Improving the *n*-pentane hydroisomerization of Pt/SO_4^{2-}(SiO_2) catalysts through mixing with ZrO_2

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The performance of Pt catalysts supported on sulfated zirconia–silica with different stoichiometries is investigated in the *n*-pentane hydroisomerization reaction. Comparatively, with respect to the Pt/SO_4^{2-}–SiO_2 or Pt/SO_4^{2-}–ZrO_2 catalysts, the sulfated mixed oxides show an enhancement of the catalytic activity that increases with the content of ZrO_2, reaching its maximum at values between 10 and 15 wt% zirconia. The characterization of the samples reveals that at this stoichiometry occurs the highest H_2-consumption of the samples as well as the top value of strong Brønsted acid sites according to the TPD-H_2 and FTIR measurements of absorbed pyridine respectively. That is, close to these percents of zirconia content one has a compound that is homogeneously mixed and above those values the segregations of the single oxides occur as verified by X-ray diffraction characterization.

Keywords: platinum; sulfated zirconia–silica catalysts; H_2-TPD; catalytic characterization; *n*-pentane hydroisomerization

1. Introduction

It is well known that some sulfate–metal oxides lead to superacid materials with surface acidity and surface areas much larger as compared with those oxides without sulfate [1]. Both features, acidity and surface, make many of these superacid compounds very active as catalysts when used in reactions that generally are catalyzed by strong acids [2]. For example, SO_4^{2-}–ZrO_2 has proved to be an efficient catalyst in the butane isomerization [3] as well as in the alkylation of isobutane with butenes [4] and in the acylation of toluene [5] among others. On the other hand, a similar enhancement in catalytic activity is also shown by non-metal sulfated materials, as is the case of the SO_4^{2-}–SiO_2 system. In fact, when the above catalyst is used in the ethanol decomposition, a higher activity than that corresponding to the unsulfated SiO_2–Al_2O_3 material has been reported [6]. Also, Sohn and Jang [7] have studied the ZrO_2–SiO_2 system unmodified or modified with H_2SO_4 in the 2-propanol dehydration and cumene dealkylation reactions. In both cases, they found an enlargement of the catalytic activity with the sulfated samples. Likewise, recently it has been pointed out that addition of Pt, Rh and Ni to sulfated-zirconia superacid catalysts improves the catalytic performance of the corresponding compound in the skeletal isomerization of alkanes, the Pt/SO_4^{2-}–ZrO_2 system being the one with highest activity [8] as well as the one with the lowest deactivation when used in reactions that are carried out in presence of hydrogen [9]. In short, although separately sulfated-silica, sulfated-zirconia, sulfated-silica–zirconia and platinum–sulfated-zirconia are very useful as catalysts or supports, the catalytic performance of the sulfated-silica–zirconia system loaded with a metal catalyst has, as far as we know, not yet been reported in the literature. Thus, the purpose of the present work is to investigate the effect that the silica/zirconia content has on the catalytic performance of Pt/SO_4^{2-}(ZrO_2–SiO_2) catalysts using, as test reaction, the hydroisomerization of *n*-pentane.

2. Experimental

Catalyst preparation: The sulfated silica–zirconia support was prepared by impregnation of dried nZr–mSi(OH)$_4$, where $m + n = 100$ wt% for $n = 0, 5, 10, 15, \cdots$ wt%, with a 1 N H_2SO_4 aqueous solution. The zirconia–silica hydroxide was sol–gel obtained from the cohydrolysis of TEOS and zirconia(IV) butoxide. The Pt/SO_4^{2-}(ZrO_2–SiO_2) catalyst was prepared by loading platinum (0.5 wt%) into the dried sulfated oxides, using H_2PtCl_6 in ethanol, i.e. in a non-aqueous solvent in order to prevent the removal of the sulfate ion. The final catalyst was obtained by drying the hydroxides at 383 K for the catalysts were reduced at 673 K during 1 h in hydrogen at a flow rate of 2 ℓ/h. It is important to notice that the activation temperature was chosen the same as the calcination temperature with the aim to avoid losing SO_4^{2-} through the mechanism $5H_2 + SO_4^{2-} \rightarrow H_2S + 4H_2O$. The reaction operation conditions were maintained at LHSV of 11.06 h^{-1}. The *n*-pentane hydroisomerization reaction was performed in a fixed bed flow reactor at different temperatures using a partial pressure of *n*-pentane of 225 Torr. The reaction products were analyzed on line by means of a 585 Tracor Gas Chromatograph equipped with FID using a 60 m SPB-1 fused silica capillary column.

3. Results and discussion

The catalytic activity of metal oxides is known to be strongly dependent on the calcination temperature [10,11]. Also, it has been reported that sulfated silica is a highly active superacid catalyst that quickly deactivates [12]. It can be assumed that Pt/SO_4^{2-}–SiO_2 follows the same behaviour. According to our results, presented in fig. 1, which correspond to a value of more than 95% selectivity towards isopentane, the deactivation of the above system is less pronounced than the one of sulfated silica alone. Furthermore, it can be seen that, when using Pt/SO_4^{2-}(ZrO_2–SiO_2), the deactivation decreases still more. That is, it seems at first glance that Pt stabilizes the deactivation of the SO_4^{2-}–SiO_2 system and this role is in addition played by zirconia in the sulfated mixed oxide leading to a lower deactivation of the catalyst.

Another feature of the Pt/SO_4^{2-}(ZrO_2–SiO_2) system is related with the dependence of its catalytic activity on the zirconia content. At this respect, the results displayed in table 1 show that catalysts supported in sulfated mixed oxides of zirconia and silica improve their catalytic activity in the *n*-pentane hydroisomerization reaction leading to an enhancement in their performance which increases with the content of ZrO_2, reaching a maximum value when the zirconia content is between 10 and 15 wt%. In order to explain these results, it is convenient to see the characterization of these materials as derived from the FTIR analysis of absorbed pyridine and H_2-TPD.

Table 1
Effect of the ZrO_2 content on the catalytic activity of Pt/(SO_4^{2-})–(ZrO_2–SiO_2) at different reaction temperatures

Support (wt% ZrO_2)	*n*-pentane conversion (mol%)		
	T = 200°C	*T* = 250°C	*T* = 300°C
0	2.13	3.05	3.27
5	8.50	8.96	14.42
10	9.36	12.65	16.68
15	10.13	14.85	24.90
20	8.62	9.88	15.63
25	8.52	12.60	19.69
100	9.50	10.16	10.60

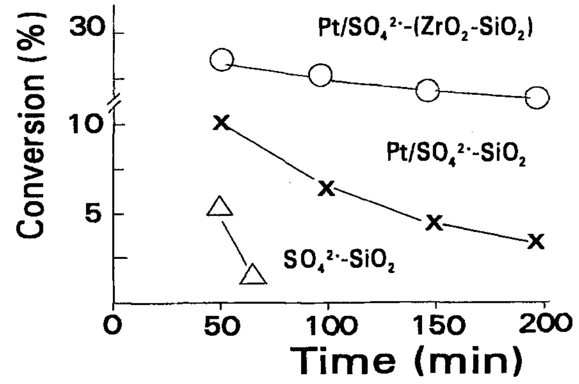

Fig. 1. Deactivation of sulfated catalyst in the *n*-pentane hydroisomerization reaction.

On the one hand, the materials used in this work can be considered as bifunctional catalysts with Lewis acidic surface properties and strong Brønsted sites, as can be seen from the FTIR spectra of absorbed pyridine shown in fig. 2, which were obtained with a Nicolet 710 spectrometer using a self-supported wafer. Accordingly with the above spectra, at 1400 cm^{-1} appears an important signal that only occurs in sulfated materials for which it can be assigned to the stretching of the S=O bond of the sulfate ion. Such a band increases with the desorption temperature indicating that, at lower temperatures, the presence of pyridine inhibits the SO_4^{2-} vibration for which its desorption in vacuum at high temperature activates the vibration associated to the sulfate ion. In consequence, the existence of the sulfate groups gives rise to strong surface Brønsted sites resulting from the activation of the terminal OH's as con-

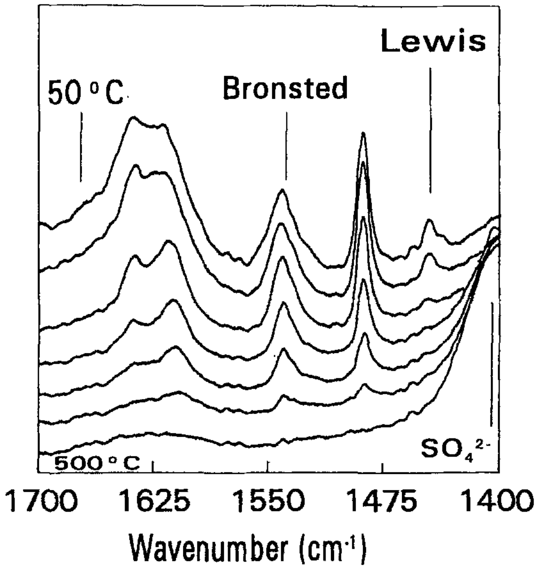

Fig. 2. FTIR spectra of absorbed pyridine in sulfated mixed oxides with a content of 10 wt% zirconia and silica outgassed at different desorption temperatures.

firmed with the band for the pyridinium ion at 1545 cm^{-1} which provides a measure for the Brønsted acid sites. This behavior is different from the well known result that the 1450 cm^{-1} band can be attributed to pyridine coordinatively bound to Lewis sites as well as to pyridine interacting with non-acidic silanol groups in the case of unsulfated samples. That is, in the isomerization case it seems plausible to assume the bifunctionality of these catalysts in such a way that the dehydrogenation–hydrogenation process takes place over the active metallic centers, while the Brønsted acid sites are able to protonate the paraffin in order to liberate molecular hydrogen to obtain the carbenium ion. Also, the Lewis acid sites, still stable at 723 K, can remove the paraffin hydride leading to the carbenium ion which leads to the branched product.

On the other hand, the content of ZrO_2 in the silica matrix modifies the total acidity of the system according to fig. 3, which shows the FTIR integrated absorbance of pyridine at 1490 cm^{-1}. This band is indicative of the total surface acidity in sulfated samples and enlarges with the increase of the metal oxide amount reaching its maximum absorbance at values around 10 wt% of zirconia. Above this stoichiometry, the integral absorbance decreases attaining the reported absorbance values associated with the silica-free metal oxide. This behavior is in good agreement with results from H_2-TPD measurements which were done using an Altamira AMI-3 system under conditions of H_2 (and Ar UHP Linde) adsorption at 303 K followed by thermodesorption up to 773 K (10 K/min) with a flux rate of 30 cm^3/min. That is, according with the results of table 2, relative to the H_2 consumption of the mixed metal oxides as function of the zirconia content, while, if the mixed metal oxide is a solid solution, the H_2 consumption increases with the content of the metal oxide. By contrast, when the content of $ZrO_2 > 15$ wt% the H_2 consumption decreases indicating a segregation of phases of the compound. This split of phases can be explained as follows: the ionic radii ratio avoids the formation of solid solutions at values higher than 10 wt% of ZrO_2 as was verified by means of X-ray diffraction characterization such as shown in fig. 4. That is, the X-ray diffractogram for SiO_2–ZrO_2 corresponds to values of $ZrO_2 > 15$ wt% and clearly contains separate information on silica and zirconia denoting in this case segregation of phases; the other two spectra are associated with compounds containing 0 and 10 wt% of ZrO_2, respectively. That is, according with Kingery [13], if the sizes of two ions differ by less than about 15%, conditions are favorable for the formation of substitutional solid solutions. In our case, this means that over 10 wt% of ZrO_2 a segregation of the separate oxides takes place giving rise to compounds with catalytic activities lower than the one found in materials without segregation. In fact, according to the H_2-TPD profiles given in fig. 5 a H_2 absorption signal clearly appears in the sulfated samples that do not contain Pt, which means that the sample with Pt contains both pieces of information: adsorption of Pt and adsorption of Zr and, by consequence, improved performance.

Table 2
Consumption of H_2 as function of the ZrO_2 wt% content

ZrO_2 wt% content	H_2 consumption (μmol/g-cat)
0	3.89
5	34.91
10	40.75
15	59.10
25	25.47

In summary, the enhanced catalytic properties of platinum are improved by using a sulfated mixture of silica and zirconia as support. This is due to the fact that the new system can be considered as a bifunctional catalyst with enlarged acid surface properties that come from the sulfation process as well as the existence of two metals that are able to absorb H_2. However, it is necessary to avoid compounds with a zirconia content higher than

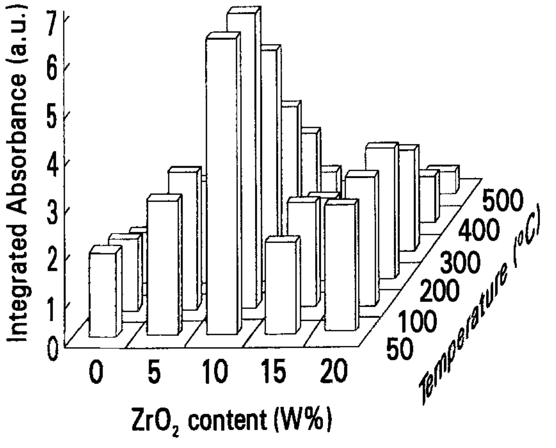

Fig. 3. Integrated absorbance of the pyridine FTIR band at 1490 cm^{-1} indicative of the total surface acidity in sulfated samples as function of the ZrO_2 content and temperature desorption.

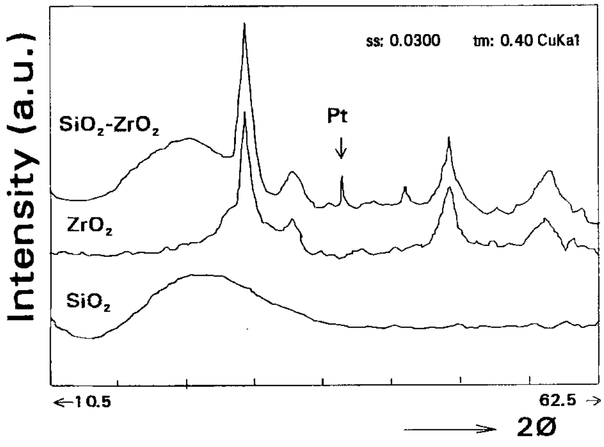

Fig. 4. X-ray diffraction spectra of Pt sulfated catalyst with different content of ZrO_2–SiO_2.

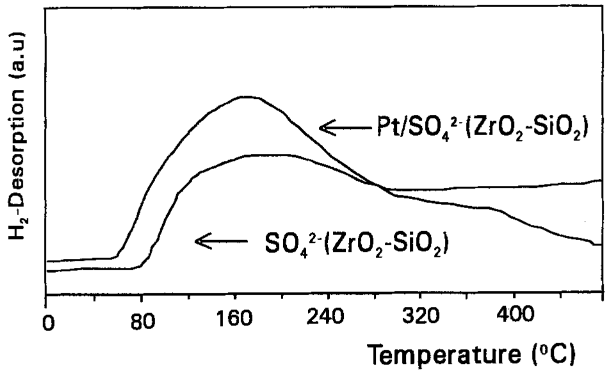

Fig. 5. H_2-TPD measurements of sulfated mixed oxide supports of zirconia silica with and without Pt.

about 15 wt% in order to prevent a segregation of phases in the support because this percentage corresponds grosso modo to the limit below which solid solutions are maintained, as shown from the X-ray diffraction characterization as well as inferred from H_2-TPD measurements.

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