

Surface properties and catalytic activity of phosphate modified zirconia

V K Smitha, H Suja, Joyce Jacob & S Sugunan*

Department of Applied Chemistry,

Cochin University of Science and Technology

Kochi 682 022, Kerala, India

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Preparation and physico-chemical characterization of phosphate modified zirconia systems and their application to Friedel-Crafts benzylation and benzoylation of toluene have been reported. The influence of transition metals on the surface properties and catalytic activity has also been discussed.

The superacidity and catalytic properties of sulphated zirconia systems have gained wide attention^{1,2} but only a few reports have appeared on phosphate modified oxides^{3,5}. Attempts to modify zirconia with phosphoric and boric acids were reported by Yadav and co-workers⁶. The present work attempts a comparative evaluation of the physico-chemical properties and catalytic activities of phosphate modified zirconia systems with those of pure zirconia. Modification with various transition metal ions has been reported to alter the properties of sulphated zirconia systems depending on the nature of the ion incorporated^{7,8}. Thus, it becomes our concern to examine the influence of certain transition metals on phosphated zirconia. Fe, Mn, Mo and W were selected as promoters for the present study. An attempt was made to optimise the phosphate content in the samples selecting pure and iron promoted phosphated zirconia as representatives. The catalytic activity of the prepared systems for Friedel-Crafts benzylation and benzoylation of toluene have also been scanned.

Experimental

Hydrous zirconium hydroxide was prepared by the hydrolysis of zirconyl nitrate (CDH Ltd.) with aqueous ammonia. The precipitate after washing and filtering was dried overnight at 120°C¹. Phosphate modified zirconia was prepared by controlled impregnation of zirconium hydroxide using 1N H₃PO₄ solution. 2.5, 5, 7.5 and 10 ml of phosphoric acid per

gram of the hydroxide was used as modifier solution and the samples were denoted as PZ-1, PZ-2, PZ-3 and PZ-4 respectively. Iron promoted systems were prepared by a single step impregnation using requisite amounts of ferric nitrate and phosphoric acid solutions (2.5, 5, 7.5 and 10 ml/g of 1 N phosphoric acid solution were used for impregnation, the samples being denoted as FePZ-1, FePZ-2, FePZ-3 and FePZ-4 respectively). Mn incorporated system was prepared from manganese nitrate, while tungsten and molybdenum were incorporated using tungstic acid and ammonium hepta molybdate respectively. The metal content in the samples was kept to 2%.

The specific surface area and pore volume of the samples were measured by BET method using Micromeritics Gemini Surface area analyzer. The crystallinity of the samples was determined by powder XRD method in an X-Ray diffractometer (Philips PW 1710 X-Ray Diffractometer) using Ni filtered Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). IR spectra were recorded by KBr pellet method in a Nicolet Impact 410 FTIR spectrophotometer. Thermal stability of the prepared samples were checked using TGA-50 Shimadzu analyzer in N₂ atmosphere at a controlled heating rate of 10°C/ min. Surface acidity of the systems was determined by temperature programmed desorption of ammonia (TPD). TPD method allows a quantitative estimation of the total acidity and acid strength distribution of the systems.

The catalytic activities of the prepared systems were tested for Friedel-Crafts benzylation and benzoylation reactions. Toluene and benzyl/benzoyl chloride in the required molar ratios were taken in a double necked R.B flask along with 0.1 g of the catalyst and magnetically stirred in an oil bath maintained at the desired temperature. Product analysis was achieved by gas chromatography using SE-30 column.

Results and discussion

Table 1 presents the results of surface area and pore volume measurements of the different catalytic systems. In comparison with pure zirconia, the modified systems exhibited higher surface area. The surface area enhancement can be attributed to the higher resistance to sintering obtained by phosphate doping. An increase in phosphate loading resulted in a

Table 1—Physico-chemical characteristics of simple phosphated and metal promoted catalysts

Catalyst	Amount of ammonia desorbed (10^{-2} mmol/g)			Total	Surface area (m^2g^{-1})	Pore Volume (10^{-2} cm^3g^{-1})
	Weak (100-200°C)	Medium (300-400°C)	Strong (500-600°C)			
ZrO ₂	2.58	11.61	5.94	20.13	34	6.31
PZ-1	3.56	15.23	7.11	25.90	100	9.78
PZ-2	15.46	2.09	9.94	27.49	99	8.07
PZ-3	14.35	8.39	6.29	29.03	89	7.41
PZ-4	13.47	8.98	3.37	25.82	35	3.32
FePZ-1	11.85	11.85	16.15	39.85	127	10.87
FePZ-2	23.58	15.72	7.87	47.17	125	9.81
FePZ-3	25.11	20.93	19.93	65.97	115	9.43
FePZ-4	9.01	11.27	10.13	30.41	63	6.89
MnPZ-3	22.43	19.48	17.04	58.95	114	8.95
MoPZ-3	18.41	14.04	13.43	45.88	108	8.73
WPZ-3	19.59	16.10	14.23	49.92	112	9.01

lowering of the surface area. The decrease was more prominent at high loadings. Same effect has been observed during sulphate modification^{1,2}. The decrease in surface area and pore volume can also be correlated with phosphate migration into the bulk phase⁹. Metal incorporation resulted in a further improvement in the surface area values. Even in the case of iron-doped systems, the trend remained the same when the phosphate loading was varied. The nature of the metal incorporated had little influence on the surface area value. The surface area of Fe, Mn, Mo and W incorporated systems were more or less of the same order.

The total pore volume of modified samples was higher when compared to pure zirconia. An increase in phosphate loading resulted in a lowering of the total pore volume, which may be assigned to the pore blockage by phosphate groups at higher loadings¹⁰.

Figure 1 depicts the XRD patterns of pure and modified zirconia samples. In agreement with the earlier reports, pure zirconia activated at 700°C showed the co-existence of tetragonal and monoclinic phases¹. However, monoclinic phase was completely absent in the case of phosphated systems indicating the stabilisation of the tetragonal phase by phosphate modification^{1,2}. The phosphate content strongly influences the crystallinity of the samples. An increase in phosphate content results in lowering of crystallinity, which may be attributed to the suppression of particle growth induced by the presence of phosphate species. The introduction of transition metal species could not produce any significant change in the XRD pattern indicating retention of crystalline nature except a slight lowering in the degree of crystallinity. The absence of

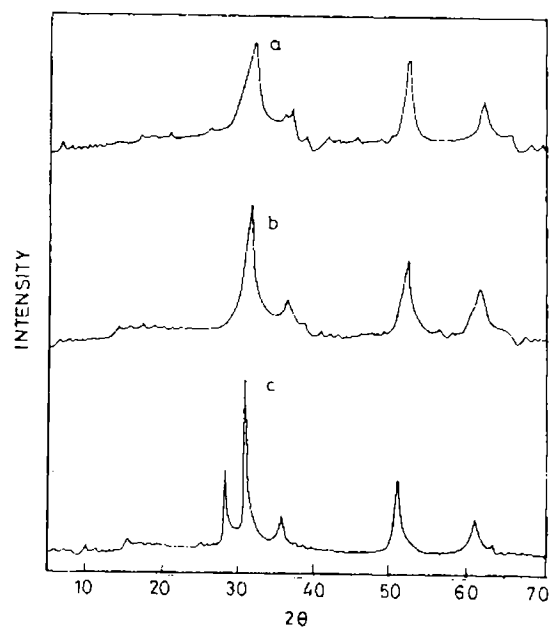


Fig. 1—XRD patterns of (a) pure ZrO₂, (b) phosphate modified ZrO₂ and (c) Fe modified ZrO₂

characteristic peaks corresponding to the metal oxide species implies that it is present in the form of solid solution or it is highly dispersed on the ZrO₂ surface.

A comparison of the FTIR spectra of pure zirconia with modified samples confirms the incorporation of phosphate groups (Fig. 2). The IR spectrum of phosphated and metal incorporated systems show a broad peak around 1070 cm^{-1} , which is absent in the case of pure zirconia. The peak can be assigned to the P-O stretching mode of PO₄³⁻ anion. The band near 1620 cm^{-1} denotes the bending vibrational modes of -OH if the hydrogen of the OH group belongs to molecularly adsorbed water¹¹. The band in the region

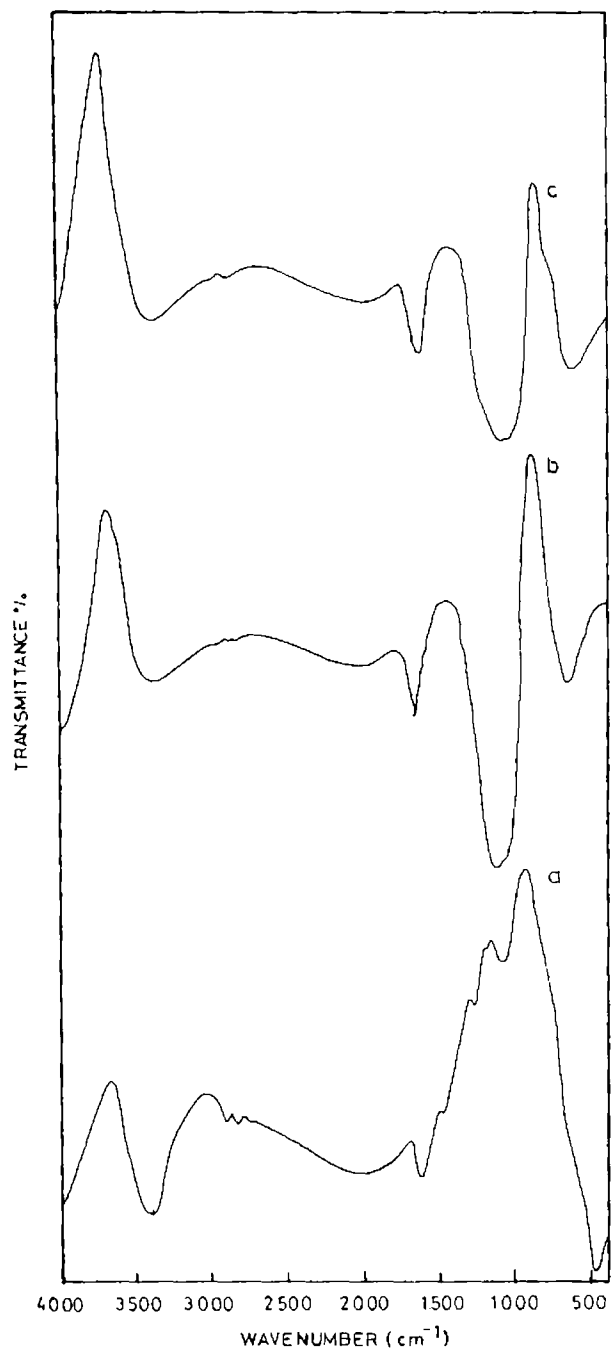


Fig. 2—IR spectra of (a) pure ZrO_2 , (b) phosphate modified ZrO_2 , and (c) Fe modified ZrO_2

$3300-3600\text{ cm}^{-1}$ corresponds to the $-OH$ groups¹². Incorporation of transition metal species could not produce any significant change in the IR spectrum.

The thermogravimetric analysis reveals the thermal stability of the phosphated samples (Fig. 3). In the case of pure zirconia, the TG curve shows a continuous weight loss in the whole range scanned.

This may be due to the dehydration occurring *via* loss of water molecules from adjacent OH groups. In the case of phosphated systems a distinct weight loss was registered in the range $100-300^\circ\text{C}$, which can be attributed to the loss of moisture¹³. No further weight loss could be detected up to 800°C indicating the thermal stability of the phosphate species incorporated. Enhanced thermal stability of phosphated anatase has been previously reported³.

Acidity measurement by ammonia TPD method establishes the enhancement of acidity by phosphate modification. The increase in acidity may be accounted for on the basis of the electron withdrawing nature of the surface phosphate group, which makes the metal centre more electron deficient. Metal incorporation causes a further increase in the acidity. The acid strength distribution at different phosphate loadings in the case of simple and iron promoted phosphated zirconia as obtained from the TPD studies is provided in Table 1. An increase in phosphate content results in an increase in the total acidity up to a certain loading and thereafter the acidity value decreases. Significant changes could be detected in the acid strength distribution also. Among the different metal incorporated systems, iron doped system showed maximum acidity. TPD curves of different metal incorporated systems are illustrated in Fig. 4.

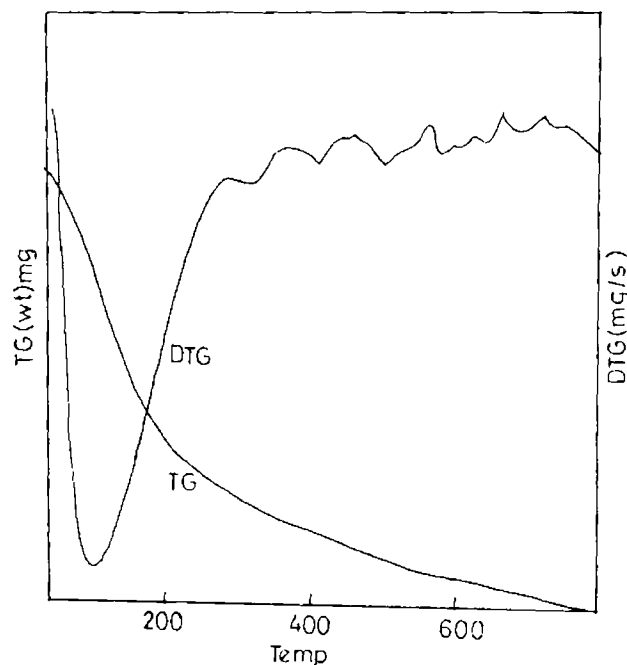


Fig. 3—TG-DTG curves of phosphate modified ZrO_2

Table 2—Benzylation of toluene over different systems
 Reaction conditions—^aCatalyst weight : 0.1g ; time : 1 h; temp : 110°C; toluene: benzyl chloride molar ratio : 5:1
^bCatalyst weight :0.1g; time :30 min; temp:80°C; toluene:benzyl chloride ratio: 10:1

Catalyst	PZ-1	PZ-2	PZ-3	PZ-4	FePZ-1	FePZ-2	FePZ-3	FePZ-4	MnPZ-3	WPZ-3	MoPZ-3
Conversion (%)	29 ^a	51 ^a	57 ^a	24 ^a	88 ^b	94 ^b	99 ^b	77 ^b	96 ^b	95 ^b	88 ^b

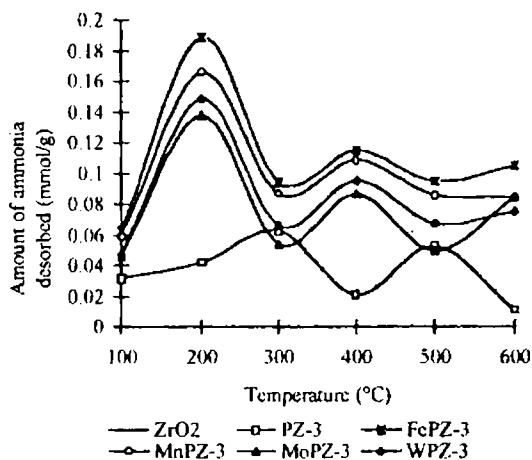


Fig. 4—Acid strength distribution for different metal promoted systems

Table 3—Benzoylation of toluene over different systems

Reaction conditions:
 0.1 g catalyst; time-1 h; temp.=110°C; toluene:benzoyl chloride molar ratio-5:1

Catalyst	Conversion (%)
ZrO ₂	3.45
PZ-3	20.61
FePZ-3	56.13
MnPZ-3	50.31
MoPZ-3	33.09
WPZ-3	42.44

Catalytic activity

Friedel-Crafts benzylation and benzoylation were chosen as test reactions for the present study. The results of benzylation of toluene over different phosphate loaded systems are presented in Table 2. In comparison with pure zirconia, simple phosphated systems did not show much activity enhancement in spite of the greater acidity after phosphation. An increase in phosphate loading resulted in an increase in the percentage conversion values up to a certain loading and thereafter it decreased. It is clear that the catalytic activity is a function of total surface acidity.

Benzoylation of toluene over pure zirconia and simple phosphated systems were carried out at refluxing temperature. Under these conditions, metal promoted systems showed complete conversion within 5 to 10 minutes. So, for the sake of comparison, the catalytic activity measurements were conducted at 80°C. Also the toluene to benzyl chloride molar ratio was changed from 5:1 to 10:1. The same reactivity order as in the case of simple phosphated systems was maintained in the case of iron promoted systems also. However, in this case the reactivity order followed the same pattern as obtained from surface area and acidity measurements. The low activity of high phosphate loaded systems may be explained on the basis of the low surface area and acidity values. Only monoalkylated products were obtained with no trace of dialkylation, a serious drawback of homogeneous catalysis. Among the different metal incorporated systems, iron promoted systems was found to be the most active, which may be accounted for on the basis of its higher acidity and redox properties of iron.

The metal promoted phosphated zirconia systems were also tested for their activity for benzoylation of toluene Table 3. Pure ZrO₂ showed poor activity for benzoylation reaction while metal incorporated systems gave satisfactory results.

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