Effect of operational conditions during n-hexane isomerization over platinum on tungsten-oxide-promoted zirconia

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The influence of total pressure, temperature and $H_2:N_2$ molar ratio on both catalytic activity and selectivity during n-hexane isomerization over platinum impregnated on tungsten-oxide-promoted zirconia was studied. It was found that the increase in pressure up to 6 kg cm^{-2} increases catalytic activity. The higher the temperature, the larger the catalytic activity. Selectivity to isomers remains practically constant, only decreasing when temperature is increased above 225 °C. In the absence of hydrogen, a rapid deactivation is observed as well as a different product distribution.

Keywords: platinum on tungsten-oxide-promoted zirconia, isomerization, operational conditions, n-hexane

1. Introduction

The isomerization of linear alkanes has taken importance during the last years as a way to improve the octane number in reformulated gasolines in view of the regulations that decrease their aromatic content. The isomerization reaction is favored at low temperatures due to thermodynamic restrictions. Catalysts such as sulfate-promoted zirconia (with or without platinum) [1–3] have been proposed for the reaction. Sulfur leaching during reaction [4], which induces a change from tetragonal to monoclinic phase of zirconia [5], has been observed on these catalysts. Hino and Arata [6,7] proposed some years ago a new catalyst for isomerization of alkanes: tungsten-oxide-promoted zirconia. This material, with the addition of platinum, has proven to be active, selective and stable for the isomerization of n-hexane [8], n-heptane and higher hydrocarbons [9]. Preparation conditions appeared to be very important in order to obtain a good catalytic activity [8,10]. Nevertheless, there is no information available about the optimal operational conditions to achieve the best catalytic activity, selectivity and stability.

The objective of this paper is to study the influence of total pressure, temperature and hydrogen partial pressure on catalytic activity and selectivity of platinum over tungsten-oxide-promoted zirconia during the n-hexane isomerization.

2. Experimental

Zirconium hydroxide was prepared from an aqueous solution containing 11% zirconium oxychloride by adding dropwise an ammonium hydroxide solution up to pH 10, as previously described [11]. An ammonium metatungstate solution of adequate concentration such as to obtain about 15 wt% tungsten over the dried hydroxide, was added by the incipient wetness technique. The sample was placed in a desiccator for 12 h, then in a stove at 110 °C for 12 h and finally calcined at 700 °C in an air stream for 3 h. This material will be called WZ. After calcination, the sample was impregnated by the incipient wetness technique with a hexachloroplatinic acid (Alfa Chemicals, 40 wt% platinum) solution of a concentration such as to obtain a catalyst containing about 0.4 wt% platinum. The material was dried in a stove at 110 °C for 12 h and then calcined at 500 °C for 3 h in an air stream heating at 2 °C min^{-1}. This catalyst will be identified as Pt + WZ.

The platinum and tungsten contents were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES), tungsten at Galbraith Laboratories. Catalyst characterization was made by nitrogen and hydrogen chemisorption, X-ray diffraction and laser Raman spectroscopy, as previously described [8].

The catalytic behavior during the n-hexane isomerization was studied in a flow fixed-bed tubular reactor; 1 g of catalyst sieved to 35–80 mesh was charged for each test. The catalyst was calcined at 500 °C for 3 h in an air stream, cooled overnight to room temperature in a nitrogen flow and then reduced with hydrogen (22 cm^3 min^{-1}, 1 kg cm^{-2}) at 250 °C for 1 h. The reaction was performed feeding n-hexane (Merck p.a.) at WHSV 4 h^{-1} and $H_2:n$-hexane molar ratio 7 during 240 min. Operational conditions used were: temperature from 175 to 250 °C, total pressure between 1 and 11 kg cm^{-2} and different hydrogen partial pressures 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. From these data, catalytic activity and selectivity to the different reaction products (on a carbon basis) were

Table 1
Platinum and tungsten contents and properties of Pt + WZ.

Tungsten (%)	18
Platinum (%)	0.4
Surface area ($m^2\ g^{-1}$)	98.0
ZrO_2 crystalline structure	Tetragonal
S_{WA} (tungsten atoms × nm^{-2})	5.2
Platinum dispersion (%)	24

calculated. n-hexane and its isomers were identified using a Shimadzu QP-2000 mass spectrometer coupled with a Shimadzu 14 APT gas chromatograph.

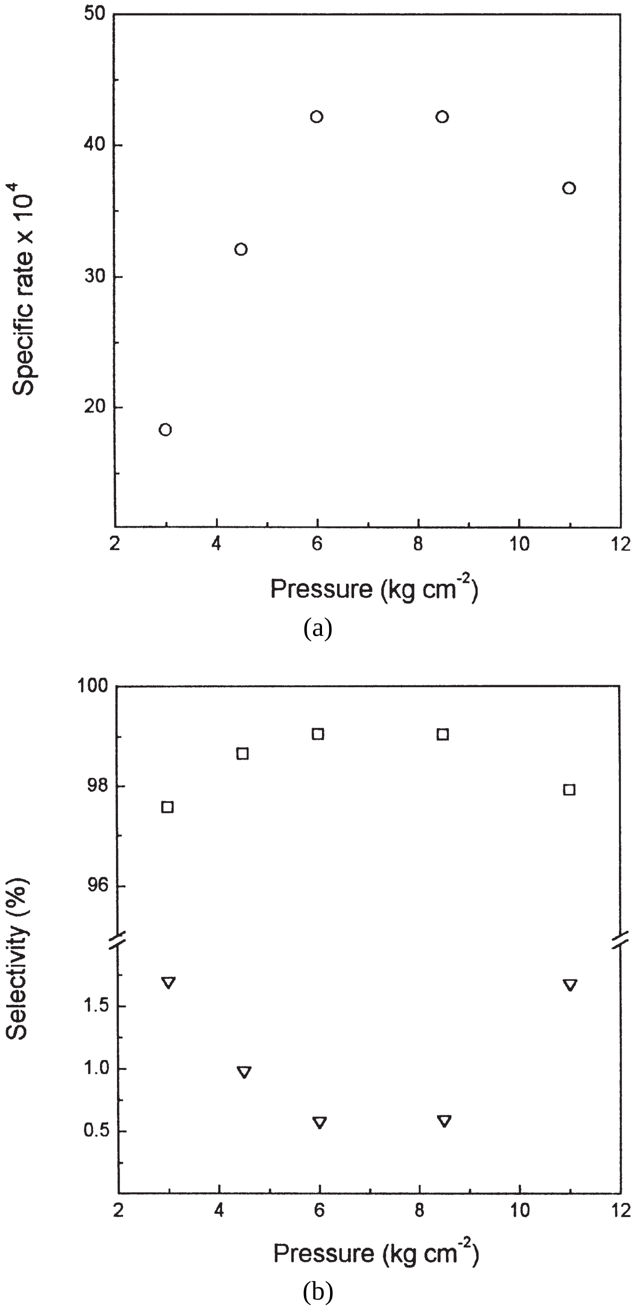
3. Results and discussion

The properties of Pt + WZ are presented in table 1. The high surface area is related to the calcination temperature that was selected because calcining at 700 °C, the maximum activity (expressed as specific rate, moles of n-hexane converted × (tungsten atoms density)$^{-1}$ × (time)$^{-1}$) is achieved [10]. The XRD pattern indicates that the zirconia crystalline structure is tetragonal. The surface density of tungsten atoms, S_{WA}, corresponds to about a tungsten oxide monolayer over zirconia, according to Iglesia et al. [9]. Because of the preparation technique, platinum preserves its metallic properties, it chemisorbs hydrogen indicating a 24% dispersion. For platinum over sulfated zirconia, platinum does not present metallic properties due to the coverage by either a platinum oxide layer [12] or by sulfur species [13]. Laser Raman studies have shown that tungsten species present are WO_3 crystallites as well as an amorphous phase in octahedral coordination [10].

Under the different operational conditions used studying the n-hexane reaction, an induction period of about 30 min was observed. This induction period was previously attributed to a transient in which intermediate oxidation states of WO_3, the active sites, are generated by the simultaneous presence of hydrogen and n-hexane [10]. These intermediate oxidation states may act as redox sites and transform hydrogen atoms (generated on metallic platinum) into acid protons, as proposed by Iglesia et al. [9].

The effect of total pressure on catalytic activity and on selectivity to isomers and to cracking products, at 200 °C and at constant hydrogen : n-hexane molar ratio, is shown in figure 1 (a) and (b). An important increase in specific rate is observed when increasing pressure up to 6 kg cm^{-2}, decreasing slightly at pressures higher than 8.5 kg cm^{-2}. The selectivity to isomers does not change significantly, reaching maximum values between 6 and 8.5 kg cm^{-2}, corresponding to minimum values of the selectivity to cracking products. The data presented correspond to 100 min on stream, the specific rate and both selectivities remaining constant up to the end of the runs.

The higher the temperature, the larger the specific rate. Above 225 °C, the selectivity to isomers decreases with a corresponding increase in the selectivity to cracking products, as presented in figure 2 (a) and (b). Pt + WZ is operated at a lower temperature than platinum-loaded zeolites [14,15] allowing a higher selectivity to dimethylbutanes, the n-hexane isomers having the highest octane number. Moreover, Pt + WZ is more interesting than the oldest chlorided alumina catalysts that present corrosion problems.

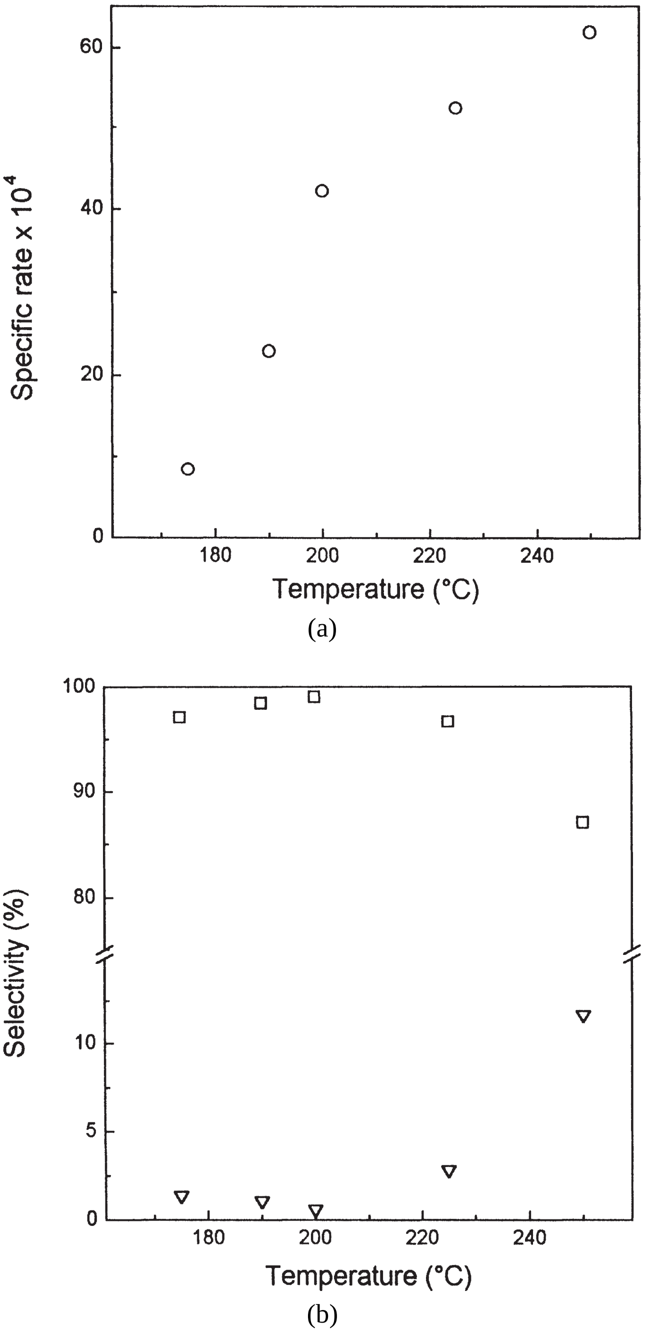


(a)

(b)

Figure 1. (a) Specific rate (moles of n-hexane converted × S_{WA}^{-1} × h^{-1}) as a function of total pressure. (b) Selectivity to isomers (□) and to cracking products (▽) as a function of total pressure. Activity test at 200 °C; WHSV = 4 h^{-1}; $H_2 : n$-hexane (molar) = 7; TOS = 100 min.

It has been previously found that the presence of hydrogen is important not only for catalyst stability, but also for catalytic activity during the n-hexane reaction over platinum-promoted sulfated zirconia [16]. For Pt + WZ we have observed a similar effect: both catalytic activity and selectivity to isomers decrease when hydrogen is di-

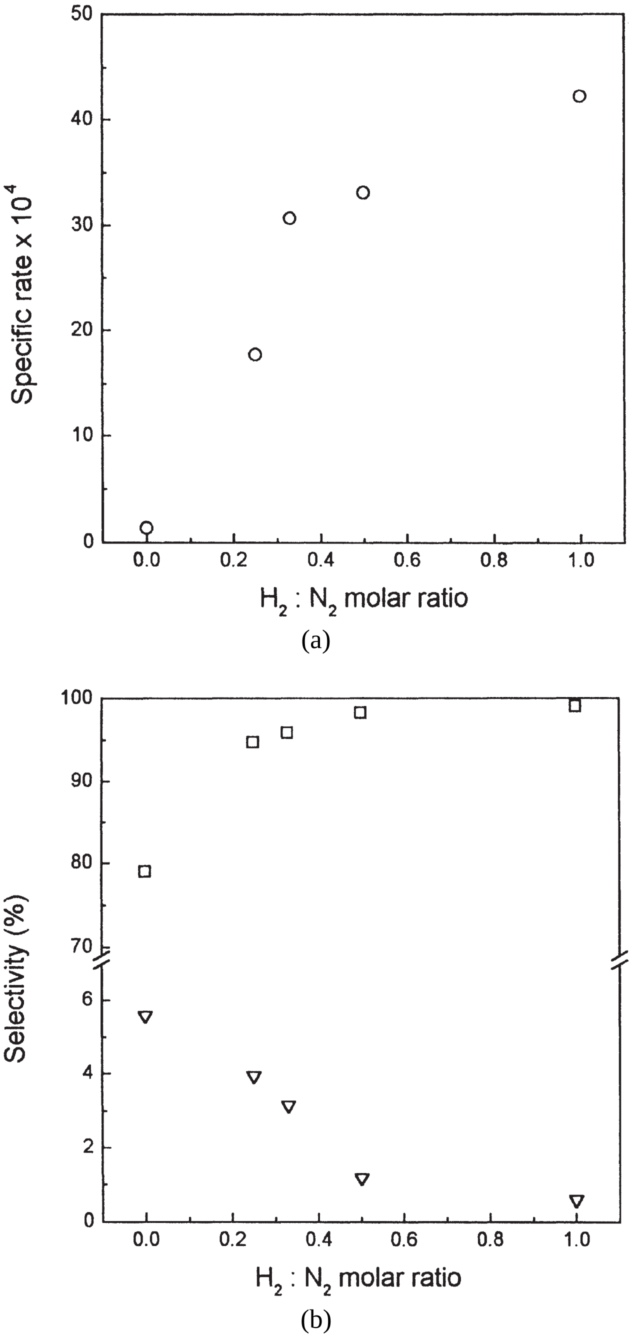


(a)

(b)

Figure 2. (a) Specific rate (moles of n-hexane converted × S_{WA}^{-1} × h^{-1}) as a function of temperature. (b) Selectivity to isomers (□) and to cracking products (▽) as a function of temperature. Activity test at 6 kg cm^{-2}; WHSV = 4 h^{-1}; $H_2 : n$-hexane (molar) = 7; TOS = 100 min.

luted with nitrogen, as presented in figure 3 (a) and (b). The effect is more noticeable when hydrogen is completely replaced by nitrogen. When hydrogen is present, although at a low $H_2 : N_2$ ratio, the activity and selectivity remain practically constant up to the end of the experiments. Nevertheless, in the absence of hydrogen, an important decrease in conversion and a change in the selectivity to isomers are observed, as shown in table 2. This behavior is similar to that found using WZ in the presence of hydrogen, also shown in table 2.



(a)

(b)

Figure 3. (a) Specific rate (moles of n-hexane converted × S_{WA}^{-1} × h^{-1}) as a function of the $H_2 : N_2$ molar ratio. (b) Selectivity to isomers (□) and to cracking products (▽) as a function of the $H_2 : N_2$ molar ratio. Activity test at 200 °C; 6 kg cm^{-2}; WHSV = 4 h^{-1}; H_2 (or $H_2 + N_2$) : n-hexane (molar) = 7; TOS = 100 min.

We have previously proposed [10] in accordance to Iglesia et al. [9] that the reaction scheme for n-hexane isomerization over Pt + WZ in the presence of hydrogen involves the dissociation of hydrogen on platinum followed by its transformation into active sites by interaction with WO_3 species. Both platinum and WO_3 species are related to isomerization activity.

At short time on stream (TOS), the activity of Pt + WZ, run with nitrogen during the n-hexane isomerization can

Table 2

n-hexane conversion (X) and selectivity to isomers (S_i) for Pt + WZ run with nitrogen [Pt + WZ(N_2)] and WZ run in the presence of hydrogen [WZ(H_2)] during the n-hexane reaction at different TOS.

TOS	X (%)		S_i (%)	
(min)	Pt + WZ(N_2)	WZ(H_2)	Pt + WZ(N_2)	WZ(H_2)
15	11.0	12.0	74	87
21	5.0	7.0	83	90
40	2.4	5.5	83	95
110	1.6	3.0	80	95
200	1.3	2.2	80	95

be associated to the fact that reduced platinum sites over Pt + WZ can dissociate and store (during the reduction step) H atoms required for hydrogen transfer and carbocation desorption [9]. Hoang and Lieske [17] observed a hydrogen uptake after hydrogen treatments of ZrO_2 and Pt/ZrO_2. The uptake increases with temperature. Desorption was observed at the uptake temperature when changing the surrounding atmosphere from hydrogen to inert gas. Platinum promotes this process, possibly via a spillover mechanism. The mechanism proposed is the same reported by Dall'Agnol et al. [18], who considered an increase in the concentration of surface OH^- groups due to the surface reaction $Zr–O–Zr + H_2 \rightarrow ZrOH + Zr \cdots H$. For WZ, the isomerization capacity in the presence of hydrogen at short TOS can be also explained by considering that some WO_x species, which are rapidly deactivated, may produce hydrogen dissociation.

Product distribution as well as the n-hexane conversion for different operational conditions, at 100 min on stream are presented in table 3. The main product is 2-methylpentane (2MP) followed by 3-methylpentane (3MP) and 2,3-dimethylbutane (23DMB). 2,2-dimethylbutane (22DMB) is produced in small amounts. Propane, isobutane and pentane (mainly isobutane) are the only cracking products present, as methane and ethane were never detected. This result is indicative that cracking proceeds via the β-scission of bi- or trimolecular intermediates [19,20]. Methylcyclopentane (MCP), cyclohexane (CH) and higher hydrocarbons (C_{7+}) are also produced. Platinum does not show hydrogenolytic activity, although it could be expected for the metal dispersion value. Hydrogenolysis is a demanding reaction requiring an ensemble of several metal atoms as active site [21]. Larger metal ensembles are required for hydrogenolysis than for isomerization [22]. Then, it can be considered that platinum is highly dispersed. Regalbuto et al. [23] reported a decrease in CO chemisorption upon introduction of W over Pt/SiO_2. It was argued that decoration of platinum crystallites by WO_x moieties was causing a partial physical blockage of the adsorption sites. Hoang-Van and Zegaoui [24] also found, using platinum on WO_x (for reduction temperatures in the 200–400 °C range) that tungsten suboxides are formed at the Pt–WO_x interface. These suboxides can migrate onto platinum particles, preferentially near the support surface. For our catalyst the chemisorption capacity and the absence of hydrogenolysis can be associated to a well-dispersed metal which could be partially covered by WO_x moieties considering the tungsten loading.

The product distribution remains constant with TOS and it is similar for the different pressures and temperatures below 225 °C when both platinum and hydrogen are present. Cracking products increase at 250 °C. The larger the conversion, the higher the 22DMB (isomer of high octane number) fraction. For example, with increasing temperature, conversion increases from 9.5 to 69.1% while the

Table 3

n-hexane conversion (X), product distribution and isomer ratios for different operational conditions.[a]

Operational conditions	X	Product distribution (%)										$\frac{2MP}{3MP}$	$\frac{MP}{23DMB}$	$\frac{22DMB}{23DMB}$
	(%)	C_3	C_4	C_5	2MP	3MP	23DMB	22DMB	MCP	CH	C_{7+}			
$T = 200$ °C; $H_2 : nC_6 = 7$														
P (kg cm^{-2}) 3.0	20.7	0.2	1.1	0.4	51.2	31.2	12.7	2.5	0.3	0.2	0.2	1.6	6.5	0.2
4.5	36.9	0.1	0.6	0.2	52.5	31.9	10.8	3.5	0.2	0.1	0.1	1.6	7.9	0.3
6.0	47.7	0.1	0.3	0.2	51.1	31.9	12.2	3.8	0.2	0.1	0.1	1.6	6.8	0.3
8.5	47.6	0.1	0.2	0.2	51.2	31.9	12.2	3.6	0.3	0.1	0.2	1.6	6.8	0.3
11.0	41.6	0.4	0.9	0.4	51.2	30.3	12.2	4.2	0.2	0.1	0.1	1.7	6.7	0.3
$P = 6$ kg cm^{-2}; $H_2 : nC_6 = 7$														
T (°C) 175	9.5	0.1	1.0	0.3	51.3	34.4	10.4	0.9	0.8	0.4	0.4	1.5	8.2	0.1
190	25.9	0.7	0.3	0.1	53.3	31.9	10.9	2.2	0.3	0.2	0.1	1.7	7.8	0.2
200	47.7	0.1	0.3	0.2	51.1	31.9	12.2	3.8	0.2	0.1	0.1	1.6	6.8	0.3
225	59.4	0.7	1.4	0.7	49.3	30.5	12.0	4.9	0.1	0.1	0.3	1.6	6.7	0.4
250	69.1	3.2	5.6	2.8	44.8	27.6	9.1	5.9	0.2	0.2	0.6	1.6	7.9	0.6
$T = 200$ °C; $P = 6$ kg cm^{-2}														
$H_2 : N_2$ (molar) 1	47.7	0.1	0.3	0.2	51.1	31.9	12.2	3.8	0.2	0.1	0.1	1.6	6.8	0.3
0.50	37.3	0.1	0.7	0.4	51.7	31.8	11.6	3.1	0.2	0.1	0.3	1.6	7.2	0.3
0.33	34.7	0.3	1.8	1.1	49.5	30.1	13.0	3.2	0.2	0.1	0.7	1.6	6.0	0.2
0.25	20.1	0.3	2.3	1.2	50.6	29.6	12.4	2.3	0.3	0.2	0.8	1.7	6.5	0.2
0	1.6	0.2	2.6	2.8	32.8	36.7	8.7	0.8	6.9	0.5	8.0	0.9	8.0	0.1

[a] TOS: 100 min.

22DMB fraction increases from 0.9 to 5.9%. According to the thermodynamic equilibrium, the formation of 22DMB is markedly unfavored by increasing temperature [25]. This means that kinetic factors favor the formation of 22DMB when increasing temperature. When hydrogen or platinum are not present (meaning that dissociated hydrogen is not available) the behavior is different, as presented in tables 2 and 3. The fraction of 2MP, 22DMB and 23DMB are lower and those of MCP and C_{7+} are higher and increase with TOS. It can be supposed that the carbocation corresponding to 2MP could be cyclized and desorbed as MCP. It is possible that the 2MP corresponding carbocation is sterically favored for cyclization referred to the carbocation that produces 3MP. Moreover, it has been reported that under certain conditions surface intermediates of isomerization are desorbed as MCP rather than as isomers [26]. In the absence of hydrogen the intermediates also remain longer on the surface producing more polymerized species (C_{7+}).

The product distribution observed under the different operational conditions, in the presence of hydrogen, as well as the 2MP/3MP, MP/23DMB and 22DMB/23DMB ratios (shown in table 3) are similar to those obtained under the same conditions using platinum over sulfate-promoted zirconia (PtSZ) as catalyst [16]. In the presence of hydrogen, the 2MP/3MP ratio practically reaches the equilibrium value (1.7 [25]) while the 22DMB/23DMB ratio is far from the equilibrium (2.8 [25]). Consequently, a reaction scheme similar to the one proposed for PtSZ [16] can be considered. The positive effect of hydrogen can be ascribed to the necessary presence of dissociated hydrogen to allow the carbocations desorption, thus producing a small coke deposition that is always about 0.1%. A negative effect of hydrogen, indicating a classical bifunctional mechanism [27], was previously reported for n-hexane [28] and n-heptane [29] isomerizations on Pt-containing zeolites. In our case, the classical bifunctional mechanism needs further evidence, because of both, the low temperature (that unfavored dehydrogenation reactions) and the induction period observed at the beginning of the run. The positive effect of hydrogen may be associated with the generation of the partially reduced WO_3 species in the presence of hydrogen and n-hexane. These intermediate oxidation states were previously proposed [10] as the active sites for n-hexane isomerization over Pt + WZ.

Taken into account that when the $H_2:N_2$ ratio is only 0.2, the increase in activity is important, we can agree with Iglesia et al. [9] that hydrogen dissociation is not the limiting step in the reaction mechanism. But according to our results, the isomerization may not be the (only) rate-limiting step, as proposed by van Runstraat et al. [30] for n-hexane isomerization on platinum-containing zeolites. They argued that differences in activity might be a combination of diffusion and adsorption effects. For our catalyst, diffusion effects may be neglected because the mean pore diameter of the catalyst is about 100 nm [10].

4. Conclusions

The operational conditions are very important for catalytic activity of Pt + WZ during the n-hexane isomerization in the presence of hydrogen. Activity increases with temperature in the whole range (175–250 °C) studied while when increasing pressure the activity increases only up to 6 $\mathrm{kg\,cm^{-2}}$, showing a slight decrease for pressures higher than 8.5 $\mathrm{kg\,cm^{-2}}$. The selectivity to isomers decreases for temperatures above 225 °C. The presence of both platinum and hydrogen is essential to keep catalytic activity and selectivity. In the absence of one of them, a rapid catalyst deactivation occurs. Hydrogen has a positive effect on catalytic activity and a classical bifunctional mechanism can be neglected.

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