

Simultaneous Hydroconversion of *n*-Hexane and Benzene over Pt/WO₃–ZrO₂ in the Presence of Sulfur Impurities

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The properties of a commercial Pt/WO₃–ZrO₂ for the simultaneous hydro-isomerization of *n*-hexane and benzene have been assessed at varying values of total system pressure, fixed reaction temperature (300 °C), and molar ratio H₂/HC = 6. A total pressure of 20 atm was satisfactory for performing both the hydrogenation of benzene and the isomerization of C₆ at convenient reaction rates. Greater pressures increased the cracking and formation of light gases. Also, the total conversion was decreased at higher pressures. Benzene conversion proceeded by metal-catalyzed hydrogenation and subsequent acid-catalyzed ring contraction with no occurrence of ring opening. The results show that the presence of a small amount of benzene (3%, vol/vol) is beneficial for the hydro-isomerization of *n*-hexane over Pt/WO₃–ZrO₂. Hydrocracking is largely suppressed, and both the liquid C₅₊ yield and the selectivity to branched isoparaffins are enhanced. Sulfur impurities in the feed decrease the *n*-hexane and benzene conversion by poisoning the metallic function, and their concentration should be lowered to less than 10 ppm to avoid producing an important inhibiting effect.

Introduction

In the last few years, benzene has been targeted as a noxious compound to be removed from gasoline because of its carcinogenic effect to humans and its relatively long life and mutagenic activity in the environment.^{1,2} The removal of benzene or aromatics from gasoline leaves the latter without the main contributor to its antiknocking properties. These properties which are chemical in nature are rather empirically described by the research octane number (RON). A fundamental model on the dependence of RON on the chemical nature of each molecule would be fairly complex³ and is currently unavailable. Some empirical rules do exist and indicate some orders of RON contribution, such as aromatics > naphthenes > isoparaffins > olefins > *n*-paraffins. Benzene removal and aromatics reduction have prompted refiners to replace them by other RON contributors. Alkylate, isomerizate, and MTBE were all first used with this purpose, but MTBE use has been lately abandoned because of environmental concerns on the leakage from storage tanks and the contamination of ground waters.⁴

Branched paraffins for the gasoline pool are mostly produced in isomerization units that convert virgin C₅–C₆ naphtha cuts. The most popular process has been the Penex (UOP) that uses a highly acidic Pt/Al₂O₃–Cl catalyst and operates at low temperatures.⁵ Other catalysts are Pt-loaded acidic zeolites, such as H-mordenite. These catalysts need a higher temperature to operate and provide fewer RON points, but they have an improved thermal stability and are less sensitive to poisons. The

last generation of isomerization catalysts is comprised of oxoanion-promoted zirconia catalysts, SO₄²⁻–ZrO₂ (SZ) and WO₃–ZrO₂ (WZ). These catalysts are highly active at low temperatures and have a higher selectivity to isoparaffins than acid zeolites. Pt/SZ is the most active of the two and is the catalyst of the Par-Isom process (UOP).⁶ Its main disadvantage is that it is permanently deactivated by sulfur loss in the event of a temperature runaway, especially in a reducing atmosphere. Pt/WZ is less active, but it has an improved selectivity to isoparaffins and a lower coking activity. It is thermally robust and is not decomposed.⁷

Despite being undesired in gasolines, benzene is a very valuable commodity, extensively used in petrochemistry. It is mainly produced in the catalytic reformer by dehydrocyclization of *n*-C₆, provided that this compound is not removed from the feed, and it can also be produced by toluene and ethylbenzene dealkylation. Smaller percentages of benzene are also present in the distillate virgin naphtha and naphthas coming from the coker, fluidized catalytic cracking (FCC), and hydrocracking units.⁸

Some new refinery lay-outs have made it possible that meaningful amounts of benzene appear in isomerization streams. For example, to reduce benzene in reforming naphtha, the *n*-C₆ fraction can be diverted from the feed of the reformer to the feed of the isomerization unit.⁹ This scheme reduces benzene by avoiding its production in the catalytic reformer. The relevant components are cyclohexane (CH), methylcyclopentane (MCP), and indigenous benzene (Bz). The new naphtha splitting

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operation must cut deep to remove all of the precursors. Another scheme is that found in HDS/octane recovery units for the treatment of FCC and pyrolysis naphtha.¹⁰ If a conventional HDS unit is used to eliminate sulfur compounds, the octane loss produced by the hydrogenation of the olefins must be recovered by isomerization of the hydrotreated product after the sulfur is stripped away. These new refinery lay-outs generate uncommon feedstocks to the isomerization units with relatively high benzene and aromatics. The subject of the removal or the transformation of benzene in isomerization feedstocks has been revised in some industrial^{11,12} and scientific reports. Arribas et al.¹³ studied the simultaneous conversion of *n*-heptane and benzene on Pt/WZ catalysts, while Shimizu et al.¹⁴ did the same in the case of the Pt/SZ catalysts. More recently, Benitez et al.¹⁵ studied Pt/WZ catalysts in the hydro-isomerization of *n*-C₆ and benzene and reported that, at low pressures, the system is severely thermodynamically constrained. Other reports on the occurrence of a second simultaneous reaction in isomerization reactors have been disclosed by Watanabe et al.,¹⁶ who studied simultaneous HDS of sulfur containing light naphtha over Pt/SZ, and Kustov et al.,¹⁷ who studied the hydrogenation/ring opening of aromatics over Pt/WZ.

In this work, the problem of the hydro-isomerization of *n*-paraffins in the presence of benzene is revisited. *n*-C₆ is used as a model compound. High-pressure, near industrial conditions are used to provide a practical insight for modern refineries. Thermodynamic basic data and kinetic models are used to explain the results. The influence of the presence of sulfur compounds in the feeds up to 10 ppm was also assessed to measure the resistance to sulfur-poisoning compounds found in coker or FCC naphtha feeds.

Experimental Section

Catalyst Preparation. Commercial tungsten zirconia was supplied by MEL Chemicals as hydroxide (WZOH) in the form of a white powder with an average 200 meshes particle size. To be used, the powder was compressed into cylinders with a hydraulic press and then ground and sieved to 35–80 meshes. Then, they were calcined in static air at 700 °C to obtain the oxide form (WZ). Pt/WZ catalysts were prepared by incipient wetness impregnation of WZ with an aqueous solution of chloroplatinic acid (H₂PtCl₆·6H₂O, Aldrich, 99.9%). The volume of impregnation was adjusted to obtain 0.6% Pt on the final catalysts. After impregnation, the catalysts were oven-dried at 110 °C overnight and then they were calcined again in static air 1 h at 500 °C to decompose the platinum precursor. Finally, the calcined catalyst was reduced in hydrogen (60 cm³ min⁻¹ g⁻¹) 1 h at 300 °C and was cooled in hydrogen to room temperature.

Catalyst Characterization. The quantity and strength of acid sites on the catalysts surface were assessed by means of temper-

ature-programmed desorption (TPD) of pyridine. A total of 200 mg of the catalyst was first immersed in a closed vial containing pure pyridine (Merck, 99.9%) for 4 h. Then, the catalysts were taken out from the vial, and excess pyridine was removed by evaporation at room temperature under a fume hood. Each sample was then charged to a quartz micro-reactor, and a constant nitrogen flow (40 cm³ min⁻¹) was established. Weakly adsorbed pyridine was first desorbed in a first stage of stabilization by heating the sample at 110 °C for 2 h. The temperature of the oven was then raised to 600 °C at a heating rate of 10 °C min⁻¹. The reactor outlet was directly connected to a flame ionization detector (SRI on a 110 chassis) to measure the desorption rate of pyridine.

TPD of methylcyclopentane (MCP), benzene (Bz), cyclohexane (CH), *n*-hexane (*n*-C₆), *n*-hexene-1 (*n*-C₆=), and 2,3-dimethylbutane (2,3-DMB) were performed in the same way to determine the relative affinity of all possible adsorbates for the surface of the catalysts. The samples were first stabilized in flowing nitrogen at 50 °C for 2 h before starting the TPD tests.

Reaction Tests. Before starting any test reaction, the catalysts were calcined in air at 500 °C to remove strongly chemisorbed water and then they were reduced in hydrogen at 300 °C for 1 h. All reactions were performed in a steel tubular reactor, 1/4 in. internal diameter. A total of 0.5–1 g of the catalysts were placed on a wool plug in the middle of the reactor. Temperature was measured with a K-type thermocouple in contact with the catalyst bed. Stainless-steel tubing (1/16 in. i.d.) was used for liquid injection, while 1/8 in. i.d. tubing was used for gas and reactor exhaust connections. The total pressure was regulated with a Swagelok backpressure regulator. The hydrogen gas flow rate was regulated with a Cole–Parmer mass flow controller. Liquids were metered with a high-performance liquid chromatography (HPLC) Cole–Parmer pump. Hydro-isomerization of *n*-hexane (*n*-C₆): the reaction was performed under the following conditions: pressure, 5–30 MPa; reaction temperature, 300 °C; catalyst mass, 2 g; molar ratio of H₂/*n*-C₆, 3; flow rate of *n*-C₆, 15 cm³ h⁻¹. Hydro-isomerization of *n*-C₆ in the presence of benzene: a model mixture of *n*-hexane/benzene [93% (vol/vol) of *n*-hexane] was used. The reaction conditions were the same as the previous test. Hydro-isomerization of *n*-C₆ in the presence of CS₂ and Bz: a model mixture of *n*-hexane/benzene [93% (vol/vol) of *n*-hexane] with 10 ppm of carbon disulfide was used. The reaction conditions were the same as those of the hydro-isomerization of *n*-hexane.

Thermodynamic Modeling. A reaction network was made explicit, and thermodynamic constants were calculated from Gibbs free energy of reaction (ΔG_r) data. The data were extracted from the tables of Stull et al.¹⁸ A schematic graph of a simplified reaction network is included in Figure 1. The estimated constants have been written in Table 1.

RON Calculation. RON values of the products mixture were estimated with the method by Nikolaou et al.¹⁹

Results and Discussion

Before discussing the results in detail, a summary of the results of our previous contribution¹⁵ should be recalled. In this contribution, the influence of the reaction temperature at 1 atm total pressure during the simultaneous hydro-isomerization of benzene and *n*-hexane was assessed. As seen in Figure 2, the system is very much constrained by the thermodynamics of benzene hydrogenation and the activation energy for isomerization. If the reaction is carried out at 200 °C, full benzene conversion can be achieved but with negligible conversion of *n*-hexane (not shown). At 250 °C, 90% benzene conversion is achieved but the *n*-hexane conversion is still negligible. At low temperatures also, the acid sites responsible for isomerization

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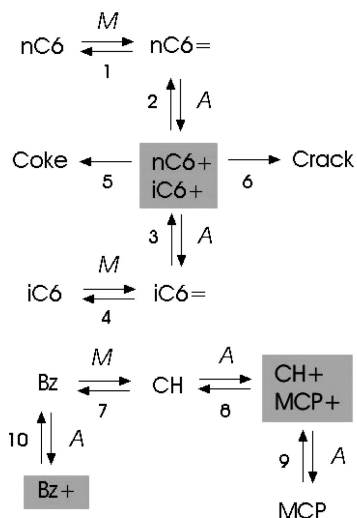


Figure 1. Reaction network based on a classical bifunctional mechanism for the isomerization of paraffins.

of *n*-hexane are more severely poisoned by benzene. If the reaction is carried out at 300 °C, the conversion of *n*-hexane is improved but the conversion of benzene is greatly disfavored. The teachings of such antagonistic behavior are that, at low hydrogen pressure, both reactions are mutually exclusive. A study of the feasibility of carrying out both reactions with good yield at higher pressures was therefore carried out in this work.

Results related to the physicochemical properties of the catalysts have been included in Table 2. The catalyst had a relative low surface area. This is mainly a consequence of the relatively high calcination temperature needed to activate this kind of catalyst and the relatively low sintering resistance of zirconia. Recent studies indicate that temperatures as high as 700–800 °C are crucial for enabling the spreading of WO₃ over zirconia.²⁰ Zirconia begins to massively lose water in an oxolation process simultaneous with crystallization at about 400 °C.²¹ Ionic mobility during the amorphous to crystalline phase change leads to extensive sintering if the surface or the bulk are not promoted with texture-stabilizing anions or cations. WO₃ overlayers delay the crystallization process and act as textural promoters, both increasing the final surface area and stabilizing the tetragonal phase of zirconia. This is considered the most active phase of the oxoanion-promoted zirconia catalysts used in acid-catalyzed reactions.²² The catalyst was completely tetragonal, with no trace of monoclinic phase that could be detected by inspection of the 28° zone, where the characteristic peak appears. The catalyst was mainly mesoporous, with an average Wheeler's radius of 15.5 nm. There should be no possible internal diffusion problems because of the great molecule/(pore size) ratio.

Pt impregnation, calcination, and reduction produced a catalyst with decreased chemisorption capacity at room temperature (H/Pt = 0.095). This is a common feature of all oxoanion-promoted zirconia catalysts and is due to the strong interaction between the Pt particles and the support.²³

The pyridine TPD results are plotted in Figure 3. Sites desorbing pyridine between 110 and 250 °C were considered

weak acid sites. Those desorbing between 250 and 400 °C were considered mild acid sites, and those desorbing at higher temperatures were considered strong acid sites. Similar assignments can be found elsewhere.²⁴ The Pt/WZ catalyst had only a small amount of strong sites, and most sites were of the mild type. These have been routinely quoted to be the most appropriate for isomerization²⁵ because weak acid sites cannot activate C–C bonds to a great extent to perform skeletal branching, while acid sites that are too strong decrease the selectivity of the catalyst by promoting cracking and polymerization reactions. The TPD trace was deconvoluted into three main peaks at 180, 230, and 340 °C. An assignment of surface species to these peaks without the aid of spectroscopical data is not possible. Detailed reports by some authors^{25,26} have indeed thoroughly characterized the sites of WZ, but an assignment of specific structures to sites of different acid strength has not been performed. In the case of sulfated zirconia, sites of increasing acid strength have been assigned to densely grafted sulfate groups (weak), (SZ) sulfates on regular planes (mild), and isolated sulfates on defective sites (strong). An analogy between the two catalysts is however not possible because SZ catalysts of widely varying sulfate density can be active, while WZ catalysts display meaningful activity only after achieving monolayer WO₃ coverage.

TPD data of the adsorbates of interest were included in Figure 4. These were representative of the species taking place in the reaction network. The size and position of the peaks reflect the chemical nature of the adsorbates and their interaction with the catalyst surface. Qualitatively, these can be explained by common acid–base and steric hindrance rules. The traces with the biggest areas were also those with peaks at the highest temperatures. According to the temperature of the last peak in the trace, the order was 2,3-DMB < *n*-C₆ < *n*-hexene-1 < MCP < CH < Bz. This order naturally conforms to the following rules: branched < linear (inverse to steric hindrance), paraffin < olefin < naphthene < aromatic (basicity). The fraction of the initial adsorbate that would only be desorbed at temperatures higher than 300 °C (reaction temperature) (Φ^{300}) was calculated and included in the last rows of Table 2. The only adsorbates being retained on the surface at the reaction temperature and in meaningful amounts are CH and Bz. Benzene has long reported to be a strong adsorbate and poison of the acid sites of oxoanion-promoted catalysts.²⁷ Cycloparaffins are known to be adsorbed as carbocations on hydro-isomerization catalysts and compete for adsorption sites; i.e., they are mild poisons.²⁸

The most important adsorbate in acid-catalyzed reactions is the so-called “carbenium ion”. The carbenium ion theory has proven invaluable in the understanding and modeling of acid-catalyzed reactions taking place in units of FCC, isomerization, alkylation, reforming, etc. However, such a thing as a carbenium ion has only been proven to exist in superacidic media, such as HF–SbF₅.²⁹ *In situ* C nuclear magnetic resonance (NMR) experiments of adsorption of olefins on zeolites have shown that, rather than full ionic separation, alcoxy-like bonds form

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Table 1. Gibbs Free Energy and Equilibrium Constants of the Reactions Involved in the Simultaneous Hydro-isomerization of *n*-Hexane and Benzene, at Three Different Temperatures^a

reaction	reaction ΔG (kJ mol ⁻¹)			reaction K_{eq}		
	200	300	400	200	300	400
<i>n</i> -C ₆ isomerization						
<i>n</i> -C ₆ → 2-MP	-0.77	0.18	1.13	1.22 × 10 ⁰	9.63 × 10 ⁻¹	8.16 × 10 ⁻¹
<i>n</i> -C ₆ → 3-MP	-0.77	0.18	1.13	1.22 × 10 ⁰	9.63 × 10 ⁻¹	8.16 × 10 ⁻¹
<i>n</i> -C ₆ → 2,3-DMB	-1.54	0.36	2.27	1.48 × 10 ⁰	9.27 × 10 ⁻¹	6.67 × 10 ⁻¹
<i>n</i> -C ₆ → 2,2-DMB	9.65	13.53	17.42	8.59 × 10 ⁻²	5.83 × 10 ⁻²	4.43 × 10 ⁻²
olefin isomerization						
<i>n</i> -C ₆ = → <i>i</i> -C ₆ =	49.59	49.39	49.20	3.31 × 10 ⁻⁶	3.12 × 10 ⁻⁵	1.51 × 10 ⁻⁴
olefin hydrogenation						
<i>n</i> -C ₆ = → <i>n</i> -C ₆	-58.19	-45.38	-32.45	2.69 × 10 ⁺⁶	1.38 × 10 ⁺⁴	3.31 × 10 ⁺²
2,2-DMB = → 2,2-DMB	-65.77	-53.15	-40.54	1.85 × 10 ⁺⁷	7.04 × 10 ⁺⁴	1.41 × 10 ⁺³
<i>n</i> -C ₆ hydrogenolysis						
<i>n</i> -C ₆ + H ₂ → CH ₄ + <i>n</i> -C ₅	-34.36	-42.35	-50.43	6.26 × 10 ⁺³	7.29 × 10 ⁺³	8.25 × 10 ⁺³
<i>n</i> -C ₆ = hydrocracking						
<i>n</i> -C ₆ = + H ₂ → C ₂ H ₆ + <i>n</i> -C ₄ =	52.39	46.97	41.42	1.63 × 10 ⁻⁶	5.20 × 10 ⁻⁵	6.08 × 10 ⁻⁴
benzene hydrogenation						
Bz + H ₂ → CH	-40.56	-12.16	16.37	2.69 × 10 ⁺⁶	1.38 × 10 ⁺⁴	3.31 × 10 ⁺²
cyclohexane ring contraction						
CH → MCP	15.33	21.58	27.83	2.02 × 10 ⁻²	1.08 × 10 ⁻²	6.90 × 10 ⁻³
MCP ring opening						
MCP + H ₂ → <i>n</i> -C ₆	22.23	13.8	5.31	3.50 × 10 ⁻³	5.48 × 10 ⁻²	3.87 × 10 ⁻¹

^a *n*-C₆, normal hexane; 2,2-DMB, 2,2-dimethyl-butane; *n*-C₆ =, *n*-hexene-1; MCP, methylcyclopentane; 2,3-DMB, 2,3-dimethyl-butane; CH, cyclohexane; Bz, benzene.

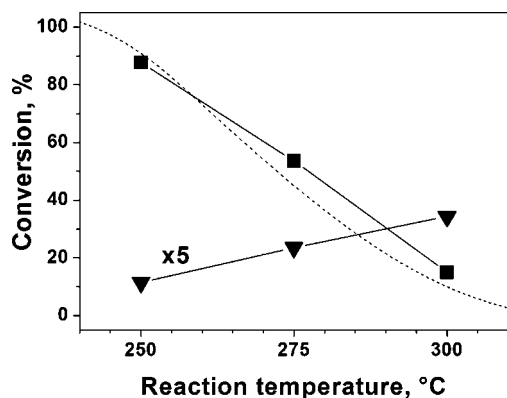


Figure 2. Results of a previous contribution (Benitez et al.⁷). Influence of the reaction temperature on the catalytic activity for the conversion of a benzene/hexane mixture. Time-on-stream, 1 h; *P*, 0.1 MPa; H₂/mixture, 15; WHSV_{mixture} = WHSV_{hexane}, 4 h⁻¹. (---) Equilibrium conversion of Bz into CH at 0.1 MPa. (▼) *n*-Hexane conversion. (■) Benzene conversion.

Table 2. Average Physicochemical Properties of the Pt/WZ Catalyst

property	value
hydrogen chemisorption capacity (H/Pt atomic ratio)	0.095
specific surface area (m ² g ⁻¹)	98
pore volume (cm ³ g ⁻¹)	0.37
micropore–mesopore volume fractions	0.05–0.95
total acidity (μmol g ⁻¹)	28.12
weak acidity (Py 110–250 °C), % (w/w)	41.9
medium acidity (Py 250–400 °C), % (w/w)	55.0
strong acidity (Py > 400 °C), % (w/w)	3.1
Φ ^{300a} (<i>n</i> -C ₆ /2,3-DMB/ <i>n</i> -C ₆ =)	1.09/2.54/0.96
Φ ^{300a} (MCP/CH/Bz)	10.48/20.7/46.2

^a Φ³⁰⁰ = fraction of adsorbed molecules desorbing at temperatures higher than 300 °C (reaction temperature).

between the carbon and the oxygen group of the catalyst surface.³⁰ Computer modeling of adsorbed olefins has further confirmed that the effective charge on the carbon of the adsorbed

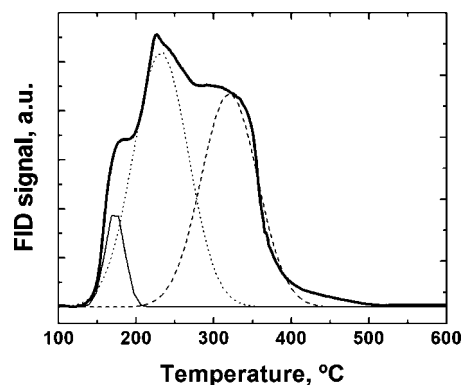


Figure 3. TPD of pyridine adsorbed on Pt/WZ.

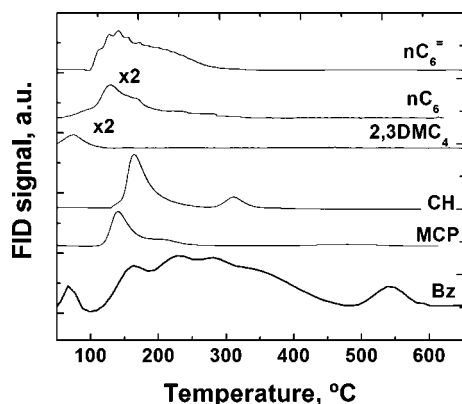


Figure 4. TPD of benzene (Bz), cyclohexane (CH), methylcyclopentane (MCP), *n*-hexane (*n*-C₆), *n*-hexene-1 (*n*-C₆ =), and 2,3-dimethyl-butane (2,3-DMB).

intermediate is much smaller than that of an ion.³¹ Despite this, the predictive power of carbenium ion theory is so good that the model continues to be used with no modifications. Carbenium ions are hypothetically formed by olefin protonation, hydride abstraction from paraffins, or H₂ loss from a carbonium ion (after direct paraffin protonation). Carbenium ions in the adsorbed state can undergo a series of elemental reactions that lead to molecular alkylation, isomerization, cracking, etc.

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To rationalize the upcoming results, a simple model was written based on the carbenium ion theory and the bifunctional mechanism of paraffin isomerization early proposed by Weisz³² (see Figure 1). In this mechanism, olefins are first formed on metal sites (1–2). Then, they migrate to an acid site, where they are branched (2–3). Finally, they are hydrogenated on a metal site to form an isoparaffin (3–4). This mechanism involves a much lower activation energy than the direct isomerization of the paraffin on an acid site. On the acid site, isomerization occurs by adsorption of the olefin and formation of a carbenium ion. This carbenium ion can be isomerized by methyl shift or formation of a protonated cyclopropane intermediate. If it undergoes β scission, a cracking product is formed and a shorter adsorbed species remains (6). If it polymerizes with other olefins, larger cations are formed and, eventually, the site develops a coke deposit (5). Until here, the important adsorbate is only the carbenium ion. Olefins on metals have a fast adsorption/desorption and reaction equilibrium, and they do not pose a kinetic limitation. As seen in previous paragraphs, other important adsorbates because of their high affinity for the catalyst surface are benzene (Bz) and cyclohexane (CH). Their adsorption equilibrium over the acid sites has been written in reactions 8 and 10. Besides acting as a poison of the acid sites, benzene can be adsorbed over a metal site and become hydrogenated to cyclohexane (7). Cyclohexane on an acid site can be isomerized to methylcyclopentane (MCP) (8) and then desorbed (9). Note that all adsorbed species in the mechanism have been noted with a shaded background in Figure 1. Elemental steps in the adsorbed state (methyl shift, hydride transfer, etc.) have not been considered in detail. Parallel reactions of co-adsorption and removal of sulfur species have not been included for the sake of simplicity, although they are present in the case of the reaction tests with the sulfur-doped feedstock.

In this mechanism and reaction network, some simplifying assumptions have been made: (i) Contributions to cracking by direct paraffin protonation were disregarded. (ii) All branched isomers of six carbons atoms were lumped into *i*-C₆= iso-olefins and *i*-C₆ isoparaffins. (iii) No hydrogenolysis with methane formation was supposed to take place. This is based on the inhibited nature of Pt in Pt/WZ that reportedly has negligible hydrogenolytic activity.³³ (iv) Acid sites of only one kind were considered irrespective of their strength. The same for metal sites. (v) No ring opening of MCP was thought to take place. This is thermodynamically favored (see Table 1) but kinetically constrained by the inhibition of the Pt metal function.¹⁵ (vi) Cracking and coke formation are considered essentially irreversible (see Table 2). (v) The contribution of a monomolecular acid mechanism of isomerization was considered to be negligible.

Reactions (7–9) are of utmost importance for many reasons. Benzene must be eliminated because of its noxious environmental effect. However, from the point of view of the product quality, it should be conveniently converted into some other hydrocarbon of high RON because its loss produces a decay of the RON. The values of blending RON of Bz, CH, and MCP are 120, 84, and 96. Also, Bz and CH should be rapidly converted into MCP because of their poisoning effect. Therefore, both from the point of view of the quality of the product and the operation of the reactor, the desired product is MCP and it should be rapidly obtained. Ring-opening and isomerization

could also be desirable,²⁸ but this solution is not likely with oxoanion-promoted zirconia catalysts having an inhibited metal function.

An approximate formula for the rate can be obtained by applying the Hougen–Watson formalism to the reactions 1–4 and not including the side reactions 5 and 6. If reactions 1–4 are considered to be much faster than the surface reaction involving the skeletal branching of the adsorbed carbenium ion, this surface reaction is rate-determining and reactions 1–4 can be considered in equilibrium.

Equation 1 is the expression of the global chemical conversion rate obtained using these assumptions. The equation contains both catalyst properties (k , k^{-1} , C_A , K_1 , K_2 , K_3 , and K_4) and process variables, P_{n-C_6} and P_{i-C_6} , i.e., the partial pressure of the reactant and the product.

$$r = \frac{kK_1K_2C_A \left[P_{n-C_6} - \frac{P_{i-C_6}}{K_{eq}} \right]}{(P_{H_2} + K_1K_2P_{n-C_6} + K_3K_4P_{i-C_6})} \quad (1)$$

K_1 , K_2 , K_3 , and K_4 are the equilibrium constants for adsorption and dehydrogenation of reactions 1–4 in Figure 1, respectively. k and k^{-1} are the direct and inverse reaction constants of the direct and inverse surface reactions of isomerization of the unbranched adsorbed carbenium ion into a branched one, respectively. K_{eq} is the global reaction thermodynamic equilibrium constant. C_A is the total concentration of acid sites involved in the adsorption of olefins.

At the beginning of the reaction, the concentration of isohexanes is negligible and eq 1 can be reduced to eq 2, which corresponds to the initial value (maximum) of the reaction rate. This is the same expression obtained by Vu et al.³⁴ for the isomerization of paraffins on WZ. This equation predicts some trends: (i) for a constant partial pressure of *n*-C₆, the rate decreases with an increasing partial pressure of hydrogen; (ii) for a constant total pressure, the reaction rate decreases with an increasing H₂/HC ratio; (iii) for a constant H₂/HC ratio, the rate does not depend upon the total pressure (eq 3, $\gamma = H_2/HC$ molar ratio).

$$r^0 = \frac{kK_1K_2C_A P_{n-C_6}^0}{(P_{H_2} + K_1K_2P_{n-C_6}^0)} \quad (2)$$

$$r^0 = \frac{kK_1K_2C_A}{(\gamma + K_1K_2)} \quad (3)$$

Both in the work of Vu et al.³⁴ and in this work, conversion data are quite high and, therefore, the expressions of the initial rate are of little value. Inspection of the K values (see Table 1) for the isomerization of *n*-C₆ to each to its skeletal isomers also indicates that these are close to unity because of the small value of the isomerization free-energy change. Therefore, the constant $K_{eq} \approx 3$ –4, and the second term of eq 1 cannot be neglected. At high conversion values, the reactor is also already working in integral mode and, therefore, the integrated form of eq 1 should be used. This is eq 4. In eq 4, $x = x_{n-C_6}$ is the conversion of *n*-hexane and $\beta = 1 + (1/K_{eq})$. This equation has four unknown parameters, (K_1K_2), (K_3K_4), (kC_A), and K_{eq} . If K_{eq} is available, then only three parameters need to be determined. In the other parameter groups, K_2 should be slightly larger than K_3 , according to the principle that branched olefins are more sterically hindered for adsorption. K_1 and K_4 are related to the

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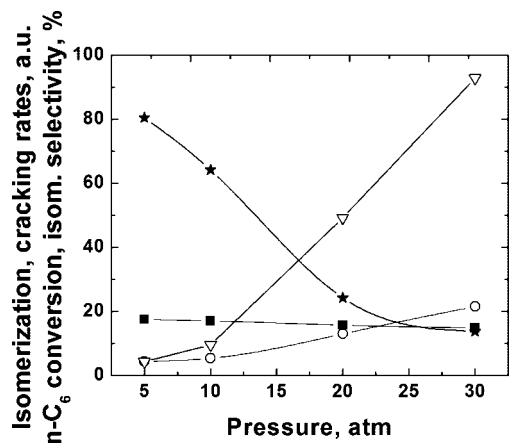


Figure 5. Isomerization rate (■), cracking rate (▽), conversion of *n*-hexane (○) and selectivity to branched isomers (*) as a function of the total pressure. Feed: pure *n*-hexane. $H_2/HC = \text{constant}$.

Gibbs free energy of hydrogenation of branched and linear olefins and, therefore, should be fairly similar (see Table 1). As a rough approximation, we could make $K_1K_2 = K_3K_4$ and $K^{eq} = 4$. Then, W/F would be given by eq 5 in the range of $X = 0-0.8$ (upper limit). This nonlinear equation can be solved to obtain the conversion of *n*-hexane as a function of the residence time W/F ($W = \text{catalyst mass}$ and $F = \text{molar feed flow rate}$) and the H_2/HC feed ratio. We can see again that the bimolecular model with no side reactions predicts that, for any value of W/F , the conversion is only a function of the process variable γ (the H_2/HC ratio).

$$\frac{W}{F} = \frac{\gamma}{kK_1K_2C_A} \left(\frac{-1}{\beta} \right) \ln(1 - \beta x_{n-C_6}) + \frac{1}{kC_A} \left(\frac{-1}{\beta^2} \right) [(\beta - 1) \ln(1 - \beta x_{n-C_6}) - \beta x_{n-C_6}] + \frac{K_3K_4}{kK_1K_2C_A} \left(\frac{-1}{\beta^2} \right) [\ln(1 - \beta x_{n-C_6}) + \beta x_{n-C_6}] \quad (4)$$

$$\frac{W}{F} = \frac{(\gamma/(K_1K_2) + 1)}{kC_A} \left(\frac{-1}{\beta} \right) \ln(1 - \beta x_{n-C_6}) \quad (5)$$

Figure 5 is a plot of the experimental isomerization rate, the cracking rate, the conversion of *n*-hexane, and the selectivity to branched isomers as a function of the total pressure with $H_2/HC = \text{constant}$. The isomerization rate was calculated as the output rate of all branched C_{4-6} isomers. In this way, we plotted a good approximation to the value of the virginal isomerization rate of *n*- C_6 into *i*- C_6 before cracking took place. It can be seen that the isomerization rate is not exactly constant, as predicted by eq 3 or 5 but varies in a fairly narrow range. The isomerization rate varies only 15% when the pressure is increased 6 times. Conversely, the cracking rate was increased 20 times. The cracking rate was calculated from the yield to C_{2-5} products. No C_1 was observed. This last fact was related to the inhibition of the hydrogenolytic activity of Pt by the strong Pt-support interaction. C_2 was negligible, and therefore, only products of primary cracking were found. Although the C_1 yield was null, some C_5 was found among the products. This should come from the cracking of adsorbed oligomers. In any case, the yield of C_5 was lower than 5%.

The pattern of cracking activity with total pressure is nonlinear in general. The dependence of the cracking rate with total pressure at a constant H_2/HC molar ratio had a positive order in hydrogen. The cracking rate was approximately proportional to $P^{1.5}$. Both isomerization and cracking of paraffins on common

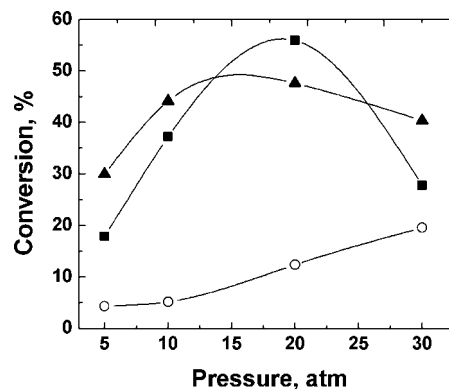


Figure 6. Conversion of *n*-hexane on Pt/WZ as a function of the system pressure. Influence of the presence of impurities in the feed. (○) Pure *n*- C_6 . (■) Feed containing benzene. (▲) Feed containing benzene and CS_2 .

bifunctional catalysts have been largely reported to be first-order in hydrocarbon pressure and (-1) in hydrogen pressure.^{35,36} This is in accordance with a rate governed by the cracking of the adsorbed carbenium ion on an acid site, as in eq 1 for the isomerization rate. A similar equation for monomolecular acid cracking of the adsorbed hydrocarbon would yield a constant rate for the constant H_2/HC ratio. The evident positive order with respect to total pressure at the constant H_2/HC ratio as seen in Figure 5 can have two explanations: (i) The limiting step elemental may not be monomolecular but bimolecular, as is the case with the hydride transfer to adsorbed carbenium ions. (ii) The concentration of acid sites responsible for cracking is not constant but is increased at higher pressures. Both explanations point to the existence of a nonclassical bifunctional mechanism when WO_3-ZrO_2 catalysts are used, as pointed out by Parera and Figoli³⁷ and Hattori and co-workers.³⁸ In this mechanism, hydrogen is first dissociated on the catalyst surface. Then, it is transformed into acidic protons by means of electron abstraction on surface cationic sites. The formation of additional, dynamic, Brönsted acid sites would explain the role of hydrogen in enhancing acid-catalyzed cracking. The formation of surface hydride could explain the positive role of hydrogen pressure in enhancing hydride transfer. The structural reasons for the existence of such a behavior in WO_3-ZrO_2 have been revised by Baertsch et al.³⁹ Polytungstate domains prevalent at intermediate surface densities are both accessible and partially reducible and are able to stabilize Brönsted acid sites via redox processes on WO_3-ZrO_2 . The density of these sites formed from H_2 is, however, small (about 0.02 H/W), and their formation is apparently linked to H_2 dissociation on the ZrO_2 support. Despite their small number, these sites would be more active than normal Brönsted acid sites. On easily reducible polytungstate domains, not only Brönsted acid can be formed but also charge transfer to form carbenium might be easier because of the ability of these structures to transfer and accommodate electronic charge.

Figures 6 and 7 contain additional data of conversion and selectivity with feedstocks of *n*-hexane that were contaminated with benzene and carbon disulfide. In the case of benzene, one clear result is that surface poisoning by benzene produces a

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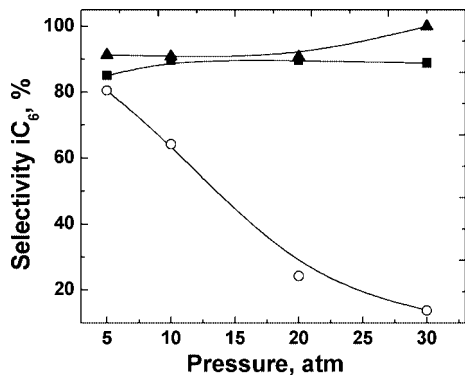


Figure 7. Influence of the presence of impurities on the selectivity to branched hexanes. (O) Feed of pure *n*-C₆. (■) Feed containing benzene. (▲) Feed containing benzene and CS₂.

beneficial effect on both the selectivity and the conversion, greatly increasing the net isomerization rate. At pressures equal to 10 atm or greater, the cracking activity is practically completely suppressed and the selectivity to isomers is almost complete. The conversion shows a “volcano” pattern, indicating that the beneficial effect is counteracted by another phenomenon increasing at higher pressures. At 30 atm, the conversion is almost similar to that of the pure *n*-hexane feed.

The beneficial effect of benzene could be related to the existence of two different kind of sites, one for isomerization and another for cracking. It could be *a priori* supposed that mild acid sites supply the population of active sites for isomerization. Strong acid sites would be responsible for cracking. Poisoning of strong acid sites by benzene would decrease cracking of branched C₆, and therefore, the selectivity to isoparaffins and the liquid yield would be increased. Benzene adsorption is supposed to be reflected in the isomerization rate expression as an additional term in the sum of the denominator of eq 1:

$$r^0 = \frac{kK_1K_2C_A P_{n-C_6}^0}{(P_{H_2} + K_{Bz}P_{Bz}^0 + K_1K_2P_{n-C_6}^0)} \quad (6)$$

For a constant feed composition, the fraction of available acid sites should be constant and independent of the total pressure. In the results of Figure 7, the selectivity to isoparaffins is about 90% and remains constant practically at all pressure values. This indicates that the cracking rate was greatly suppressed in the entire pressure range. This equation predicts that for constant H₂/HC and Bz/*n*-C₆ the conversion because of isomerization alone should be constant. Again, one possible explanation for the conversion increase is the additional creation of acid sites at higher pressures, leading to a bigger C_A term. If the additional sites have an increased turnover with respect to normal Brønsted sites, only a minor increase in their concentration would be sufficient for an important increase in activity.

It is also possible that coking plays an important role in shaping the activity pattern. When coking phenomena are invoked, the rise in *n*-C₆ conversion can be attributed to the increase of the concentration of free acid sites not covered by coke. Higher pressures would promote the hydrogenation of coke precursors. Cracking is usually accompanied by coking because strong acid sites capable of cracking are also active in oligomerization. The high acid strength augments the residence time of the adsorbed olefinic species, and then also, the possibility of reacting with another olefin to form oligomeric species is increased. After a critical size is reached, the oligomeric species can no longer leave the acid site and coke

is formed unless the species is hydrogenated. The coking rate always negatively depends upon the hydrogen partial pressure. Progressively higher values of P_{H₂} should decrease the effective coking rate and increase the fraction of acid sites available for reaction. This effect would be maximal for a pressure of 20 atm.

With respect to the decline in the conversion at pressures higher than 20 atm, this cannot be attributed to an increase in coking because no simple mechanism can be invoked to explain it. The conversion decline also affects the isomerization and cracking rates simultaneously as reflected by the constant values of selectivity to branched isomers. Then, the only suitable explanation seems to be the competitive adsorption of hydrogen. In the case of sulfated zirconia, the chemisorption of hydrogen over acid sites needed for isomerization has been pointed out in the past by Garin et al.,⁴⁰ who found volcano activity plots during the isomerization of *n*-butane over Pt-free sulfated zirconia at variable hydrogen partial pressures.

Vu et al.³⁴ have explained the inhibiting effect of high hydrogen partial pressures resorting to eq 2. They argued that high pressures shift the equilibrium of olefin formation to the left and decrease the concentration of adsorbed carbenium ions. This is not possible in our case because the same eq 2 cannot explain the appearance of a volcano pattern when the H₂/HC is constant and the total pressure is varied.

It is clear at this point that a simple and classical bifunctional model as depicted by the reaction network 1–4 cannot adequately describe the behavior of the system. At a minimum, reactions of cracking, coking, competitive chemisorption of hydrogen and benzene, and dynamic formation of Brønsted acid sites must be taken into account to correctly predict the response of the system upon the modification of some process variables.

In any case and only analyzing the empirical evidence, one clear conclusion from the analysis of Figures 6 and 7 is that a small amount of benzene in the feed is beneficial for the selectivity to branched isomers. An optimum level of conversion and iso-C₆ yield is obtained at 20 atm total pressure.

With respect to the results of the reaction with feeds doped with benzene and CS₂, the volcano pattern was again obtained in the *n*-C₆ conversion curve. The height was lower than in the previous case. In this case, the decreased activity would be due to a decreased activity of the metal sites for performing the de/hydrogenation reactions related to the olefinic intermediates. The effect at 10 ppm sulfur poisoning is however not very drastic. This might be due to the facts that the olefin equilibrium concentration is dictated by thermodynamics only and the de/hydrogenations are very fast reactions in comparison to the acid-catalyzed ones. If only a few sites are needed to achieve the olefin/paraffin equilibrium ratio, a more convincing explanation for the flattening of the conversion curve is that sulfur poisoning decreases the ability of metal sites to activate hydrogen and eliminate adsorbed coke precursors. Sulfur-poisoned catalyst would have a lower concentration of available acid sites and hence a lower activity for all acid-catalyzed reactions.

Our attention should now be turned to the conversion of benzene. The relevant results are plotted in Figures 8 and 9. In comparison to our previous results of Figure 2, it can be readily seen that, at pressures equal or higher than 5 atm, the system is no longer constrained by the thermodynamics of benzene hydrogenation. In Figure 8, the curve of selectivity to MCP has an identical shape to that of conversion of *n*-hexane, with a maximum of 70% at 20 atm. This is not surprising, because

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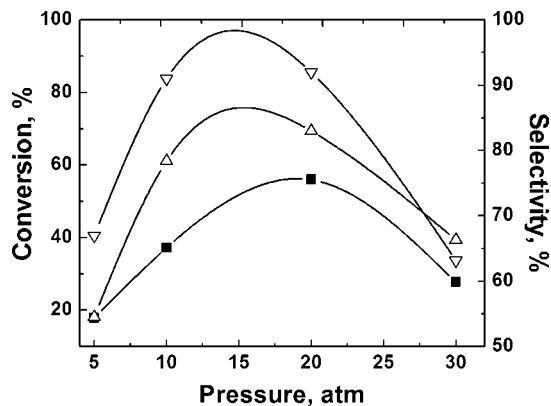


Figure 8. Conversion of *n*-hexane and benzene as a function of the pressure during the simultaneous hydro-isomerization of a benzene-containing feed. (■) *n*-C₆ conversion. (Δ) Bz conversion. (∇) MCP selectivity.

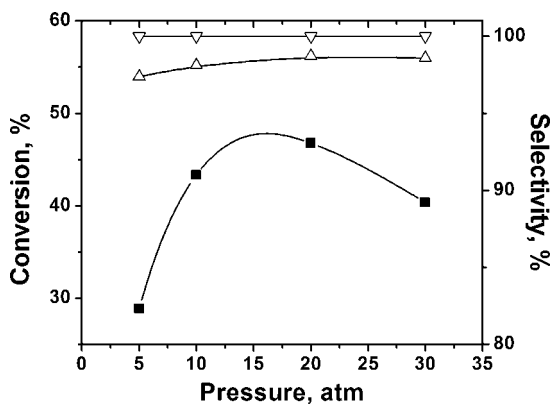


Figure 9. Conversion of *n*-hexane and benzene as a function of the pressure during the simultaneous hydro-isomerization of a feed containing both benzene and CS₂. (■) *n*-C₆ conversion. (Δ) Bz conversion. (∇) MCP selectivity.

both *n*-hexane isomerization and cyclohexane ring contraction depend upon the activity of the acid function. The selectivity of the conversion of Bz to MCP is far from the equilibrium value, indicating that the ring contraction is kinetically limited. At equilibrium conditions, the molar ratio MCP/CH should be equal to 5. Benitez et al.¹⁵ reported a higher MCP yield at the same reaction temperature when using the same catalyst, but they used different space velocity and hydrogen pressure. The kinetic limitation for ring contraction is much smaller than that for *n*-hexane isomerization. The results of Figure 9 indicate that sulfur poisoning at 10 ppm has a small inhibiting effect on the conversion of *n*-hexane, with about a 10% decrease in conversion at 20 atm. In the case of benzene, the maximum conversion value at 20 atm decreased from 70 to 55%. The selectivity to MCP is improved in the entire pressure range probably because of the lower activity in the competing reaction of isomerization of *n*-hexane.

With respect to the antiknocking quality of the product stream and the liquid yield obtained with this catalyst, both the RON and the C₅₊ liquid yield have been plotted in Figure 10 for the

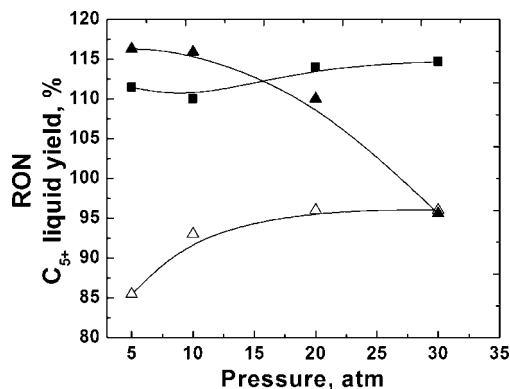


Figure 10. Processing of benzene-containing feedstock: (Δ) C₅₊ liquid yield and (■) product RON. Processing of benzene- and CS₂-containing feedstock: (▲) product RON.

case of the benzene-doped feed. The RON of the product is fairly insensitive to the process total pressure, while the liquid yield reaches a plateau at pressures higher than or equal to 20 atm. Therefore, the most convenient point of operation seems to be 20 atm. At this pressure and in the presence of CS₂ in the feed, the liquid yield is almost the same. At higher pressures, the RON of the isomerizate decreases sharply and, therefore, the process pressure should not be higher than 20 atm.

Conclusions

The simultaneous hydrogenation and isomerization of benzene present in paraffinic streams can be performed in the same isomerization reactor and over catalysts of the Pt/WO₃-ZrO₂ type. At 300 °C and pressures higher than 5 atm, the system is no longer constrained by the thermodynamics of benzene hydrogenation. The best condition of working total pressure was found to be 20 atm. At this value, *n*-hexane conversion reached 60%, with 90% selectivity to branched isomers.

The presence of benzene in small amounts in the feed (<7% in volume) is greatly beneficial for the hydro-isomerization of *n*-hexane because cracking on strong acid sites can be suppressed by competitive adsorption of benzene and its product of hydrogenation, cyclohexane.

The presence of sulfur compounds in the feed decreases both the activity in *n*-hexane isomerization and benzene hydrogenation. At the low level of 10 ppm, the inhibiting effect is not drastic but sufficiently important. Therefore, sulfur in the feed should be removed to smaller concentration values before entering the hydro-isomerization reactor.

In the conditions used in this work, the conversion of benzene contained in paraffinic streams is performed preserving the integrity of the ring (cyclohexane and methylcyclopentane are the only products) and precluding the formation of acyclic isomers of lower average RON.

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