Liquid phase reactions catalyzed by Fe- and Mn-sulphated ZrO2

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Fe- and Mn-promoted sulphated ZrO$_2$ as liquid phase catalysts

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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 FT-IR 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 benzylolation of toluene.

**Keywords:** metal promoted sulphated zirconia; liquid media catalyst; surface functionalities; structural characterizations; $^1$H MAS NMR.

**Introduction**

Sulphated zirconia (ZS) has attracted great interest as solid acid catalyst for low temperature alkane isomerization and also for other acid catalized 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 1-2 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 un-promoted materials [20]. Recent results [30,31] support Adeeva et al. conclusions; Vedrine et al. [31] show that the acid strength of Fe and Mn promoted samples is somewhat smaller than that of un-promoted 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 et al. [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 un-promoted 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 acrylyc 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 benzylolation of toluene over iron promoted ZS is investigated.
In this case the 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 (NH₄)₂SO₄ 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 ZrO₂ is the procedure reported by Pereira et al. in which ZrOCl₂ and iron nitrate are simultaneously hydrolyzed by NH₃ [21].

The structural features of the present products are investigated in detail since the possible incorporation of lower valence cationic species in the ZrO₂ lattice may bear relevance to the actual role played by the metals on the reactivity of the catalysts.
acidity features of the samples are analyzed by both FTIR and $^1$H MAS NMR. XPS analyses are performed to obtain indications on the surface features of the catalysts.

2. Experimental 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$_4$)$_2$SO$_4$): 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: 0.15mm; 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 × 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 (BE) 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 vR 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.

FT-IR 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 (~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]. Briefly, 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.

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 reaction [16]. As the boiling point of methanol is 338 K, the operative way may be described as a modified “batch process”, where the reagents are put altogether in the reactor and methanol is continuously added and taken off by distillation together with water. The amount of 5 g/L of catalyst was added into the reactor, and samples of 5 ml of the reaction mixture were picked up to test the catalytic performance as a function of the reaction time.

3. Results

3.1 Morphological, structural and XPS characterizations

The specific surface areas of the present samples are reported in Fig. 1a. The addition of iron provokes only a slight increase in the extension of the surface area with
respect to un-doped ZS, only in the case of impregnated sample, while the presence of Mn provokes a decrease in surface area up to about 20% for the sol-gel, “one pot” sample. Literature data [35] report that iron promoted ZS show a larger surface area while the addition of Mn produces a slight depression with respect to ZS. Pereira et al. [21] report for a different synthetic route that sulphated iron zirconia samples did not show significant changes in the specific surface area as compared to iron free samples.

All the present samples are mesoporous (Fig. 1b); the presence of Mn leads to a larger total pore volume especially for the pore sizes in the range 6<d<20 nm.

Experimental X-ray diffractograms of all samples were elaborated by the Rietveld method (using the TOPAS® v. 3.0 software (Bruker AXS GmBH - Germany)) to obtain structural parameters (Tab. 1). The phase composition (columns 2 and 3) changes from a mixture of monoclinic (M) and tetragonal (T) polymorphs in the case of untreated zirconia (Z) to pure tetragonal for ZS and one-pot metal promoted samples. The effect provoked by sulphates on the phase composition of nanocrystalline zirconia is well documented in the literature [16], the tetragonal phase being stabilized by the reduced size of the crystalline domains. The addition of metals does not, as a rule, affect the structural phase of ZS [32], as for the present one-pot catalysts. In the case of the impregnated samples, instead, appreciable fractions of monoclinic phase are observed, and increase passing from ZSFe_imp to ZSMn_imp.

The analysis of the diffraction profile was performed by Whole Powder Pattern Modelling (WPPM) [40,41], assuming the presence of spherical crystalline domains, with a lognormal distribution of the diameters. A secondary contribution to line broadening due to lattice distortions was also considered, including the effect of dislocations in the primary slip system of fluorite-type structures ([001]<110>). Details
for calculating the anisotropic line broadening effects of dislocations can be found elsewhere [42]. Figures 2 and 3 show, respectively the result of the modelling for sample ZSMn and the corresponding lognormal size distribution. For all samples both the mean diameter ($<D>$) and the volumetric average size (actual domain size, $<D>_v$) i.e. Scherrer size, are reported in columns 4 and 5 of Tab.1. In the case of iron doping (both one-pot and impregnated samples) the domains are slightly smaller than in ZS and Mn doped samples, and possibly show a larger component due to lattice distortions. Dislocations density of $8\times10^{15}$ and of $2\times10^{15}$ m$^{-2}$ were obtained, respectively in the case of Fe and Mn doped one-pot samples. Line defects may easily originate as growth defects, as well as a result of point defects coalescence, like oxygen vacancies balancing the presence of Fe and Mn ions.

The cell volumes of the various samples are reported in column 8 of Tab. 1. It can be observed that in the case of the iron doped samples the unit cell shrinks with respect to both ZS and Mn promoted samples, the more so in the case of the impregnated samples. The shrinkage of the unit cell has been reported previously in the literature [29], in the case of Fe and Mn promoted ZS, and was interpreted as the result of the incorporation in the lattice of metal cations with different sizes and charges. The observed shrinkage of unit cell, more appreciable in the case of iron-promoted samples, can be considered as a different evidence of the larger dislocation density, reported above.

Survey XPS spectra were recorded for all samples. No significant presence of impurities was observed, except for the ubiquitous carbon contaminant. In the case of the latter element, only the C 1s peak at 284.6 eV (due to –CH– species) was present. The peak of the Zr 3d doublet was found to be in any case regular with BE values
(182.2–184.6 eV) consistent with literature data relative to Zr(IV) species in the oxide phase [2,6]. The distortion of the Zr 3d peak introduced by the presence of the metals reported by Vedrine et al. [31] was not observed for any of the present samples.

The spectrum of S 2p was never intense, due to the low intrinsic sensitivity factor of this element, and could be fitted by a single component at BE = 169.3 eV, in agreement with that expected for sulphur in sulphates and consistent with previous results relative to other ZS samples [2,6,8,23]. The S/Zr atomic ratios (Tab. 2, 2nd column) are fully comparable with the values reported previously for ZS samples prepared by similar procedures and are not significantly affected by the presence of the metals. The metal/Zr atomic ratios vary by about one order of magnitude in passing from the sol-gel to the impregnated samples (see Table 2, 3rd column).

The oxygen 1s peak, in the case of ZS catalysts, shows in any case the presence of more than one species. The fitting procedure of O 1s spectral components was adopted previously [2,3,6,8,9,16] and is based on BE values present in the literature and verified by us on reference materials (ZrO₂, Zr(SO₄)₂); the main component, at lower binding energies, is assigned to reticular O²⁻ in the oxide (530.0 eV), the second component is attributed to oxygen in sulphates (531.6±0.5 eV), and the third component at higher BE is due to surface OH groups (532.6±0.4 eV). The shape of the peak is generally broad; in the present case the situation is even more complex, since oxygen species related to the presence, at the surface, of metal oxides can also concur to broaden the peak. Table 2 (4th column) shows that the O_{tot}/Zr atomic ratio is not affected by the composition of the samples. The presence of the metals determines, instead, a lowering of the OH/O_{tot} ratio, the more so in the case of Fe-promoted catalysts and of impregnated samples.
3.2 Catalytic tests

The activity of ZS systems as heterogeneous catalysts in liquid media has been much less investigated with respect to gas phase reactions [16,39,43-45].

In the present tests, the powders have been used as heterogeneous catalysts for the benzylation of toluene and for the esterification of benzoic acid with methanol. Leaching tests, aimed at verifying the possible release of sulphates from the catalysts during the course of the reactions, were in any case negative, allowing the catalysis to be considered as heterogeneous [16].

The two catalytic processes are performed in significantly different experimental conditions which mainly concern the temperature of the reaction, the concentrations of the reagents and the presence of an inert solvent in the case of the benzylation reaction.

The benzylation of toluene over ZS catalysts was studied recently in our laboratory and a kinetic model was proposed [39]. The reaction mechanism was observed to be quite similar to the one previously proposed for the same reaction over Nafion–silica [46]. The benzylation reaction was carried out in cyclohexane and the toluene/BzOH ratio was kept high (> 20) to avoid the formation of oligotoluenes; the temperature was fixed at 353 K. Fig. 4a reports the trend of the % conversion of BzOH (the limiting agent) as a function of time for a representative sample. This reaction profile is common to all the present catalysts. The linear trend of the experimental data suggests their interpretation by an empirical rate equation zero-order with respect to BzOH. The kinetic constants (k_{cat}, Tab. 3, 2nd column) are all of the same order of magnitude, but, it can be observed that the Fe-promoted one-pot sample shows a larger k_{cat} value, while the one-pot Mn-promoted sample presents a significantly lower
constant than in the case of un-promoted ZS. No kinetic data could be obtained in the case of the Mn-impregnated catalyst since the supernatant could not be separated efficiently from the solid even upon prolonged ultracentrifugation at 11000 rpm.

In the case of the esterification reaction 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 reaction. As the boiling point of methanol is 338 K, the operative way may be described as a modified “batch process”, where the reagents are put altogether in the reactor and methanol is continuously added and taken off together with water [16].

Fig. 4b reports the trend of the % conversion of benzoic acid as a function of time. By comparing Fig. 4a and b, the two reactions appear to proceed by different kinetic paths. For the esterification of benzoic acid to methyl-benzoate a quasi-plateau conversion region follows an initial rising part. No appreciable differences in the reaction profiles were observed by changing the catalysts. Tab. 3 (3rd column) reports the kinetic constants obtained by elaboration of the experimental results by a pseudo-first order kinetic model. No large differences between the obtained kcat values can be appreciated. The samples promoted by Fe show values comparable to un-promoted ZS while, as in the case of benzylolation, the presence of Mn leads to lower kinetic constants. Fig. 5 shows the reagents % conversion, at fixed time, for the two reactions in order to offer a more immediate comparison between the activity of the same catalysts towards the two different reactions. While the presence of iron promotes the benzylolation reaction and not significantly the esterification, the addition of Mn, both by impregnation and one pot, depresses both reactions.
With the aim to highlight possible characteristic features of the catalysts producing the above described different activities, the three one pot samples (showing the largest variations) were submitted to solid-state NMR and FTIR analyses.

3.3 Acidity and surface functionalities (Solid-State NMR Spectroscopy and FTIR)

The $^1$H MAS NMR spectra of “one pot” samples, recorded in a temperature range of 300 K are reported in Fig. 6. The spectra of zirconia (Z) and sulphated zirconia (ZS) samples are characterized by the presence of a very broad signal at low field (6-7 ppm) and of a sharper signal at high field (2 ppm). The mobility plays a relevant role in the width of NMR line shape, indeed the broader signal can be ascribed to the rigid water molecules with restricted mobility near the surface region of the material, with respect to the sharper signal relative to water with more freedom degrees [47-51]. This behavior suggests the presence of different kinds of interaction between the water molecules and the zirconia surface. To support these assignments, solid echo experiments were performed to highlight the different nature of the water molecules. It is known that the echo signal in the region of restricted mobility depends, among other parameters, also on the correlation time $\tau_c$, which is related to molecular motion. In our case the Z spectrum (as a representative curve) showed (see Fig. 6, inset) peaks with opposite phase. The on-phase broad peak is relative to the less mobile water molecules, fast relaxing and with long $\tau_c$. The out-of-phase, narrow peak is relative to more mobile water molecules which are slower relaxing and with short $\tau_c$. The sulphate modification induces, in agreement with literature results [48], a significant downfiled shift of ca. 1 ppm (see Fig. 6) of the broader signal, which suggests a strongly enhanced proton acid strength relative to pure ZrO$_2$. 
The spectra of sulphated zirconia doped with Fe and Mn promoters (ZSMn and ZSFe, respectively) showed only the signal at high field (Fig. 6). In this case it is possible that the downfield signal might have become so broad to vanish in the noise. The absence of the broad downfield peaks corresponds to a lower degree of coverage by the less mobile, rigidly structured water, or of OH groups directly bound to the oxide. This observation is in agreement with the lower OH/O\textsubscript{tot} ratio, observed by XPS in the case of metal doped samples (Tab. 2).

FTIR spectroscopy of a basic probe molecule, such as 2,6-dimethylpyridine, 2,6-DMP, adsorbed onto promoted and unpromoted ZS-based systems has been resorted to in order to test their total, \textit{i.e.} Lewis and Brønsted, surface acidity. All samples were inspected using the 2,6-DMP adsorption/desorption (in mild conditions) procedure [52], which briefly consists of (i) the admission of large pressure (~ 5 Torr) of the base at BT (IR beam temperature) onto the sample activated surface (in the present case, all samples were activated at 423 K), (ii) the evacuation of the base excess at BT for increasing times up to 15 min, and (iii) the desorption of the strongly bonded 2,6-DMP fraction at 423 K.

As it can be observed in Figure 7, all ZS-based samples exhibit a common behaviour upon 2,6-DMP uptake: in fact, no peculiarities due to either presence or absence of the promoting agents is evident. In particular, protonic (\textit{i.e.}, Brønsted) acidity is always present for all samples, as indicated by the presence of the characteristic envelope of bands at \(\nu > 1620 \text{ cm}^{-1}\) [52]. This is not unexpected in the presence of surface anions: in fact, sulphation of oxides induces protonic acidity [2]. Besides this envelope, some other bands are evident at lower \(\nu\): if the spectrum is obtained in the presence of an excess of 2,6-DMP (curves 1 in each set of spectra), the usual two-bands profile is
observed [52]. These bands, centred at ~1580 and ~1594 cm⁻¹, are ascribed to physisorbed and H-bonded 2,6-DMP species, respectively. Moreover, the shoulder at higher ν (~1605 cm⁻¹) is ascribable, on the basis of its spectral behaviour and of literature data [53], to the 8a mode of Lewis-coordinated 2,6-DMP species interacting with cus ( coordinatively unsaturated) Zr⁴⁺ cations.
Upon evacuation of the base excess at BT (curves 2 in each set of spectra), some important features can be evidenced:

(i) There is a drastic and overall decreasing of the intensity of the envelope located at ν < 1620 cm⁻¹, as expected for H-bonded and physisorbed species. Within this envelope, the band at ~1606 cm⁻¹, ascribable to the 8a mode of Lewis-coordinated 2,6-DMP, is now better evident, in particular in the case of Fe and Mn-promoted samples;

(ii) on the contrary, the broad envelope located at ν>1620 cm⁻¹ (due to Brønsted-bound 2,6-DMP species) turns out to be very little affected by the evacuation, remaining strong and complex as it was from the beginning. If the evacuation of the base is carried out at 150°C (curves 3 in each set of spectra), the bands due to protonated 2,6-DMP remain almost unaltered, whereas the residual concentration of the aprotic fraction becomes almost negligible.

In order to get some more information about both intrinsic and added functionalities present at the surface of these ZS materials, we examined the FTIR background spectra of the samples.

Figure 8 reports the spectral features relative to the same ZS-based (promoted and unpromoted) materials for which we tested the total surface acidity.
As for the intrinsic functionalities (namely, OH surface species), it can be observed (Fig. 8a) that all spectra exhibit the two-bands OH profile typical of all catalytically active ZS-based systems [2]: in fact, in the 3950-2900 cm\(^{-1}\) spectral range, the main absorptions are due to the stretching modes of mono-(or terminal) and tri-coordinated OH species (\(~3760\) and \(~3655\) cm\(^{-1}\), respectively). In the case of the plain ZS material (and partly for the Mn-promoted ZS sample), two more important \(v_{\text{OH}}\) components are present: the former is located at \(~3585\) cm\(^{-1}\) and, on the basis of its spectral behaviour, it can be ascribed to the \(v_{\text{OH}}\) vibration of almost H-bonding free oxonium ions [54] present at the surface of these medium-low dehydrated materials. The latter is represented by a broad and unresolved envelope located at \(v < 3500\) cm\(^{-1}\): it can be ascribed to the stretching mode of OH species interacting by H-bonding.

As for the added functionalities, we can observe the presence of the characteristic spectral features of surface sulphates at \(v < 1500\) cm\(^{-1}\) (see figure 8b). Two main IR absorptions are present at \(~1370\) and \(~1030\) cm\(^{-1}\): they are characterised by a fairly large spectral separation (\(\Delta v \approx 300\) cm\(^{-1}\)). This spectral behaviour is typical of non coupled \(v_{\text{S=O}}\) and \(v_{\text{S-O}}\) vibrational modes of isolated (i.e., with almost no mutual perturbations) and covalent poly-dentate sulphates [55,56] which can be present at the surface of tetragonal ZS-based materials brought to a medium dehydration stage [2]. In this latter spectral region one more important absorption is present for the plain ZS sample (and partly for the Mn-promoted material): in fact, a band located at \(~1600\) cm\(^{-1}\) is evident and can be assigned to the vibration of either a neutral [57] or a protonated water molecule [52, 58, 59]. The presence of spectral components typical of either oxonium ions or OH species interacting by H-bonding might be an indication of an intrinsic higher affinity to retain water (hydrophilicity) to (i) a major extent for plain ZS...
catalysts, (ii) a very minor extent in the case of Mn-promoted systems and almost null in the case of Fe-containing samples. These considerations are in total agreement with both XPS and solid-state NMR observations.

Discussion

The procedure of addition of the metals to sulphated zirconia, either during the oxide synthesis ("one pot") or by impregnation, leads to samples showing slight differences, between each other, both concerning the structure and the morphology. However the nature of the metal itself, either Fe or Mn, plays the major role in imposing the physicochemical features of the calcined oxides.

The XPS metal/Zr surface atomic ratio changes by almost one order of magnitude for impregnated or "one pot" samples while it is comparable for Fe and Mn, for both addition procedures. Only a very slight larger surface iron amount, with respect to manganese, can be appreciated in the case of one pot samples. Actually some literature results show a larger incorporation in the lattice of Mn with respect to iron [35].

In the case of the present Mn-promoted samples, the structural features are very similar to those of the un-doped ZS, both concerning crystal size and cell volume. Apparently the incorporation of Mn cations in the lattice is not such as to provoke important modifications of the structure. The present XPS results do not allow the actual valence of Mn to be assessed due to the very low surface amount. Literature results are rather controversial on this point; Jentoft et al. [29] conclude that the valence of Mn in the ZS lattice may vary from 2 to 4, and other authors suggest the formation of surface-MnSO$_4$ referring to Mn K edge XAS spectra [57]. The presence of bivalent Mn
surface species, also in the case of the present samples, would justify the lower catalytic activity, especially shown by ZSMn, in the case of the benzylation of toluene. In fact the catalyst for the Friedel-Crafts reaction needs to show, for the reaction to start, a relevant electron attracting power, which is not typical for Mn(II) species.

In the case of iron promoted ZS the metal is in any case considered to be speciated as ferric species; Schethauer et al. [58] and Tabora et al. [59] report the formation of small Fe₂O₃ rafts at the surface of heavily doped ZS samples. In the present case the addition of iron, provokes larger structural modifications than Mn, i.e. smaller crystal sizes (the more so in the case of the impregnated sample) and the significant formation of growth defects supported by both line broadening components and shrinkage of the unit cell; these effects are presumably to be related to the incorporation in the lattice of a lower valent cation with respect to Zr.

The growth defects present in the bulk and, presumably, also at the surface of the iron doped samples, can be considered to be responsible, at least in part, of the better performance of these samples. In fact the catalytic action of the oxide could be promoted by adsorption sites which are more reactive and which may regenerate themselves by exchange with the sub-surface defects. With reference to the excellent performance of iron-containing samples with respect to the benzylation of toluene, it can be recalled that ferric salts are commonly used as catalysts for the Friedel-Crafts reaction [60].

The doping by Mn, while not relevantly affecting the structural and defective features of the oxide, introduce instead variations in the morphology. The surface area is reduced, especially for one pot samples. Literature results show, also in the case of Mn promoted ZS prepared by incipient wetness [35], a contraction of the surface area upon
Mn addition. The present Mn promoted samples, besides showing a smaller surface area, present also a larger pore volume, especially concerning the small pore size region, with respect to the other samples. It can be suggested that the lower surface area and the concomitant more porous network, implying less accessible sites for the species present in solution, may concur to determine the lower performance of the Mn doped samples.

FTIR characterizations indicate that the acidity features are not significantly different among the various samples. All ZS-based catalysts present a common behaviour, showing both protonic (i.e. Bronsted) and Lewis sites. The present results consequently support the more recent literature results indicating no actual difference in the acid features of promoted ZS with respect to un-promoted materials. One aspect, however, emerges clearly from the joint analyses of FTIR, \(^1\)H MAS NMR, and XPS. The metal promoted samples are less hydrophobic than ZS, the more so in the case of iron doped samples which show an almost null affinity to retain water. The scarce hydrophobicity of iron doped samples may make them more compatible with the apolar medium of the benzylation of toluene reaction and gives rise consequently to the top catalytic conversion shown by these samples.

In the light of what exposed above, the present results, on one side, support the more recent literature conclusions which, in the case of alkane isomerization reactions, attribute the improved catalytic activity of metal promoter ZS, not to more numerous or stronger acid sites, but to a different electronic environment of surface sulphates. On the other side, these results show that in the case of catalytic reactions performed in solution like the present ones, other parameters like the accessibility of the catalyst surface sites or the conditions of “wettability” of the material in the reaction medium may concur to impose the overall performance of the catalyst.
Conclusions

Fe and Mn promoted sulphated zirconia (ZS) powders were prepared by two different procedures: a single step sol–gel reaction and the impregnation of the zirconia hydrous precursor. Materials prepared by impregnation show a much larger surface metal amount (almost one order of magnitude) with respect to one pot samples, but do not show improved catalytic activity with respect to either the esterification of benzoic acid with methanol or the benzylation of toluene. The surface metal amount appears therefore not to be directly related to the activity of the catalysts. The same can be said for the acidity features which appear not to be significantly different among the various samples thus supporting the more recent literature results which attribute, in the case of alkane isomerization reactions, the improved catalytic activity of metal promoted ZS, not to more numerous or stronger acid sites, but to an enhancement of the activity of surface sulphates.

In the present case, Mn-doped catalysts show a lower activity, with respect to un-doped ZS, for both the studied liquid phase catalytic reactions. This behaviour is attributed to the possible presence at the surface of bivalent Mn sites and also to morphological effects, i.e. to the sample lower surface area and to a lower accessibility of the catalyst surface sites due to its larger degree of porosity.

Iron promoted samples, instead show a significantly higher activity, especially for the benzylation of toluene reaction, the more so for one-pot samples. This improved activity is attributed to the presence growth defects localized both in the bulk and at the surface of these samples which may offer adsorption sites which are more reactive and which may regenerate themselves by exchange with the sub-surface defects. A further aspect which may concur to improve the activity of these samples is the consistently
lower affinity to retain water showed by these samples which can result therefore more compatible with the apolar medium of the benzylaion reaction.

Acknowledgment

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References


Figure legends

FIGURE 1. a) BET surface area and b) relative pore volume distribution for all samples.

FIGURE 2. WPPM results for ZSMn sample: experimental data (dot), modelled pattern (line) and difference between experimental and modelled data (residual, line below); the inset shows the same pattern in Log scale.

FIGURE 3. WPPM results: refined distribution of spherical domain diameters for the sample of Figure 2. In addition to the arithmetic mean size (<D>), it is also shown the "Scherrer Size" (<D>v), which is inversely proportional to the peak width [40]

FIGURE 4. Reaction profile (conversion vs time) for ZS sample. a) benzylation of toluene; b) esterification of benzoic acid with methanol.

FIGURE 5. Esterification (8h) and benzylation (100 min) final conversion for all the catalysts.

FIGURE 6. 1H NMR MAS spectra of “one pot” samples. Δν½ is the line width in Hz at half peak height. Inset: solid echo 1H Z spectrum.

FIGURE 7. Differential absorbance (background subtracted ) FTIR spectra in the 8a-8b ring stretching modes (1700-1550 cm⁻¹) of 2,6-DMP adsorbed/desorbed on the various catalysts activated in vacuo. In each set of spectra curves 1 refer to adsorption (∼ 2 Torr) at BT, whereas curves 2 and 3 refer to 2,6-DMP evacuation at BT (15 min).

FIGURE 8. Absorbance FT-IR spectra in the 3850–3000 cm⁻¹ range (a) νOH stretching region) and in the 1800–850 cm⁻¹ range (b) νSO stretching region) of the various samples activated in vacuo.
<table>
<thead>
<tr>
<th>sample</th>
<th>% T</th>
<th>% M</th>
<th>&lt;D&gt;</th>
<th>&lt;D&gt;v</th>
<th>a</th>
<th>c</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>31.5</td>
<td>68.5</td>
<td>6.9 ± 0.5</td>
<td>10.7 ± 0.7</td>
<td>3.5947</td>
<td>5.1784</td>
<td>66.915</td>
</tr>
<tr>
<td>ZS</td>
<td>97.5</td>
<td>2.5</td>
<td>4.5 ± 0.2</td>
<td>6.8 ± 0.2</td>
<td>3.5949</td>
<td>5.1739</td>
<td>66.864</td>
</tr>
<tr>
<td>ZSFe</td>
<td>100</td>
<td>---</td>
<td>4.1 ± 0.2</td>
<td>6.8 ± 0.2</td>
<td>3.5916</td>
<td>5.1692</td>
<td>66.680</td>
</tr>
<tr>
<td>ZSMn</td>
<td>100</td>
<td>---</td>
<td>4.6 ± 0.1</td>
<td>7.2 ± 0.2</td>
<td>3.5931</td>
<td>5.1760</td>
<td>66.824</td>
</tr>
<tr>
<td>ZSFe_imp</td>
<td>97.7</td>
<td>2.3</td>
<td>3.8 ± 0.2</td>
<td>6.0 ± 0.2</td>
<td>3.5903</td>
<td>5.1654</td>
<td>66.583</td>
</tr>
<tr>
<td>ZSMn_imp</td>
<td>92.7</td>
<td>7.3</td>
<td>5.2 ± 0.1</td>
<td>6.9 ± 0.2</td>
<td>3.5922</td>
<td>5.1692</td>
<td>66.703</td>
</tr>
</tbody>
</table>

Table 1. Quantitative phase composition (T = tetragonal, M = monoclinic), mean diameter (<D>), volumetric average size, Scherrer size (actual domain size, <D>v) and unit cell parameters.
<table>
<thead>
<tr>
<th>sample</th>
<th>S/Zr</th>
<th>metal/Zr</th>
<th>O/Zr</th>
<th>OH/O_{tot}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>—</td>
<td>—</td>
<td>1.8</td>
<td>0.10</td>
</tr>
<tr>
<td>ZS</td>
<td>0.16</td>
<td>—</td>
<td>2.1</td>
<td>0.19</td>
</tr>
<tr>
<td>ZSFe</td>
<td>0.17</td>
<td>0.007</td>
<td>2.3</td>
<td>0.06</td>
</tr>
<tr>
<td>ZSMn</td>
<td>0.18</td>
<td>0.005</td>
<td>2.2</td>
<td>0.14</td>
</tr>
<tr>
<td>ZSFe_imp</td>
<td>0.17</td>
<td>0.04</td>
<td>2.2</td>
<td>0.07</td>
</tr>
<tr>
<td>ZSMn_imp</td>
<td>0.16</td>
<td>0.03</td>
<td>2.1</td>
<td>0.11</td>
</tr>
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</table>

**Table 2.** XPS surface ratios for all the present samples.
<table>
<thead>
<tr>
<th>sample</th>
<th>$k_{\text{cat}} \times 10^5$ (Lmin$^{-1}$g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>benzylolation (353 K)</td>
</tr>
<tr>
<td>ZS</td>
<td>5.2 ± 0.2</td>
</tr>
<tr>
<td>ZSFe</td>
<td>6.8 ± 0.6</td>
</tr>
<tr>
<td>ZSMn</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>ZSFe_imp</td>
<td>5.2 ± 0.2</td>
</tr>
<tr>
<td>ZSMn_imp</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

**Table 3.** Kinetic constants for benzylation (zero order) and esterification (pseudo first order) reactions
FIGURE 1

(a) B.E.T. surface area (S, m²/g) for different samples:
- Z
- ZS
- ZSFe
- ZSMn
- ZSFe_imp
- ZSMn_imp

(b) Pore volume (V, ml/g) for different particle sizes:
- d>80 nm
- 20<d<80 nm
- 6<d<20 nm
- d<6 nm

Z
ZS
ZSFe
ZSMn
ZSFe_imp
ZSMn_imp
FIGURE 2
FIGURE 3

Mean diameter
$\langle D \rangle = 4.6 \text{ nm}$

Scherrer size
$\langle D \rangle_v = 7.2 \text{ nm}$

Mean diameter
$\langle D \rangle = 4.6 \text{ nm}$

Scherrer size
$\langle D \rangle_v = 7.2 \text{ nm}$
a) benzylation

b) esterification
$\Delta \nu_{1/2} = 1400$ Hz

$\Delta \nu_{1/2} = 300$ Hz

$\Delta \nu_{1/2} = 1800$ Hz

$\Delta \nu_{1/2} = 300$ Hz

$\Delta \nu_{1/2} = 600$ Hz

$\Delta \nu_{1/2} = 300$ Hz
FIGURE 8