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Structural and catalytic characterization of mechanical mixtures of Pt/WOx–ZrO_2 and Al_2O_3

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ABSTRACT

The effect of the Brønsted/Lewis acid ratio on isomerization of n-heptane using Al_2O_3 as a source of Lewis acidity and WOx/ZrO_2 as a source of Brønsted and Lewis acidity was studied and controlled using mechanical mixtures of these solids. These mixtures were characterized by surface area, infrared spectroscopy of pyridine, X-ray diffraction and Raman spectroscopy. It was found that the presence of W═O stretching mode which was consistent with the presence of oxotungstate species which were the precursors of the acid sites. It was found out that as the oxotungstate structures increased, the selectivity to n-heptane isomers increased while the hydrocracking and dehydrocyclization selectivity decreased. The presence of Brønsted acidity of the WOx/ZrO_2 domains, the increase of Knudsen diffusivity and the loss of Pt metallic area by strong interaction of the Pt with the WOx/ZrO_2 explain this catalytic behavior.

1. Introduction

Due to the great technological interest of the tungstated zirconia much attention has recently been devoted to the role of the Brønsted–Lewis acidity in its connection with the isomerization reactions of hydrocarbons. The investigations on catalysts of Pt supported on these solids containing Brønsted acid sites can be combined with other solids containing Lewis acid sites such as γ-Al_2O_3 in order to increase the catalytic conversion of reactions of normal hydrocarbons [1]. Recently, low quantities of Al to the sulfated zirconia improved the activity and stability for the isomerization of the n-butane [2,3]. Some studies with ZrO_2–SO_4 and Al_2O_3 with high area and selectivity to n-hexane isomerization were carried out [4]. Other studies using Pd and Pt–Pd/WOx–Al_2O_3–ZrO_2 catalysts have shown that Al avoided the formation of monoclinic WO_3 bulk phase [5]. This promoting effect of Al on ZrO_2–SO_4, TiO_2–SO_4 and Fe_2O_3–SO_4 catalysts was also studied [6]. The addition of Al_2O_3 to tungstated zirconia made the zirconia tetragonal phase more stable [7] and converted large hydrocarbon molecules, such as n-cetane fractions which are between n-C_{14} and n-C_{20}, into small useful fractions [8]. Other study was the use of Al_2O_3 with WOx (39%), Ce and Pt producing a high selectivity of n-pentane isomerization [9]. Other study of supported WO_3 catalysts on Al_2O_3, Nb_2O_5, TiO_2 and ZrO_2 [10] showed that reactivity trends reflected the influence of the specific support cation electronegativity on the acid character of the bridging W–O–support bond.

In this study, mechanical mixtures of WOx–ZrO_2 and Al_2O_3 were made to control the Brønsted/Lewis acidity ratio, porosity and area in order to attempt to know their effect on the isomerization selectivity and conversion of n-heptane.

2. Experimental

The catalysts were prepared making a mechanical mixture of a Al_2O_3 sol–gel and a WOx–ZrO_2 catalyst previously made by refluxing method [11] in which the $ZrO(OH)_2 \cdot nH_2O$ was obtained by precipitation using the $ZrOCl_2 \cdot 8H_2O$ (Aldrich) and NH_4OH (pH of 9–10). The $ZrO(OH)_2 \cdot nH_2O$ was stirred in refluxing for 192 h. W (10 wt%) was added to the refluxed slurry by incipient wetness impregnation using an ammonium metatungstated solution for 1 h. The resulting material was dried at 110 °C and calcined at 800 °C for 3 h in static air (sample WZ). The Al_2O_3 sol–gel was obtained from aluminum trisecbutoxide (Aldrich) and ethyl alcohol (at 1/50 molar ratio) which were mixed together under continuous vigorous stirring for 1 h at 60 °C, dried at 110 °C (24 h) and calcined at 500 °C (3 h). Both WOx/ZrO_2 and Al_2O_3 were mixed in several proportions, from 50 wt% of [WOx/ZrO_2] up to 90 wt% (Table 1). Each mechanical mixture was made using the Al_2O_3 sol–gel and WOx–ZrO_2 powders which were sieved using the 200 US Tyler sieve. The mixture was made using an electric mixer (120 rpm) for 1 h and the average particle size was 0.074 mm. Each mixture was impregnated with an aqueous solution of H_2PtCl_2, (0.5 wt% Pt) dried and calcined at 500 °C for 3 h (named WZ + A). A sample of low concentration in Al_2O_3 was made [1] from a mixture of $Al(OH)_3$ (Aldrich) and $ZrO(OH)_2 \cdot nH_2O$ with 2.5 wt% of Al_2O_3 (ZAW) and ammonium metatungstate (10 wt% W). The W and Pt amounts and thermal treatments were similar to those of the WZ sample. A Pt/Al_2O_3 catalyst was prepared with H_2PtCl_6, was dried at 110 °C for 24 h and then calcined at 500 °C for 3 h (sample P).

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Table 1
Metal content, textural properties and Knudsen diffusivity of n-Heptane of the Pt[a]/[WOx/ZrO_2 + Al_2O_3] catalysts.

Catalyst	Nominal content (wt.%)			Surface area (m^2/g)	Pore vol. (cc/g)	Pore diam. (Å)	D_k ($\times 10^3$ cm^2/s)
	ZrO_2	W	Al_2O_3				
WZ	90	10	0	43	0.087	114	2.7
ZAW	86.5	11.2	2.3	39	0.080	103	2.5
P	0	0	99.5	170	0.40	79	1.9
[WOx–ZrO_2] and Al_2O_3 sol–gel							
WZ + A1	45	5	50	153	0.33	85	2.0
WZ + A2	54	6	40	139	0.34	98	2.3
WZ + A3	63	7	30	143	0.36	94	2.3
WZ + A4	72	8	20	118	0.33	112	2.7
WZ + A5	81	9	10	114	0.36	125	3.0

D_k = Knudsen diffusivity.

[a] Pt concentration was 0.5 wt.% in all the samples.

In order to know the surface area, the samples were analyzed by N_2 adsorption in an ASAP-2000 (Micromeritics). The determination of acid sites was made using the infrared spectroscopy of pyridine adsorbed from 25 up to 400 °C. The acidity measurement was made on self-supported wafers (0.02 g) in a glass adsorption cell equipped with KBr windows. This cell was mounted on a Nicolet 560 spectrometer. Each wafer was preheated at 400 °C under vacuum for 30 min to take off the water and other gases adsorbed then the heat was suspended under vacuum and the wafer at room temperature was stabilized for 30 min. A mixture of pyridine and N_2 was introduced into the adsorption cell for 20 min and then vacuum was made in order to take off the pyridine physisorbed. An infrared beam went through the wafer and pyridine adsorbed after each temperature (25 up to 400 °C). The wavenumber range was 1700–1400 cm^{-1} for pyridine adsorption and the number of averaged scans was 50. The sensitivity of this technique was 0.5 μg mol of pyridine per g of catalyst and the procedure to calculate the concentration of Brønsted and Lewis acid sites was described in [12]. The XRD patterns of the WZ + A samples after calcination were obtained in a Phillips X'pert diffractometer using CuKα radiation. Diffraction intensity was measured in the 2θ range between 20 and 70° with a 2θ step of 0.02° with 8 s per point, the samples were analyzed directly at room temperature. The Raman spectra of the WZ + A samples were analyzed using a Thermo Nicolet Raman apparatus (Almega model). Spectral range 10–4000 cm^{-1}, spectral resolution 2 cm^{-1}, sensitivity was less than 0.1 of the monolayer. The analysis was made with a pulsed Nd–YAG laser.

The catalytic evaluations were made in a microactivity plant, in a glass fixed-bed microreactor connected on-line to a gas chromatograph (Varian CP-3380) in a continuous flow at 0.9 atm. n-Heptane (Aldrich), H_2, N_2 and compressed air (Praxair) were used. In all the evaluations, 0.1 g of catalyst was loaded (particle size of US mesh 100–200). The catalyst was activated with a flow of H_2 (1 ml/s), for 2 h at 350 °C; and the reaction was made with a mixture of H_2–n-heptane with a H_2/n-heptane molar ratio of 16 at 25 °C, WHSV was 4.8 h^{-1}. The temperature was increased from 200 up to 350 °C. The reaction products were grouped in accordance with their selectivity for isomerization (Si %), hydrocracking (Sh %), dehydrocyclization (Sc %) and finally the conversion (X %).

3. Results and discussion

The addition of 2.3% of Al_2O_3 to WZ did not produce any increment of the area (Table 1), the values are close to those reported in the literature [1]. This preparation method produced areas of 133 m^2/g close to the average area of 136 m^2/g which was calculated using the area of the WZ sample (43 m^2/g) and the area of the Al_2O_3 sol–gel (230 m^2/g). These values suggested that each material contributed independently with its surface area. The pore diameter increased as the WOx–ZrO_2 increased and therefore the calculated Knudsen diffusivity of the n-heptane in H_2 increased. As the WOx–ZrO_2 increased, the mass transport of the n-heptane by diffusion increased in the pores of the mechanical mixtures and their residence time decreased compared with the catalyst containing only Al_2O_3 (for example the catalyst P). The pore diameter of the sample without Al_2O_3 (sample WZ) was 114 Å and for the catalyst of Pt/Al_2O_3 (sample P) was 79 Å. The Knudsen diffusivity is proportional to the pore diameter [13].

In the case of the acidity studies, the WZ catalyst showed a main band at 1541 cm^{-1} due to Brønsted acidity (Fig. 1) and a band at 1444 cm^{-1} due to Lewis acidity [14] and its Brønsted/Lewis acid sites ratio (B/L) at 200 °C was close to 0.3 (Fig. 2). The addition of

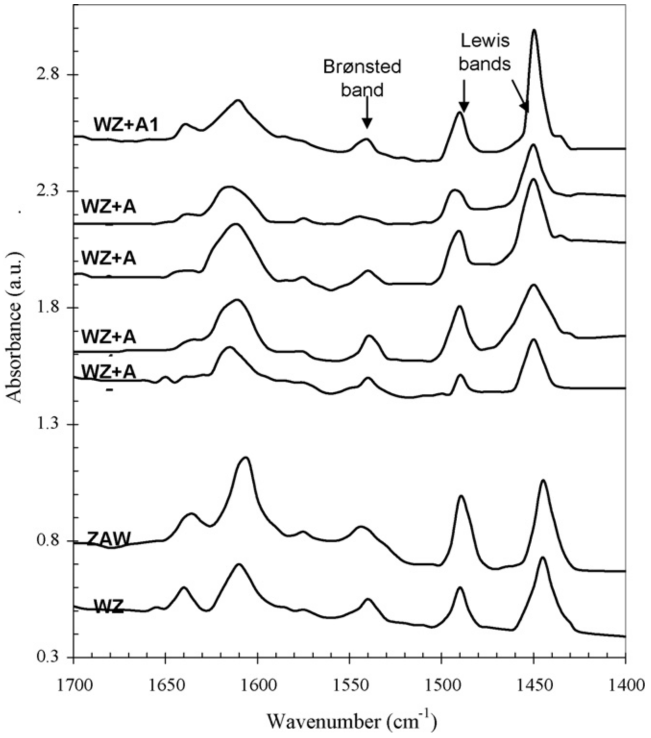

Fig. 1. IR-spectra of pyridine adsorbed on WZ + A catalysts at 200 °C. It was included the sample ZAW.

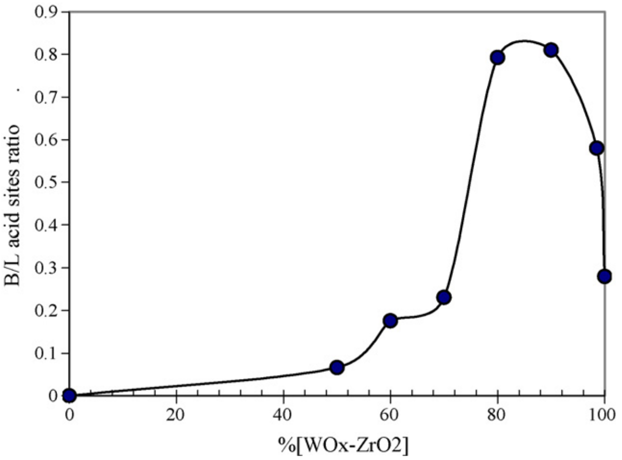

Fig. 2. Brønsted/Lewis acid ratio versus the concentration of [WOx/ZrO_2] at 200 °C.

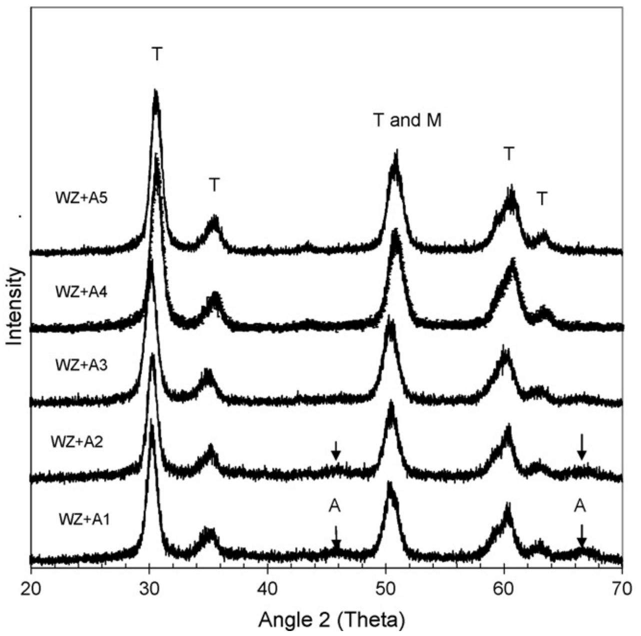

Fig. 3. XRD of WZ + A samples, where T and M are the tetragonal and monoclinic reflections of the WOx–ZrO_2 and A are the reflections of the Al_2O_3 component.

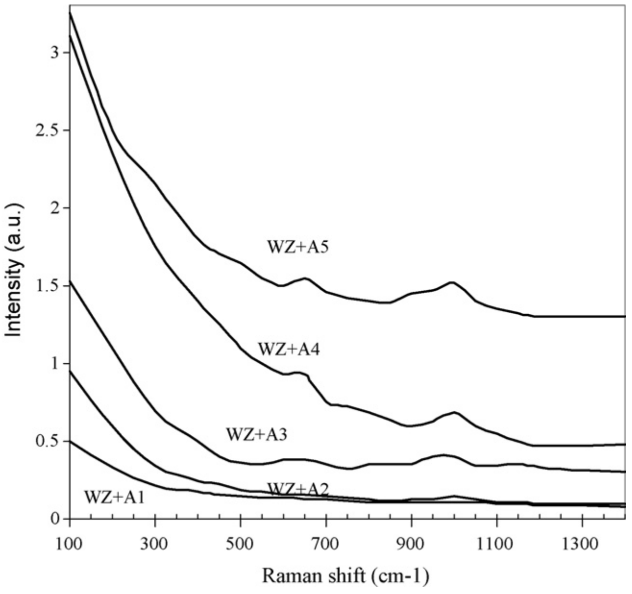

Fig. 4. Raman spectra of the WZ + A samples.

2.5% of Al to WZ catalyst produced the catalyst ZAW. This addition of WOx–ZrO_2 increased the B/L acid sites ratio from 0.3 to 0.58 (Fig. 2). This increase of the acidity produced by the presence of Al has already been observed using a new method with ^1H NMR of titration of acid sites [15]. For the samples prepared by the mechanical mixture a maximum of this B/L ratio was obtained between 80 and 90 wt% WOx–ZrO_2. Also a maximum in acidity at 80 wt% was detected in the case of ZrO_2–SO_4–Al_2O_3 catalysts [4].

The XRD patterns of the WZ + A samples after calcinations are shown in Fig. 3. All the solids presented crystallinity showing the characteristic peaks of tetragonal zirconia phase (T in Fig. 3) i.e. $2\theta = 30, 35, 50.5$ and 60° [16], also the monoclinic phase (M in Fig. 3) was identified. It was observed a progressive evolution of the X-ray reflections with the content of alumina, as illustrated by the gradual appearance of the characteristic peaks (A in Fig. 3) at 46 and 67° (2θ)) for samples WZ + A2 and WZ + A1 (having 40 and 50 wt% Al_2O_3).

The Raman spectra of the WZ + A1 to WZ + A5 samples are shown in Fig. 4. The spectra showed the presence of the tetragonal ZrO_2 phase located at 652 cm^{-1}. The spectra also depicted a main band located at 926 cm^{-1} assigned to W=O stretching mode of tungstate monomeric species in tetrahedral coordination. Other band at about 1010 cm^{-1} corresponds to the W=O stretching mode which was consistent with the presence of oxo-tungstate species. Both intensities of the Raman signals of ZrO_2 and W=O decreased as the concentration of Al_2O_3 increased, these oxo-tungstate species can be reduced by H_2 at several temperatures. We have observed the presence of reduction bands from 600 to more than 1000 °C with Pt/WOx–ZrO_2 catalysts [17]. In that study we identified three reduction steps as the temperature increased producing three superficial species of $WO_{2.9}$, WO_2 and W. Some studies of H_2 reduction of metal oxides have been used in order to analyze the domain sizes [18] and the high temperature required to reduce the oxotungstate species. The metal oxides supported tended to reduce at higher temperatures than bulk crystallites due to a strong metal–oxygen bond with the oxide surface and an absence of metal oxide nearest neighbors to share the reduced charge. WOx species on ZrO_2 were reduced at lower temperatures than WOx on Al_2O_3 at similar W concentrations [19–21] this fact is important because at low WOx surface concentration, the reduction temperature of these species is determined by the strength of the tungsten–oxygen (W–O) bonds that contain oxygen shared with the support. Therefore, the higher reduction temperature of the WOx–Al_2O_3 sample suggests that the W–O–Al bonds are stronger than the W–O–Zr bonds. The WOx polyhedra at high W concentration are connected by W–O–W bonds and the first two reduction steps of these polytungstate domains on ZrO_2 occurred at temperatures similar to those required for the reduction of WOx domains in heteropolyacids such as $H_3PW_{12}O_{40}$ [21]. The presence of Pt on WOx/ZrO_2 affected the reduction of the first reduction step and slight reduction can occur during H_2 pretreatment and during n-heptane reactions at 170 and 350 °C [21]. This property of WOx domains to undergo slight reduction by delocalizing the net negative charge has been proposed by Iglesia et al. [21] and they suggested that reduced state of WOx domains may be linked with the strong acidity appearing on WOx domains on ZrO_2 for which the domain sizes become large enough to delocalize the electron charge over several W atoms. These WOx domains partially reduced could act as redox sites required for the formation of H^+ species from H_2 and alkanes on WOx-based solid acids [20,21].

3.1. Isomerization selectivity (Si)

2-Methyl-hexane (2MH) and 3-methyl-hexane (3MH) were the main isomerization products (Fig. 5). These products have been

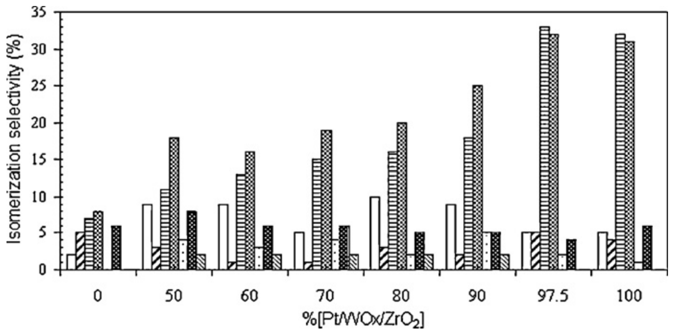

Fig. 5. Isomerization selectivity of n-heptane over the Pt/[WOx–ZrO_2] and sol–gel Al_2O_3 catalysts prepared by reflux method at 350 °C.

obtained in the literature using WOx/ZrO_2 and Al_2O_3 [1]. The production of these monobranched isomers form rapidly and dominate at all practical conversions, whereas multibranched isomers appeared more slowly with conversion. 2,3- and 2,4-dimethyl pentanes were the dominant dibranched isomers at low selectivities. The presence of dibranched isomers has been related to the Pt metal-to-acid ratio [22].

The Al_2O_3 in these mechanical mixtures diluted the isomerization sites located mainly on the WOx/ZrO_2 domains. We observed a negative order in the partial pressure of H_2 (0 to −0.5) as H_2 pressure increased and this kinetic order has been previously reported for Pt/WOx/ZrO_2 catalysts [20–22]. This behavior are related with quasi-equilibrated H_2 transfer steps, which lead to short surface lifetimes, low steady-state carbocation coverages and desorption of these carbocations before β-scission occurs, such as Barton et al. [21] have suggested. Also the Knudsen diffusivity increased when the concentration of WOx/ZrO_2 increased (Table 1) and the residence time of n-heptane and probably the isoolefins in the pores of the rich WOx/ZrO_2 particles could be smaller than in samples with high Al_2O_3 concentration and also low β-scission happened.

Products from cracking and isomerization reactions were obtained such as 2-methyl butane and 2-methyl pentane. The isomerization selectivity was related to the concentration of Brønsted acid sites created by the polytungstate species. Isoheptanes could be produced both mono- and bimolecularly via oligomerization and β-fission of a chemisorbed C_{14}-carbenium ions [20,21].

3.2. Hydrocracking selectivity (Sh)

The effect of concentration of WOx/ZrO_2 in the hydrocracking of n-heptane showed an inverse behavior in relation with the isomerization selectivity (Fig. 6). For example samples with 50 and 60 wt% of WOx/ZrO_2 showed high hydrocracking of $C_1 + C_2$ and C_3 and the sample WZ (free of Al_2O_3) showed very low hydrocracking of these products. In fact it seemed that catalysts with 97.5% (sample ZAW) and 100% (sample WZ) made the scission or cracking in the middle of n-heptane molecule. In general, all isomers increased as the concentration of WOx/ZrO_2 increased (Fig. 5) while all the hydrocracked products increased as the concentration of Al_2O_3 increased (Fig. 6).

The hydrocracking products varied from n-C_1 to n-C_6 and $C_1 + C_2$ and C_3 were obtained mainly in the samples with low WOx/ZrO_2 (Fig. 6). This behavior could be related with the steps of low H_2 transfer, which lead to long surface lifetimes of carbocations in the pores and their β-scission in accordance with Barton et al. [21,22]. Also the Knudsen diffusivity contributed because it decreased when the concentration of WOx/ZrO_2 decreased (Table 1) for example the sample P (free of WOx/ZrO_2) had a $D_k = 1.9 \times 10^{-3}$ cm^2/s while the sample WZ (free of Al_2O_3) had a $D_k = 2.7 \times 10^{-3}$ cm^2/s. Then the residence time of isoolefins in the pores of samples with high Al_2O_3 content was higher than in samples with high WOx/ZrO_2 and therefore the β-scission happened.

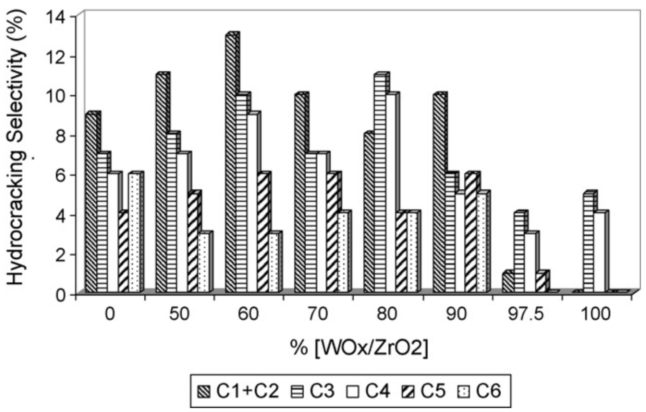

Fig. 6. Hydrocracking selectivity of n-heptane over the Pt/[WOx–ZrO_2] catalysts at 350 °C.

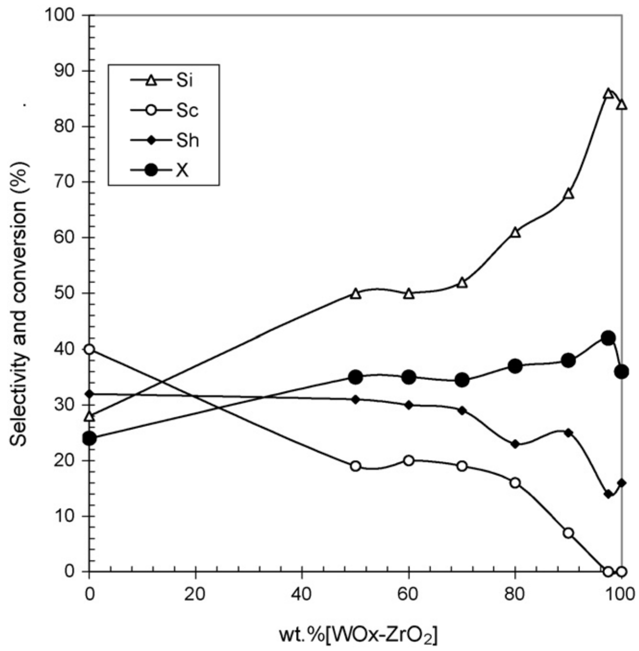

Fig. 7. Conversion and selectivity of n-heptane as a function of the concentration of [WOx/ZrO_2] at 350 °C.

3.3. Dehydrocyclization selectivity (Sc)

Toluene was the main product of the n-heptane dehydrocyclization reaction. Its selectivity decreased as WOx/ZrO_2 increased and samples WZ + A5, ZAW and WZ showed low selectivity (Fig. 7) and the highest value corresponded with the Pt/Al_2O_3 catalyst (sample P) free of WOx/ZrO_2 and the lowest selectivity was for the WZ catalyst. This reaction occurs either on the Pt metal or the acid sites of the Al_2O_3 [23]. The cyclization reaction on Al_2O_3 without Pt occurs via heptenes but the dehydrocyclization rate depends on Pt surface area [24]. The effect of Pt surface area on dehydrocyclization rate of n-heptane has been demonstrated [23,24] and a direct relationship was found. Then the Pt function is very important to produce toluene. In our samples, it seemed that as WOx/ZrO_2 concentration increased the active Pt metal decreased. This loss of metallic properties by strong interaction of the Pt with the WOx/ZrO_2 has been proposed [25,26] or also as a loss in metal surface area [27]. However, it seems, that only a few metal centers were necessary to promote isomerization over WOx/ZrO_2 whereas substantial amounts of small Pt particles favor the formation of light products by hydrogenolysis [28,29].

4. Conclusions

As the [WOx/ZrO_2]/Al_2O_3 ratio increased the selectivity to n-heptane isomers increased and the hydrocracking decreased. Two catalyst properties produced these phenomena; one chemical; the increase of the Brønsted/Lewis acidity ratio and one physical, the increase of Knudsen diffusion due to the increase of the pore diameter. The Raman spectra showed the presence of W=O stretching mode which was consistent with the presence of oxotungstate species which were the precursors of the acid sites. The isomerization selectivity of samples with high WOx/ZrO_2 was related with the steps of H_2 transfer, which led to short surface lifetimes of carbocations and their desorption before β-scission happened. The presence of Brønsted acidity of the WOx/ZrO_2 domains, the increase of Knudsen diffusivity and the loss of Pt metallic area by strong interaction of the Pt with the WOx/ZrO_2 contributed to explain the isomerization, hydrocracking and dehydrocyclization selectivity on n-heptane.

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