Liquid phase reactions catalyzed by Fe- and Mn-sulphated ZrO$_2$

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ABSTRACT

Fe- and Mn-promoted ZrO$_2$–SO$_4$ (ZS) powders were prepared both by a single step sol–gel reaction and by impregnation of the zirconia hydrous precursor. The samples were calcined at 890 K and characterized for the structural (XRD) and morphological features (BET method). Surface functionalities were investigated by XPS, ^{1}H MAS NMR and FTIR analyses. The liquid medium catalytic activity was tested with respect to both the esterification of benzoic acid to methylbenzoate and the benzylation of toluene. The acidity features appeared not to be significantly different among the various samples while all surface characterizations showed a lower affinity to retain water by the metal-promoted samples with respect to ZS, the more so in the case of iron-containing samples. The presence of Mn reduced the surface area and depressed the catalytic activity. Iron-doped catalysts appeared, instead, to be more efficient than ZS especially for the benzylation of toluene.

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1. Introduction

Sulphated zirconia (ZS) has attracted great interest as solid acid catalyst for low temperature alkane isomerization and also for other acid catalyzed processes like alkylation and esterification reactions [1–17].

It was also shown that the activity and stability of ZS could be improved by the addition of transition metal promoters, mainly Fe and Mn cations. Hsu et al. [18] reported that Fe- and Mn-promoted sulphated zirconia catalysts have more numerous and stronger acid sites than ZS and that the activity for butane conversion is improved by one to two orders of magnitude. The promoter effect has been confirmed by several groups [19–28] and Mn was generally reported to be a more effective promoter than Fe [29]. The actual role played by the metals in promoting the isomerization reaction is yet not fully clarified and controversial hypotheses are present in the literature. Adeeva observed no actual difference in the acid features of promoted sulphated zirconias with respect to unpromoted materials [20]. Recent results [30,31] support Adeeva et al. conclusions; Vedrine and co-workers [31] show that the acid strength of Fe- and Mn-promoted samples is somewhat smaller than that of unpromoted ZS and that the Fe-promoted samples present a higher proportion of Lewis sites with respect to unpromoted and Mn-promoted ZS. Other authors [32], instead,

found by ^{31}P MAS NMR a pronounced increase in both concentration and strength of acid sites in the case of Fe-promoted catalysts.

Several authors suggest that the alkane reaction may not be entirely acid catalyzed and that, in the case of promoted zirconias a bifunctional mechanism based on a metallic redox site and an acid site in close proximity takes place [33,34]. Jentoft and co-workers [35] conclude that the promoters enhance the oxidation potential of the sulphate and thus facilitate initiation of the reaction via oxidative dehydrogenation.

Hino and Arata [36] observed that Mn- and Fe-promoted ZS were much more active than unpromoted catalysts for the reaction of butane to isobutane and reported a key role played by the conditions of preparation of the catalysts. Specifically the features of the zirconia gel, of the metal salt solution concentration and of the temperature of the final annealing step were observed to affect the final performance of the catalysts.

The literature discussion concerning the catalytic activity of Fe- and Mn-promoted ZS catalysts is mainly relative to alkane isomerization reactions. To the authors' best knowledge only two papers are present in the literature concerning the activity of Fe- and (in one case) Mn-promoted ZS with respect to a reaction performed in liquid phase [31,37]. In the article by Vedrine et al. [31] the esterification of acrilylic acid with but-1-ene is catalyzed by Fe- and Mn-promoted ZS. The main result is that Mn and Fe do not improve either the acidity or the activity of the catalysts but they strongly improve the catalyst resistance to deactivation. In the paper by Suja et al. [37], instead, the liquid phase benzylation of toluene over iron-promoted ZS is investigated. In this case the

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authors observe both an increase in the acid strength of the catalysts and also a progressive increase in the conversion with increasing the iron content of the catalysts.

In this work we report on the activity of Fe- and Mn-promoted ZS catalysts, with respect to two different reactions performed in liquid phase, the esterification of benzoic acid with methanol and the benzylation of toluene by benzylic alcohol. The two reactions are performed in very different conditions (temperature, reagent concentrations, reaction medium, etc.) in order to possibly highlight the role played by the catalyst features, independently of the specificity of the liquid phase process.

A relevant aspect of the present work concerns the catalyst synthesis. Two different routes have been adopted to introduce the promoters: the first one follows the common procedure adopted in the literature and consists in the impregnation, by incipient wetness, of the zirconia hydrous precursor with the iron (III), manganese (II) and $(NH_4)_2SO_4$ salt solutions followed by the calcination. By the second route the catalysts are synthesized directly by a sol–gel procedure through a one-pot reaction in which metal salts and sulphates are directly added to the starting reaction mixture. The xerogel is then submitted to the calcination step. No result could be found, in the literature, concerning a one-pot sol–gel synthesis of metal-promoted ZS catalysts. The sole result in which the promoter is added directly to the synthetic mixture of ZrO_2 is the procedure reported by Pereira et al. in which $ZrOCl_2$ and iron nitrate are simultaneously hydrolyzed by NH_3 [21].

The structural features of the present products are investigated in detail since the possible incorporation of lower valence cationic species in the ZrO_2 lattice may bear relevance to the actual role played by the metals on the reactivity of the catalysts. The acidity features of the samples are analyzed by both FTIR and ^1H MAS NMR. XPS analyses are performed to obtain indications on the surface features of the catalysts.

2. Materials and methods

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

2.1. Sample preparation

The zirconia hydrous precursors were prepared by a sol–gel method by using zirconium *n*-propoxide, $Zr(OPr)_4$, as the reagent, and adopting water/alkoxide, i-PrOH/alkoxide and HNO_3/alkoxide molar ratios, respectively of 30, 15 and 0.21. Two different procedures were adopted to add the Fe, Mn metal promoters (from $Fe(NO_3)_3$ and $MnSO_4$ salts) and the sulphating agent $((NH_4)_2SO_4)$: (a) directly during the sol–gel synthesis (one pot) and (b) by impregnation through incipient wetness of the zirconia hydrous precursor, with a single solution, containing both the metal salts and the sulphating agent. By both procedures the promoter and the sulphate content were, respectively 3 and 15 mol%. The gels were dried as xerogels at 353 K at atmospheric pressure for 15 h. The xerogels were all calcined at 893 K for 5 h in an oven under an oxygen flux.

A reference ZrO_2 (no metals, no sulphate, named Z) sample was also obtained for the sake of comparison.

2.2. Sample characterization

Specific surface areas and pore volume distribution were determined by the classical BET procedure using a Coulter SA 3100 apparatus.

X-ray diffraction (XRD) patterns were collected on a Rigaku PMG powder diffractometer using Cu Kα radiation. The selection of narrow slits (Soller: 2°; DS: 1°; RS: 0.15 mm; AS: 1°), and the use of a graphite bent-crystal analyzer are such to produce a relatively narrow (full width at half maximum ~0.04° at 30° 2θ) and symmetrical instrumental peak profile throughout the entire range of analysis. For all studied samples, powder patterns were collected with a counting time of 30 s for each a 0.05° step [38].

XPS analyses were obtained using an M-probe apparatus (Surface Science Instruments). The source was monochromatic Al Kα radiation (1486.6 eV). A spot size of 200 μm × 750 μm and a pass energy of 25 eV were used. 1s level hydrocarbon-contaminant carbon was taken as the internal reference at 284.6 eV. The accuracy of the reported binding energies (BEs) can be estimated to be ±0.2 eV.

^1H MAS NMR spectra were recorded with a Bruker Avance 500 spectrometer equipped with a 4 mm magic angle spinning (MAS) broad-band probe (spinning rate ν_R up to 15 kHz), at a temperature of 300 K and 5 kHz of spinning. The standard zg and solid-echo Bruker software sequences were used. ^1H MAS spectra were recorded on solid samples, typically 0.15 g, which have been pretreated at 600 K under vacuum for 3 h and stored under vacuum for the exclusion of moisture. Each sample was packed into a 4-mm MAS rotor (50 μl sample volume) and spun at 5 kHz at a temperature of 300 K.

FTIR spectra were obtained at 2 cm^{-1} resolution with a Bruker 113v spectrophotometer equipped with a MCT cryodetector. All samples were inspected in the form of thin-layer deposition ($\sim$10 mg cm^{-2}) on a Si platelet starting from an aqueous suspension. Before being inspected, all samples were activated at the desired temperature in a quartz cell (equipped with KBr windows) connected to a conventional vacuum line (residual pressure $p < 10^{-5}$ Torr, in order to perform strictly *in situ* adsorption/desorption experiments).

2.3. Catalytic tests

Details of experimental procedures of the catalytic reactions of both benzylation of toluene and esterification of benzoic acid have been reported previously [16,39].

The reaction of toluene with benzylic alcohol (BzOH):
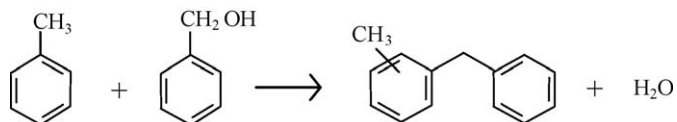
is known to produce dibenzylether as an abundant and undesired byproduct.

In the present case the benzylation of toluene by BzOH was studied at 353 K, with $C_0^{BzOH} = 0.07$ mol/L; $C_0^{TOL} = 1.6$ mol/L; $C^{cat} = 5$ g/L. Due to the large excess of toluene ($C_0^{TOL}/C_0^{BzOH} = 23$), this hydrocarbon was considered to have an approximately constant $C^{TOL} (= C_0^{TOL})$ during the runs. The reaction was performed in cyclohexane.

Gas chromatographic analysis was performed on a HP5890 series II apparatus with a capillary HP-5 column, 30 m long, 0.32 mm i.d., 0.25 mm film, operated at temperatures from 40 to 280 °C, observing the already reported retention times [39].

The esterification reaction of benzoic acid to methylbenzoate:
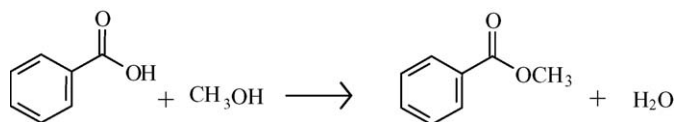
is an equilibrium one and the temperature of the process was fixed at 433 K in order to shift the equilibrium to the products, by the continuous distillation of the water produced during the