products were analyzed by gas chromatography [85]. Isomerization was carried out with heteropolyacid alone also and the results were compared with that used in combination with Ce-Ni/Ce-Pd oxides. It was observed that in the presence of heteropoly acid alone, the conversion increased with the loading of HPA, though it was low, but it was associated with the drawback of its rapid poisoning with time (even after only 22 min). On the other hand, when silica-supported heteropolyacids were used in combination with Ce-Ni/Ce-Pd oxides, no deactivation was observed even after 4 h. It was explained as cerium probably acted as an electronic promoter due to the Ce^{+4}/Ce^{+3} redox system; which improved the rate of reducibility of nickel and palladium ions during the reaction. It was concluded from the reaction that for mechanical mixtures with nickel-based oxide, the optimum amount of NiCe is 30%, which does not correspond exactly to the higher value of dimethylbutane (DMB) obtained; for the mixture with the Pd-based oxide, the best mixture was constituted of 50% $Pd_{0.1}CeO$, which corresponds to the larger DMB percentage. Among various heteropolyacids used, the conversion proceeded in the following order: HPW>HSiW>HBW, which is consistent with the order of their acid strength. On the basis of the studies, it was concluded that mechanical mixtures of mixed Ni/Pd-Ce oxides and silica-supported heteropolyacids have a synergistic effect on n-hexane isomerization. Reduced metal oxides provide metallic species for hydrogenation/dehydrogenation function and the acidic properties come from the silica-supported heteropolyacids. In addition to this,Ni-based system helps in the maintaining the Keggin structure of heteropolyacid and prevents the coke deposition, as a result of which lowering of activity by poisoning can be totally inhibited.

The activation of C-H bond of n-hexane was performed on heteropoly compounds catalysts in order to compare their catalytic performance for linear alkanes. Conversion of n-hexane was observed at 473–623 K using $HPMo_{12}O_{40}$, $FePMo_{12}O_{40}$ and $PMo_{11}FeO_{39}$ as catalysts. Results indicated heteropoly compounds to be serving two purposes, dehydrogenation and oxidation with the observation that the catalytic activity of the solids was very sensitive to the reaction temperature and nature of the co-ordination (Mo^{+6}, Fe^{+3}) or counter (H_3O^+, NH_4^+, Fe^{+3}) ion [86].

Isomerization of n-Heptane

Nickel containing silicotungstic acid has been used for the hydroisomerization of n-heptane. Catalyst was prepared by 4% Ni loading on 30% $H_3SiW_{12}O_{40}$ supported on MCM-41. Reaction was carried out at 573 K after pretreating the catalyst (calcination temperature 673 K, reduction temperature 673 K for 5 h, reducing the hydrogen flow rate 40 mL/min). 18.5 and 74% activity and selectivity was observed for the reaction [87]. Gheribet al.[88, 89] prepared $H_3PW_{12}O_{40}.18H_2O$, $H_4SiW_{12}O_{40}.19H_2O$ and $H_5BW_{12}O_{40}.16H_2O$ by classical method [42, 89] and impregnated them on silica by wet incipient method [90]. Pt-Ce oxides were prepared separately by co-precipitation method [91]. Catalysts before reaction were first reduced at 498 K for 4 h in

hydrogen with a flowing rate of 21.8 ml/h under atmospheric pressure and then their catalytic properties were evaluated under the same conditions but hydrogen was passed through a saturator containing n-heptane. The WWH (wt of n-heptane per wt of catalyst per hr) was 0.40 h^{-1} and the products were analyzed by gas chromatography with a SE-30 non-polar capillary column. As a result, it was observed that both the conversion and the selectivity towards branched products were nearly constant over the entire time range for all the catalysts and stationary conversion and selectivity were obtained after two hours of reaction. Further, selectivity in isomerization increased slowly with the reduction in temperature of reaction, whereas the conversion of n-heptane and the selectivity of all the products of cracking decreased quickly. Among different heteropoly acids used, the conversion of n-heptane and the TON (Turn over Number) was in the order HPW (65.2%)>HSiW (48.12%)>HBW (22.78%) [82], which is in accordance with the classification of their acid strength. However, selectivity in isomerization followed HSiW (97.64%)>HPW (95.21%)>HBW (64.40%), which could be explained on the basis of strong interaction between heteropoly acid and protonated silanol group on the surface.

The bimetal-bearing (CePt or LaPt) 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$ (PW)) catalysts supported on de-aluminated USY zeolite (DUSY) were prepared and tested for the hydroisomerization of n-heptane with a continuous atmospheric fixed-bed reactor[92]. It was observed that Pt-bearing catalysts doped with Ce or La, especially Ce, exhibit much higher catalytic activity and selectivity than the catalysts without dopants at lowered reaction temperatures. At the optimal reaction conditions, i.e., the reaction temperature of 250°C and WHSV of 1.4 h^{-1}, the catalyst with a Pt loading of 0.4%, PW loading of 10% and a molar ratio of Ce to Pt of 15:1 shows a conversion of n-heptane of 70.3% with a high selectivity for isomerization products of 94.1%.Skeletal isomerization of n-heptane in the presence of hydrogen has been studied over silica-supported bifunctional catalysts, Pd-$H_4SiW_{12}O_{40}$/SiO_2 with different loadings of $H_4SiW_{12}O_{40}$[93]. The catalytic performances of these catalysts have been compared with those of typical bifunctional catalysts such as Pd-H-β zeolite, Pt-SO_4^{2-}/ZrO_2, and Pd-WO_3/ZrO_2. The Pd catalysts with low loadings of $H_4SiW_{12}O_{40}$, such as 2 wt.% Pd-10, 15 and 20wt.% $H_4SiW_{12}O_{40}$/SiO_2, were found to exhibit very high selectivity toward branched heptanes comparable to that of Pd-H-β zeolite. Selectivity towards branched heptanes was sensitive to the loading amount of $H_4SiW_{12}O_{40}$; the selectivity increased with a decrease in $H_4SiW_{12}O_{40}$ loading amount. Few cracking products werealso obtained, which were considered to be produced from dibranched heptenes.

II.   Conclusion

Isomerization is the reaction used to enhance the octane number of gasoline and thereby helps in increasing the life of the automobile engines. Although a number of methods are known, researchers are still struggling for a low cost catalytic material in order to replace the previous expensive ones. Heteropoly acid has come out as one of the promising alternatives to meet the requirements and is considered to be a bi-functional catalyst performing dehrdrogenation and isomerization followed by hydrogenation through its special structural features.

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