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Hydroisomerization of *n*-hexane on Pt/SO_4^{2-}–ZrO_2: effect of total and hydrogen partial pressure

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The effect of both total pressure and hydrogen partial pressure during the *n*-hexane isomerization on Pt/SO_4^{2-}–ZrO_2 at 200°C and 4 h^{-1} weight hourly space velocity was studied. Total pressure was varied between 1.0 and 10.0 kg cm^{-2}; different hydrogen partial pressures were obtained by dilution with nitrogen keeping the total pressure at 6 kg cm^{-2}. The *n*-hexane isomerization activity increases when increasing either total pressure or hydrogen partial pressure. Methylpentanes are the C_6 isomers formed in major proportion and the 2-methylpentane/3-methylpentane ratio practically reaches the equilibrium value in most of cases. Isomerization is always accompanied by hydrocracking. Hydrogenolysis products were not observed, the main cracking products being propane, isobutane and isopentane; then, the cracking product distribution cannot be interpreted by considering an intramolecular rearrangement of carbocation intermediates. A slight deactivation takes place with time-on-stream. The lifetime of surface intermediates is longer in the absence of hydrogen or at a low hydrogen partial pressure; it allows oligomerization and cracking to prevail at short times and polymerization and coke formation at long times.

Keywords: platinum, sulfated-zirconia, *n*-hexane, isomerization, total pressure, hydrogen partial pressure

1. Introduction

The isomerization of linear alkanes plays an important role as an alternative to improve the octane number in reformulated gasolines. Solid superacids are attracting considerable interest as potential catalysts for this reaction; among them, sulfate-promoted zirconia (SZ) is being widely studied [1,2]. SZ shows a fast deactivation [3] and platinum is added to improve the stability [4]. The isomerization of C_5–C_8 hydrocarbons on Pt/SO_4^{2-}–ZrO_2 (Pt/SZ) with good catalytic performance, has been reported [5]. The studies of *n*-hexane isomerization on Pt/SZ are generally carried out at pressures higher than atmospheric; neither a systematic study nor the selection of this parameter can be found in the literature. Similarly, although there are papers which indicate that hydrogen is necessary for the reaction [6], a complete analysis of the influence of the hydrogen partial pressure is not available. Both parameters influence the hydride transfer on the surface, postulated as the limiting step of the reaction mechanism [7].

It is the objective of this paper to study the effect of the total pressure and the hydrogen partial pressure on the catalytic behavior of Pt/SZ during *n*-hexane isomerization. A reaction scheme is proposed.

2. Experimental

2.1. Catalyst preparation and characterization

Zirconium hydroxide was prepared from an aqueous solution of zirconium oxychloride (Strem Chemicals) by adding dropwise an ammonium hydroxide solution, up to pH 10. The precipitated hydrogel was aged, filtered, thoroughly washed, and dried. The zirconium hydroxide sample was impregnated by the incipient wetness technique using $H_2PtCl_6 \cdot 6H_2O$ aqueous solutions, and then dried. This material was sulfated by dipping in a 0.5 M sulfuric acid solution, filtered and dried. More details about the preparation method have been previously published [8].

Pt/SZ, calcined at 550°C for 3 h, was characterized using techniques previously mentioned [8]. It has 120 m^2 g^{-1} BET specific surface area; 0.14 cm^3 g^{-1} cumulative pore volume; mainly tetragonal phase; 2.34% sulfur; 0.56% platinum; and mainly S^{6+} and Pt^0 as surface species.

2.2. Catalytic test

Catalytic activity and selectivity were measured in a fixed-bed tubular flow reactor, as previously described [8]. The catalyst was calcined at 550°C for 3 h in an air stream, cooled overnight to room temperature in a nitrogen flow and then reduced with hydrogen up to reaction temperature. The reaction was performed feeding

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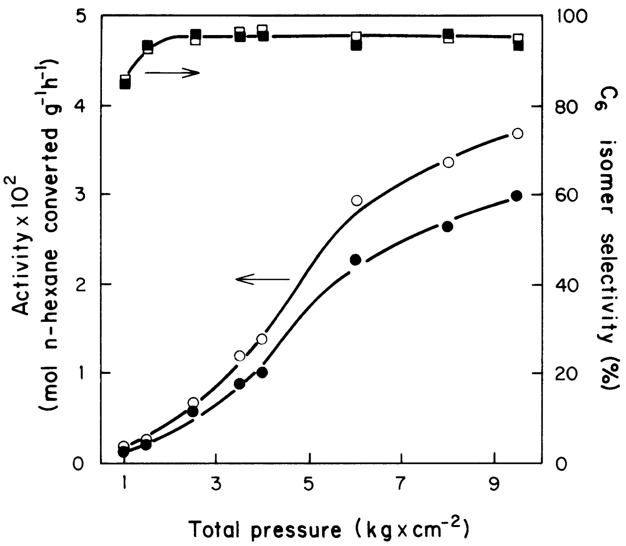


Figure 1. Catalytic activity and selectivity to C_6 isomers as a function of total pressure at 5 min (open symbols) and 300 min (filled symbols) time-on-stream. Activity test at 200°C; WHSV = 4 h^{-1}; hydrogen/*n*-hexane molar ratio = 7.

6 ml h^{-1} *n*-hexane (Merck p.a.) during 360 min at 200°C. Different total pressures with a hydrogen/*n*-hexane molar ratio about 7 or different hydrogen partial pressures at a 6 kg cm^{-2} constant total pressure, were used. The different hydrogen partial pressures were obtained by dilution with nitrogen. *n*-hexane and reaction products were analyzed by on-line gas chromatography using a 30 m long, 0.32 mm o.d. Heliflex bonded FSOT RSL-150 (Alltech) column, operated isothermally at 30°C.

3. Results

The effect of total pressure over the catalytic activity (expressed as moles of *n*-hexane converted h^{-1} g^{-1}) and the selectivity to isomerization products, at a constant hydrogen : *n*-hexane molar ratio, is shown in figure 1. The higher the total pressure, the higher the catalytic activity. A decrease in activity as a function of time-on-stream is observed; this decrease (in percentage) is lower when pressure increases. The selectivity to C_6 isomers is practically constant at pressure higher than 2.5 kg cm^{-2}; it does not change with time-on-stream.

Table 1 presents the product distribution (as weight%) for different pressures; the corresponding *n*-hexane conversions are also mentioned. C_1 and C_2 are not detected, the C_3–C_5 fraction mainly consists of propane, isobutane (the largest) and isopentane, and the C_4 and C_5 linear fraction is very small. The C_5/C_3 ratio is above one in all cases. The C_6 isomers produced in higher amounts are 2-methylpentane (2-MP) and 3-methylpentane (3-MP). Dimethylbutanes show a different behavior; 2,3-dimethylbutane (2,3-DMB) has a smooth maximum between 2.5 and 4.0 kg cm^{-2}. 2,2-dimethylbutane (2,2-DMB) is the C_6 isomer present in the smallest amount; it increases continuously with pressure, reaching a proportion similar to 2,3-DMB at 9.5 kg cm^{-2}. The C_6 isomers do not significantly change with time-on-stream. An important proportion of methylcyclopentane (MCP) appears at atmospheric pressure and it increases with time-on-stream, but a fast decrease is observed when increasing pressure. Cyclohexane (CH), although being in low concentrations, presents a behavior similar to MCP. Heavier hydrocarbons are practically not found. Table 1 also shows the ratios between

Table 1
n-hexane conversion, product distribution, and C_6 isomer ratios at different total pressures [a]

	Total pressure (kg cm^{-2})							
	1.0	1.5	2.5	3.5	4.0	6.0	8.0	9.5
n-hexane conversion (%)	2.9	4.3	13.5	19.1	19.3	50.8	55.2	63.4
product distribution (wt%)								
C_3	0.5	0.5	0.7	0.7	0.6	1.4	1.1	1.3
C_4	1.1	1.2	1.3	1.8	1.9	3.0	2.9	3.1
C_5	0.8	0.7	0.8	1.2	1.2	1.9	1.8	2.0
2-MP	44.8	49.8	50.9	50.6	50.6	47.4	47.0	45.9
3-MP	26.8	28.8	29.2	29.0	29.2	28.5	28.3	27.0
2,3-DMB	12.0	12.2	12.8	12.6	12.6	11.3	10.9	10.4
2,2-DMB	1.5	1.9	3.0	3.4	3.1	6.2	7.9	10.2
MCP	11.0	3.6	0.7	0.4	0.5	0.2	0.1	< 0.1
CH	1.5	0.7	0.6	0.3	0.3	< 0.1	< 0.1	$\ll 0.1$
C_6 isomer ratios								
2-MP / 3-MP	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
MP / 2,3-DMB	6.0	6.4	6.3	6.3	6.3	6.7	6.9	7.0
2,2-DMB / 2,3-DMB	0.1	0.2	0.2	0.3	0.3	0.6	0.7	1.0

[a] Activity test at 200°C, WHSV = 4 h^{-1}, hydrogen/*n*-hexane molar ratio = 7, time-on-stream = 300 min.

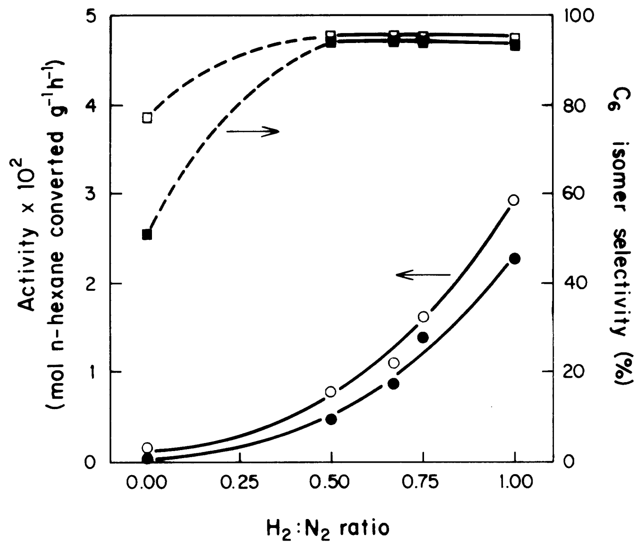


Figure 2. Catalytic activity and selectivity to C_6 isomers as a function of hydrogen partial pressure (expressed as hydrogen : nitrogen ratio) at 5 min (open symbols) and 300 min (filled symbols) time-on-stream. Activity test at 200°C; 6 kg cm^{-2}; WHSV = 4 h^{-1}.

C_6 isomers; the equilibrium value of 2-MP/3-MP, MP/2,3-DMB and 2,2-DMB/2,3-DMB ratios, at 200°C, are 1.7, 5.0 and 2.8, respectively [9].

Figure 2 shows the effect of the hydrogen partial pressure (expressed as hydrogen/nitrogen molar ratio) on catalytic activity and on selectivity to isomerization products at both constant *n*-hexane flow rate (6 ml h^{-1}) and constant total pressure (6.0 kg cm^{-2}). The activity is very low when only nitrogen is present, but it increases 5.7 times for a 0.50 : 0.50 hydrogen : nitrogen ratio, the increment being even higher for higher hydrogen partial pressures. A decrease in activity with time-on-stream is observed. The selectivity to C_6 isomers does not change, neither with time-on-stream nor when hydrogen is present, reaching the lowest value when hydrogen is absent.

Table 2 presents the product distribution (as weight%) for different hydrogen : nitrogen molar ratios at two times-on-stream and the corresponding *n*-hexane conversions. C_1 and C_2 are not detected; the C_3–C_5 fraction is mainly formed by propane, isobutane and isopentane. Isobutane is the cracking product present in the largest amount. The C_5/C_3 ratio is always above one, increasing with time-on-stream. When only nitrogen is present, the amount of *i*-C_4 and *i*-C_5 increases significantly at short times-on-stream, while there are no cracking products at the longest times-on-stream. Methylpentanes are the C_6 isomers produced in larger amounts. For high hydrogen partial pressures, 2-MP and 3-MP levels are practically constant, independent of the time-on-stream. When only nitrogen is present, the behavior is different: 2-MP and 2,3-DMB decrease, while 3-MP increases with time. 2,2-DMB, an important C_6 isomer because of its high octane number, reaches the largest amount when nitrogen is not present. A small proportion of MCP appears only at long times-on-stream when nitrogen is not present. In the absence of hydrogen or when both hydrogen and nitrogen are present, MCP appears from the beginning of the run, increasing with time. Cyclohexane is produced in a small proportion, and C_{7+} products are not observed. Table 2 also shows the ratios between C_6 isomers.

Table 2
n-hexane conversion, product distribution, and C_6 isomer ratios at different hydrogen partial pressures (expressed as hydrogen/nitrogen ratio) and 15 and 300 min time-on-stream [a]

	H_2 : N_2 (molar)									
	1 : 0		0.75 : 0.25		0.66 : 0.33		0.50 : 0.50		0 : 1	
	15 min	300 min	15 min	300 min	15 min	300 min	15 min	300 min	15 min	300 min
conversion (%)	65.5	50.8	35.1	33.9	21.3	18.7	17.2	10.1	3.0	0.5
product distribution (wt%)										
C_3	1.2	1.4	0.7	0.8	0.9	0.8	1.1	0.6	1.6	0
C_4	2.5	3.0	2.1	2.7	2.6	2.5	2.6	2.8	11.1	0
C_5	1.5	1.9	1.2	1.7	1.9	1.7	1.5	1.5	7.7	0
2-MP	47.5	47.4	49.9	50.3	49.9	50.3	49.2	46.7	41.5	11.1
3-MP	28.7	28.5	29.6	28.8	28.6	28.8	28.7	32.7	24.0	40.0
2,3-DMB	11.6	11.3	11.8	11.0	12.4	12.2	12.9	12.0	10.9	0
2,2-DMB	6.9	6.2	4.2	3.9	3.2	3.0	3.6	2.8	1.0	0
MCP	0	0.2	0.3	0.5	0.3	0.4	0.3	0.5	2.2	48.9
CH	0	< 0.1	0.2	0.3	0.2	0.3	0.1	0.4	0	0
C_6 isomer ratios										
2-MP / 3-MP	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.4	1.7	0.3
MP / 2,3-DMB	6.6	6.7	6.7	7.2	6.3	6.5	6.0	6.6	6.0	–
2,2-DMB / 2,3-DMB	0.6	0.6	0.4	0.4	0.3	0.3	0.3	0.2	0.1	–

[a] Activity test at 200°C; 6 kg cm^{-2}; WHSV = 4 h^{-1}.

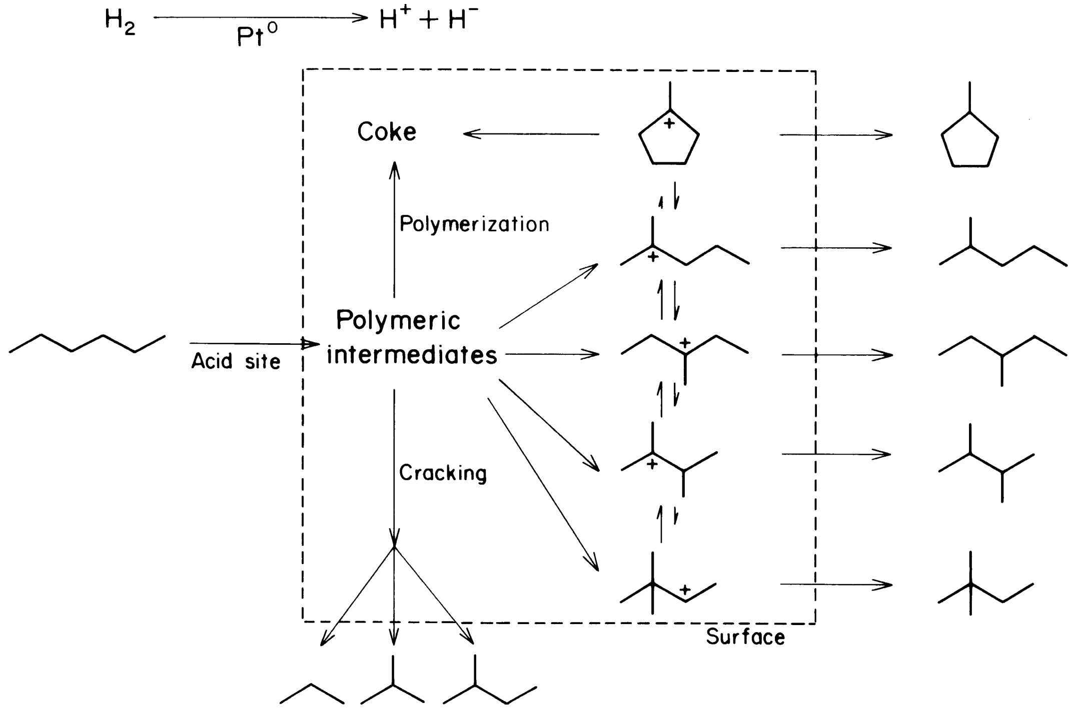
4. Discussion

Our experimental results show that *n*-hexane conversion on Pt/SZ increases by increasing total pressure; a similar qualitative behavior has been previously observed for this system at 5, 10 and 15 bars [5]. *n*-hexane conversion also increases when increasing hydrogen partial pressure. In the absence of hydrogen (nitrogen present) and at short time-on-stream (3 min), a high activity (2.50×10^{-2} moles of *n*-hexane converted g^{-1} h^{-1}) is reached, the selectivity being 60 and 40% to cracking and isomerization, respectively, although a fast deactivation takes place and *n*-hexane conversion decreases to very low levels at 9 min-on-stream [10]. We have observed a decrease in activity with time-on-stream for all the operational conditions used, which can be ascribed to coke deposition [10], although other factors, such as sulfur loss and changes in the sulfur oxidation state have been mentioned as possible factors of catalyst deactivation [11].

It can be considered that hydrogen has a stabilizing effect, removing coke precursors. Nevertheless, our data show a positive order of the hydrogen pressure and a small effect of the hydrocarbon pressure. Consequently, the effect of hydrogen is not only to inhibit catalyst deactivation; it can be assumed that there exists a limiting action of hydrogen on the lifetime of reaction intermediates on the catalyst surface. Differently from the Pt/mordenite system, the classical bifunctional mechanism [12] does not allow one to explain the catalytic behavior of Pt/SZ because of the low reaction temperature (which does not favor the alkane to alkene dehydrogenation) and the positive effect of hydrogen. Platinum would allow the dissociation of hydrogen which spills over the SZ surface, H^+ perhaps related to acid sites and H^- being necessary to desorb products from the surface. Iglesia et al. [7], studying C_5–C_8 *n*-alkane isomerization on Pt/SZ, proposed a reaction mechanism where the rate determining step is the hydride transfer. In order to understand the catalytic behavior and product distribution during *n*-hexane conversion on Pt/SZ, the reaction pathway presented in scheme 1 is proposed.

The cracking products distribution cannot be interpreted considering an intramolecular rearrangement of carbocation intermediates. It can be assumed that cracking products are formed through polymeric intermediates, as previously suggested for H/mordenite [13] and for Pt/SZ [7]. We observed that isomerization is always accompanied by hydrocracking, independently of reaction conditions, allowing us to consider a common intermediate for both processes. The C_5/C_3 ratio higher than one, reaching the largest value in the absence of hydrogen, could indicate that other cracking processes take place under some conditions. Finally, the cracking product distribution does not show hydrogenolytic activity; this behavior can be associated with a platinum which does not show typical metallic properties on the SZ surface [14].

The selectivity to C_6 isomers is very high except either at atmospheric pressure or in the absence of hydrogen. Product distributions indicate that 2-MP and 3-MP are the isomers appearing in major proportion and the 2-



Scheme 1. Proposed *n*-hexane reaction pathway on Pt/SZ.

MP/3-MP ratio reaches practically the equilibrium value in most of the cases. The proportion of 2,3-DMB remains practically constant under different conditions but the equilibrium value is never reached. Considering that tertiary carbocations are favored to desorb from intermediates [13], the distribution of the previous isomers is in accordance with a carbocation chain mechanism: the isomerization between 2-MP and 3-MP is markedly faster than other isomerizations, reaching the equilibrium, while the lower proportion of 2,3-DMB is understood considering that it is generated from a tertiary carbocation with lower stability than the tertiary carbocations that produce methylpentanes, which have a longer main chain [15]. During *n*-hexane isomerization, the 2-MP/3-MP ratio remains near equilibrium with increasing conversion, whereas, when feeding *n*-heptane, the methylhexanes ratio (2-MH/3-MH) decreases with increasing conversion by virtue of the easier cracking propensity of the 2-MH; in this last case, cracking selectivity increases abruptly because oligomerized precursors are no longer required before acid-catalyzed cracking steps [7]. 2,2-DMB is the isomer far away from the equilibrium value; it could be understood by the carbocation chemistry: 2,2-DMB, containing a quaternary carbon, is formed from a secondary carbocation which is less stable than the tertiary ion that generates 2,3-DMB [15]. The relative stability of the carbocations was clearly shown some years ago for *n*-heptane isomerization over Friedel–Crafts catalysts [16] supporting the behavior observed. Surface intermediates should remain long times in order to form the secondary carbocations. Nevertheless, this explanation does not allow to explain the increase in 2,2-DMB by increasing total pressure, which corresponds to a decrease in the lifetime of surface intermediates. The behavior can be understood considering that all *n*-hexane isomers can desorb from polymeric intermediates according to polymerization–cracking processes. The higher the total pressure or the hydrogen partial pressure, the shorter the lifetime of intermediates on the surface; under these conditions the typical equilibria of carbocation chemistry are not reached. By decreasing the hydride transfer availability, which corresponds to an increase in the lifetime of the surface intermediates, those equilibria begin to govern and influence the product distribution. The major limitation in hydride transfer is the absence of hydrogen; accepting that tertiary carbocations corresponding to methylpentanes are favored to desorb and to reach the equilibrium ratio, in the absence of hydride the carbocation corresponding to 2-MP could be cyclized and desorbed as MCP. It is possible that the 2-MP corresponding carbocation is sterically favored for cyclization referred to the carbocation that produces 3-MP. Paál et al. [17] studying the isomerization reaction on Pt/SiO_2, stated that the common surface intermediate of isomerization and cyclization is desorbed as MCP rather than as isomers, under certain conditions. Considering that the hydride transfer is unfavored at low pressure and that it is impossible when no hydrogen is present, in both cases the residence time of the intermediates on the surface will be long, the isomerization products being unfavored meanwhile strongly adsorbed species can either become oligomerized and cracked or polymerized giving coke.

5. Conclusions

n-hexane isomerization activity on Pt/SZ increases with total pressure (at a constant hydrogen : *n*-hexane ratio) and with hydrogen partial pressure (at both constant total pressure and *n*-hexane flow rate). Methylpentanes are the C_6 isomers formed in major proportion. Isomerization is always accompanied by hydrocracking while hydrogenolysis products are not observed. The catalytic behavior could be explained by relating the lifetime of polymeric intermediates on the surface with the hydride availability.

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