Influence of the crystalline structure of ZrO_2 on the metallic properties of Pt in $Pt/WO_3–ZrO_2$ catalysts

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The influence of the crystalline structure of ZrO_2 on the metallic properties of Pt, when supported on $WO_3–ZrO_2$, was studied. Pt supported on tetragonal zirconia loses its metallic properties while when supported on monoclinic zirconia it presents good metallic activities. WO_4^{2-} deposited on amorphous $Zr(OH)_4$ before calcination generates an active material for n-butane isomerization. The larger the fraction of the tetragonal phase of zirconia in this material, the higher the isomerization activity and the lower the metallic activity of Pt.

Keywords: Pt metallic properties, $Pt/WO_3–ZrO_2$ catalysts

1. Introduction

The promotion of zirconium oxide with metallic oxoanions (SO_4^{2-} and WO_4^{2-}) has received considerable attention from research groups interested in the study and development of catalytic materials suitable for the isomerization of light paraffins at a low temperature [1,2]. The use of tungstate as catalytic promoter has been less studied when compared with sulfate. Nevertheless some characteristics and effects of both promoters are similar and are not found in other acidic materials. When Pt is supported on ZrO_2 promoted with sulfate or tungstate, its metallic properties are modified (i.e., activation and dissociation of chemisorbed hydrogen, hydrogenating/dehydrogenating capacity, $H_2–D_2$ exchange) [3,4]. We concluded in a previous work that the presence of W modifies the metallic properties of Pt in a different way when the metal is supported on $WO_3–ZrO_2$ (WZ) [4]. The main effects of oxoanion addition are a delayed crystallization on thermal treatments and the stabilization of the tetragonal zirconia phase. This crystalline form strongly influences both the acidic properties and the catalytic activity of $WO_3–ZrO_2$ [5].

The main objective of this work is to study the influence of the crystalline structure of ZrO_2 on the metallic properties of Pt when it is supported on $WO_3–ZrO_2$. The metallic state of Pt will in turn strongly affect the catalytic reaction paths.

2. Experimental

2.1. Catalyst preparation

ZOH: $Zr(OH)_4$ was obtained from zirconium oxychloride hydrolysis with aqueous ammonia. The precipitate was rinsed with distilled water and oven dried at 110 °C overnight.

WZA: ZOH was impregnated with ammonium metatungstate solution using the incipient wetness technique, with the amount of salt required to obtain a final solid material with 15% W. Impregnated ZOH was oven dried and then calcined at 800 °C under flowing air for 3 h.

WZB: ZOH was impregnated with an ammonium metatungstate solution previously stabilized at pH = 6 during one week (liquid to solid ratio: 15 ml/g) to obtain 15% W in the final solid material. The impregnated solid was dried and calcined in the same way as WZA.

WZN_2: was prepared in the same way as WZB, but N_2 was used instead of air in the calcination step.

WZM: a commercial monoclinic zirconia (Strem Chemicals) was impregnated using the same procedure as in the case of WZB.

Z: ZrO_2 was obtained from the prepared $Zr(OH)_4$ by calcination at 800 °C under air for 3 h.

ZT: a commercial tetragonal zirconia doped with 5.2% Y_2O_3 (Strem Chemicals) was calcined at 800 °C under air for 3 h, the presence of Y_2O_3 stabilizes the tetragonal phase of ZrO_2.

WZT: a commercial tetragonal zirconia doped with Y_2O_3 (Strem Chemicals) was impregnated using the same procedure as for WZB.

Pt was incorporated into the prepared materials (after calcination at 800 °C) as chloroplatinic acid using the incipient wetness technique and the acid concentration required to obtain 1% Pt in the final solid. Impregnated samples were oven dried at 120 °C overnight and calcined under flowing air at 500 °C for 2 h.

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2.2. Materials

Ammoniun metatungstate ($(NH_4)_6(H_2W_{12}O_{40})\cdot nH_2O$) was provided by Fluka. Chloroplatinic acid ($H_2Cl_6Pt\cdot 6H_2O$) was from Strem Chemicals. The gases were n-butane (99.9%), pure air, nitrogen and hydrogen from AGA.

2.3. Hydrogen adsorption and specific surface area

Hydrogen adsorption isotherms were determined to calculate Pt metallic dispersion. First, samples were heated at 300 °C and reduced in hydrogen atmosphere during 1 h. Then, at the same temperature, they were evacuated during 2 h. The isotherms of total and reversible hydrogen adsorption were measured at room temperature. The amount of chemisorbed hydrogen was obtained by subtracting the two isotherms and the H/Pt ratio or metal dispersion was calculated assuming dissociative adsorption of hydrogen on the Pt atoms. For the specific surface area, the catalyst samples were degassed at 200 °C for 2 h, and then the nitrogen adsorption isotherm was determined at liquid-nitrogen temperature. A Micromeritics 2100E equipment was used for both determinations.

2.4. XRD measurements

The XRD measurements were performed on a Shimadzu DX-1 diffractometer with Cu Kα radiation filtered with Ni. Spectra were recorded in the 20°–65° 2θ range and scanning at a rate of 1.2°/min. The percentage of tetragonal phase of different samples was calculated according to Mercera et al. [6].

2.5. Temperature-programmed reduction

TPR analyses were made in an Ohkura TP2002 equipped with a thermal conductivity detector. Samples were pretreated *in situ*. After pretreatments, they were heated from room temperature to 950 °C at 10 °C/min in a gas stream of 4.8% hydrogen in argon.

2.6. Catalytic tests

n-butane isomerization was carried out using a fixed-bed quartz reactor operated under isothermal conditions at atmospheric pressure. The reactor outlet passed through a sampling valve connected to a chromatograph. Flow reaction conditions were: $T = 350$ °C, WHSV = 1.0, 0.5 g of catalysts and $H_2/n\text{-}C_4 = 6$. Reaction products were analyzed in an on-line chromatograph with a FID detector. A 6 m long, $1/8''$ diameter column packed with 25% dimethylsulfolane on Chromosorb P was used.

Cyclohexane dehydrogenation. The test conditions for cyclohexane dehydrogenation were: $T = 270$ °C, WHSV = 10, 0.1 g of catalysts and molar ratio $H_2/CH = 30$. Reaction products were analyzed in an on-line chromatograph with a FID detector. A 2 m long, $1/8''$ diameter column packed with FFAP on Chromosorb P was used.

3. Results and discussion

The main physical, chemisorptive and catalytic properties of the different catalyst types are shown in table 1. The addition of Pt does not modify the specific surface area and the ZrO_2 crystalline phase of the calcined supports.

When $Zr(OH)_4$ is calcined at 800 °C, the obtained solid (Z) has a monoclinic structure (the characteristic peak of the tetragonal phase at $2\theta = 30°$ was not detected) and a low surface area. The commercial sample of ZrO_2 doped with W (WZM) also has a purely monoclinic structure, but its surface area is greater. The commercial sample doped with Y_2O_3 (ZT) has a purely tetragonal structure (no diffraction peaks corresponding to monoclinic phase were detected at $2\theta = 28°$ and 31°) and the smallest surface area. WZA, WZB and WZN_2 present a mixed monoclinic/tetragonal structure, the percentage of tetragonal ZrO_2 being the highest for WZB. It can be concluded that the conditions of impregnation as well as the type of thermal treatment (atmosphere) have a major influence on the crystalline structure of the prepared materials. In contrast, the surface area is not significatively affected by the relative amounts of crystalline phases in the solids with mixed structure, but considerable variations were detected for the samples with pure tetragonal or monoclinic structure. All samples with Pt, except Pt/ZT and Pt/WZT (not shown in table 1), have some hydrogen adsorption capacity, but samples without Pt did not chemisorb hydrogen.

Values for cyclohexane conversion (TON) obtained at a time on stream of 5 min are also presented in table 1. Selectivity to benzene was 100% in all cases. This reaction is accepted to be non-demanding (catalytic activity is directly proportional to the amount of exposed metallic atoms). It can be observed that dehydrogenating activity decreases while the amount of tetragonal phase increases, the catalyst without W (PtZ) being the most active. Catalyst Pt/ZT, with a pure tetragonal structure, has no measurable dehydrogenating activity. In ascending order of catalytic activity, catalyst Pt/WZB follows, which has the highest percentage of tetragonal phase between the W-promoted samples. It could be supposed Pt dispersion would be higher in the samples with a predominant monoclinic phase, but measurements of metallic dispersion show the opposite ($D_{Pt/WZB} = 66\%$, $D_{Pt/Z} = 44\%$). Another possibility is the partial blockage of Pt atoms by W species as a consequence of surface migration during the calcination step in air at 500 °C after chloroplatinic acid impregnation, thus hindering the access of reactant molecules to the active sites. This "decorating effect" was proposed by Regabulto et al. [7]. This course of reasoning can be disregarded in this case as long as all samples were prepared according to the same procedure and such phenomena should be independent of the crystalline "habitat" of the support. In the case of Pt/ZT, the absence of W on the surface makes impossible such type of blockage. Another possibility is the partial oxidation of Pt due to electron transfer to ZT to form some PtO_x species.

Table 1
Surface area (Sg), crystalline phases, percent of tetragonal ZrO_2, chemisorbed H/Pt ratio and dehydrogenating activity of catalyst samples.

Catalyst	Specific surface area (m^2/g)	ZrO_2 crystalline phase[a]	Tetragonal ZrO_2 (%)	H/Pt ratio (%)	Dehydrogen. activity TON[b]
Pt/WZA	40	M,T	60	30	0.245
Pt/WZB	42	M,T	75	66	0.085
Pt/WZN_2	38	M,T	64	60	0.161
Pt/WZM	14	M	0	50	0.271
Pt/Z	8	M	0	44	0.301
Pt/ZT	3	T	100	0	0

[a] M: monoclinic, T: tetragonal.
[b] TON: reacted molecules cyclohexane/exposed Pt atoms × second.

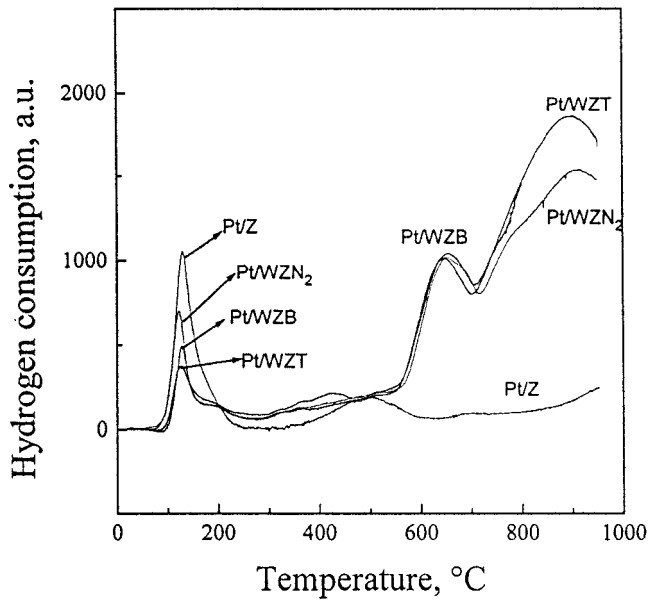

Figure 1. Temperature-programmed reduction of samples containing Pt.

Temperature-programmed reduction spectra are shown in figure 1 for some of the samples containing Pt. Pt/Z exhibits a broad but well defined peak in the 100–200 °C range which could be assigned to Pt oxide reduction. Such low reduction temperature range (as compared to Pt deposited on other supports such as Al_2O_3) corresponds to a low dispersed metallic phase with a large crystallite size and low interaction with the support. Pt/WZM has a similar reduction pattern (not shown), with a somewhat smaller Pt reduction peak. In contrast, Pt/WZN_2 has a smaller reduction peak. At temperatures higher than 500 °C, the reduction of different W species starts in the surface of the catalysts. The largest decrease of Pt reduction peak is observed for Pt/WZT and Pt/WZB. Large Pt reduction peaks are observed for samples with a monoclinic structure (Pt/Z and Pt/WZM (not shown in figure 1)). In contrast, small Pt reduction peaks are observed for samples with major proportion of tetragonal phase (Pt/WZN_2, Pt/WZT and Pt/WZB). It can be concluded that Pt reducibility is affected when deposited on WZ catalysts. In a previous work [4], we postulated that the presence of W could be the cause of such anomalous behavior. Regarding the results obtained now with samples with the same W content (Pt/WZM and Pt/WZB) it can be concluded that the operating mechanism is more complex being additionally associated to the type of crystalline structure present and that this effect is more important when the proportion of tetragonal phase increases.

Table 2 shows the total conversion of n-C_4 and the selectivity to reaction products ($S_{i\text{-}C_4}$ (isomerization reaction), and $S_{C_1+C_3}$ (hydrogenolysis reaction) and $S_{C_{4+}}$ (n- and i-C_5 as deproportionation products)) at two times on stream. Values of i-C_4 yield% (total conversion × i-C_4 selectivity) are also included. In the case of Z, the material is not active and the introduction of Pt produces the appearance of the hydrogenolysis reaction, typical of the metallic function. In a "classical" bifunctional reaction scheme, this behavior corresponds to a metallic function well in excess with respect to the acidic one, or it is due to an acid strength too low to isomerize the olefins formed on the metallic sites. The alkenes formed in the first reaction step can so hydrogenolyze to C_1 and C_3 hydrocarbons.

A similar behavior of Pt/WZM was observed regarding both conversion and selectivity. This indicates that the presence of W on a monoclinic support does not bring iso-

Table 2
n-butane conversion and products selectivity of different samples at two times on stream.

Catalyst	Time (min)	X[a] (%)	i-C_4 yield (%)	Products selectivity (%)		
				$S_{C_1+C_3}$	$S_{i\text{-}C_4}$	$S_{C_{4+}}$
Pt/WZA	5	73.3	20.5	71.6	28.0	0.4
Pt/WZA	60	15.3	13.3	10.8	87.0	2.2
Pt/WZB	5	32.1	27.6	12.8	86.0	1.2
Pt/WZB	60	16.1	15.6	1.6	97.0	1.4
Pt/WZN_2	5	60.0	11.2	81.0	18.6	0.4
Pt/WZN_2	60	11.2	7.3	34.2	65.0	0.8
Pt/WZM	5	47.1	2.7	94.2	5.7	0.3
Pt/WZM	60	3.6	1.2	64.8	34.7	0.5
Pt/Z	5	49.4	3.7	91.0	7.5	1.5
Pt/Z	60	26.2	2.3	91.0	8.8	0.2
Pt/WZT	5	0	0	0	0	0
Pt/WZT	60	0	0	0	0	0
Pt/ZT	5	0	0	0	0	0
Pt/ZT	60	0	0	0	0	0

[a] X total conversion of n-C_4.
[b] S selectivity of n-C_4 to each product. C_{4+} is formed by n-C_5, i-C_5 and a little of n-C_4 alkenes.

merizing activity to the catalyst. In a previous work [5], we found that both the W precursor and the preparation technique have influence on its surface state in catalysts WZ. A higher "spreading" of W on the catalyst surface leads to a solid with a higher percentage of ZrO_2 in tetragonal structure. In this case, W is mainly an amorphous surface structure of the WO_x type. Such W species in octahedral coordination are apparently responsible for the onset of the isomerizing activity which increases when W is more dispersed or covers a larger fraction of the zirconia surface.

Pt/WZB catalysts have the highest i-C_4 production (highest i-C_4 yield) though the total conversion is the lowest due to a strongly decreased formation of $C_1 + C_3$ hydrocarbons. It can be concluded that a good metal/acid balance exists in this catalyst. Pt content is the same for all catalysts and the materials with the lowest hydrogenolysis in table 2 present the lowest cyclohexane dehydrogenation activity in table 1.

Pt loses its hydrogenolysis activity more rapidly than the acid sites of WZ lose their isomerization activity, then an increase in isomerization selectivity can be seen. The catalyst deactivation is produced by carbonoceous deposits that are produced firstly on the metallic function decreasing the Pt atoms ensemble demanding hydrogenolysis.

Pt/ZT and Pt/WZT catalysts do not exhibit any n-C_4 isomerizing activity, thus indicating that both catalytic functions do not operate. A statement repeatedly found in the literature about superacidic ziconia catalysts says that tetragonal structure is the dominant crystalline phase present in catalytically active materials [8]. Taking into account the results, it can be stated that this condition is not sufficient to bring about the catalytic activity. The promotion with WO_4^{2-} or SO_4^{2-} ions is necessary in order to obtain active catalysts and the promotion would be done to amorphous $Zr(OH)_4$.

In Pt/WZ catalysts, when WO_x is uniformly distributed on ZrO_2, this oxide crystallizes in the tetragonal phase, the acid activity for n-C_4 isomerization is maximum and the hydrogenolysis activity of Pt is minimun. For catalysts rich in monoclinic phase ZrO_2, the isomerization activity is lower and the hydrogenolysis metallic activity is higher. Pt supported on tetragonal ZrO_2 is inactive for dehydrogenation and does not present other metallic properties.

4. Conclusions

Pt supported on tetragonal zirconia loses its metallic properties while supported on monoclinic zirconia it presents good metallic activities. WO_4^{2-} deposited on amorphous $Zr(OH)_4$ after calcination generates an active material in isomerization but little activity in dehydrogenation. The larger the fraction of the tetragonal phase of zirconia in this material, the higher is the isomerization activity and the lower the dehydrogenation activity.

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