

## Influence of $\text{SO}_4^{2-}$ , $\text{Cr}_2\text{O}_3$ , $\text{MoO}_3$ , and $\text{WO}_3$ on the stability of $\text{ZrO}_2$ -tetragonal phase

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Zirconia is an oxide with high melting point (2973 K), a low thermal conductivity, and a high resistance for corrosion. Therefore, it has been widely used for various purposes such as refractors, pigment, piezo electric devices, ceramic condensers, and oxygen sensors.  $\text{ZrO}_2$  is increasingly used in catalysis both as a support and as a catalyst [1, 2]. It efficiently catalyzes hydrogenation of CO [3, 4], olefins [5], and dienes [6]. Among the notable, the sulfated zirconia has attracted much attention recently because of its ability to catalyze many acid catalyzed reactions such as cracking, alkylation, isomerization, and condensation [7]. Recently, Hino and Arata [8] reported that  $\text{WO}_3$  doped  $\text{ZrO}_2$  is another alternative catalyst in reactions requiring stronger acid sites. Reddy *et al.* [9, 10] observed that  $\text{MoO}_3$  incorporated  $\text{ZrO}_2$  also catalyzes various acid catalyzed reactions more effectively. The major advantages of Mo- or W- modified  $\text{ZrO}_2$  over sulfated zirconia are that the former catalysts do not suffer from dopent loss during thermal treatments and also undergo significantly less deactivation during catalytic reactions. However, the exact role of these dopents on the genesis and stabilization of strong acidic properties of zirconia is not fully understood.

The primary objective of this investigation was to understand the precise role of  $\text{Cr}_2\text{O}_3$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ , and  $\text{SO}_4^{2-}$  on the physicochemical characteristics of  $\text{ZrO}_2$ . For this purpose a hydrated zirconia and a  $\text{ZrO}_2$  support were prepared and doped with equal amounts of the above dopents under identical conditions and investigated by X-ray diffraction and other methods.

The zirconium hydroxide was first prepared from  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (Loba Chime, GR grade) by hydrolysis with dilute aqueous ammonia solution. For this purpose, the requisite quantity of zirconium oxychloride was dissolved in doubly distilled water and to this clear solution the aqueous  $\text{NH}_3$  was added drop wise with rigorous stirring until the pH of the solution reached 8. The obtained precipitate was washed several times until free from chloride ions and dried at 393 K for 24 h. Thus accomplished hydrous zirconia was divided into two equal portions and a portion of which was calcination at 923 K for 6 h to obtain the  $\text{ZrO}_2$ . On the prepared  $\text{Zr(OH)}_4$  and  $\text{ZrO}_2$  supports a constant 6 mole % of chromium, molybdenum, tungsten, and sulfate ions were doped by adopting a wet impregnation method. To achieve this, the requisite quantities

of ammonium heptamolybdate (J T Baker, England, GR grade), ammonium tungstate (BDH Chemical Ltd., England), ammonium dichromate (Loba Chemie, GR grade), and  $\text{H}_2\text{SO}_4$  (Loba Chemie, GR grade) were dissolved in doubly distilled cold or hot water. To these clear solutions the desired quantity of  $\text{Zr(OH)}_4$  or  $\text{ZrO}_2$  in fine powder form were added and the excess water was evaporated on a water bath. The resulting samples were oven dried at 393 K for 24 h and calcined at 923 K for 6 h in a flow of oxygen. The X-ray powder diffraction (XRD) patterns were recorded on a Siemens D-5000 diffractometer using  $\text{Cu K}_\alpha$  radiation source and a scintillation counter detector. The XRD phases present in the samples were identified with the help of ASTM Powder Data Files. The amount of monoclinic and tetragonal phase present in the samples was estimated by comparing the areas under the characteristic peaks of the monoclinic phase ( $2\theta = 28.5^\circ$  and  $31.6^\circ$  for the (111) and (111) reflections respectively) and the tetragonal phase ( $2\theta = 30.4^\circ$  for the (111) reflection) [6]. Gaussian curves were first fitted to the XRD pattern at the characteristic peaks and the height  $h$  and width at half-height  $w$  were then obtained. The percent composition of each phase was calculated from the Gaussian areas  $h \times w$ :

$$\% \text{ Monoclinic} = \frac{\sum (h \times w)_{\text{monoclinic}}}{\sum (h \times w)_{\text{monoclinic and tetragonal}}}$$

$$\% \text{ Tetragonal} = \frac{\sum (h \times w)_{\text{tetragonal}}}{\sum (h \times w)_{\text{monoclinic and tetragonal}}}$$

The X-ray line broadening technique was used to determine the crystallite size for each phase from XRD data of monoclinic (111) and tetragonal (111) reflection by using the Debye-Scherrer equation [11].

The XRD patterns of  $\text{Zr(OH)}_4$  and  $\text{ZrO}_2$  samples impregnated with various dopents are shown in Figs 1 and 2, respectively. The percent composition of monoclinic and tetragonal phases and their crystallite size are presented in Table I. As can be noted from these figures and Table I that the pure  $\text{ZrO}_2$  obtained by calcining the hydrated zirconia at 923 K is in the crystalline state with monoclinic  $\text{ZrO}_2$  phase dominating over the tetragonal phase. A dramatic influence on the monoclinic to tetragonal phase formation and their crystallite size can be noted when various dopents are added

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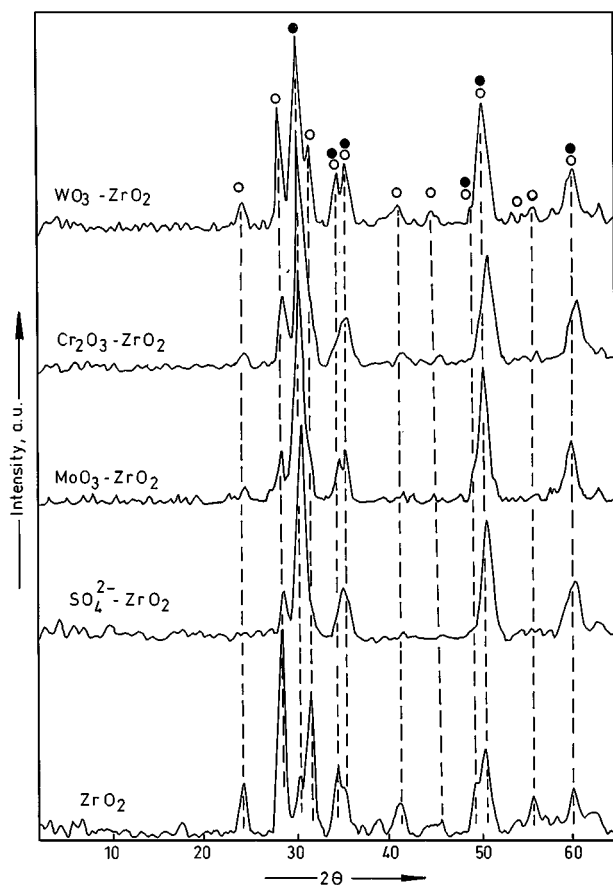


Figure 1 XRD patterns of various dopants containing  $ZrO_2$  samples. Dopants were impregnated on  $Zr(OH)_4$  and calcined at 923 K: (○) characteristic lines due to monoclinic phase; (●) lines due to tetragonal phase.

to the zirconia. Most importantly, this influence is more prominent when these dopants are incorporated to the  $Zr(OH)_4$  rather than to  $ZrO_2$ . In the case of  $SO_4^{2-}/ZrO_2$  sample, the tetragonal  $ZrO_2$  dominates over the monoclinic phase. A much similar behavior can be noted in the case of  $MoO_3/ZrO_2$  sample. However, the  $Cr_2O_3$  and  $WO_3$  are not as effective as  $MoO_3$  and  $SO_4^{2-}$ . As can be noted from these results that the monoclinic to tetragonal phase change has been facilitated when the support employed is hydrous zirconia instead of  $ZrO_2$ . This is due to the incorporation of cations or anions into the solid solution, which substantially decreases the specific surface free energy of zirconia and favors the tetragonal phase that has a low surface free energy than the monoclinic form [12–14].  $ZrO_2$  normally exists in the monoclinic, tetragonal and cubic structure

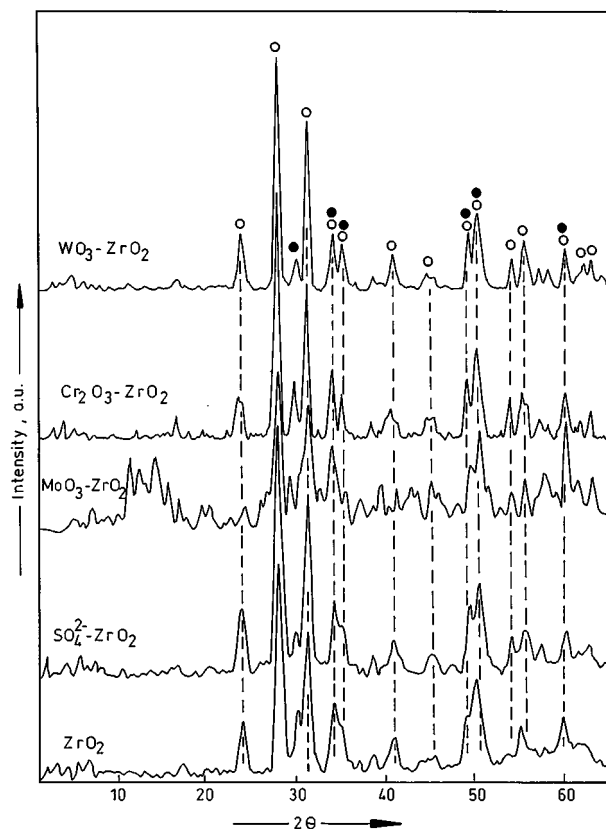


Figure 2 XRD patterns of various dopants containing  $ZrO_2$  samples. Dopants were impregnated on  $ZrO_2$  and calcined at 923 K: (○) characteristic lines due to monoclinic phase; (●) lines due to tetragonal phase.

[15]. The pure  $ZrO_2$  monoclinic phase, in the absence of impurities, is stable up to 1373 K, and transforms to tetragonal as the temperature increases to 1473 K. On cooling this high temperature tetragonal phase transforms back to the monoclinic phase with a large hysteresis, so that the tetragonal to monoclinic transition occurs between 1273 K and 1123 K [16, 17]. However, stabilization of the tetragonal phase well below 1373 K is very important in the use of  $ZrO_2$  for catalytic applications.

The structure of sulfated zirconia and Mo- or W-promoted zirconia catalysts were investigated by various techniques [18–20]. These studies revealed that the zirconia is predominantly present in tetragonal modification and the retained sulfate ions are mostly located on the zirconia surface in the case of  $SO_4^{2-}/ZrO_2$  samples. In the case of W- or Mo-doped catalysts, the tungsten or molybdenum oxides exist both as crystallites of

TABLE I Amount of monoclinic and tetragonal phases of  $ZrO_2$  and their crystallite size in various samples prepared by impregnation of various dopants on  $Zr(OH)_4$  or  $ZrO_2$  and calcined at 923 K

Sample	$Zr(OH)_4$				$ZrO_2$			
	Monoclinic		Tetragonal		Monoclinic		Tetragonal	
	Amount (%)	Size (nm)	Amount (%)	Size (nm)	Amount (%)	Size (nm)	Amount (%)	Size (nm)
$ZrO_2$	76	11.2	24	13.0	—	—	—	—
$SO_4^{2-}/ZrO_2$	20	07.3	80	12.3	85	11.3	15	14.8
$Cr_2O_3/ZrO_2$	23	10.3	77	11.4	80	14.4	20	16.5
$MoO_3/ZrO_2$	16	08.5	84	14.3	82	10.4	18	22.5
$WO_3/ZrO_2$	32	11.9	68	16.2	79	15.0	21	10.9

WO<sub>3</sub> or MoO<sub>3</sub> and in the dispersed state along with tetragonal form of ZrO<sub>2</sub> [19, 21]. It appears from the present study that the strong acidity of sulfated ZrO<sub>2</sub> and W- or Mo-promoted zirconia catalysts is mainly due to the preparation process. In the normal preparation, the amorphous Zr(OH)<sub>4</sub> loses water and crystallizes predominantly to monoclinic zirconia with some small amount of tetragonal ZrO<sub>2</sub> upon calcination at elevated temperatures. The modifiers such as sulfuric acid, ammonium molybdate, and others profoundly change this crystallization phenomenon. These modifiers influence the crystallization characteristics of the zirconia and results in the formation of tetragonal zirconia. Additionally, these modifiers also stabilize the formed tetragonal zirconia. Thus, doping of metal cations and SO<sub>4</sub><sup>2-</sup> anions to hydrated zirconia and calcination at 923 K results in the formation of tetragonal phase, which is very active for the observed, many organic transformations.

The following conclusions can be drawn from this study: (1) The various dopents such as Cr-, Mo-, W- of SO<sub>4</sub><sup>2-</sup> influence differently when impregnated on Zr(OH)<sub>4</sub> or ZrO<sub>2</sub>. (2) Incorporation of these dopents to Zr(OH)<sub>4</sub> is more preferred in terms of the favored tetragonal phase formation. (3) Among various dopents the SO<sub>4</sub><sup>2-</sup> is more effective followed by MoO<sub>3</sub> for the desired tetragonal ZrO<sub>2</sub>. Finally, further studies are highly essential in order to understand fully the microscopic mechanism of the transformation of monoclinic to tetragonal phase under the influence of chromium, molybdenum, tungsten, and sulfate ions at low temperatures.

### Acknowledgments

Thanks are due to Council of Scientific & Industrial Research, New Delhi, for the award of a senior research fellowship to V.R.R.

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*Received 29 April  
and accepted 18 November 1999*