

Influence of sulphate content on the physico-chemical properties and catalytic activity of some sulphated zirconia systems

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Received 1 August 2002; revised 25 June 2003

The present work attempts a systematic examination of the effect of sulphate content on the physico-chemical properties and catalytic activity of sulphated zirconia and iron promoted sulphated zirconia systems. Sulphate content is estimated by EDX analysis. The amount of sulphate incorporated has been found to influence the surface area, crystal structure and the acid strength distribution. Ammonia TPD and adsorption studies using perylene have enabled the determination of surface acidic properties. The results are supported by the thermodesorption studies using pyridine and 2,6-dimethylpyridine. The catalytic activity towards benzoylation reaction has been correlated with the surface acidity of the systems.

Hydrous zirconium oxide, when modified by anions like sulphate, has been reported to form highly acidic or superacidic catalyst depending on the treatment conditions¹⁻³. The type of precursor and precipitating agent, solution pH, sulphating agent employed, method of impregnation, calcination temperature etc. play a crucial role in deciding the final properties⁴⁻⁷. A major shortcoming of this category of catalysts is the rapid deactivation due to coke formation at high temperatures. Modification with various transition metal ions has been reported to alter the properties of the system depending on the nature of the ion incorporated^{8,9}.

The present investigation sets out to study the effect of calcination temperature and sulphate content on the physico-chemical properties and catalytic activity of sulphated zirconia systems and to estimate the influence of Fe(III) as promoter.

Materials and Methods

Catalyst preparation

Hydrous zirconium oxide was prepared by the hydrolysis of zirconyl nitrate, $\text{ZrO}(\text{NO}_3)_2$ (CDH Ltd) with 1:1 ammonia at 80°C and at a pH 10. The precipitate was filtered, washed and dried overnight at 120°C.

Sulphated zirconia samples were obtained by impregnating hydrous zirconium oxide with the requisite amount of 1N H_2SO_4 solution. Wet-impregnation was carried out by stirring zirconium hydroxide with the modifier solution for 4 hours and

then evaporating the solution under continued stirring. Iron promoted sulphated zirconia was prepared from zirconium hydroxide by single step impregnation using ferric nitrate solution and requisite amount of 1N H_2SO_4 solution. The iron loading in the samples was kept to 2%. The samples were designated based on the amount of H_2SO_4 solution (2.5, 5.0, 7.5 and 10 ml) used per gram of hydrous zirconium oxide. The samples after overnight drying at 120°C were calcined at the required temperature for 3 hours.

Prior to the characterisation and catalytic activity tests, the samples were activated at the corresponding calcination temperature for half an hour.

Catalyst characterisation

Surface area and pore volume were measured by BET method in a Micromeritics Gemini surface area analyser by nitrogen adsorption at liquid nitrogen temperature (P/P_0 range 0.1-0.9). The crystallinity of the samples was determined by the powder XRD method in an X-ray diffractometer (Rigaku D-Max C X-Ray Diffractometer) using a Ni filtered Cu-K radiation ($\lambda=1.5406 \text{ \AA}$). Thermal stability was examined using a Shimadzu thermogravimetric analyser (TGA-50) in nitrogen atmosphere at a heating rate of 20°C/min. IR spectra of the samples were recorded in a Shimadzu spectrophotometer (DR 8001). Selected samples were subjected to Laser Raman spectroscopic analysis (Dilor-Jobin spectrophotometer). The sulphate content was obtained by EDX analysis (Stereoscan 440 Cambridge, UK).

The evaluation of surface acidic properties was carried out by temperature programmed desorption of ammonia¹⁰ (TPD) and electron acceptor studies using perylene^{11,12}. The results were supported by TG studies after adsorption of 2,6-dimethylpyridine^{13,14}.

For TPD, pelletised samples were activated at 300°C inside the reactor under nitrogen flow for half an hour. After cooling to the room temperature, ammonia was injected in absence of the carrier gas flow and the system was allowed to attain equilibrium. The excess and physisorbed ammonia was then flushed out by a current of nitrogen. The temperature was raised to 600°C in a stepwise manner at a linear heating rate of about 20°C/min. Ammonia desorbed at intervals of 100°C was trapped in dilute sulphuric acid solution and estimated volumetrically by back titration with NaOH.

Electron-acceptor studies were carried out by stirring a weighed amount of the catalyst with different concentrations of perylene in benzene solvent. The amount of perylene adsorbed was determined by measuring the absorbance ($\lambda_{\max}=439$ nm) of the solution in a UV-vis spectrophotometer (Shimadzu UV-160 A) before and after adsorption. The limiting amount of perylene adsorbed was obtained from the Langmuir plots.

For thermodesorption studies, activated samples were kept in a dessicator containing 2,6-dimethylpyridine under vacuum for 48 hours to allow equilibrium adsorption and then subjected to thermal analysis in N₂ atmosphere at a heating rate of 20°C/min.

Catalytic activity

Benzoylation of toluene with benzoyl chloride was used as a test reaction for a comparative evaluation of the catalytic activity of different samples. The reaction was carried out in a 50 ml double-necked flask fitted with a spiral condensor. The temperature was maintained using an oil bath. In a typical run, toluene (10 ml) and benzoyl chloride in a molar ratio 5:1 was added to 0.1 g of the catalyst in the R.B. flask and the reaction mixture was magnetically stirred. The product analysis was done using a Chemito 8610 Gas Chromatograph equipped with a flame ionisation detector and SE-30 column.

Results and Discussion

Surface area and pore volume

Calcination temperatures from 500°C to 700°C were tried in the present study for optimisation.

SZ(10) and FeSZ(10) were selected as representative systems for the purpose. After calcination at 500°C catalyst systems were all hygroscopic in nature due to their high sulphate content and this nature was completely eliminated by high temperature calcination. The results of the physico-chemical characterisation at different calcination temperatures are given in Table 1. An increase in calcination temperature results in a lowering of surface area.

The variation in the surface area and pore volume with sulphate loading for sulphated zirconia and iron promoted sulphated zirconia after calcination at 700°C is presented in Table 2. The sulphated samples showed a higher surface area as compared to pure zirconia. This can be explained on the basis of higher resistance to sintering as well as the delayed transformation from amorphous to crystalline state acquired by doping with sulphate ions^{5,15,16}. Sulphate doping suppresses particle growth and also facilitates the dispersion of the zirconia particles resulting in a higher surface area.

An increase in sulphate loading resulted in a decrease in the surface area value. The decrease was only marginal in the case of low sulphate loaded samples, whereas for high loaded samples the decrease was quite noticeable. Thus it can be assumed that for low sulphate loadings the stabilising effect of the sulphate ions is prominent. At high sulphate loadings plugging of the pores may result in a reduction in the surface area¹⁷. The decrease in surface area can also be correlated with sulphur migration into the bulk phase and to an alteration of crystalline structure⁶. Even though the sulphur migration into the bulk predicts a decrease in the surface area, the lower degree of crystallinity tends to increase the value and the observed surface area may be due to a fine balance between the two.

The iron promoted samples showed a higher surface area as compared to their simple sulphated analogues. The dispersed Fe₂O₃ particles along with the SO₄²⁻ species prevent the agglomeration of zirconia particles leading to an enhanced surface area. In the case of iron promoted samples also an increase in sulphate content resulted in a decrease in surface area value, but the extent of reduction was much lower. Thus it can be assumed that the incorporation of iron aids in resisting the surface area loss during high temperature calcination.

The pore volume of the samples also showed a decreasing trend with increased sulphate loading

Table 1 — Influence of calcination temperature on the physico-chemical properties

Calcination temperature (°C)	Catalyst	Surface area (m ² /g)	Sulphate content (wt %)	% sulphate retained	Perylene adsorbed (10 ⁻⁶ mol/g)
500	SZ	125	29	81	0.59
	FeSZ	160	32	90	1.01
550	SZ	99	27	77	0.98
	FeSZ	123	32	90	1.59
600	SZ	79	26	72	1.22
	FeSZ	99	31	88	2.16
650	SZ	66	20	58	1.69
	FeSZ	85	31	87	2.98
700	ZrO ₂	35	-	-	0.09
	SZ	45	18	51	2.75
	FeSZ	61	30	85	3.67

Table 2 — Influence of sulphate loading on the physico-chemical properties

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Sulphate content (wt %)	% Sulphate retained	Perylene adsorbed (10 ⁻⁶ mol/g)
ZrO ₂	35	0.065	-	-	0.08
SZ-2.5	80	0.087	2.9	21	1.90
SZ-5.0	78	0.081	5.9	24	2.16
SZ-7.5	70	0.079	10	33	2.39
SZ-10	55	0.069	19	48	2.75
FeSZ-2.5	83	0.098	5	43	2.38
FeSZ-5.0	79	0.096	12	47	2.86
FeSZ-7.5	66	0.087	23	74	3.16
FeSZ-10	61	0.082	30	85	3.67

which again supports the pore blockage at higher sulphate concentrations. The pore volumes of the iron incorporated samples were higher when compared to their simple sulphated analogues.

XRD patterns

The XRD patterns of pure and sulphated samples at different calcination temperatures are illustrated in Fig. 1. Pure ZrO₂ was crystalline at 500°C with only tetragonal phase, whereas the sulphated samples were amorphous at this temperature. Above 500°C, traces of monoclinic phase, were also detected in the XRD pattern of pure zirconia, the intensity of which increased with the increase in calcination temperature. The gradual transformation of the tetragonal phase into thermodynamically stable monoclinic phase with an increase in the calcination temperature has been reported earlier¹⁸⁻²⁰. However, in the present case, a predominance of the tetragonal phase was observed even after calcination at 700°C. It may be due to the existence of an activation energy for the transformation arising from kinetic factors since all the potentially tetragonal crystallites are not converted into the monoclinic phase under the conditions

employed. On the basis of thermodynamic considerations, Garvie and co-workers²¹⁻²³ and Pyun *et al.*²⁴ attributed the stabilisation to surface and strain energy effects; these effects allowed the calculation of a critical crystallite size below which the tetragonal phase was more stable than the monoclinic modification. In the thermodynamic standard state of macroscopic crystals, monoclinic zirconia is stable while cubic and tetragonal forms are metastable. However, for small particles, tetragonal ZrO₂ has a lower Gibbs free energy than monoclinic ZrO₂. Agglomeration of zirconia particles beyond a critical crystallite size will lead to ZrO₂(t) transformation into ZrO₂(m)^{21,22}.

Prevention of agglomeration *via* sulphation accounts for the stabilisation of the tetragonal phase^{5,25,26}. Lowering of peak intensities in the XRD patterns supports a gradual decrease in the degree of crystallinity with an increase in the sulphate concentration (Fig. 2). An increased sulphate content delays the particle growth. The development of crystallinity could be observed in low loaded samples even after calcination at 600°C, while samples with high sulphate loadings were amorphous (Fig. 3). At

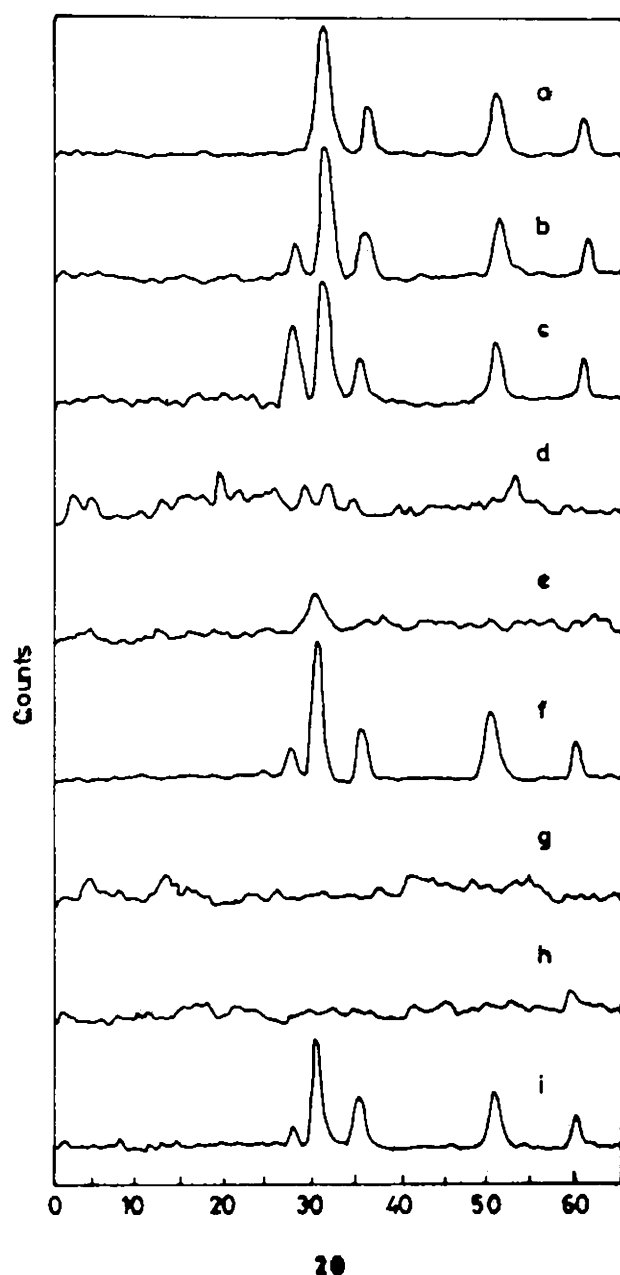


Fig. 1 — Influence of calcination temperature on the XRD attens of pure and modified zirconia

- a) ZrO_2 (500°C) b) ZrO_2 (600°C) c) ZrO_2 (700°C)
 d) SZ-10 (500°C) e) SZ-10 (600°C) f) SZ-10 (700°C)
 g) FeSZ-10 (500°C) h) FeSZ-10 (600°C) i) FeSZ-10 (700°C)

700°C, both SZ(10) and FeSZ(10) were crystalline with a predominant tetragonal phase and traces of monoclinic phase. Traces of monoclinic phase could also be detected in the XRD pattern at high sulphate loading. The intensity of the monoclinic bands was considerably lowered in the sulphated samples when compared with pure zirconia at the same temperature.

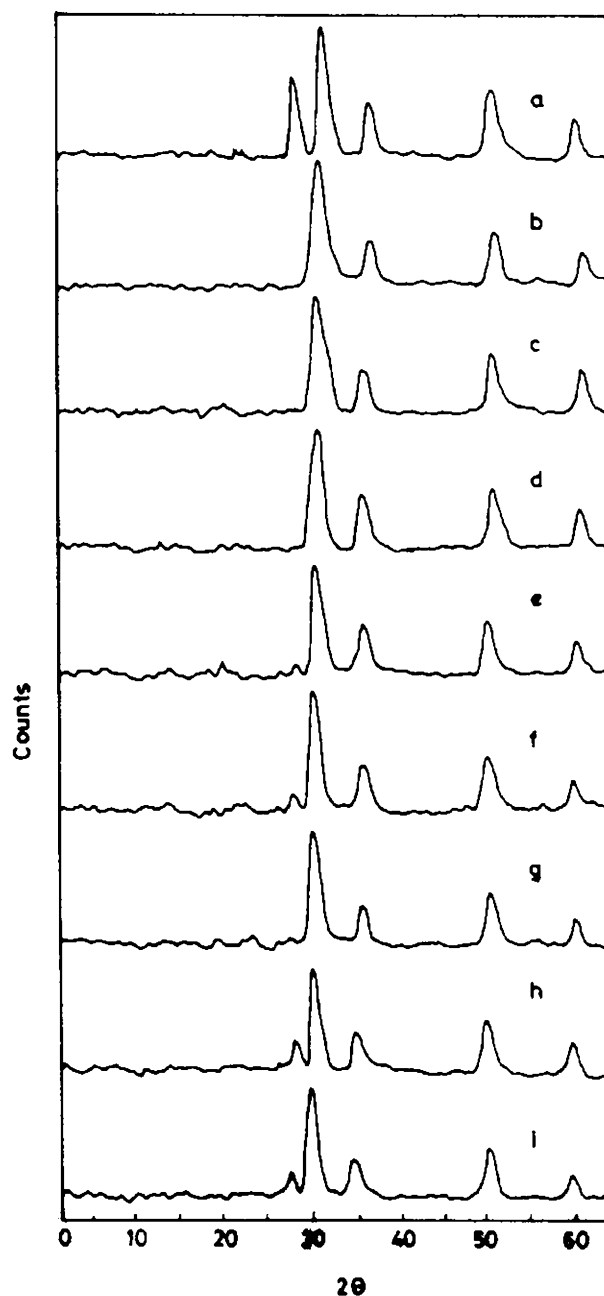


Fig. 2 — Influence of sulphate content on XRD patterns

- a) ZrO_2 b) SZ-2.5 c) FeSZ-2.5
 d) SZ-5.0 e) FeSZ-5.0 f) SZ-7.5
 g) FeSZ-7.5 h) SZ-10 i) FeSZ-10

It can be concluded that sulphated zirconia with low or medium sulphur content crystallises only in the tetragonal form, whereas at higher sulphate content a minor fraction of monoclinic phase also appears⁶.

Incorporation of iron had no significant effect on the XRD patterns except for a slight lowering in the degree of crystallinity. The intensity of the

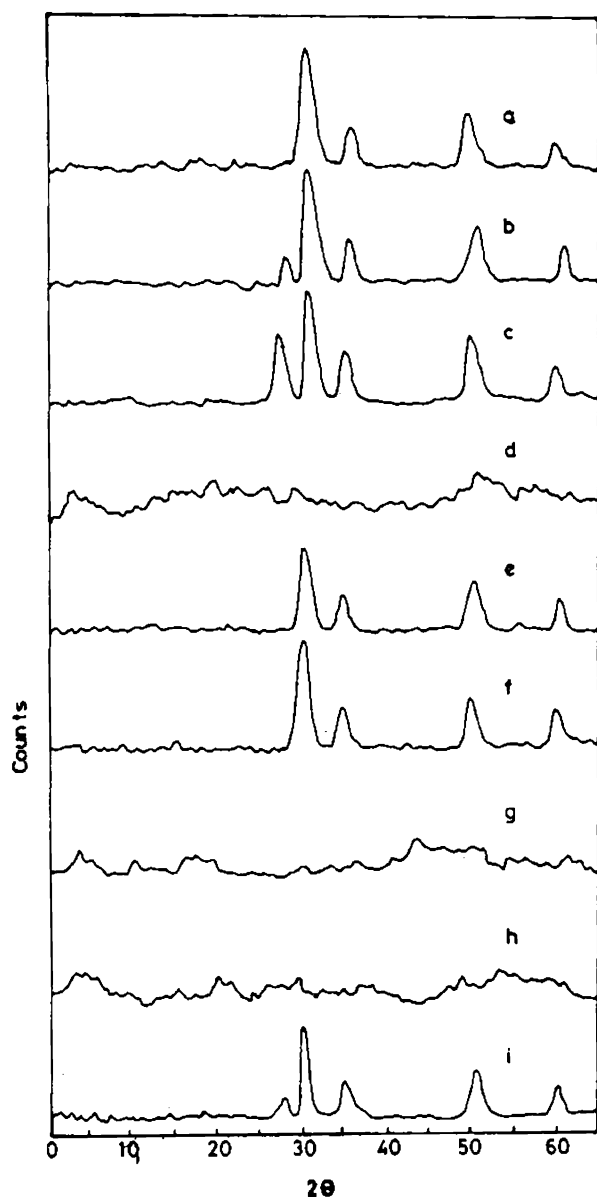


Fig 3— Influence of sulphate content in the development of crystallinity at different calcination temperatures

- a) ZrO_2 (500°C) b) ZrO_2 (600°C) c) ZrO_2 (700°C)
 d) FeSZ-2.5 (500°C) e) FeSZ-2.5 (600°C) f) FeSZ-2.5 (700°C)
 g) FeSZ-10 (500°C) h) FeSZ-10 (600°C) i) FeSZ-10 (700°C)

monoclinic peak was considerably lower in the iron promoted sample indicating a further stabilisation of the tetragonal phase by the incorporation of iron moieties. The absence of characteristic peaks corresponding to Fe_2O_3 implies that the metal oxide is present in the form of solid solution or it is highly dispersed on the ZrO_2 surface. The dispersion of Fe_2O_3 particles causes the stabilisation of the tetragonal phase and also imparts higher surface area.

TG-DTA analysis

TG pattern of hydrous zirconia is typical of that found with a gel-dehydration occurring continuously over the entire temperature range studied. The sulphated samples showed an initial weight loss at around 100°C, which can be due to the removal of surface adsorbed water of hydration. The onset of sulphate decomposition was observed around 650°C for simple sulphated systems. An increase in sulphate loading shifts this decomposition to higher temperature. In the case of SZ-10, the decomposition was found to set in around 690°C. Iron promoted samples exhibited a higher thermal stability and the commencement of decomposition occurred only above 700°C. Thus, it can be inferred that besides delaying the crystallisation process the addition of iron also serves to stabilise the surface sulphate species. As for simple sulphated systems the decomposition temperature showed an upshift with an increase in sulphate content. In the case of FeSZ-10, the initiation of decomposition occurred around 750°C.

The DTA analysis of ZrO_2 shows an exothermic peak with peak maxima around 410°C, which can be due to a phase transition from an amorphous into a crystalline form of zirconia. Srinivasan *et al.*²⁷ observed that the exothermic peak appears at the same temperature for samples that after calcination lead to pure monoclinic or tetragonal zirconia. The delay in the transition from amorphous to crystalline material by sulphate doping is supported by the DTA results. An increase in the sulphate loading shifted the peak maxima towards the high temperature region. In low sulphate loaded samples the peak maximum was obtained at around 430°C, whereas for high loaded system the maxima was observed at 472°C. Further stabilisation of the tetragonal phase by incorporation of iron is also established by the exothermic peak maxima in iron promoted samples at 500–550°C. The bandwidth of the peak suggests that the crystallisation may be occurring over a temperature range. This explains why the high loaded samples seemed amorphous in the XRD pattern even at 600°C, while the exothermic maximum was obtained at 472°C. The exothermic peak may be considered to represent the initiation of the crystallisation process.

EDX analysis

EDX results revealed a lowering of the sulphate content with an increase in calcination temperature (Table 1). At 700°C only strongly bonded sulphates

are retained which in turn contributes to the high activity of the systems. The sulphate content of different systems as obtained from EDX analysis is given in Table 2. The sulphate content increases with an increase in the amount of acid used as modifier solution per gram of hydrous zirconium oxide. The sulphate concentration was found to be very low when compared to the values estimated based on the amount of acid used for impregnation. This may be due to the sulphate removal induced by high temperature calcination. The low sulphate loaded systems showed a poor retention. This along with the surface area results lends support to the proposed migration of sulphate into the bulk at high loadings⁶. It may be assumed that, at high sulphate loadings part of the sulphate is present in the bulk phase, rather than on the surface.

The incorporation of iron was found to improve the sulphate retaining ability of the systems. The iron promoted samples showed a higher sulphate content and the presence of iron stabilises the surface sulphate species. This is also in agreement with the thermal analysis results, which predicts a higher stability and decomposition temperature after incorporation of iron. In the case of unpromoted systems the sulphate retaining ability varied from 20 to 47%, whereas for iron incorporated samples the corresponding values were in the range 42 to 84 %. Presence of iron also resists the sulphate loss at high calcination temperature (Table 1). An increase in the calcination temperature from 500°C to 700°C caused only a minor decrease in the percentage sulphate retained (90.46% to 84.70%), while the decrease was rather steep for simple sulphated system (81% to 51%).

IR spectra

The IR analysis of the sample reveals a broad peak with shoulders at around 1200 cm^{-1} corresponding to the S-O mode of vibration. The peaks at 1029, 1076 and 1222 cm^{-1} are typical of a chelating bidentate sulphate species co-ordinated to a metal cation²⁸ (Fig.4). The peak at 1380 cm^{-1} arises from the covalent character of S=O on a highly dehydrated oxide surface. The absence of peak around 1400 cm^{-1} suggests the absence of polynuclear sulphate species²⁰ in spite of the high sulphate loading.

Surface acidity

The surface acidic properties at different calcination temperatures were estimated by ammonia TPD and the distribution profiles are presented in

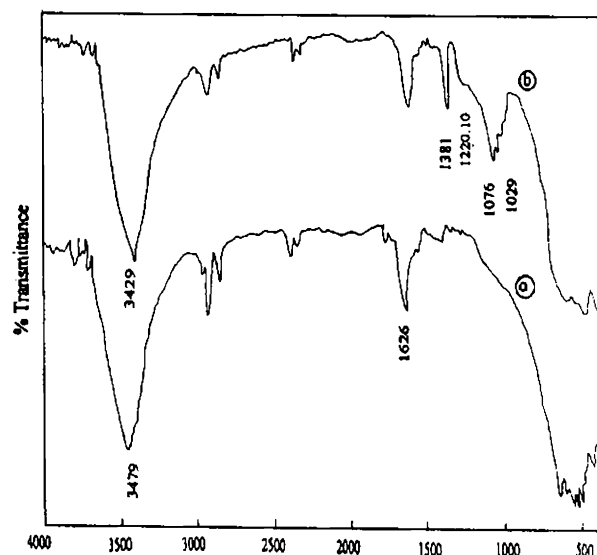


Fig. 4—FTIR spectra of pure and modified zirconia systems
a) ZrO_2 b) FeSZ (10)

Table 3. In the case of pure zirconia no significant change could be noticed in the total acidity values with increase in calcination temperature. However, an enhancement in the amount of strong acid sites was quite evident at high calcination temperatures. In the case of SZ(10) and Fe(10)SZ systems a gradual increase was observed in the total acidity values with an increase in the calcination temperature. The distribution curves in all the cases showed a shift favouring the formation of strong acid sites. This supports the view that high temperature calcination is necessary for the generation of strong acidity in sulphated metal oxides^{5,18}.

Effect of sulphate loading on the surface acidity for various systems is given in Table 4. A gradual increase in the total acidity was observed with an increase in sulphate loading. However, the prominent effect was a considerable enhancement in the amount of strong acid sites at the expense of weak acid sites. Thus, it may be inferred that even though the nature of sulphate species is important than the sulphate content, an abundance of surface sulphate species corresponds to an increase in the surface acidity and surface active sites.

In the case of strong acid sites it can be either Lewis sites or Brønsted sites adjacent to Lewis acid sites as proposed by Clearfield *et al.*²⁹. The enhancement of Lewis acidity can be attributed to the increase of the electron accepting properties of the three co-ordinated zirconium cations *via* the inductive

Table 3—Acid strength distribution at different calcination temperatures

Calcination temperature (°C)	Catalyst	Amount of ammonia desorbed (mmol/g)			Total
		Weak 100-200°C	Medium 200-400°C	Strong 400-600°C	
500	ZrO ₂	0.12	0.08	0.11	0.32
	SZ(10)	0.39	0.26	0.20	0.85
	FeSZ(10)	0.41	0.29	0.24	0.93
550	ZrO ₂	0.09	0.09	0.12	0.30
	SZ(10)	0.35	0.27	0.28	0.90
	FeSZ(10)	0.38	0.29	0.31	0.99
600	ZrO ₂	0.08	0.10	0.14	0.31
	SZ(10)	0.33	0.29	0.34	0.96
	FeSZ(10)	0.32	0.31	0.43	1.06
650	ZrO ₂	0.08	0.08	0.15	0.31
	SZ(10)	0.29	0.32	0.41	1.01
	FeSZ(10)	0.29	0.34	0.51	1.14
700	ZrO ₂	0.09	0.05	0.17	0.31
	SZ(10)	0.23	0.30	0.52	1.05
	FeSZ(10)	0.26	0.38	0.60	1.24

Table 4—Acid strength distribution for different sulphated systems

	Amount of ammonia desorbed (mmol/g)			Total
	Weak 100-200°C	Medium 200-400°C	Strong 400-600°C	
ZrO ₂	0.07	0.05	0.19	0.31
SZ-2.5	0.33	0.21	0.33	0.86
SZ-5.0	0.26	0.37	0.42	1.05
SZ-7.5	0.25	0.34	0.49	1.07
SZ-10	0.23	0.30	0.52	1.05
FeSZ-2.5	0.277	0.35	0.28	0.90
FeSZ-5.0	0.26	0.36	0.49	1.11
FeSZ-7.5	0.27	0.37	0.58	1.22
FeSZ-10	0.26	0.38	0.60	1.23

effect of the sulphate anions, which withdraw electron density through the bridging O atom³⁰. The removal of sulphate from the surface sites induced by high temperature calcination can also result in the generation of strong co-ordinatively unsaturated Zr(IV) Lewis acid sites³¹.

The iron promoted samples was found to have a higher acidity as compared to the simple sulphated samples which may be partially attributed to their higher sulphate content. The structural changes accompanied by incorporation of iron moieties may also be contributing to the acidity enhancement. At low sulphate loadings weak and strong acid sites were obtained in almost equal proportions, while considerable enhancement of the strong acid sites was observed at high sulphate loading.

Perylene adsorption study is based on the ability of the catalyst surface site to accept a single electron

from an electron donor like perylene to form charge transfer complexes. The adsorption of perylene from a solution in benzene was done at room temperature. The pale yellow or white colour of the samples was changed into green after adsorption. Perylene after electron donation gets adsorbed on the Lewis sites as radical cation. As the concentration of perylene in the solution increases, amount adsorbed also increases up to a certain limiting value after which it remains constant. The limiting amount adsorbed is a measure of the Lewis acidity or the electron accepting capacity. The results of the perylene adsorption studies on the systems at different calcination temperatures are presented in Table 1. A well-defined enhancement in the Lewis acidity was obtained at high calcination temperature, which may be due to the gradual removal of adsorbed water during high temperature calcination. Such an increase in the Lewis acidity at the expense of Bronsted acidity

during high temperature calcination has been reported²⁰.

The reversible transformation of Lewis acid sites into Brönsted acidic sites was also confirmed by thermodesorption studies using 2,6-dimethylpyridine. The formation of weak bonds between 2,6-DMP and Lewis acid sites has been observed in alumina, boron phosphates and zeolites at low temperatures^{13,32}. Thus, we presume that the amount of 2,6-DMP desorbed at temperatures above 300°C originates exclusively due to desorption from Brönsted acid sites³³. The relative percentage weight loss upon thermal treatment may be taken as a measure of the Brönsted acidity of the systems and the results are presented in Table 5. As expected, an increase in the calcination temperature resulted in a lowering of the total Brönsted acidity. However, there was a pronounced enhancement in the amount of medium and strong Brönsted acid sites at the expense of weak sites. This may be accounted for on the basis of the increase in the Lewis acidity at high calcination temperatures. Lunsford *et al.*³⁴ pointed out that strong Brönsted acidity requires the interaction of the bisulphate groups with the adjacent Lewis acid sites. Presence of Lewis acid sites adjacent to Brönsted acid sites results in enhancement of the Brönsted acidity due to the electron withdrawing inductive effect.

The results of adsorption studies given in Table 2 clearly show a considerable enhancement of Lewis acidity on sulphation. The Lewis acidity was found to increase with an increase in the sulphate loading. This is in contrast to the earlier reports, which predicts an increase in Brönsted acidity at high sulphate loading when sulphates mostly exist in the form of polynuclear pyrosulphates²⁰. This can be explained on the basis of the IR results, which indicates the absence of the polynuclear species in our systems in spite of high loading. It is generally agreed that most sulphate groups which form on the exposed patches of regular crystalline planes can induce protonic acidity, especially if they are in the form of complex polynuclear sulphates favoured at high loadings²⁰. The high calcination temperature employed may also be a reason for the high Lewis acidity of the samples. The same trend was observed for the iron promoted samples also, the Lewis acidity being higher when compared to their simple sulphated analogues.

Catalytic activity

The sulphate content remarkably affects the physico-chemical properties like surface area, crystallinity and even the acidic properties. Thus, the sulphate content should have a deciding hand on the catalytic performance. The influence of sulphate

Table 5—Variation in Brönsted acidity with calcination temperature

Calcination temperature (°C)	2,6-DMP desorption (relative percentage weight loss)			
	Weak (300-400°C)	Medium (400-500°C)	Strong (500-700°C)	Total
500	1.10	1.59	1.21	3.91
600	0.76	0.97	1.44	3.17
700	0.31	0.89	1.70	2.90

Table 6—Influence of sulphate loading on catalytic activity
Reaction temperature — 110°C, Catalyst — 0.1 g; Duration — 1 hour, Molar ratio
(toluene/benzoyl chloride) — 5:1,

Catalyst system	Perylene adsorbed (10 ⁻⁶ mol/g)	Conversion (%)	Selectivity (%)	
			<i>Ortho</i>	<i>Para</i>
ZrO ₂	0.09	3.5	-	100
SZ-2.5	1.90	19.7	15.8	84.2
SZ-5.0	2.16	22.5	16.9	83.2
SZ-7.5	2.39	28.5	17.0	83.0
SZ-10	2.75	34.4	16.1	83.9
FeSZ-2.5	2.38	56.4	18.5	81.5
FeSZ-5.0	2.86	64.8	18.0	82.0
FeSZ-7.5	3.16	71.6	16.6	83.4
FeSZ-10	3.67	79.6	15.2	84.8

Table 7 — Influence of calcination temperature on catalytic activity and selectivity
Reaction temperature — 110°C, FeSZ(10) catalyst — 0.1 g, molar ratio (toluene/benzoyl chloride) — 5:1

Calcination temperature (°C)	Perylene adsorbed (10 ⁻⁶ mol/g)	Conversion (%)	Selectivity (%)	
			Ortho	Para
500	1.01	8.6	-	100
550	1.59	15.1	3.5	96.5
600	2.16	23.7	12.7	87.3
650	2.98	49.8	14.7	85.3
700	3.67	79.6	15.2	84.8

content on the catalytic activity towards benzoylation of toluene over different sulphated zirconia and iron incorporated sulphated zirconia systems was determined and the results are presented in Table 6. The percentage conversion increased with increasing sulphate content in the samples. The same trend was observed in the case of iron promoted systems also. Benzoylation of toluene resulted in the formation of *ortho* and *para* methylbenzophenones, with a selectivity of around 80-85% to the *para* isomer. The selectivity remained almost impassive to the sulphate content.

An attempt was made to correlate the catalytic activity with the acidic characteristics determined by the TPD and adsorption studies. The increase in the percentage conversion correlated with the increase in the Lewis acidity of the samples obtained by perylene adsorption studies. Considering the acid site distribution from the TPD measurements, the increase in the strong acid sites with increasing sulphate content is in agreement with the enhanced activity at high sulphate loadings. Thus, strong acid sites may be considered to be involved in the Friedel-Crafts benzoylation of toluene. The conversions obtained for the iron promoted systems when compared with simple sulphated systems was much higher than expected from the Lewis acidity values as well as the amount of strong acid sites.

Table 7 illustrates the dependence of the catalytic activity on the calcination temperature of the catalyst, taking the specific case of FeSZ(10). An increase in calcination temperature was found to facilitate the reaction. At low calcination temperatures (500°C) only *para* isomer was obtained which may be due to the extremely low conversion. The increase in conversion was followed by a concomitant decrease in the selectivity.

Keeping in mind the correlation observed between the catalytic activity and Lewis acidity, we attempted to find a correlation between the two in this case also.

IR studies on adsorbed pyridine by Morterra *et al.*³⁵ support the gradual elimination of all but a small fraction of the Brönsted acid sites after high temperature calcination and the reversible transformation of Lewis to Brönsted acidity upon exposure of the sample to moisture. The increase in the catalytic activity observed with increasing calcination temperature parallels the enhancement of Lewis acidity of the samples obtained by perylene adsorption studies. A rather sharp rise in the conversion was obtained when the calcination temperature was increased from 600°C, while the Lewis acidity showed a gradual increase in this range. This may be partially attributed to the development of the catalytically active tetragonal phase in the sample during this temperature range.

To confirm the involvement of Lewis acid sites in catalysing the reaction, the influence of moisture on catalytic activity was tested. The activated catalyst was kept in a desiccator containing water for 48 hours before testing for the catalytic activity. Parallel runs were conducted using fresh catalyst. The adsorption of moisture resulted in a loss of catalytic activity (80% for fresh catalyst and 67% for moisture adsorbed sample). This may be correlated with the reversible transformation of the Lewis acid sites into Brönsted acid sites upon exposure to moisture.

The reusability and stability of the catalyst is an important aspect in catalysis. No significant loss in catalytic activity was detected in the iron incorporated system FeSZ(10), even after five recycling operations while simple sulphated system showed deactivation. The deactivation in the simple sulphated system may be a consequence of the sulphate leaching during the reaction as confirmed by the EDX analysis. The absence of dark brown colour of the solution after the reaction points to the absence of Fe³⁺ in solution. To confirm this, the catalyst (Fe(2)SZ) was filtered out and the reaction was continued for 15 to 30 minutes. No noticeable change in conversion could be detected

indicating the absence of metal leaching. The retention of the iron content was also confirmed by the EDX analysis of the sample after the reaction (Fe content- 1.95%). We conclude that iron chloride if at all formed by the probable reaction of benzoyl chloride or HCl evolved in the reaction with the iron component of the catalyst exists on the catalyst surface. Thus, the reaction can be assumed to be mainly heterogeneous in nature. The low iron content may be the reason for the heterogeneous character of the reaction. Iron seems well dispersed on the catalyst surface as a part of the complex structure, which explains its stability.

Acknowledgement

The financial support from CSIR to Suja Haridas, Deepa C S and Sreeja Rani K is gratefully acknowledged.

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