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MODIFICATION OF THE PERFORMANCE OF WO_3-ZrO_2 CATALYSTS BY METAL ADDITION IN HYDROCARBON REACTIONS

Gerardo Carlos Torres, Debora Laura Manuale, Viviana Mónica Benítez, Carlos Román Vera y Juan Carlos Yori*
Instituto de Investigaciones en Catálisis y Petroquímica, Facultad de Ingeniería Química, Universidad Nacional del Litoral, Consejo Nacional de Investigaciones Científica y Técnicas, Santiago del Estero 2654, 3000 Santa Fe, Argentina

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A study of the different hydrocarbon reactions over Ni doped WO_3-ZrO_2 catalysts was performed. Ni was found as NiO at low Ni concentration while at high Ni concentrations a small fraction was present as a metal. For both cases, Ni strongly modified total acidity and concentration of strong acid sites. In the cyclohexane dehydrogenation reaction, Ni addition promotes both benzene and methyl cyclopentane production. The hydroconversion activity (n-butane and n-octane) increases with the augment of total acidity produced by Ni. The selectivity to reaction products is modified according to the acid strength distribution changes produced by Ni addition.

Keywords: tungstated zirconia; Ni addition; hydrocarbon reactions.

INTRODUCTION

Most world countries are adopting increasingly stringent laws to protect the environment. Particularly they have adopted regulations limiting the kind and amount of contaminants in motor fuels. Though product specifications vary from country to country the objectives for gasoline and diesel are roughly the same. Both sulfur and aromatics must be reduced. In the case of gasoline the loss of octane points produced by the elimination of aromatics must be compensated by the addition of other octane boosters. In this sense the acid-catalyzed isomerization of short paraffin and the isomerization-cracking of long paraffins have a role of increasing importance among refinery units for fuel production. Isomerization units produce high octane C_5-C_6 cuts while the isocracker can produce gasoline, kerosene and lube oils.[1] C_5–C_6 isomerizate is produced from light straight-run naphtha and is commonly added to gasoline labelled as environmentally friendly or ‘‘ecologic’’.[2-5] Other contributors to the gasoline pool are the reformate from the catalytic reformer and the hydrotreated naphtha from FCC. The high octane number supplied by branched paraffin compensates the octane loss produced by the elimination of environmental noxious aromatic compounds. Mild isomerization of heavier n-paraffin C_7–C_{15} is sometimes used for the production of diesel fuels with high cetane number and improved cold flow properties (viscosity, pour point, freezing point).[1,6,7] Deeper branching of this cut could be used for producing isomerizate of high octane number for the gasoline pool, if the molecular size is adjusted aftwerwards or simultaneously. The unit operation involving the simultaneous molecular branching and size adjustment is called isomerization--cracking. Many reactors containing an acid catalyst can perform this operation but it has been thoroughly demonstrated that the best suited reactor is the hydrocracker.

If a stress is put on environmental issues, catalysts might also be scrutinized. In this sense environmentally friendly isomerization--cracking catalysts, non-corrosive and non-polluting, are to be preferred. From a process point of view, one desirable feature is the operation at low pressures in order to decrease compression, equipment and catalyst regeneration costs. Low hydrogen pressures dictate that the catalysts also have an adequate resistance to coke deposition. Research efforts have been extensively reported in which new formulations are proposed to phase out technologically obsolete, corrosive and environmentaly non-friendly catalysts such as HF, H_2SO_4, Al_2O_3-$AlCl_3$, etc.[8-11]

Since the isoparaffin/n-paraffin ratio is thermodynamically favored at low reaction temperatures one common target of both isomerization and isomerization-cracking operations is to find catalysts with high activity at low temperatures. For this reason considerable efforts have been invested on the understanding of the reaction network that leads to the formation of isomers and cracked products from normal and branched paraffin. In spite of this the complex reaction mechanism is still not completely understood and is still a matter of controversy among scholars.

In previous works we have reported data concerning the isomerization of n-butane and the production of isoparaffins in the C_4-C_6 range by means of isomerization-cracking of n-octane over sulfated zirconia (SZ) and tungstated zirconia (WZ) catalysts promoted with Pt, Pd and Pt-Pd.[12-18] We found that Pt/SZ is the most active catalyst but it deactivates both by coking and by loss of sulfur. Pt/WZ is a more robust catalyst and the results revealed a strong influence of the calcination temperature on the metal/acid balance. The higher the calcination temperature the higher the promoting action of W for generating strong acid sites.

In other papers Ni instead of Pt was used as active metal phase of different acid solids and the catalysts formed were tested in hydrocarbon reactions.[19-21] Ni is cheaper than noble metals like Pt or Pd and its use would be highly justified on a cost basis. The hydroisomerization and/or the hydrocracking of n-hexadecane, Fischer-Tropsch waxes and polyolefins was performed by Wender and coworkers using Pt/SZ and WZ promoted with Ni and Pt.[19,20] The hydroisomerization of n-octane over Ni-WO_3/ASA catalysts was reported by Rezgui *et al.*.[21] They found that the main reaction pathways over the prepared solids were isomerization, cracking and hydrogenolysis.

In a previous paper we studied the convenience of adding Pt or Ni to sulfated-zirconia (SZ) for isomerizing-cracking n-octane to C_4–C_6 branched isoalkanes. We found that Pt enhanced the activity and stability of the catalysts. Ni mainly improved the selectivity to isoparaffins (maximum yield at 1% Ni).[14] In other paper[15] we analyzed the variation of the isomerizate quality due to Ni and Pt addition to WZ catalysts.

This study aims to explore the causes of the change in the performance of WZ catalysts for different hydrocarbon reactions by the incorporation of Ni. The performance of the catalysts was studied using

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*e-mail: jyori@fiq.unl.edu.ar

three different molecules to model the feedstocks: n-butane, cyclohexane and n-octane. Activity, stability and selectivity were correlated to different properties of the prepared catalysts, particularly metal content, total acidity and concentration of acid sites of different strength.

EXPERIMENTAL

Preparation of catalysts

$Zr(OH)_4$ (ZH) was obtained by hydrolysis of zirconium oxychloride ($ZrOCl_2.8H_2O$, Strem Chemicals, 99.998%) in an ammonia solution. The precipitate was washed and dried in a stove at 110 ºC for 24 h. WO_3-ZrO_2 (WZ) was obtained by incipiente wetness impregnation of ZH with a solution of ammonium metatungstate ($(NH_4)_6(H_2W_{12}O_{40}.nH_2O$, Fluka, 99.9%), previously stabilized at pH = 6 for 7 days. The impregnating volume was of 15 cm^3 g^{-1} of ZH with an adequate concentration in order to obtain 15% W in the final catalyst. After the impregnation (24 h at room temperature) the support was dried in a stove at 110 °C overnight. Then it was calcined in air at 800 ºC for 3 h.

A portion of WZ (35-80 meshes) was impregnated to incipient wetness with an aqueous solution of nickel nitrate ($Ni(NO_3)_2.6H_2O$, Merck, >99.0%). The concentration values of the different impregnating solutions were adjusted in order to obtain catalysts with different Ni contents (0.1, 0.5, 1.0 and 5% Ni). Then the catalysts were dried at 120 °C and calcined in air (10 ml/min) for 3 h at 450 °C. The catalysts were named 0.1Ni/WZ, 0.5Ni/WZ, 1.0Ni/WZ and 5.0Ni/WZ.

Catalyst characterization

Ni and W loadings in each catalyst were determined by ICP in an Optima 21200 Perkin Elmer equipment.

In order to identify the different crystalline phases present in the ZrO_2 catalysts XRD measurements were taken in a Shimadzu XD-1 diffractometer using CuKα radiation filtered with Ni. The spectra were recorded in the 2θ = 20-65º range and with a scanning rate of 1.2 º min^{-1}.

The specific surface area of the catalysts was measured by treating the samples for 2 h at 200 ºC and in a vacuum and by taking nitrogen adsorption isotherms at the temperature of liquid nitrogen in a Micromeritics 2100 E equipment.

The reducibility of the samples was analyzed by means of temperature programmed reduction (TPR) in an Ohkura TP2002 equipment having a thermal conductivity detector. The samples were stabilized in argon at 25 ºC and then they were heated up to 800 ºC at a heating rate of 10 ºC min^{-1} in a stream of 4.8% H_2 in Ar.

The measurement of the total acidity and the distribution of acid strength of the catalysts was performed by means of temperature programmed desorption of pyridine (Merck, >98%). It must be recalled that pyridine TPD cannot distinguish between Brönsted and Lewis sites and therefore it can only assess the total acidity and the acid strength of the sites. In each experiment the samples were first immersed in a volume of pyridine for 6 h at room temperature. Then they were filtered and dried at room temperature, placed in a quartz microreactor and stabilized in nitrogen flow for 1 h at 110 °C. Then they were heated from this temperature to 650 ºC at 10 ºC min^{-1}. The desorbed products were continuously sent to a flame ionization detector and the signal was recorded in a computer.

Catalytic tests

Before measuring the catalytic activity, all samples were pretreated *in situ* in the reactors. First they were calcined in air (1 h, 450 °C) and then in hydrogen (1 h, 300 °C). At the pressure, temperature and flow rate conditions chosen for the three reactions, neither internal nor external mass transfer limitations in the catalyst particles were found, as confirmed by the calculation of the Weisz-Prater modulus (Φ< 0.01) and the Damköhler number ($Da \approx 0$). No equilibrium limitations were observed

Isomerization of n-butane: this reaction was carried out in a quartz reactor operated at atmospheric pressure, 350 ºC, WHSV = 1 h^{-1}, molar ratio H_2/n-C_4 = 6 and with a catalyst mass of 0.5 g. The reaction products were analyzed on-line in a gas chromatograph equipped with a flame ionization detector and a 6 m long, 1/8" diameter column, packed with 25% dimethylsulfolane supported over Cromosorb P.

Dehydrogenation of cyclohexane: the reaction was performed in a quartz reactor at 300 ºC, 0.1 MPa total pressure, WHSV = 12.6 h^{-1}, molar ratio H_2/CH = 1.4 and catalyst mass = 0.1 g. The reaction products were analyzed with a chromatograph equipped with a flame ionization detector and a 1/8" diameter column, packed with FFAP supported over Chromosorb P.

Hydroisomerization-cracking of n-octane: this reaction was performed in a steel reactor loaded with 0.25 g of catalyst. Reaction conditions were: 0.1 MPa, 300 ºC, WHSV = 4 h^{-1}, molar ratio H_2/nC_8 = 6. The products were analyzed on-line with a chromatograph with a FID and a 100 m long capillary column coated with a squalane stationary phase.

In all the catalytic tests the catalysts used were previously ground and sieved to 35-80 meshes.

RESULTS AND DISCUSSION

Catalysts characterization

ICP chemical analysis confirmed the theoretical metal amounts of W and Ni in each catalyst within a 5% error margin that was considered negligible.

After being calcined at 800 °C in air WZ had a surface area of 39 m^2 g^{-1}. The addition of Ni did not modify the surface area substantially. Only in the case of the 5% Ni sample the surface area was decreased slightly (36 m^2 g^{-1}).

The phase of the ZrO_2 catalysts was purely tetragonal. No peaks that could be addressed to the monoclinic phase were found at 28.2°. Segregated WO_3 crystals appeared as a separate phase in the patterns. The stabilization of the tetragonal structure of zirconia by calcination of ZH impregnated with tungsten oxo-species was consistent with the reports of Hino and Arata.[22] The details of the mechanism of stabilization are still controversial.

Figure 1 shows the TPR traces of the catalysts. Comparing the TPR results of the Ni-loaded samples with the corresponding to WZ, we can conclude that when Ni is deposited over WZ a different reduction pattern can be expected depending on whether the catalysts have a low Ni content (between 0.1-0.5%) or a high Ni content (between 1-5%). At low Ni contents the consumption of hydrogen begins smoothly at 300 °C. At this temperature the reduction of surface W species also begins and therefore it is difficult to detect if Ni species are also being reduced.[23] At high Ni contents a reduction peak can be seen at 250-400 °C. The consumption of H_2 is higher as the Ni content increases. Several reports define different temperature ranges for Ni reduction that depend basically on the content and nature of Ni:[24-26] "bulk" NiO with a low interaction with the support is reduced in the 250-320 °C range, NiO highly dispersed with a strong interaction with the support is reduced at high temperatures, 400-700 °C. The found TPR pattern would therefore correspond to Ni present as a segregated phase, with little interaction with the support. In the samples with low Ni content no reduction peaks can be seen in the zone where the reduction of bulk NiO occurs and therefore in this case Ni species are highly dispersed and interacting strongly with the support.

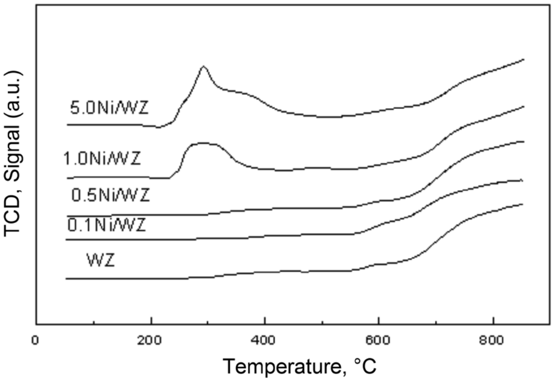

Figure 1. *TPR traces of the metal promoted WZ catalyst*

As a conclusion it can be said that at the conditions of the tests Ni is found as NiO at low Ni content, while at high Ni contents one part of the Ni is present as a metal.

Figure 2 contains the results of total acidity and acid strength distribution of the samples. WZ has a high concentration of weak and moderate acid strength sites. The addition of Ni (0.1% Ni) produces initially a decrease of the total acidity of WZ and an increase of the concentration of strong acid sites (sites retaining pyridine in the 500-600 °C range). For Ni contents up to 1% an increase can be seen both in the total amount of sites and in the amount of strong ones. Higher Ni contents (up to 5%) practically do not modify the acidity or the acid strength distribution. Ni addition increases the total acidity of WZ by 85%. The effect is stronger in the case of the strong acid sites. There is a 7-fold increment of their concentration related to Ni addition. The change in the total acidity and acid strength distribution of WZ due to the addition of Ni is really surprising, and in principle there is not a clear explanation for this effect.

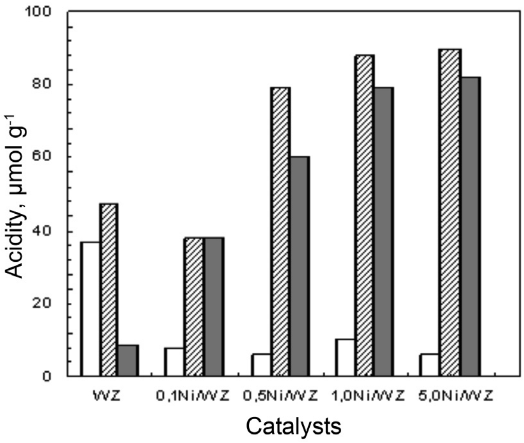

Figure 2. *Results of temperature programmed desorption of pyridine. Acid strength distribution: weak sites (white, 150-300 °C), moderate sites (gray, 300-500 °C), strong sites (black, 500-600 °C)*

Trying to elucidate the reasons of this singular effect exceeds this work and will be the cause of further studies. However, the possibility to properly modify the total acidity and acid strength distribution of WZ catalysts in reactions catalyzed by acids is essential and it must be confirmed in order to avoid erroneous conclusions. Much has been written regarding the validity of the characterization results obtained using TPD of probe molecules. Then it is necessary to confirm the TPD results by analyzing the reaction behavior of these catalysts.

Figure 3 shows results of n-C_4 conversion as a function of time-on-stream. The values of conversion of the fresh catalyst (TOS = 5 min) indicate that the addition of Ni improves the performance of WZ in the reaction. The highest conversion values (60-70%) were obtained with the catalysts of high Ni contents. During the experiments the catalysts suffered deactivation by coking. Ni catalysts lost their activity faster. This is likely related to the lower capacity of Ni to generate "activated hydrogen" that hydrogenates coke precursors and also to the high population of strong acid sites responsible for coke formation.

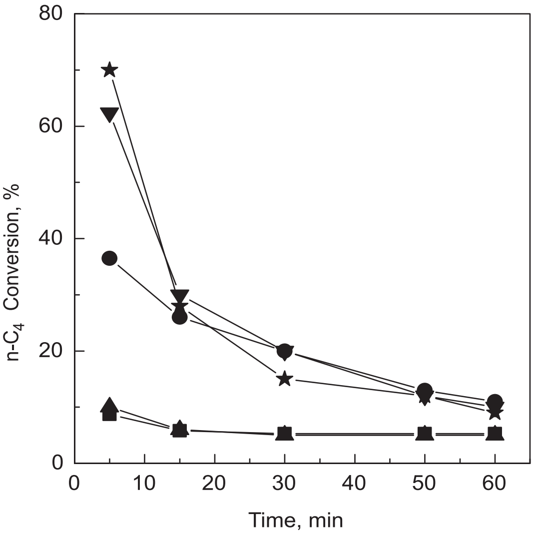

Figure 3. *n-Butane isomerization. Conversion as a function of a function of time-on-stream. (■) WZ. (▲) 0.1Ni/WZ. (●) 0.5Ni/WZ. (▼) 1.0Ni/WZ. (★) 5.0Ni/WZ*

Table 1 shows the activity results corresponding to the isomerization of n-butane and the dehydrogenation of cyclohexane, expressed as a yield to different reaction products at 5 min of time-on-stream. In the n-butane reaction, WZ has a relatively low yield of skeletal isomers. The addition of Ni to the catalyst produces an increase in the activity of WZ with a great increment of the C_1-C_3 fraction that is detrimental to the formation of i-C_4. The production of C_2 is specially enhanced while the levels of C_1 and C_3 are maintained at low levels. This means that the formation of C_2 is produced by the cracking of n-C_4 over the acid function and not by hydrogenolysis over the metal function. Cracking is a reaction that needs strong acid sites and these activity results correlate with the acidity results because the addition of Ni produces an increase of the concentration of strong acid sites of WZ. Figure 4 shows an approximately exponential relation between the population of strong acid sites and the yield to cracking products (Y_{C2}) for the studied catalysts.

Figure 5 shows an approximately linear relation between total acidity and n-C_4 conversion values for the studied catalysts. It has been thoroughly reported that the skeletal rearrangement of n-butane is the most demanding of the reactions of isomerization of short paraffins. This is related to the occurrence of a primary carbenium ion in the slowest rate-limiting step of the monomolecular acid mechanism. In this sense the found results are related to the high relative proportion of strong acid sites in the total population of acid sites. As a result in the case of the Ni doped WZ catalysts the intrinsic activity for hydroconversion of short paraffins is directly related to the total amount of surface acid sites. A more general conclusion is that in the case of the isomerization of short paraffins, the catalytic behavior of the catalysts is completely correlated to the characterization results of temperature programmed desorption of basic probe molecules.

Table 1. Catalytic tests results. Yields to different products

	Reactant			
	n-Butane		Cyclohexane	
Catalysts	Y_{iC4}, %	Y_{C2}, %	Y_{MCP}, %	Y_{Bz}, %
WZ	8.1	2.1	--	--
0.1Ni/WZ	6.5	12.0	--	0.23
0.5Ni/WZ	4.8	32.1	0.38	0.38
1.0Ni/WZ	1.7	60.6	1.55	0.75
5.0Ni/WZ	0.8	70.1	2.0	1.25

iC_4= isobutane; C_2= ethane; MCP=methylcyclopentane; Bz= benzene.

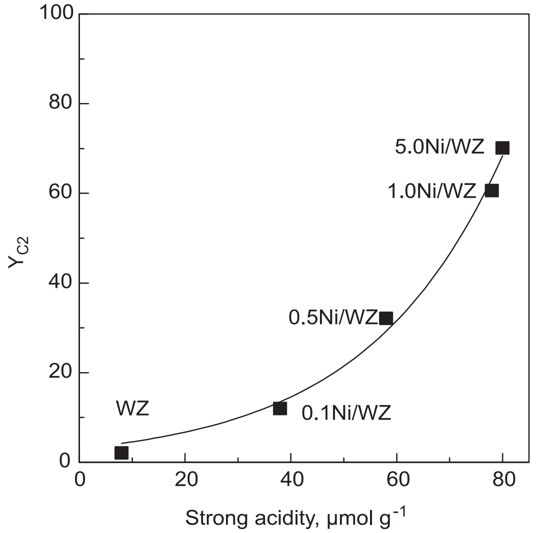

Figure 4. *n-Butane isomerization. Yield to C_2 fraction as a function of the concentration of strong acid strength sites*

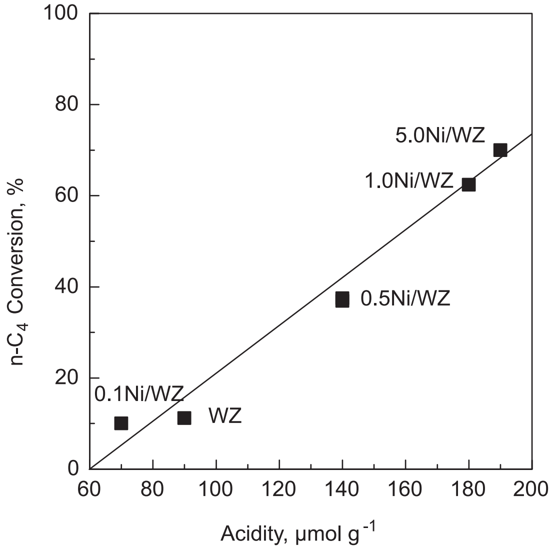

Figure 5. *n-Butane isomerization. Conversion as a function of the total acidity*

The dehydrogenation of cyclohexane is commonly used to measure the metal activity of the catalysts because this is a structure-insensitive reaction for which the activity is proportional to the number of exposed active metal atoms.[29] When the metal is deposited over a neutral support or an only slightly acidic one the only reaction taking place is the dehydrogenation of cyclohexane to benzene (Bz). When the support has a high acidity not only the metal sites lose dehydrogenating capacity because of some deleterous interaction with the support but also cyclohexane can be isomerized over the acid sites to methyl cylopentane (MCP). This reaction proceed through the adsorption and dehydrogenation of an intermediate cyclohexene species.[30] WZ has no dehydrogenating or isomerizing activity (ring contraction) by itself. However when Ni is added, the catalyst becomes active and the production of Bz is increased. The production of MCP is also concurrently increased. It is important to note that the reaction of ring contraction demands strong acid sites. The increase of the yield of MCP and Bz indicates an augment of both the metal activity and the acid activity of the WZ catalyst. The increase of the metal activity coincides with the presence of metallic Ni in the catalysts of high Ni content. In turn, the increase of the ring contraction activity coincides with an augment in the population of strong acid sites in the catalysts of high Ni content.

Figure 6 shows results of n-C_8 conversion as a function of time-on-stream. The values of conversion of the fresh catalyst (TOS = 5 min) indicate that in general (except for 0.1% NiWZ) the addition of Ni improves the performance of WZ in the reaction. This behavior coincides with the pattern of total acidity of the Ni doped catalysts. During the experiment the catalysts suffered deactivation by coking and after 4 h they reached a pseudo steady-state. The stable conversion value increased with the addition of Ni. Such as it was previously mentioned Ni in the metallic form is necessary for increasing the capacity for activating hydrogen. Activated hydrogen is an inhibitor for the formation of coke precursors responsible for the deactivation of the catalyst.

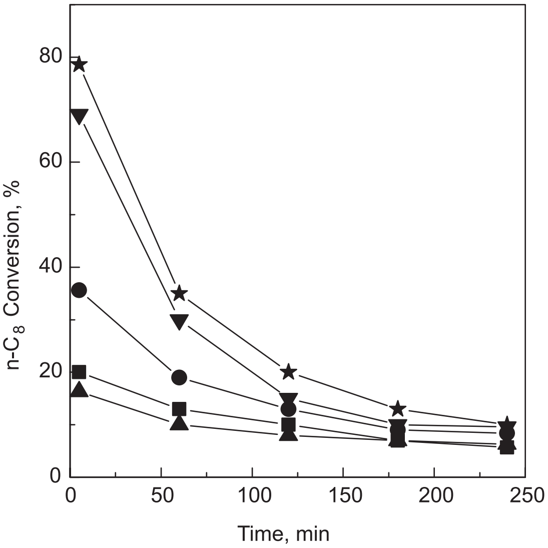

Figure 6. *Isomerization-cracking of n-octane. Total conversion of n-octane as a function of time on stream. Symbols as in Figure 3*

Figure 7 is a plot of the n-C_8 conversion at 5 min time-on-stream, as a function of total acidity. It can be seen that the activity of the WZ promoted catalysts during the hydroconversion of long-paraffins is directly related to the amount of surface acid sites. The dependence is seemingly exponential. This is similar to that observed for short paraffin hydroconversion, thus indicating that both reactions are rate-limited by the acid function.

These findings on the general relation between the acidity and the activity of metal promoted oxoanion promoted zirconia catalysts confirm some similar results reported elsewhere.[14,15] It can be specifically said that: the effect of Ni addition on the acidity and acid strength distribution are different for SZ and WZ; for both systems the total conversion for n-C_8 correlates directly to the total acidity of the catalysts.

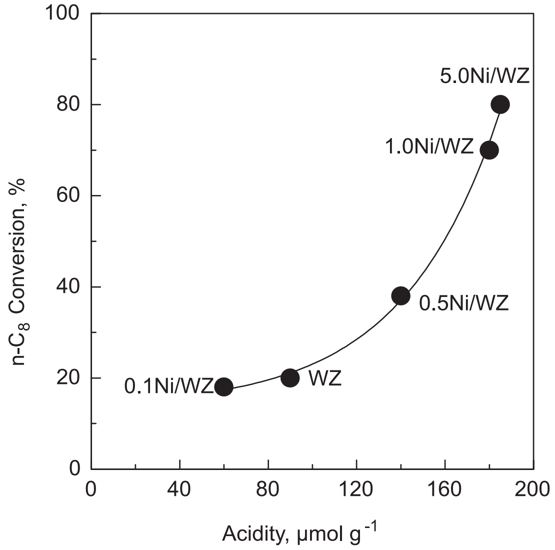

Figure 7. *Isomerization-cracking of n-octane. n-C_8 conversion as a function of total acidity*

At this point some mechanistic issues should be discussed. Ni addition augments the concentration of acid sites. If we recall the classical bifunctional bimolecular mechanism for n-paraffin isomerization, the global reaction should be controlled by the activity of the acid site since the slowest elemental step is the skeletal rearrangement of carbenium ions on the acid site. In this sense the results might indicate that the reaction proceeds in accord with an acid-limited, classical mechanism with olefinic intermediates. The increase in the concentration of active sites though leading to a greater overall reaction rate it might not lead to a greater isoparaffins yield. This is due to the possible modification of the strength of the acid sites. If the concentration of strong acid sites is increased, the isomerization of the chemisorbed carbenium ions can be followed by cracking.

Cracking is a secondary reaction that occurs preferentially on skeletally branched carbenium ions. This is related to the relatively growing stability of primary, secondary and tertiary carbenium ions. For this reason the usual reaction path begins with the adsorption of the hydrocarbon, the formation of the carbenium ion and the skeletal rearrangement in the adsorbed state. Depending on the strength of the site the ion will be either desorbed or cracked.

Another possibility is that the underlying reaction mechanism is a non-classical one.[31-33] In this case the main role of the metal is to supply activated hydrogen and enhance hydride transfer steps rather than to form olefinic reaction intermediates. Activated hydrogen is crucial for hydrogenating coke precursors and also generates "dynamic" Brönsted acid sites highly active for isomerization. Despite the different role of hydrogen, here again the overall activity would be related to the concentration of active sites because dynamic sites are formed by electron transfer from hydrogen to strong surface Lewis sites. Even in the case that the rate controlling step is posed to be the hydride transfer to adsorbed carbenium ions, hydride formation is not only linked to the formation of atomic hydrogen on metal sites but to the concentration of strong acid sites that can produce the transformation of hydrogen atoms into hydride ions.

On the other hand, the change in the total acidity and acid strength distribution of WZ due to the addition of Ni is remarkable. How this metal modifies the total acidity and the acid strength distribution of WZ is a pending question that requires further research.

Table 2 shows values of selectivity to several reaction products for the Ni promoted WZ catalysts at 5 min time-on-stream (results corresponding to the fresh, coke free catalysts). All the catalysts showed a similar pattern of product distribution. The main features are: most products are normal paraffins and isoparaffins; cyclization (to aromatic compounds) reactions occurs with yields lower than 1%; the iso/normal paraffins ratio is greater than one in all the catalyst series; i-C_4, i-C_5 and i-C_8 dominate the isoparaffins distribution while i-C_6 and i-C_7 yields are negligible; the i-C_4/n-C_4 ratio is equal to 1.8-2.0, above the thermodynamic equilibrium value;[34] the fraction of the C_8 isomers is mainly composed of mono-branched isomers (2-methyl heptane and 3-methyl heptane) in a 3-5:1 ratio with respect to the multi-branched isomers. The isomers abundance order is mono > di > tribranched; compounds with more than eight carbon atoms were not detected.

Table 2. n-C_8 reaction, products distribution. Results for metal promoted WZ catalysts at 5 min time-on-stream

Catalysts	0.1Ni/WZ	0.5Ni/WZ	1Ni/WZ	5Ni/WZ
Methane	0.02	0.08	1.83	4.07
Ethane	0.004	0.02	0.56	0.95
Propane	0.41	2.71	9.47	9.5
Isobutane	1.19	7.97	27.48	28.80
Butane olefins	0	0	0	0
n-butane	0.59	4.14	15.01	15.98
Isopentane	0.46	2.71	7.62	7.41
pentane olefins	0.01	0.03	0.11	0.06
n-pentane	0.16	1.36	3.91	4.81
2,2-dimethylbutane	0	0	0.03	0.05
2,3-dimethylbutane	0	0	0	0
2-methylpentane	0.01	0.05	0.48	0.46
3-methylpentane	0.005	0.02	0.24	0.25
n-hexane	0.01	0.04	0.34	0.46
methylcyclopentane	0	0	0	0.05
Benzene	0	0	0.03	0.03
Cyclohexane	0	0	0.03	0.05
2,4-dimethylpentane	0	0	0	0
2,2,3-trimethylbutane	0	0	0	0
3,3-dimethylpentane	0	0	0	0
2-methylhexane	0.02	0.03	0.03	0.13
2,3-dimethylpentane	0	0	0	0
3-methylhexane	0.02	0.05	0.05	0.18
3-ethylpentane	0	0	0	0.008
n-heptane	0.03	0.04	0.04	0.27
Toluene	0.01	0.02	0.22	0.41
methylciclohexane	0	0	0	0
Ethylciclohexane	0	0	0	0
2,5-dimethylhexane	0.21	0.23	0.05	0.22
2,4-dimethylhexane	0.52	0.47	0.05	0.12
2,2,3-Trimethylpentane	0.55	0.59	0.02	0.25
3,3-dimethylhexane	0.14	0.16	0.03	0.18
2,3,4-trimethylpentane	0	0	0.01	0
Dimethylheptane	3.93	3.19	0.23	0.99
2,3-dimethylheptane	1.58	1.31	0.13	0.51
Trimethylheptane	5.71	4.57	0.63	1.64
n-octane	83.64	69.42	30.87	21.35
octane olefins	0.44	0.27	0.05	0.07
Ehtylbenzene	0.03	0.05	0.02	0.030
p-xilene	0.04	0.08	0.05	0.11
m-xilene	0.10	0.18	0.18	0.33
o-xilene	0.05	0.06	0.06	0.11

The greater concentration of isoparaffins can be expected from thermodynamics. As indicated earlier the well-accepted classical mechanism of isomerization and cracking of a linear paraffin necessarily begins with a first step of adsorption of a carbenium ion. This is likely firstly isomerized in the adsorbed state by any of the accepted mechanisms such as methyl shift or formation of protonated cyclopropanes. Cracking is a consecutive reaction. The branched isomer (mono, di or tri) can be cracked on the same site or can be readsorbed on another site and be cracked there. Cracking can only proceed on acid sites with a strong acidity. In an ''ideal'' isomerization-cracking scheme molecules resulting from primary cracking are desorbed and are not subjected to secondary cracking and in this way the formation of light gaseous products is minimal.[1,35,36] Considering that the step of isomerization of n-C_8 produces mainly monobranched isomers, n-C_8 can be cracked to the following pairs: i-C_4+n-C_4, i-C_5+C_3, i-C_6+C_2. The latter pair is the least feasible. The two first ones are more likely because long molecules tend to get broken in middle positions. As it can be seen in Table 2 in all cases i-C_4 is the most abundant isomer thus confirming that cracking in the middle position of a long paraffin molecule is favored. i-C_5 is produced to a lower extent than i-C_4. The yield to i-C_4 and i-C_5, both products of isomerization-cracking, increases with Ni content and is maximal for the 1.0 and 5.0Ni/WZ catalysts. The latter demands a high acid strength and therefore it can be confirmed, as in the case of the test of n-C_4, that the addition of Ni modifies both the acidity and distribution of acid strength of WZ. On the other side a value greater than one for the i-C_4/n-C_4 and C_3/n-C_5 molar ratio rules out other mechanisms such as direct cracking of n-C_8 into 2 n-C_4 or C_3+n-C_5 pairs. Moreover it would indicate that the formation of i-C_4 not only comes from the cracking of monobranched i-C_8. Two other possible routes are: the isomerization of n-C_4, a product of the cracking of i-C_8 and the cracking of dibranched i-C_8. Of the two possibilities the most feasible is the last one because in reactions of hydrocracking branched products cannot be formed by secondary isomerization of the linear fragments since the competitive adsorption at the acid sites becomes less favorable for the fragments of decreasing chain length.[37] Besides it is well-known that cracking reactions are slower than isomerization reactions and that the formation of cracking products must follow the formation of branched isomers. It has been reported that for the hydroconversion of n-$C_{8,}$ the ratio of mono to multi-branched isomers increased with space velocity. Therefore isomerization first mainly leads to mono--branched isomers and then to multi-branched ones.[23] Multibranched isomers are also more easily cracked than monobranched isomers.

Ni incorporation produces greater amounts of undesirable products of hydrogenolysis (C_1) and successive cracking (C_2). The yield to C_1 and C_2 increases with Ni content and is maximal for 5.0Ni/WZ. Again, this behavior is coincident with the changes in acid strength distribution produced by Ni incorporation.

The absence of compounds with more than eight carbon atoms excludes the possible pathway of dimerization of n-C_8. Finally, according to the obtained results we can conclude that Ni addition increases the activity of WZ in isomerization-cracking of long paraffins. Addition of 1.0 wt% Ni to WZ produces practically the same catalytic effect on the activity than the addition of 5.0 wt%. Both catalysts produce high amounts of isomerization-cracking products (i-C_4 and i-C_5). The reaction behavior can be explained by the acid strength distribution of both catalysts. 1.0Ni/WZ has a good performance for isomerization-cracking.

CONCLUSIONS

Addition of Ni modifies both the total acidity and the acid strength distribution of WZ catalysts. The effect is really surprising and not only the total acidity is increased but also the concentration of strong acid sites.

The performance of WZ catalysts in hydrocarbon reactions confirms that the catalytic activity and selectivity may be properly regulated by metal addition. For all the reaction tests (isomerization of n-butane, cyclohexane dehydrogenation and isomerization-cracking of n-octane), the behavior in reaction of the catalysts may be explained from the TPD and TPR results.

In the cyclohexane dehydrogenation reaction, Ni addition promotes both benzene (Bz) and methyl cyclopentane (MCP) production in different ways.

In the case of n-C_4 isomerization, Ni addition increases the activity of WZ, especially promoting cracking reactions. This is in accord with the acidity results because Ni addition increases the population of strong sites responsible of cracking.

The n-C_8 isomerization-cracking results for fresh catalyst (5 min time-on-stream) are indicative that Ni addition improves the performance of WZ. The conversion to isoparaffins is increased at high Ni contents. This is so because Ni addition increases the concentration of strong sites responsible of cracking.

Finally, it can be concluded that the performance of WZ catalysts in hydrocarbon reactions may be properly regulated by metal addition.

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