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Effects of the precursor features and treatments on the catalytic performance of SO_4/ZrO_2

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SO_4/ZrO_2 powders, showing different phase compositions, have been coupled with a traditional catalyst in Fischer–Tropsch synthesis (FTS) to convert synthesis gas to branched hydrocarbons. The isomerization efficiency, introduced by the doped oxide, was measured as a function both of the calcination temperature of the treated zirconia precursor and of the concentration of the H_2SO_4 used in the sulphation. Determinations of the actual acidity pK_a and density of the oxide surface sites have been obtained by a revised Hammett–Bertolacini technique and the results are cross-compared with the catalytic data. XPS spectra of Zr 3d are discussed in respect to the conditions of the powders preparation and their phase composition. A relation between the isomerization efficiency and the pattern of Zr 3d XPS spectra is apparent. The results of the different characterisations are discussed with regard to one another and to literature data.

Keywords: sulphated zirconia, isomerization catalyst, superacid powders

1. Introduction

In recent years SO_4-doped zirconia powders have attracted great interest as strong acid catalysts for isomerization, acylation and esterification reactions [1–15]. These compounds are active in hydrocarbon conversion at temperatures lower than most of the generally used solid acid catalysts. In respect to zeolite, sulphated zirconia allows the same hydrocarbon conversion level to be obtained at temperatures from 100 to 200°C lower. This fact, besides reducing energy consumption, significantly favours isomerization over cracking [16,17].

The literature concerning both fundamental and applicative aspects of sulphated zirconia is very ample and often controversial. The catalytic performance of SO_4/ZrO_2 powders is reported to depend on several factors, mainly on the temperature and sequence of the powders calcination and on the nature and concentration of the sulphating agent [18,19].

The powders activity is generally found to increase with the temperature of calcination up to a maximum which occurs in a rather wide range between 550 and 750°C, but is, more frequently, centred around 550–630°C; the catalytic efficiency is not a simple function of the concentration of the sulphating agent although it is higher for samples treated with sulphuric acid than for the ones treated with sulphate salts [18–24].

The above mentioned effects of temperature and concentration are not totally independent of one another as they both affect the sulphur content of the particles, this being, in its turn, related to the catalytic activity [19]. Several authors report that maximum efficiency occurs in correspondence of a monolayer coverage of ZrO_2 by sulphates but large debate exists about the actual acid nature, either purely Lewis or Lewis–Brønsted, of the catalytically active sites [19,20,23].

Other aspects appear to be controversial in the literature or need better clarification. For example, Yamaguchi et al. [15] report that the catalytic performance of the oxides is more affected by the presence of the tetragonal polymorph than by the sulphur content. On the other hand other authors [21,22] report that samples, treated with H_2SO_4 after the calcination, although being purely tetragonal, strongly acid and with high sulphur content, are totally inactive catalytically.

In order to bring some further evidence concerning the above debated points, in this paper, we report results relative to the isomerization efficiency, acid characterisation and surface chemical state of SO_4/ZrO_2 powders as a function of the calcination temperature and the H_2SO_4 concentration used in the treatment. The samples were obtained from precursors prepared by different procedures but aimed in any case at producing oxides (in the absence of sulphate treatment) not only composed of tetragonal polymorphs.

2. Experimental

All the chemicals were of reagent grade purity and were used without further purification; doubly distilled water passed through a Milli-Q apparatus was used to prepare solutions and suspensions.

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2.1. Sample preparation

ZrO_2 powders were prepared by calcining for 5 h at 470, 600 and 700°C hydrous zirconia precursors obtained following a previously reported pathway [25,26] which implies the hydrolysis, at the boiling point, of $ZrCl_4$ acid solutions, by KOH dropwise additions (about 60 drops/min) under vigorous stirring. The pH of the suspension was never raised over pH = 7.0–7.3 during the reaction. The final product purified by centrifugation/resuspension and dialyses was dried, calcined and stored as a powder (samples A). The phase composition of these precursors, in absence of any H_2SO_4 treatment and calcined for 5 h at 470°C, was a mixture of metastable and monoclinic polymorphs (roughly about 1 : 1 M/T).

A second series of samples (samples B) was prepared by following the procedure reported by Clearfield [27] which essentially consists in a room temperature, fast precipitation at acid pH (never higher than 2.5) of an hydrous precursor, by NH_3, from $ZrCl_4$ solutions, followed by prolonged refluxing of the suspension (96 h). Purification, calcining and storage as for samples A. By X-ray diffraction these samples, calcined at 470°C and in absence of H_2SO_4 treatment, resulted to the purely monoclinic.

Both precursors were treated with H_2SO_4 at different concentrations (in the range 1 M–5×10^{-2} M) by equilibration of the powders in the solutions at room temperature and under stirring for 1 h, keeping the powder weight/solution volume ratio constant in the different experiments. The solids were then filtered, dried at 100°C and successively calcined at the given temperature for 5 h. Structurally the calcined and treated A samples were mainly composed of the metastable polymorphs, although the occurrence of traces of the monoclinic phase, in the case of samples treated at the lower H_2SO_4 concentration and temperature, could not be excluded. In the case of the B samples the phase was in any case purely monoclinic, the H_2SO_4 treatment provoking only a drastic decrease of the degree of crystallinity.

2.2. Sample characterisation

All the zirconia powder characterisations refer to “fresh”, as-prepared samples.

The specific surface area was determined by the classical BET procedure using a Sorptomatic Carlo Erba apparatus.

X-ray photoelectron spectra were taken in an M-probe apparatus (Surface Science Instruments). The source was monochromatic Al Kα radiation (1486.6 eV). A spot size of 200×750 μm and a pass energy of 25 eV were used. The energy scale was calibrated with reference to the $4f_{7/2}$ level of a freshly evaporated gold sample, at 84.00 ± 0.1 eV, and with reference to the $2p_{3/2}$ and 3s levels of copper at 932.47 ± 0.1 and 122.39 ± 0.15 eV, respectively 1s level hydrocarbon-contaminant carbon was taken as the internal reference [28] at 284.6 eV. The accuracy of the reported binding energies (BE) can be estimated to be ± 0.2 eV. With a monochromatic source, an electron flood gun is required to compensate the build up of positive charge on the samples during the analyses, when insulating samples are analysed: a value of 3 eV has been selected.

The surface acidity features of the samples were determined by a modification of the Hammett–Bertolacini technique [29,30]. This method relies on a selective adsorption of dye molecules, with different pK_a values, on the oxide surface. The operative techniques essentially consist in successive colorimetric titrations of the oxide suspension in benzene under N_2 bubbling and stirring. The titrant was a 0.1 N *n*-butylamine solution added dropwise by a microsyringe into the vial which was tightly protected from any contact with atmospheric moisture.

2.3. Catalytic tests

The isomerization efficiency of the zirconia samples was investigated by coupling them with a classical FTS catalyst to obtain directly branched hydrocarbons from synthesis gas [11]. Each run was performed with a “fresh” amount of both the catalyst components to avoid effects due to deactivation. Reaction tests were performed in a stainless steel tubular reactor, coated with copper, designed especially for Fischer–Tropsch synthesis of hydrocarbon (C_n: $n < 15$) and described elsewhere [31]. The reaction was performed with a mixture of high-purity CO and H_2 (SIAD) (the H_2/CO molar ratio of the inlet mixture was 2), at 548 K, 500 kPa and a space velocity of 9.0×10^{-2} mmol-CO/(mmol-Ru s). The catalyst was loaded in two separate layers in the reactor, first 0.8 g of Ru 1% Al_2O_3 and then 0.2 g of SO_4/ZrO_2 placed at the end of the catalytic bed after the conventional catalyst, thus the mainly linear hydrocarbons generated on the FTS catalyst would isomerize on the acid catalyst before leaving the reactor. A blank test using only SO_4/ZrO_2, carried out under the same conditions, gave no conversion, implying that only the FTS catalyst was responsible for CO conversion. The catalytic performance was evaluated by using on-line gas chromatography and by GC-MSD for the C_4 fraction [32]. Particularly the iso-C_4 conversion of the samples in respect to the traditional catalyst was studied; the efficiency was calculated as iso-$C_4/C_{4\,\mathrm{tot}}$ ratio.

3. Results and discussion

Deactivation of SO_4/ZrO_2 catalysts during isomerization reactions is reported to occur in the literature [2,18,23]. In the present case each catalytic test (performed in any case with a “fresh” amount of both catalysts) was followed for 24 h and during this time no deactivation of the catalysts was appreciable, the efficiency conversion keeping a steady-state plateau value. In order to allow consistent comparison between the catalytic performance and the powder features, all the catalyst characterisations in the following refer to "fresh", as-prepared samples.

Figure 1 reports the isomerization efficiency of the sulphated zirconia powders (samples A) as a function of the calcination temperature of the treated hydrous zirconia precursor. The oxide calcined at the lower temperature (470°C) shows the higher activity; a sharp decrease occurs upon firing at 600°C and the efficiency reduces to zero for the 700°C sample. The decreasing trend of the catalyst efficiency apparent in figure 1 is at variance with the major part of literature data which show, upon increasing the firing temperature, first an increase of the activity up to a maximum (centred in a broad range, 550–720°C, but generally higher than 470°C) and subsequently a decrease [18–24].

The decreasing trend in figure 1 finds direct support from the observation of the acidity features of the samples reported in figure 2. The pK_a values of the surface sites decrease (become less acid) significantly in passing from 470 to 600°C while no further decrease appears between 600 and 700°C. The total site densities, which have been reported per unit gram in order to better reflect the catalytic procedure conditions, embed also the decrease in specific surface area ensuing the thermal treatment and show a continuous decrease with the temperature. In the light of data in figures 1 and 2 it could be said that the intrinsic acid strength of the surface sites and the site densities play a synergetic role in affecting the isomerization performance of the powders; the comparison between the 600 and 700°C samples shows that the sole reduction of the site density is sufficient to produce definite depression of the powders catalytic efficiency.

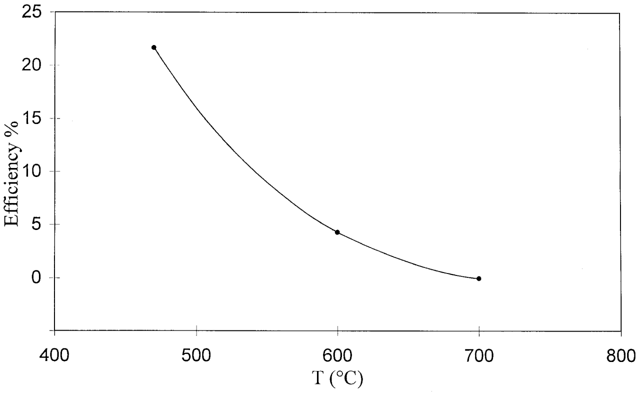

Figure 1. Isomerization efficiency of samples A, treated with 0.5 M H_2SO_4, as a function of the calcining temperature. The values of the percent efficiency have been calculated from the ratios between the relative iso-C_4/C_4 amounts (by gas-chromatography) and fixing at zero the "traditional" FTS catalyst activity.

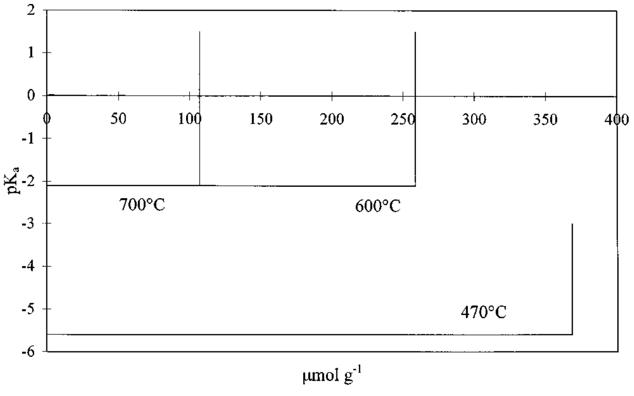

Figure 2. Dependence of the acid features (pK_a, site densities) of samples A, treated with 0.5 M H_2SO_4, on the calcining temperature.

A lowering of the acidity of sulphated zirconia samples, with increasing the firing temperature, has been reported previously [14,19,23]. As a general rule, the increase in the firing temperature provokes a lowering of the sulphur content of the oxide. To this end, Parera et al. [23] suggest that the maximum in the activity vs. temperature curve is the result of a balance between the decreasing sulphur content and the progressive dehydration of the surface yielding catalytically active Lewis acid surface sites. This seems not to apply to the present case. Apparently other factors, as surface structure-faceting, related to the phase composition of the untreated precursor, may superimpose their effect on the "classical" parameters ruling the material performance.

The dependence of the isomerization efficiency on the H_2SO_4 concentration (used in the treatment) is reported in figure 3. The variation of the acid concentration of one order of magnitude (from 5×10^{-2} to 0.5 M) does not introduce significant modifications in the catalyst activity while it almost doubles for 1 M H_2SO_4 concentration. The absence of marked effects of the catalytic activity for acid concentrations between

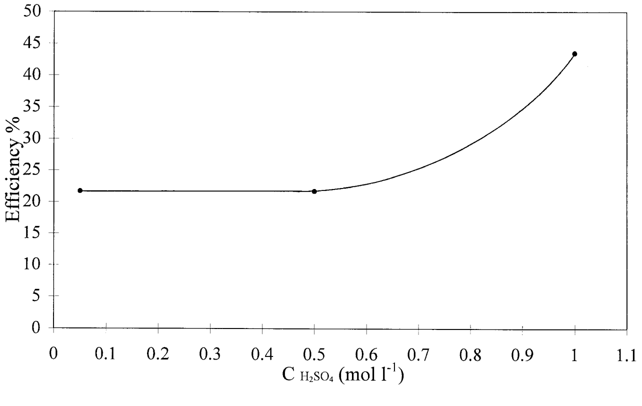

Figure 3. Isomerization efficiency of samples A, calcined at 470°C, as a function of the H_2SO_4 concentration used in the treatment.

5×10^{-2} and 0.5 M has been reported previously by Arata [12], the catalyst showing also the same sulphur content. Nascimento [19] reports that when monolayer coverage of ZrO_2 with sulphates is reached no further increase in the activity is observed. As a matter of fact also in the case of samples previously obtained, in our laboratories, by following the same procedure of the present ones the sulphur coverage reached a plateau for concentrations of about 10^{-2}–5×10^{-2} M [33,34]. The definite enhancement produced by the increase in acid concentration up to 1 M is instead less expected and in partial disagreement with some literature results. In fact consistently with the above mentioned considerations relative to the absence of catalytic improvement after the monolayer coverage, Morterra [20] concludes that at high coverage, Brønsted acid sites prevailingly form, these sites being ineffective catalytically.

The acid characterisation of the powders reported in figure 4 can bring some insight into the argument. As observed in the case of figure 2 the two acid parameters, intrinsic acidity and site density, play a parallel and synergistic role. The pK_a values of the sites increase with the acid concentration. The site density of the 5×10^{-2} M samples is, however, almost twice the one of the 0.5 M samples. The intrinsic acidity of the sites of the 5×10^{-2} M catalyst is lower than the one of the 0.5 M sample but the almost double site density apparently makes it efficiency fully comparable with the 0.5 M sample. The isomerization reaction is apparently not severely selective in respect to the energetic interactions with the catalyst. The 1 M sample shows both strongly acid sites, with a broad energy distribution, and also a much higher density of sites in respect to the other samples. The very low (acid) values of the pK_a suggest strong interactions between H_2SO_4 and ZrO_2 to take place in the case of the 1 M samples. These observations, although fully congruent with the trend in figure 3, seem to be somewhat at variance with the literature conclusions that for acid concentrations exceeding the monolayer coverage the interactions could be looser and yielding thermolable sulphur species [20,35].

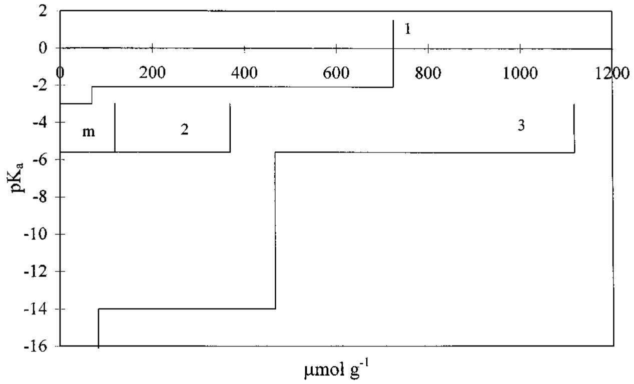

Figure 4. Dependence of the acid features of samples calcined at 470°C, on the H_2SO_4 concentration used in the treatment (1, 2, 3) Samples A, treated respectively at 5×10^{-2}, 0.5 and 1 M. "m" refers to sample B treated with 0.5 M H_2SO_4.

Independent evidence on the nature of the oxide–sulphate interactions can be found from the comparison of XPS spectra of ZrO_2 samples both H_2SO_4 treated and untreated. Figure 5a, relative to an untreated A sample, shows the regular Zr 3d doublet, with BE values in agreement with literature data for Zr(IV) in the oxide [36–38]. Upon treatment with H_2SO_4 the peak becomes broad and complex and a one-component curve-fitting yields no acceptable results. This effect has been observed previously to occur in the case of treated metastable, tetragonal and cubic (if any), zirconia polymorphs while it was absent in the case of the treated pure monoclinic samples [34]. The peaks of figures 5b and 5c (0.5 M, 1 M H_2SO_4) are best fitted by assuming the presence of two zirconium(IV) components. The BE of the lower energy component is in the range of Zr(IV) in ZrO_2 while the higher energy component corresponds to the formation of a Zr(IV) species bound to a more electron attractive species, although being not relative to a $ZrSO_4$ species [34,39]. From the figure the definitive increase of the intensity of the higher energy Zr(IV) component for the 1 M H_2SO_4 treated sample (figure 5c) can be immediately appreciated. Very interesting observations result

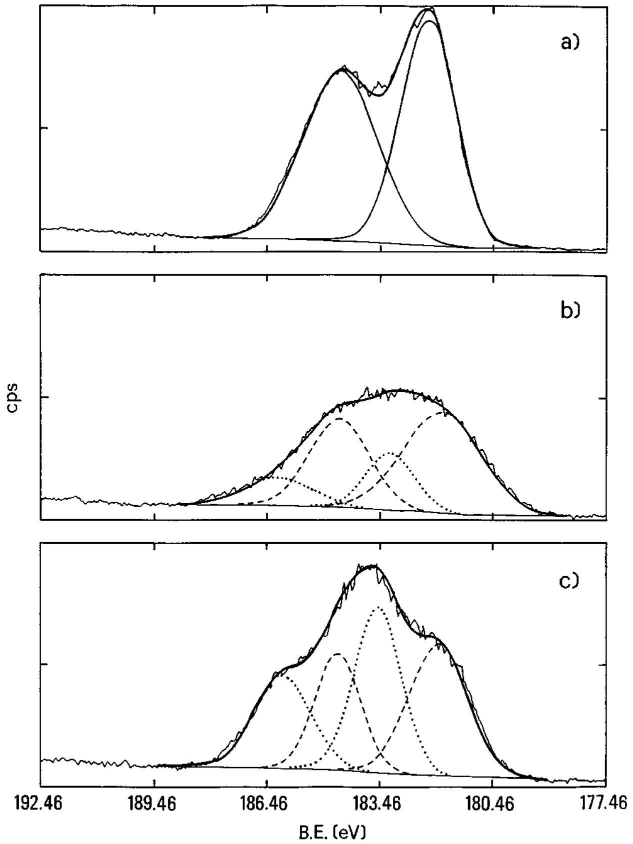

Figure 5. XPS spectra of the Zr 3d doublet of samples calcined at 470°C. (a) Untreated sample A, (b) sample A treated with 0.5 M H_2SO_4, (c) sample A treated with 1 M H_2SO_4.

Table 1
Atomic ratios of the Zr(IV) and S spectral components

	$Zr(IV)_{tot}/S$	$Zr(IV)_{ox}/ZrSO_4$ [a]	$Zr(IV)_{SO_4}/S$ [a]
Sample B1, 0.5 M H_2SO_4	3.9	3	1
Sample B2, 1 M H_2SO_4	4.2	1	2

[a] $Zr(IV)_{ox}$ = lower energy Zr(IV) component, $Zr(IV)_{SO_4}$ = higher energy Zr(IV) component.

from the analysis of the atomic ratios of the Zr(IV) spectral component reported in table 1.

The $Zr(IV)_{tot}/S$ can be considered to be invariant with the H_2SO_4 concentration, in agreement with the literature results. The ratio between the two Zr(IV) components, instead, undergoes deep variation, the $Zr(IV)_{SO_4}$, component increasing sharply. This increase is reflected in the parallel value of the $Zr(IV)_{SO_4}/S$ ratio, which doubles for the 1 M H_2SO_4 sample. The above reported data suggest that although showing a constant sulphur content, the 1 M H_2SO_4 samples present a higher density of the "doped sites" due to a variation in the stoichiometry of the Zr–SO_4 surface sites. These conclusions are fully congruent with the data in figure 4 which showed a definitive increase of both the sites densities and of the pK_a values (absolute data) upon 1 M H_2SO_4 treatment.

Catalytic tests have been performed also coupling samples of pure monoclinic ZrO_2 powders (samples B). The isomerization efficiency over the traditional FT catalyst was found to be zero. The absence of catalytic activity of monoclinic samples is in agreement with literature results which report that the catalytic efficiency is improved by increasing contents of the tetragonal component [15]. The acidity data in figure 3 show that the site density is very low (comparable with the one of the 700°C sample) although the pK_a values show a relatively high acid strength. No effect on the XPS spectra of Zr 3d doublet was observed.

4. Conclusions

SO_4/ZrO_2 samples prepared by precipitation at the boiling point from $ZrCl_4$ acid solutions, by KOH, purified, dried and treated with H_2SO_4 at different concentrations, have been calcined at 470–600 and 700°C respectively. All the oxides have been tested for the isomerization efficiency by combining them with a classical Fischer–Tropsch catalyst.

The trend of the catalytic performance as a function of both the temperature of calcining and the H_2SO_4 concentration is closely reflected by the relative dependencies of the "acid" parameters of the samples, pK_a values and site densities. By increasing the temperature the samples show a decrease of the catalytic efficiency and a congruent decrease of the (absolute) pK values and site densities. The effects of the H_2SO_4 concentrations are less forward. For concentrations between 0.05 and 0.5 M no appreciable effects on the catalytic activity are observed while a variation of the sites pK is compensated by an opposite effect on the site densities. For 1 M H_2SO_4 concentrations a definite increase in both catalytic activity and acid features is observed.

XPS determinations performed both on the untreated and on 0.5 and 1 M treated samples, show the occurrence of a second Zr(IV) component in the Zr(IV) doublet, at higher binding energies in respect to Zr(IV) in the oxide. The analysis of the atomic ratio of the elements and of the Zr(IV) doublet components allow considerations on the site stoichiometry to be made.

The isomerization efficiency of 0.5 M H_2SO_4 treated monoclinic samples was found to be zero. The samples showed intermediate pK values and very low site densities. No effect of the sulphur treatment was observed in the XPS Zr(IV) spectrum.

The actual isomerization performance of the ZrO_2–SO_4 samples appears to be the result of a delicate interplay between precursor preparation conditions, its structure, and temperature and acid concentration. The catalytic efficiency is mirrored by the acid features of the samples; the appearance of a second Zr(IV) component in the XPS Zr(IV) spectrum seems to reflect the formation of catalytically active species.

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