JOURNAL OF MATERIALS SCIENCE 30 (1995) 6355–6358

Structural modification of zirconia and its influence on the catalytic activity

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X-ray diffraction, differential thermal analysis and specific surface area measurements have been employed to understand the structural properties of ZrO_2 and sulphate-modified ZrO_2 calcined at different temperatures. Calcination facilitates the transformation of ZrO_2 from cubic to monoclinic phase. Addition of SO_4 ion to $Zr(OH)_4$ helps to retain the cubic phase up to 550 °C, and to maintain the surface area through a surface complex formation mechanism. The modified ZrO_2 acts as a superacid catalyst and enhances the vapour-phase aniline alkylation.

1. Introduction

Zirconium oxide is an important transition metal oxide which is useful as a catalyst and a support [1]. It is probably the only oxide that possesses acidic, basic, oxidizing and reducing properties. These properties are influenced by the pretreatment conditions. The catalytic activity and selectivity of zirconia are thus dependent on the preparation methods and activation conditions [2].

It has been reported [1, 3, 4] that the addition of anions such as SO_4^{2-}, PO_4^{3-} to zirconia modifies the structural and catalytic behaviour. It is also believed that these anions enhance the acidity of zirconia and make it a superacid catalyst [1]. Furthermore the anions disturb the transition of one crystallographic form of zirconia to another. This in turn affects the catalytic properties of zirconia.

The present investigation is directed at understanding the structural changes that take place in zirconia due to calcination and on the addition of sulphate ions. The overall catalytic activity of an acid-catalyzed vapour-phase aniline alkylation reaction on zirconia and modified zirconia is studied. A correlation between structural modification and catalytic activity is established.

2. Experimental details

Zirconium hydroxide, $Zr(OH)_4$, was prepared by the hydrolysis of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$; LOBA CHEMIE) with an aqueous ammonia solution (25% w/w) at a constant pH of 10.5. The precipitate was filtered and washed with deionized water until no chloride ion was detected in the filtrate. It was dried at 110 °C for 24 h.

A series of zirconia samples were prepared by calcining the dried $Zr(OH)_4$ for 3 h in air at different temperatures in the region 350 to 750 °C.

Another series of zirconia samples containing 5 wt % sulphate ion was prepared by impregnating $Zr(OH)_4$ with an aqueous solution of ammonium sulphate and dried at 100 °C for 24 h. It was subjected to different calcination temperatures (350 to 750 °C) in air for 3 h.

X-ray diffraction patterns of zirconia and sulphated zirconia (ZrO_2–SO_4^{2-}) calcined at different temperatures were taken using a Philips PW 1051 X-ray diffractometer with Ni-filtered FeK_α radiation ($\lambda = 0.19360$ nm).

Thermal analyses (DTA) were carried out on zirconia and sulphated zirconia samples using DTA equipment (Leeds and Northrup, U.S.A.) at a heating rate of 12.5 °C min^{-1} in air.

The surface areas of zirconia and sulphated zirconia at three different calcination temperatures were measured using a Micromeritics Pulse Chemisorb 2700.

Vapour-phase aniline alkylation was carried out in a vertical flow reactor using a motorized syringe. Approximately 0.5 g of the catalyst was loaded into the reactor. Aniline alkylation was carried out at 400 °C at 1 bar using aniline–ethanol mixture (1:5 w/w) with a feed of ethanol-free aniline maintained at 9×10^{-3} mol h^{-1}. Nitrogen was used as a carrier gas. The liquid products were analysed by a gas chromatograph using 10% SE 30 on a chromosorb W column. The details of the experimental set up has been described elsewhere [5].

3. Results and discussion

XRD results of zirconia calcined in air at different temperatures are shown in Fig. 1. Zirconium hydroxide dried at 110 °C is amorphous. On calcination to 350 °C, a significant formation of cubic phase ($d = 0.293$ nm) takes place with a trace of monoclinic phase. On further calcination to higher temperatures, the cubic phase disappears with the simultaneous appearance of the monoclinic phase ($d = 0.284$ nm and 0.316 nm). The intensity of the XRD peak due to monoclinic phase also depends upon the calcination

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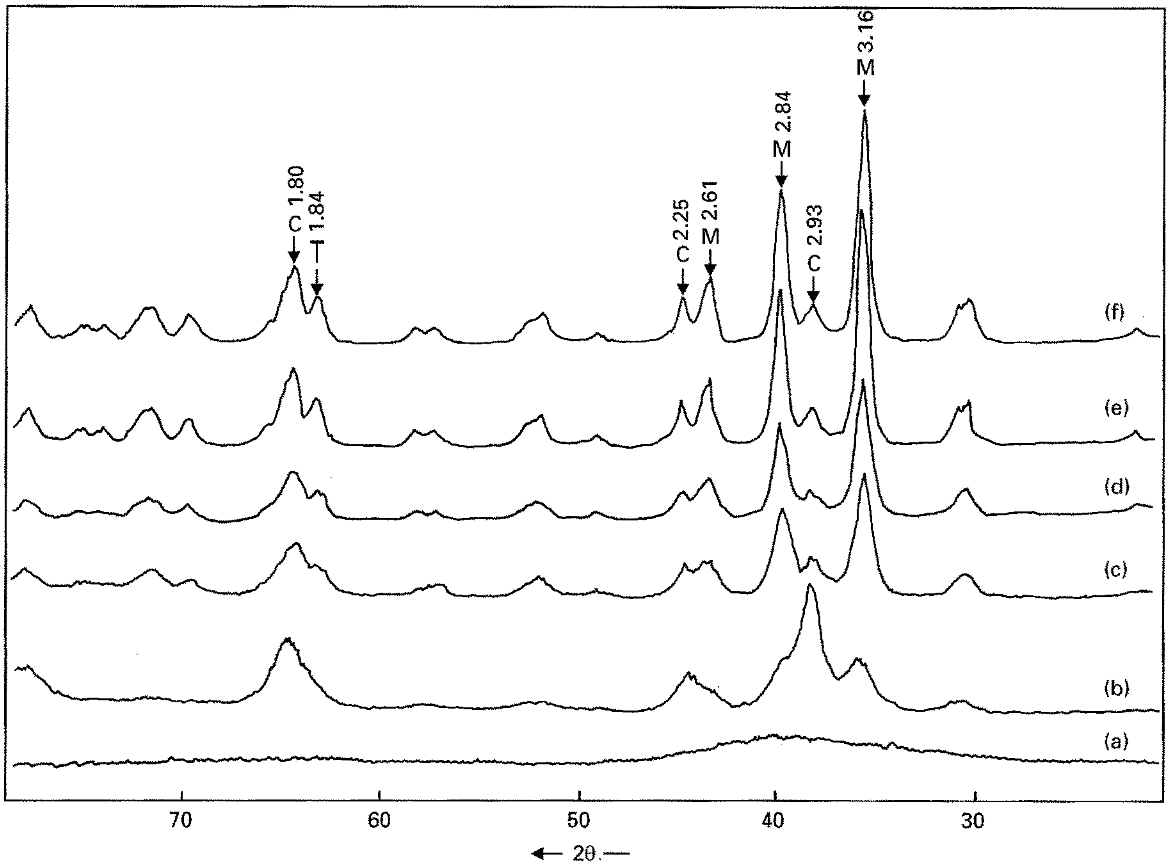

Figure 1 Effect of calcination temperature (°C) ((a) 110, (b) 350, (c) 450, (d) 550, (e) 650 and (f) 750) on the phase transformation of ZrO_2.

temperature. As can be seen, beyond 450 °C, only the monoclinic form predominates and this seems to be the transition temperature for phase transformation in unsulphated zirconia sample.

Many authors report the presence of either tetragonal phase [6] or tetragonal along with monoclinic forms [7–10] in zirconia calcined below 450 °C. However, as evidenced from XRD we see that the cubic phase is more predominant than the tetragonal phase. This does not in any way preclude the presence of tetragonal phase in small quantities as it is sometimes difficult to clearly distinguish the two phases.

In Fig. 2, the effect of calcination temperature on the phase transformation (XRD patterns) of sulphate modified zirconia is given. Sulphated zirconia (ZrO_2–SO_4^{2-}) just dried at 110 °C (curve-A) is only amorphous. On calcination to 350 °C, the cubic crystalline phase ($d = 0.293$ nm) starts to appear and is maintained up to 550 °C. Calcination beyond this temperature results in the formation of monoclinic phase with the simultaneous disappearance of the cubic phase. Comparison of high temperature calcined zirconia (Fig. 1, curves e and f) and ZrO_2–SO_4^{2-} (Fig. 2, curves e and f) shows that the unmodified zirconia seems to be more crystalline as evidenced from the intensity of the XRD patterns. It is also observed that the phase transformation from cubic to monoclinic takes place only beyond 550 °C in the case of ZrO_2–SO_4^{2-} compared to 450 °C in the case of pure ZrO_2.

This suggests that the addition of SO_4^{2-} ion before calcination is in some way responsible for inhibiting the phase transformation from cubic to monoclinic. This may be visualized due to the interaction between the hydroxyl groups of zirconia and the SO_4^{2-} ion as shown in Fig. 3.

The DTA curves of ZrO_2 and ZrO_2–SO_4^{2-} are shown in Fig. 4a and b. Pure ZrO_2 exhibits a crystallization exotherm at about 435 °C. However, the exotherm peak is shifted to 570 °C for ZrO_2–SO_4^{2-} (Fig. 4b). This observation is in agreement with Yamaguchi and Tanabe [4]. It appears that the presence of SO_4^{2-} ions seems to delay the crystallization of zirconia. This observation is also in line with that of XRD patterns. It should be noted that the influence of SO_4^{2-} ion on zirconia phase transformation is significant only when it is added to $Zr(OH)_4$ prior to calcination. Addition of SO_4^{2-} into ZrO_2 (calcined $Zr(OH)_4$ at 450 °C) does not seem to have any influence on the structural modification. The absence of an exotherm peak (Fig. 4c) and the presence of the monoclinic phase in the XRD pattern (Fig. 1c) show that the phase transformation has already taken place during calcination at 450 °C prior to SO_4^{2-} addition.

It is evident that the surface hydroxyl groups have a major role to play in the structural modification and the phase transformation of zirconia. Pure ZrO_2 on calcination easily undergoes dehydroxylation and results in the phase transformation from cubic to monoclinic accompanied by sintering and reduction in the specific surface area. Increasing the calcination temperature facilitates this process [11]. On the other hand, the addition of SO_4^{2-} ion as ammonium sulphate results in an intermediate complex as shown in Fig. 3. This inhibits the participation of surface –OH

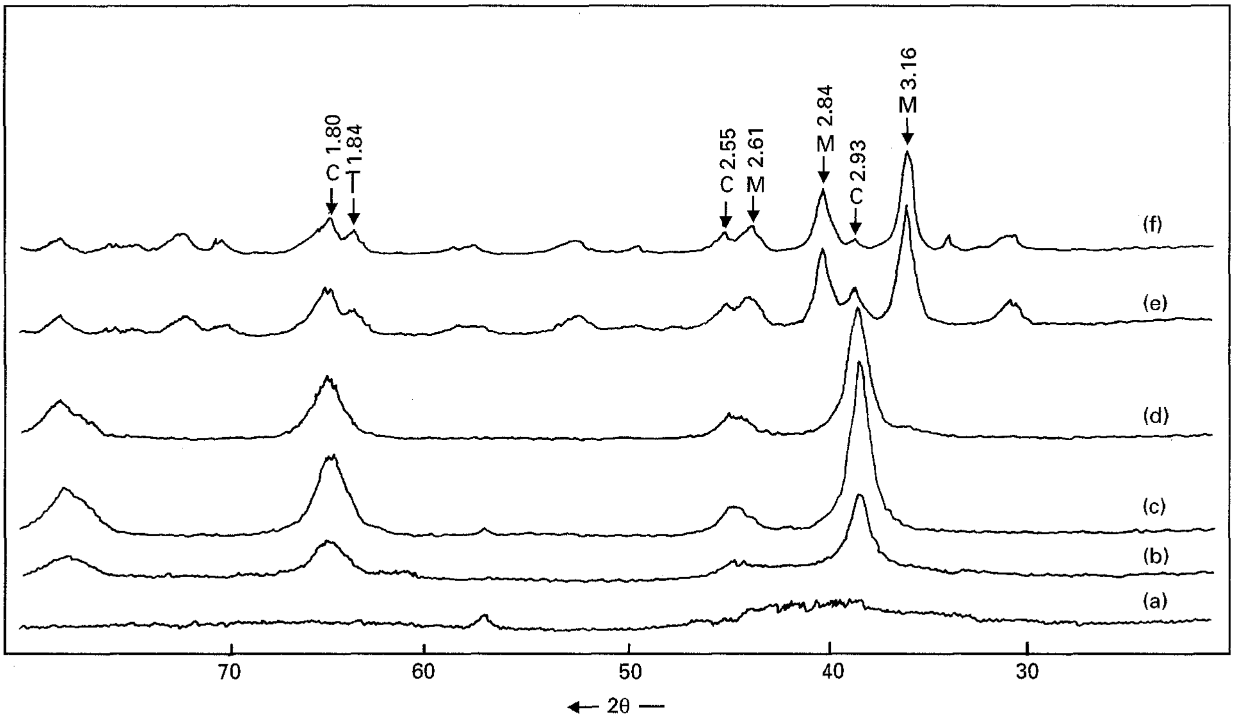

Figure 2 Effect of calcination temperature on the phase transformation of sulphated ZrO_2. Symbols (a), (b), (c), (d), (e) and (f) are the same as those given in Fig. 1.

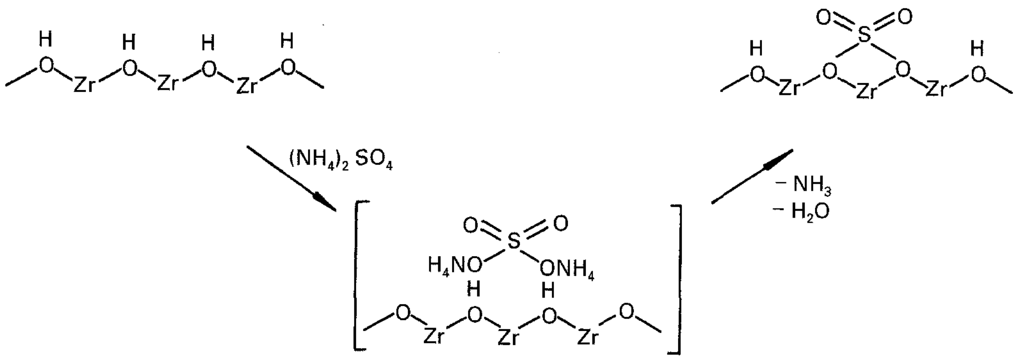

Figure 3 Proposed model for the complex formation of SO_4^{2-} with $Zr(OH)_4$ during calcination.

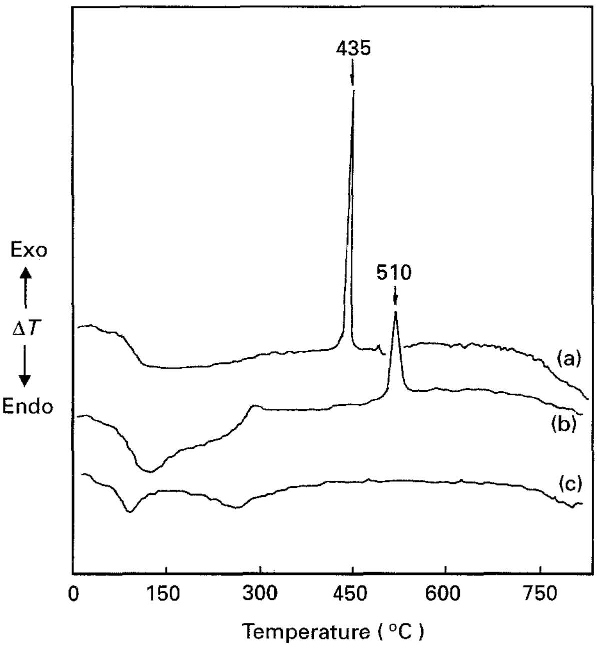

Figure 4 Thermal analysis curves of ZrO_2 and modified ZrO_2((a) pure ZrO_2 calcined at 450 °C; (b) SO_4^{2-} addition prior to calcination of ZrO_2 and (c) SO_4^{2-} addition after calcination of ZrO_2).

TABLE I Effect of calcination temperature, surface area and aniline conversion on ZrO_2 and sulphated zirconia

	Sample					
	ZrO_2			ZrO_2–SO_4^{2-}		
Calcination temperature	350	450	750	350	450	750
Surface area ($m^2 g^{-1}$)	116	58	19	164	140	36
Conversion (%)	–	–	–	71	88	26

groups in the dehydroxylation process due to calcination. This complex also helps to retain the cubic phase and the surface area. However, beyond 650 °C, due to the severity of conditions the phase transformation is accompanied by sintering or may be due to the decomposition of the sulphate complex from the surface resulting in SO_x evolution [12].

Table I gives a comparison of surface area of ZrO_2 and ZrO_2–SO_4^{2-} calcined at different temperatures. Surface area of pure ZrO_2 is generally less than that of

ZrO_2–SO_4^{2-}. The sulphated zirconia maintains the surface area as compared to pure zirconia up to 450 °C. However, at 750 °C, even the sulphated zirconia loses its surface area.

Pure ZrO_2 shows almost no activity for aniline alkylation under the given experimental conditions. However, sulphated zirconia is active. The conversion is reduced when ZrO_2–SO_4^{2-} is calcined at 750 °C. The catalytic activity seems to be dependent on zirconia phase, surface area and the acidic strength of the catalyst. It appears that the ZrO_2 with cubic phase with reasonable surface area is more favourable as a catalyst and the catalytic activity is enhanced by the addition of SO_4^{2-} ion.

The superacidity of sulphated zirconia is generated by the interaction between the oxide and SO_4^{2-} ion. The presence of an asymmetric vibrational mode of a $S=O$ is considered to be responsible for the presence of superacidity [13, 14]. The Lewis acid strength of Zr^{4+} becomes stronger by the inductive effect of $S=O$ in the complex. Hence there is a significant conversion on the sulphated zirconia catalyst as compared to the pure zirconia for the aniline alkylation reaction.

4. Conclusion

Zirconium hydroxide on calcination at 450 °C transforms into a monoclinic phase from a cubic phase. On addition of SO_4^{2-} ion prior to calcination at 450 °C, the cubic phase is maintained up to 550 °C and thereby increasing the catalytic activity of the aniline alkylation. This behaviour may be explained due to surface complex formation between SO_4^{2-} ion and zirconium hydroxide.

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Received 8 February 1994
and accepted 28 April 1995