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New formulations of oxoanion promoted zirconia catalysts for the upgrade of heavy paraffinic cuts

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Abstract

The effect of the addition of Pd on the catalytic activity and selectivity of Pt/WZ for isomerization-cracking of linear heavy paraffins was assessed using *n*-octane as model feedstock. A focus was put on obtaining an optimized catalyst with good isomerization activity and minimum cracking in order to get a product with improved RON and a minimum production of light gases. The results were compared with those obtained with a $Pt/SO_4^{2-}–ZrO_2$ (Pt/SZ) catalyst used as reference. The catalysts were further characterized by means of N_2 adsorption, X-ray diffraction, temperature programmed desorption of probe molecules and cyclohexane dehydrogenation. The n-C_8 results indicate that the simultaneous addition of Pt and Pd to a WZ catalyst produces a decrease of the total acidity and an increase of the de/hydrogenating capacity as compared to the monometallic Pt/WZ and Pd/WZ catalysts. This effects allows the tuning of the metal and acid functions of the catalysts, optimizing the balance for the mild isomerization-cracking reaction. In this sense, high values of RON gain were measured in the product and a high C_{5+} liquid yield was obtained.

Keywords: Supported superacids; Tungsta-zirconia; Pt; Pd

1. Introduction

Refinery processes reengineering and redirection of refinery feedstocks and internal streams have been occurring in the last years in order to adapt to the new fuel market needs. The main causes are the changing environmental regulations and the need for processing a wider variety of crude oils including heavy ones with a high content of metals and heteroatoms. In these conditions stocks are generated that are difficult to upgrade to valuable fuels. New technologies are needed to increase the contribution of heavy feedstocks to the diesel and gasoline pools.

Besides the development of synthetic fuels from renewable resources has appeared as an alternative to the use of petroleum fuels that have a horizon of declining supply and increasing extraction costs. In this sense the synthesis of Fischer–Tropsch (FTS) appears as an important source for the supply of synthetic fuels. This process converts a mixture of CO and H_2 (synthesis gas) into a wide variety of hydrocarbons. The low temperature FTS process (LTFT) is currently preferred in the industrial practice for the production of high quality diesel [1]. However most of the produced hydrocarbons are heavier than those boiling in the diesel range. The so-called Fischer–Tropsch waxes are long chain linear paraffins that advantageously have no sulfur or nitrogen in their composition. Only traces of polyaromatic and heavy metals can be found. These FT waxes are a source of clean feedstocks for the production of transportation fuels and base lube oils that can be used unmodified or after blending with other refinery petroleum cuts [2–5].

In this context the acid-catalyzed paraffin isomerization and paraffin isomerization-cracking processes have a role of increasing importance among refinery units for fuel production. These units can produce gasoline, kerosene and lube oils [6]. Hydroisomerization of C_4–C_7 cuts is used for the production of high octane number and environmentally friendly gasoline [7–10]. Mild isomerization of C_7–C_{15} cuts is used for the production of diesel fuel with improved cold flow properties (viscosity, cloud and pour points) [8,11,12].

The two ultimate technologies for isomerization (based on Pt/zeolite and Pt/MO_x–ZrO_2) have clear advantages over the old ones (employing corrosive H_2SO_4, HF or Friedel–Crafts

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catalysts) because they are environmentally benign, they can be regenerated are less sensitive to impurities. Processes based on MO_x–ZrO_2 catalysts have surpassed the performance of those based on zeolites because they can operate at lower temperatures with a higher selectivity to branched isomers. The first MO_x–ZrO_2 catalyst to reach the market was the Pt/SO_4^{2-}–ZrO_2 (Pt/SZ) one. This catalyst needs a relatively high hydrogen to hydrocarbon ratio in order not to deactivate by coking and can lose sulfate. For this reason it is being progressively substituted by Pt/WO_x–ZrO_2 (Pt/WZ) catalysts. This catalyst is more stable and robust and does not decompose even in highly reducing environments. It also has a higher selectivity to isomers compared to SZ under similar process conditions. This is mainly due to its lower cracking activity (WZ has a lower acid strength than SZ). WZ however has a lower activity and surface area than SZ. This is a disadvantage for its use in the revamping of process units. Other differences are less obvious. In Pt/WZ Pt addition is totally necessary for obtaining a good conversion. However a lower amount of Pt is needed in Pt/WZ to enable the onset of a bifunctional isomerization mechanism. This is due to the lower inhibiting effect of the support on the metal function in the case of Pt/WZ [13].

The objective of this work is to study the effect of the addition of a second noble metal (Pd) on the properties of a Pt/WZ base catalyst. The focus is put on the improvement of the performance of Pt/WZ for the isomerization-cracking of heavy linear paraffins. A catalyst is desired that can isomerize with minimum cracking in order to obtain an isomerizate with high octane number and with minimum production of light gases. *n*-Octane is used as a probe molecule and the results are compared with those obtained with Pt/SZ.

2. Experimental

2.1. Preparation of catalysts

$Zr(OH)_4$ (ZH sample) was obtained by hydrolisis and precipitation of zirconium oxychloride (Strem Chem., 99.99%) with an ammonium solution. The precipitate was washed and dried in a stove at 110 °C overnight.

SO_4^{2-}–ZrO_2 (SZ sample) was prepared by incipient wetness impregnation of ZH with a solution of 2N sulfuric acid. The impregnation volume used was equal to the pore volume plus a 10% excess ($0.4\ cm^3\ g^{-1}$). It was later dried at 120 °C and calcined in air ($10\ ml\ min^{-1}$, 3 h, 620 °C). Pt/SZ was prepared by incipient wetness impregnation of an aqueous solution of H_2Cl_6Pt (Merck, >99.5%) with a volume and concentration adjusted in order to obtain a 0.5% Pt in the final catalyst. Finally it was dried at 120 °C and calcined in air ($10\ ml\ min^{-1}$, 3 h, 450 °C).

WO_3–ZrO_2 (WZ) was obtained by incipient wetness impregnation of ZH with a solution of ammonium metatungstate (Aldrich, >99.9%) previously stabilized at pH 6 for a week and with a concentration in order to obtain 15% W in the WZ samples. After the impregnation the support was dried at 110 °C in a stove overnight. Then it was calcined in air for 3 h at 700 °C.

The WZ batch was divided in four parts. The first one was impregnated to incipient wetness with an aqueous solution of chloroplatinic acid ($H_2Cl_6Pt{\cdot}6H_2O$, Strem Chem. 99.9%). The concentration was adjusted to give a final 0.5% Pt concentration in the final catalyst. This catalyst was named Pt/WZ.

The second part was impregnated with a solution of palladium chloride (Cl_2Pd, Strem Chem., 99.9%) in order to obtain a catalyst with 0.5% Pd (Pd/WZ).

The last two WZ fractions were coimpregnated with a mixture of both solutions in order to obtain a 0.5% of metal (Pt + Pd) in the final catalyst. In one of the fractions the amounts of Pt and Pd were regulated in order to give a 1:1 Pd/Pt ratio. In the second one the Pd/Pt ratio was 1:2. Then the catalysts were dried at 120 °C and calcined in air ($10\ ml\ min^{-1}$, 3 h, 450 °C). These catalysts were named PtPd(1:1)/WZ and PtPd(1:2)/WZ.

2.2. Catalysts characterization

In order to assess the different crystalline structures of ZrO_2 X-ray diffraction spectra were recorded in a Shimadzu DX-1 using Cu Kα radiation filtered with Ni. The specific surface area of the catalysts was measured in a nitrogen adsorption Micromeritics 2100E equipment.

The measurement of the amount and strength of acid sites of the catalysts was done by temperature programmed desorption of pyridine (Merck, >98%). Both Bronsted and Lewis sites were titrated with this method. The samples were first immersed in pyridine in a vial for 6 h. Then they were filtered and dried at room temperature. Then they were placed in a quartz microreactor and stabilized in N_2 for 1 h at 100 °C. Finally they were heated from this temperature to 650 °C at a heating rate of $10\ °C\ min^{-1}$. The desorbed products were continuously analyzed in a flame ionization detector (SRI Instruments Inc.).

Pulse chemisorption of CO was used to measure the dispersion of the noble metal particles. Calibrated pulses of CO were injected in a stream of N_2 flowing through the sample. The reactor outlet was connected to a methanator system and then to a flame ionization detector. Pulses were sent to the reactor until the sample became saturated. At the beginning of the experiment the sample (300 mg) was reduced at 500 °C ($10\ °C\ min^{-1}$) for 1 h. Then N_2 was made to flow over the sample for 1 h at 500 °C in order to eliminate adsorbed hydrogen. Then the sample was cooled down to room temperature in a N_2 stream and then pulses of 0.6 μmole of CO were sent to the reactor. The CO that was not chemisorbed was transformed into CH_4 in a reactor containing a catalyst of Ni on Kieselgur. This reactor was fed with H_2 and the gases from the chemisorption cell. CO is transformed quantitatively in the methanator to CH_4 and then detected by the flame ionization detector. The amount of CO adsorbed over the catalysts was determined by comparing the size of the chemisorbed pulses and that of the non-chemisorbed ones (after saturation).

Cyclohexane dehydrogenation: it was performed in a quartz microreactor, at atmospheric pressure, $T = 300\ °C$, WHSV = 12.6 h^{-1}, molar ratio H_2/CH = 1.4 and a catalyst mass of 0.1 g. Before the reaction the catalyst was prereduced in situ at the reaction temperature for 1 h. Reaction products were analyzed by on-line gas chromatography in a Variar Star 3400 CX equipment with a FID detector and a 1/8″ diameter, 2 m long column packed with FFAP supported over Chromosorb P.

Hydroisomerization-cracking of *n*-octane: this reaction was performed in a stainless steel fixed bed reactor, with 0.25 g of catalyst, 0.1 MPa, $T = 300$ °C, WHSV = 4 h^{-1} and a molar ratio H_2/*n*-C_8 = 6. The products were analyzed on line by gas chromatography using the same equipment described above and a 100 m long squalane capillary column.

The calculation of the research octane number (RON) was done with a simple non-linear equation that is fed with GC compositional data [14]. The RON gain (ΔRON) was defined as the difference between the RON of the product mixture and the RON of *n*-octane. The yield of light gases was calculated by taking the whole C_1–C_4 fraction. The liquid yield was therefore calculated as that of C_{5+}.

In all the catalytic test catalysts were used with a 35–80 meshes particle size.

3. Results and discussion

3.1. Catalysts characterization

After being calcined at 700 °C WZ has a specific surface area of 63 $m^2\,g^{-1}$ and a pore volume of 0.10 $cm^3\,g^{-1}$. It has a monomodal pore size distribution spanning the 20–100 Å and centered at 65 Å. The presence of Pt, Pd or Pt + Pd in the catalyst in the studied range does not affect the values of the textural properties. The SZ catalyst had a specific surface area of 110 $m^2\,g^{-1}$, a pore volume of 0.14 $cm^3\,g^{-1}$ and a pore size distribution centered around 30 Å. When compared to SZ, WZ has one half the surface area of the latter. As indicated before this is a disadvantage for its use in the revamping of units where a high activity per unit volume is needed, like SZ. However from the point of view of the porosity, WZ has fewer problems when used for the reaction of big molecules with diffusional restrictions.

The crystalline structure of WZ is entirely tetragonal as inspected by XRD and with a high percentage of crystallinity (88%). No crystals of WO_3 as a segregated phase were detected. These results are consistent with the statement of Barton et al. [15] who considered that segregated WO_3 crystals are formed for loadings equal or higher than 1.5 monolayers (9 at. nm^{-2}). The W load was 6.2 at. nm^{-2} in our case.

Table 1 shows the results of total acidity and acid strength distribution of the catalysts, as determined by pyridine temperature programmed desorption. Pt/SZ has the highest concentration of acid sites, doubling and tripling in some cases the values displayed by the other catalysts. Pt/SZ has a greater proportion of sites of medium and strong acidity. In the case of the W promoted catalyst series Pt/WZ is the most acid one and has a greater proportion of weak and medium strength. In a previous report [16] we have indicated that the addition of Pt to WZ produces an increase of the total acidity while keeping unaltered the acid strength distribution. Pd/WZ is the second most acid catalyst of the W series. The samples double promoted with Pt and Pd have the lowest total acidity values and an acid strength distribution with dominant medium strength sites. The acidity test clearly indicate that the addition of Pd to Pt/WZ reduces the total concentration of acid sites of the catalyst and shifts the acid strength distribution to the low strength region. This is important for the isomerization-cracking of long chain paraffins because a mild cracking is desired in order to have a maximum liquid yield and reduce the amount of low-value light gases.

Table 1
Total acidity and distribution of acid strength of the catalysts

Catalysts	Acidity (μmol Py g^{-1})			
	Total	Weak 150–300 °C	Medium 300–500 °C	Strong 500–650 °C
Pt/SZ	280	56	128	96
Pt/WZ	120	44.4	63.58	12.0
Pd/WZ	104.1	30.0	53.49	20.7
PtPd(1:1)/WZ	80.3	13.0	58.5	8.8
PtPd(1:2)/WZ	85.6	14.6	61.31	9.73

Table 2 shows the results of catalytic activity of the test reaction of cyclohexane dehydrogenation. Test reactions are common means for assessing the properties of metal-acid bifunctional catalysts because under certain reaction conditions they are very selective and only a few products are produced. Cyclohexane dehydrogenation is an structure insensitive reaction that is used for the test of the metal function [17] and that can give information of the interaction of the metal with the support.

During the dehydrogenation of cyclohexane to benzene a parallel reaction occurs on acid catalysts. Cyclohexane is isomerized to methylcyclopentane, MCP, by contraction of the six-membered ring. Ring contraction requires the action of strong acid sites. Pt/SZ has a low dehydrogenating activity in agreement with the reports about the inhibition of the metal properties by the support. In contrast the yield of MCP is relatively high indicating the presence of strong acid sites. Pt/WZ displays a medium activity both for dehydrogenation and isomerization, with a lower proportion of the latter. Pd/WZ has low values of total conversion with similar values of selectivity to benzene (Bz) and MCP. However the simultaneous addition of Pt and Pd yields catalysts that have almost twice the activity of Pt/WZ. Pt–Pd(1:1)/WZ has the highest dehydrogenating

Table 2
Catalytic activity results

Catalyst	X_{Total} (%)	X_{Bz} (%)	X_{MCP} (%)
Pt/SZ	19.51	2.75	16.76
Pt/WZ	10.36	8.21	2.14
Pd/WZ	1.71	0.91	0.80
PtPd(1:1)/WZ	27.40	26.58	0.82
PtPd(1:2)/WZ	21.74	20.81	0.93

Test reaction of cyclohexane dehydrogenation.

activity. The yield of MCP both for Pt–Pd(1:1)/WZ and Pt–Pd(1:2)/WZ is low and is in accord with the low concentration of strong acid sites. An increase of the de/hydrogenating activity and a reduction of the concentration of strong acid sites (responsible for the cracking reactions) is desirable for the increase of the isomerization/cracking ratio. Besides a good level of hydrogenating activity prevents the deactivation of the catalyst by coking.

No CO chemisorption capacity was displayed by the samples. After seeing these results one reasonable doubt is if the catalysts had capacity for activating hydrogen and de/hydrogenating hydrocarbons at reaction conditions. However decreased CO or hydrogen chemisorption are typical of some supported Pt catalysts with an inhibited metal function. These limitations seem to be overcome at higher temperatures. For example Rajeshwer et al. [18], Volter et al. [19] and Burch [20] studied the chemisorption of H on Pt at temperatures higher than room temperature. Higher hydrogen uptakes at high temperatures were linked to high dispersion of the metal particles or to the negative influence of metal function promoters. Specially in the case of the report of Rajeshwer et al. [18] the addition of Sn to Pt/Al_2O_3 increased the activation energy for H chemisorption. Depending on the amount of Sn added the H/Pt ratio was decreased to almost null values. The chemisorption capacity was however high when the experiment was performed at 150 °C. Such activation barrier could be also present in the case of noble metals supported onto oxoanion promoted zirconia because the metal function is in these catalysts in strong interaction with the support.

Fig. 1 shows the results of conversion of n-octane as a function of the time-on-stream (TOS) corresponding to the W promoted samples. All the catalysts prepared have high initial conversion values, between 80 and 90%. Under similar process conditions Pt/SZ produces almost a complete conversion (99%). It must be recalled that the W catalysts have one half the specific surface area of Pt/SZ.

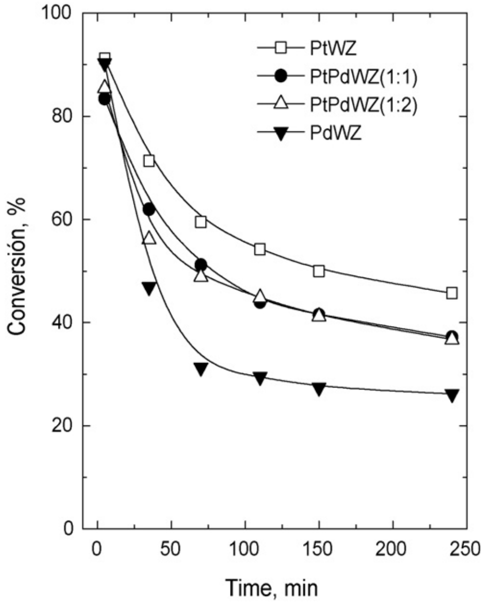

Fig. 1. Conversion of *n*-octane as a function of the time-on-stream.

At high values of time-on-stream the catalysts are deactivated by the formation of coke. The results indicate that the importance of the deactivation phenomenon follows the order: Pt/WZ ~ PtPd/WZ < Pd/WZ. After 4 h a pseudo stationary state is reached in which conversion and selectivity are almost constant. The stable conversion value is highest for Pt/WZ that is also the catalyst with the highest initial conversion (at TOS = 5 min). Pd/WZ has practically the same value of initial activity as Pt/WZ though the conversion value at

Table 3
Results of hydroconversion of *n*-octane

	Catalyst							
	PtPd(1:1)/WZ		PtPd(1:2)/WZ		Pt/WZ		Pd/WZ	
	5[a]	180[a]	5[a]	180[a]	5[a]	180[a]	5[a]	180[a]
Conversion (%)	83.43	37.21	85.45	36.74	91.18	45.71	90.27	26.22
S_{C1}	0	0	0	0	0	0	0	0
S_{C2}	0	0	0.09	0	0	0	0.04	0
S_{C3}	4.69	1.49	5.60	1.66	10.27	3.40	9.05	3.14
S_{iC4}	15.72	5.99	18.42	6.43	35.94	13.71	33.58	13.33
S_{iC5}	6.00	1.88	6.98	2.06	11.85	4.03	9.45	3.33
S_{iC6}	0.20	0	0.26	0	0.38	0.13	0.43	0
S_{iC7}	0.39	0.08	0.36	0.39	0.31	0.42	0.35	0.22
S_{iC8}	61.91	86.29	54.37	82.82	15.56	68.23	23.37	70.06
SnP_{4-7}	9.10	3.17	10.78	5.12	23.67	8.33	21.21	7.43
SiP_{5-8}	68.50	88.25	61.97	85.27	28.10	72.81	33.59	73.61
S_{ARO}	1.98	0.97	3.14	1.40	2.03	1.61	2.51	1.32
ΔRON	70.53	62.66	73.47	62.65	87.77	65.92	82.80	64.80
%Gas	23.54	3.86	28.52	4.07	59.52	10.83	53.59	6.00
η_{C5+}	76.46	96.14	71.48	95.93	40.48	89.17	46.41	94.00
$\%iC_4^{Gas}$	56.45	59.64	55.89	58.94	55.32	58.75	56.93	59.21

[a] Time (min).

TOS = 4 h is the lowest of all samples, i.e. it suffered the highest deactivation. This is because Pt has a higher capacity than Pd for activating hydrogen. Activated hydrogen acts as an inhibitor for the growth of coke precursors that deactivate the catalyst. No big differences can be seen among the PtPd/WZ catalysts, indicating that small Pt amounts in the catalysts are enough for activating hydrogen.

Table 3 shows values of selectivity to different reaction products, RON gain, yield of light gases (C_1–C_4 fraction) and selectivity to selected isomers at two values of time-on-stream (5 and 180 min). In the case of the light gases the yield of isobutane is a special case because is a highly valued petrochemical feedstock. A common feature if observed when fresh and deactivated catalysts are compared:

- the RON gain decreases;
- the production of gases decreases and the liquid yield increases;
- the yield of iC_4 decreases;
- the yield of iC_5 decreases;
- the yield of monobranched C_8 isomers increases;
- the percentage of iC_4 in the light gases is constant.

The decrease of the ΔRON is a direct consequence of the decrease of the yield of iC_5 in the liquid products that is not compensated by the increase of the amount of C_8 isomers C_8. iC_5 has a value of blending RON of 100 while mono- and dibranched C_8 isomers supply only 30 RON points to the hydrocarbon mixture. The production of light gases as a consequence of successive cracking of *n*-octane decreases because coke deposits are preferentially formed on the strong acid sites of the catalyst that are responsible for deep cracking. In this sense the production of iC_5 is decreased for the same reason. On the other side the production of C_8 isomers is less affected by coking because isomerization of long chain alkanes can proceed on sites of low acid strength.

If the ΔRON values at 5 min TOS are compared the following order can be detected: Pt/WZ > Pd/WZ > PtPd/WZ. Pt/WZ provides almost 17 additional RON points than the catalysts having both Pt and Pd. Again the differences displayed by PtPd(1:1)/WZ and PtPd(1:2)/WZ are small. These samples show a higher percentage of C_8 isomers than C_5 ones in contrast to results of the Pt or Pd catalysts. It seems that the combined effect of a greater de/hydrogenating capacity and a lower acidity yields catalysts with an improved isomers/cracked products ratio. If the liquid yield is analyzed the differences are more marked because Pt/WZ and Pd/WZ have liquid yield values of 40–45% while the PtPd catalysts have values of 72–77%. This is important from the point of view of the economy of the process. In the same reaction conditions Pt/SZ produces an increase of the RON of the liquid of 66 points, for a liquid yield of 27%. Pt/SZ mainly produces iC_4 due to its high amount and strength of acid sites.

The results indicate that PtPd/WZ is a promising alternative catalyst for the isomerization-cracking of heavy paraffins.

4. Conclusions

The simultaneous addition of Pt and Pd to a WZ catalyst produces a decrease of the total acidity and an increase of the de/hydrogenating capacity as compared to those of Pt/WZ and Pd/WZ. The metal and acid functions are thus optimized for the reaction of isomerization-cracking of heavy paraffins.

The initial activity values in isomerization-cracking of *n*-octane (5 min) indicate that the RON gain with the PtPd/WZ catalysts is somewhat lower than that obtained with Pt/WZ or Pd/WZ. The liquid yield is however greatly improved with the use of PtPd/WZ.

There are no big differences in the pattern and magnitude of deactivation between the Pt catalysts indicating that Pt has a higher capacity than Pd for activating hydrogen. Small Pt amounts are enough for producing activated hydrogen.

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