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Phosphate as promoter of zirconia for alkane isomerization reactions

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Phosphate, as catalytic promoter of zirconia, has similar effects as sulfate and tungstate anions, i.e., enhanced thermal stability with high retention of surface area and higher crystallization temperature, in comparison with unpromoted zirconia. n-butane isomerization activity increases and selectivity to isobutane decreases as phosphate content increases. For n-heptane isomerization, activity and selectivity to i-C_7 have maxima.

Keywords: phosphate-promoted zirconia, n-butane isomerization, n-heptane isomerization

1. Introduction

Much research efforts have been done in the last years in order to find a catalytic promoter better than SO_4^{2-} for the isomerizing activity of zirconia. Most of the research works were done on the WO_3/ZrO_2 system, due to the higher surface stability of tungstate as compared with sulfate [1]. It has been found that the crystalline structure of ZrO_2 must be thermally stabilized after promotion to achieve catalytic activity for both sulfate- or tungstate-promoted zirconia [2,3]. Tetragonal ZrO_2 is the predominant crystalline phase in SO_4^{2-}/ZrO_2 systems that have catalytic activity [4].

Only a few studies on PO_4^{3-}-promoted zirconia may be found in the current literature, mainly related with its physicochemical characterization [5,6]. The aim of this work is the study of the influence of phosphate content on catalytic activity for light n-paraffins isomerization, and to establish its correlation with bulk and surface properties of the catalysts. The performances of the prepared samples were compared with the corresponding of a SO_4^{2-}/ZrO_2 catalyst.

2. Experimental

2.1. Catalysts

ZrO_2 was obtained from $Zr(OH)_4$ gels after calcination at 700 or 800 °C during 3 h in flowing air. Phosphate was added by soaking of $Zr(OH)_4$ gels in phosphoric acid solutions with different concentrations (0.04, 0.3, 0.5 and 1 M). This treatment was done without stirring, with a liquid/solid ratio of 6 ml/g. After 2 h, the gel was decanted, washed and dried overnight at 120 °C. Calcination of these dried samples was done at two temperature levels (700 and 800 °C, 3 h, flowing air). All catalysts so obtained were denominated PZ.

SO_4^{2-}/ZrO_2 was prepared by sulfating $Zr(OH)_4$ with a 1.0 M H_2SO_4 solution according to [7] and is denominated SZ.

2.2. Catalyst characterization

Chemical analysis: P contents were determined by spectrophotometry after acid digestion.

Potentiometric titration: Surface charge of the samples as a function of pH was determined on solid suspensions in KNO_3 [8].

XRD: Catalysts samples were analyzed in a Shimadzu DX-1 diffractometer, using Cu Kα radiation with a Ni filter. Diffractograms were recorded at a scanning rate of 1.2°/min in the 20–60° 2θ range.

Catalytic tests: Catalytic activity (paraffin conversion) and selectivity to products were measured for n-butane (AGA, 99.5%) and n-heptane (Carlo Erba, 99.5%) at 300 °C and atmospheric pressure. n-butane catalytic conversion was evaluated in a continuous microreactor using the pulse technique with N_2 as carrier gas. For n-heptane, a conventional continuous fixed-bed reactor was used. n-heptane was fed at WHSV $= 1.0$ with hydrogen ($H_2/n\text{-}C_7 = 6$). Products were analyzed by GC.

3. Results and discussion

Specific surface area and crystalline phase of unpromoted ZrO_2 and samples promoted with different H_3PO_4 concentrations are shown in table 1. As previously observed for SO_4^{2-}–ZrO_2 [7], the incorporation of phosphate into zirconia enhances its thermal stability, leading to higher surface areas after calcination at both temperatures 700

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Table 1
Specific surface area and crystallinity at two calcination temperatures.

Catalyst	Sg[a] (BET) (m^2/g)		ZrO_2[b]	
	700 °C	800 °C	700 °C	800 °C
ZrO_2	25	8	M	M
PZ 0.04 M	108	48	M(−), T(+)	M(−), T(++)
PZ 0.30 M	120	47	T	T
PZ 0.50 M	112	46	Amorphous	T
PZ 1.00 M	72	20	Amorphous	T

[a] Sg: specific surface area.
[b] T: tetragonal, M: monoclinic.

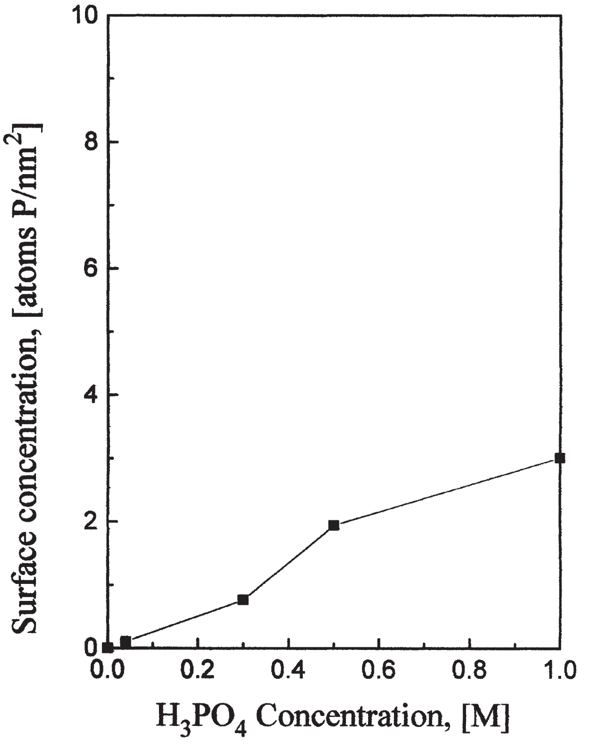

Figure 1. Surface concentration of P versus H_3PO_4 concentration of impregnating solution. Samples calcined at 800 °C.

and 800 °C. Surface area retention is high for H_3PO_4 concentrations in the impregnating solutions up to 0.5 M. For the highest acid concentration (1 M), the surface area of the calcined sample is greatly reduced. This may be caused by acid attack to zirconia with partial destruction of the porous structure and formation of bulk zirconia phosphate.

As the PO_4^{3-} content increases, a shift in the temperature of ZrO_2 transition from amorphous to crystalline state can be observed, with a predominance of the tetragonal structure over the monoclinic one. This is particularly noticeable at H_3PO_4 concentrations of 0.3 M and higher. Higher calcination temperatures are required to transform the amorphous phase into a crystalline one as acid concentration increases.

Surface coverage with phosphate ions, expressed as P atoms/nm^2, as a function of H_3PO_4 concentration in the impregnating solutions is plotted in figure 1 for samples after calcination at 800 °C. It must be pointed out that only a minor fraction of the PO_4^{3-} available in the impregnating solution remains on ZrO_2 after calcination.

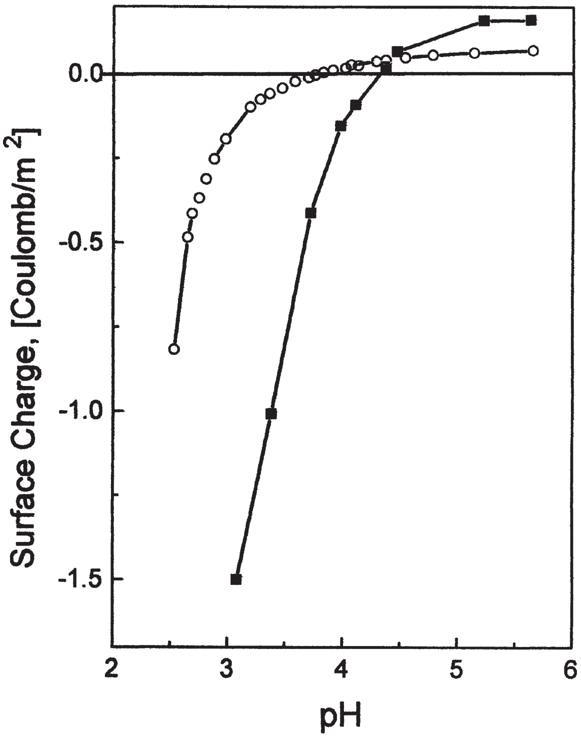

Figure 2. Potentiometric titration of catalysts calcined at 800 °C. (○) PZ 0.5 M, (■) ZrO_2.

Surface concentration of P increases, as the acid concentration increases, as expected, with the values of P coverage being similar to those previously obtained for SO_4^{2-} as promoter [7]. Low surface coverage values (0.1 at P/nm^2) are enough to achieve the promoting effect on ZrO_2, leading to a higher thermal stability with improved surface area retention after calcination.

Surface polarization plots are presented in figure 2 for representative samples. ZrO_2 has a ZPC (zero-charge point) at about 4.5 pH units. Phosphate addition shifts the ZPC to lower pH values, which can be ascribed to a higher acidity of surface OH groups remaining after calcination. This is noticeable because surface acidity plays an important role on the isomerization activity. The rest of the promoted samples exhibited a similar behavior as compared with unpromoted zirconia (not shown), the average shift being 1.0 pH units.

Values for total n-C_4 conversion and selectivity to products obtained in the first pulse are reported in table 2. Also, the results presented for SZ catalysts are indicated.

For PZ samples, it can be observed that only the catalysts previously calcined at 800 °C exhibit catalytic activity. Samples calcined at 700 °C do not have catalytic activity, although some of them have tetragonal crystalline structure of ZrO_2 (PZ 0.3 M).

Catalytic activity increases as the acid concentration in the impregnating solution increases. On the other hand, selectivity to isobutane decreases due to an increase in

Table 2

Catalytic conversion and selectivity on n-C_4 reactions over calcined phosphate–zirconia catalyst, first pulse in N_2 at 300 °C and atmospheric pressure.

Catalyst	Calcination temp. (°C)	Conversion (%)	Products selectivity (%)		
			C_1–C_3	i-C_4	C_5
PZ 0.04 M	800	2.6	38.0	62.0	
PZ 0.30 M	700	0.0			
	800	3.5	34.0	57.0	9.0
PZ 0.50 M	700	0.0			
	800	4.0	72.0	25.0	3.0
PZ 1.00 M	800	13.5	76.0	23.0	
SZ	620	20.0	16.0	73.0	11.0

Table 3

Catalytic conversion and selectivity on n-C_7 reactions at 300 °C, WHSV = 1.0, atmospheric pressure, H_2/HC = 6 at 5 min time on stream.

Catalyst	Calcination temp. (°C)	Conversion (%)	TON[a] $\times 10^3$	Products selectivity (%)		
				C_1–C_4	i-C_7	C_5–C_6
PZ 0.04 M	800	1.98	6.9	6.0	76.1	17.9
PZ 0.30 M	700	2.38	0.4	18.5	50.0	31.5
	800	3.2	1.5	14.0	53.0	33.0
PZ 0.50 M	700	2.32	0.2	21.0	62.0	17.0
	800	8.5	1.6	1.1	91.0	7.9
PZ 1.00 M	800	4.16	1.2	2.1	68.0	29.9
SZ	620	13.5	1.3[b]	80.0	7.0	13.0

[a] TON: n-C_7 reacted molecules/(s P_{atom}).

[b] TON: n-C_7 reacted molecules/(s S_{atom}).

cracking products (C_1–C_3). SZ shows a better performance than PZ catalysts. The PZ behavior is entirely different to that found for sulfate-promoted catalysts calcined at its optimum temperature, where an increase in acid concentration led to an increase on both activity and selectivity to isobutane [7,8]. If we try to explain the performance of the PZ and SZ catalysts using a conventional criterion for acid-catalyzed reactions, i.e., isomerization is a less demanding reaction as compared with cracking or disproportionation [9], then we can conclude: (a) for PZ catalysts, the treatment with increasing acid concentration produces solids with stronger acid sites, and (b) SZ has a higher concentration of sites with lower acid strength than PZ catalysts. However, this could be reversed from the expectation based on the much higher charge to radius ratio of S^{6+} versus P^{5+}. Further experiments in order to clarify these topics are in advance. Catalytic activity continuously decreases for successive pulses (not shown in the table).

Initial values (5 min time on stream) of activity and selectivity for n-C_7 isomerization reaction are shown in table 3. As observed for n-C_4, calcination at 800 °C is required to obtain higher catalytic activity, which increases as the acid concentration increases up to a maximum at 0.5 M. SZ shows higher activity values, but the selectivity to i-C_7 is poor, producing mainly cracking products (C_1–C_4 fraction). All samples deactivate with time on stream reaching a stable conversion value after 3 h. The loss of activity is about 50% of the initial conversion value. n-heptane isomerization is less demanding than n-butane isomerization on acid strength. If we take in mind the behavior of PZ samples in n-C_4 isomerization, the presence of maximum for both activity and selectivity in n-heptane conversion cannot be explained with the conventional acidity criterion quoted above. However, if we expressed the conversion results as reacted molecules of n-C_7/(s P_{atom}) (TON), it can be seen that the low P loading catalyst has higher activity per P atom than the high P loading.

Another important difference with previous works on SO_4^{2-}-promoted ZrO_2 is the existence of amorphous PO_4^{3-}/ZrO_2 samples which have catalytic activity (PZ 0.5 M/700 °C). It must be recalled that in the previous works it was found that the crystalline form of zirconia plays a role in determining catalytic activity.

4. Conclusions

Phosphate is a textural promoter with similar properties as sulfate for ZrO_2 stabilization. Temperature shifts observed for crystalline phase changes are about 100 °C higher than those observed for SO_4^{2-}/ZrO_2. The catalysts prepared have activity for light paraffins isomerization. The classical parameters used for evaluating activity of samples in acid-catalyzed reactions are not sufficient to explain the behavior of the PZ samples. Active crystallographically amorphous catalysts were obtained.

References

[1] M. Hino and K. Arata, J. Chem. Soc. Chem. Commun. (1987) 1259.

[2] C. Morterra, G. Cerrato, C. Emanuel and V. Bolis, J. Catal. 142 (1993) 349.

[3] J.C. Yori, C.R. Vera and J.M. Parera, Appl. Catal. A 163 (1997) 165.

[4] C.R. Vera, R.A. Comelli and J.M. Parera, J. Catal. 151 (1995) 96.

[5] K.M. Parida and P.K. Pattnayak, J. Coll. Interf. Sci. 182 (1996) 381.

[6] M.I. Zaki and A.M. Ali, Coll. Surf. A 119 (1996) 39.

[7] J.C. Yori and J.M. Parera, Appl. Catal. A 129 (1995) L151.

[8] C.R. Vera, Doctoral thesis, Universidad Nacional del Litoral, Santa Fe, Argentina (1995).

[9] B.W. Wojciechowski and A. Corma, in: *Catalytic Cracking. Catalyst, Chemistry, and Kinetics* (Dekker, New York) chapter 2.