Research Article

Amit Kumar, Shailey Singhal, Shilpi Aggarwal, Rajendra Prasad Badoni, Amit Kumar Sharma*

Influence of Synthetic Approach of $\text{SiO}_2\text{-ZrO}_2$ Materials

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Abstract: In the present manuscript, the effect of the synthetic route on the properties of $\text{SiO}_2\text{-ZrO}_2$ has been evaluated. Co-precipitation, sol-gel and microwave methods were adopted for synthesizing the structured oxide. The properties of the final products such as surface morphology, crystallinity, surface area, pore volume and size, particle size and total acidity were examined using standard instrumentation like Fe-SEM, XRD, BET and TPD. The results revealed that the mixed oxides were mesoporous in nature with a high BET surface area ($315\text{--}435\text{m}^2/\text{g}$). Among various methods, the microwave route achieved the highest surface area ($433\text{m}^2/\text{g}$), pore volume (0.70cc/g) and pore size (6.50nm). The total acidity of the sample synthesized by the microwave reactor was also higher (0.296mmol/g) than that resulting from other methods. Results conclude that microwave method is a suitable choice for synthesizing the structured oxides with desirable properties.

Keywords: Structured oxides, mixed oxides, nanoparticles, BET

1 Introduction

Mixed metal oxides represent a small but an important and diversified part of the entire family of inorganic compounds. They are widely used as fillers or pigments

in the paper, paint or plastic industries and are also being utilized in ceramic and electronic technology. They are thermally stable, consist of metal cations and oxygen anions and behave as a template in many of the reactions of industrial importance. However, the properties are, more or less, related to the degree of mixing of the two oxide components. In recent years, $\text{SiO}_2\text{-ZrO}_2$ mixed-oxides have been studied extensively due to their superior physicochemical properties [1–2] such as higher thermal and chemical stability, hardy mechanical strength, catalytic activity and strong surface acidity. Macro et al. 2002 synthesized a series of microporous silica-zirconia based catalysts for the oxidation of cyclohexene [3]. It is also reported in the literature that these catalysts exhibit good activity towards the isomerization of n-heptane [4].

Several strategies have been developed for the synthesis of $\text{SiO}_2\text{-ZrO}_2$ mixed-oxides, such as hydrothermal routes [5], deposition of silicate on zirconia [6], impregnation [7], co-precipitation [8], and the sol-gel method [9–10]. In contrast with traditional techniques, the solution sol-gel method gives excellent control of the properties of the products. In addition, the products prepared by conventional methods have lower surface areas and pore volumes than desired for catalytic applications. Therefore, the aim of this research is to improve the properties of the silica zirconia mixed oxide using different methods of synthesis. In this study, we have synthesized a $\text{SiO}_2\text{-ZrO}_2$ mixed oxide using tetraethyl orthosilicate (TEOS) and zirconium oxychloride through different methods and studied the various physico-chemical properties in order to choose the best strategy to obtain the required characteristics such as surface morphology, crystallinity, surface area, pore volume, pore size, particle size and total acidity.

2 Materials and Methods

Fresh solvents were employed for all synthesis work. Tetraethyl orthosilicate (TEOS) used was of Sigma Aldrich, while zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) was of LOBA

*Corresponding author: Amit Kumar Sharma, Department of Chemistry, College of Engineering Studies, University of Petroleum & Energy Studies, Dehradun (Uttarakhand), India,

E-mail: amitk@ddn.upes.ac.in, amit.orgchemistry@gmail.com

Amit Kumar, Shailey Singhal, Shilpi Aggarwal, Department of Chemistry, College of Engineering Studies, University of Petroleum & Energy Studies, Dehradun (Uttarakhand), India

Rajendra Prasad Badoni, Department of Chemical Engineering, College of Engineering Studies, University of Petroleum & Energy Studies, Dehradun (Uttarakhand), India

chemie and Ethanol. Nitric acid (HNO_3) was from Fischer scientific. All the chemicals were of AR grade.

2.1 Synthesis of Structured Oxides

Three different strategies were adopted for the synthesis of structured oxides, viz. co-precipitation, sol-gel, and microwave routes.

2.1.1 Co-precipitation method

In a flat bottom flask, TEOS (70% by wt.) was diluted two times with ethanol and stirred vigorously for 15 minutes at room temperature. A dilute solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (30% by wt.) was then added slowly with continuous stirring. The resulting solution was precipitated by the drop wise addition of ammonium hydroxide raising the pH up to 10. The mixture was then kept in oil bath at 90-100°C for 4 hr. The resulting mixed oxide was carefully filtered using a vacuum pump, and washed with distilled water until the pH of the washing solution decreased from 10 to 7. It was dried at room temperature overnight, followed by heating at 120°C in a hot air oven. After drying, the oxide was ground to the sieve size of 100 μm and then calcined at 550°C for 5 hours at the rate of 1°C/min. The sample synthesized by this method was referred as SZ1.

2.1.2 Sol-Gel method

In the sol-gel method, a similar strategy was adopted as was applied in the case of the co-precipitation method, however, the digestion of the solution was performed at 40°C for 24 h to permit the transformation to sol and gel states. The sample was referred as SZ2.

2.1.3 Microwave method

TEOS (70% by wt.) was placed into a 500ml round bottom flask and diluted with dilute nitric acid. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (30% by wt.) was dissolved in dilute nitric acid and mixed with the solution of TEOS. The resulting solution was stirred at 600 rpm in microwave reactor (Raga Tech) at 70°C for 30 min. Then the oxide was filtered, washed, dried, sieved and calcined. The sample was referred as SZ3.

The flow chart outline for the synthesis of the $\text{SiO}_2\text{-ZrO}_2$ structured oxide by different methods is represented in Scheme 1.

2.2 Characterization of Structured Oxides

The powder X-ray diffraction analyses were carried out by a Bruker D8 advance instrument using $\text{CuK}\alpha$ radiation with $\lambda = 1.541 \text{ \AA}$ and range $2\theta = 15$ to 80° at a scan rate of $10^\circ \text{ min}^{-1}$ and a step size of 0.2° . The morphology of the silica-zirconia was characterized using TESCAN, MIRA3, French. Prior to testing, the samples were gold coated using a super coater (Edward S150) to provide conductivity to the sample. Fourier transform infrared spectroscopy (FTIR; Perkin Elmer) was employed to analyse the linkages between the silica and the hetero-metal oxide network. The surface area was measured by the BET method. The pore volume, pore size distributions, and particle size was examined by a nitrogen adsorption/desorption isotherm at -196°C using the Accelerated Surface Area and Porosimetry System, Micromeritics, ASAP 2020. All the samples were degassed at 250°C for 6 hours prior to actual measurements. The profile of temperature-programmed desorption of ammonia ($\text{NH}_3\text{-TPD}$) over the catalysts was performed by a Micromeritics Chemsorb 2750. The crystallite size of the synthesized materials (SZ3) was determined applying Scherer's equation (1), where λ is the

Scheme 1. Different synthetic strategies for $\text{SiO}_2\text{-ZrO}_2$

wavelength radiation used ($\lambda = 1.5406 \text{ \AA}$), θ is the Bragg angle and β is the line width at half maximum height calculated from the full width at half maximum intensity (FWHM) of the mean reflection (101).

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

3 Results & Discussion

3.1 X-Ray Diffraction

Colorless samples were obtained from all the three methods. Figure 1b shows the development of crystalline structures is depend on the synthetic route (in the case of SZ3, crystalline in nature) and reaction conditions. The PXRD pattern of SZ3 is crystalline in nature as the all the lines are sharp in the pattern (b) as shown in Figure 1.

In the diffraction patterns of silica zirconia mixed oxide, it can be noted that in material SZ3, the SiO₂-ZrO₂ mixed metal oxide is crystalline and exhibits intense peaks at $2\theta = 30.17^\circ$, 35.07° , 50.59° and 60.11° composed of tetragonal crystalline structure of zirconia, corresponding to (101), (110), (112) and (211) planes respectively, according to pattern card number JCPDS 80-2155. Also, low intensity signals are seen at $2\theta = 27.16^\circ$, 62.84° and 74.54° that characterize the existence of zirconium oxide with a monoclinic structure as compared to card number JCPDS 7-3430. These results suggest that tetragonal and monoclinic phases coexist in this sample. In the case of SZ1, SZ2 and pure silica, a peak around 25° indicated the presence of amorphous materials (Figure 1a, c, d). It is important to note that the sample synthesized by the microwave method is crystalline in nature. The average crystallite size of the SZ3 material was around 13.83 nm calculated by Scherer's equation. The other three samples

Figure 1. XRD pattern of samples (a) silica (b) SZ1 (c) SZ2 (d) SZ3

(a)

(b)

(c)

(d)

Figure 2. Fe-SEM image of sample (a) Pure silica (b) SZ 1 (c) SZ 2 (d) SZ 3

are amorphous in nature as shown in Figure 1 and predicted on the basis of PXRD patterns.

3.2 Morphology

Scanning electron microscopy was carried out to investigate the surface morphology, shape and size of the particles, and the nature of the oxides. Figure 2 represents typical SEM photographs of the samples. It can be seen that with the addition of zirconia, modification in the morphology results in aggregates without regular shapes and distribution. The particles are bulky with irregular shapes and appear to be mesoporous. In the case of the SZ2 image, it can be clearly seen that zirconia is deposited over the crystals of silica and the surface of the silica is covered

with zirconia. This type of morphology is not observed in the other images as the resolution of SZ1 and SZ3 is low. Addition of zirconia on silica causes agglomeration with an increase in particle size.

3.3 FTIR Analysis

Figure 4 shows the FTIR spectrum of $\text{SiO}_2\text{-ZrO}_2$. A broad band around 3450cm^{-1} shows the existence of hydroxyl groups [11]. The existence of a pure silica matrix is represented by an overtone around 1632cm^{-1} in the spectra [11]. The peaks obtained at 1111cm^{-1} and 800cm^{-1} indicate asymmetric and symmetric stretching of Si-O-Si respectively, while peaks at 800cm^{-1} and 474cm^{-1} indicate the bending mode of Si-O-Si [12-15]. The Peak observed at 1069cm^{-1} is due to Si-O-Zr [16] and confirms the synthesis

of the structured oxide. The band at 1069 cm^{-1} is tentatively assigned to an asymmetric Si-O-Si stretch perturbed by the presence of Zr in its environment.

Figure 4. FTIR of samples (a) SZ 1 (b) SZ 2 (c) SZ 3 (d) Pure silica

Based upon FTIR results, it is very well confirmed that a Si-O-Zr linkage exists and the following skeletal structure can be assigned to the structured oxide synthesized Scheme 2.

Scheme 2. Skeletal structure of $\text{SiO}_2\text{-ZrO}_2$

3.4 BET Studies

The N_2 adsorption-desorption isotherms of $\text{SiO}_2\text{-ZrO}_2$ prepared by various methods are shown in Figure 5a. The results revealed that all the samples were type IV isotherms with H3 type hysteresis loops which confirm the presence of plate like particles forming slit shaped pores [17]. In addition, the existence of conspicuous hysteresis loops at high relative pressures also indicates its mesoporous nature [18]. The pore size distribution (PSD) of the material was calculated from the desorption branch of the isotherm (Figure 5b). It was observed that the $\text{SiO}_2\text{-ZrO}_2$ samples synthesized by the conventional methods (sol-gel and precipitate methods) have wider PSD than microwave synthesis method. The intercalation of oxides and reduction of particle size (13.83-19.01 nm) to nano range resulted into high surface areas and pore volumes. The surface areas of the structured oxides are in the order: SZ3 ($433\text{ m}^2/\text{g}$) > SZ2 ($324\text{ m}^2/\text{g}$) > SZ1 ($315\text{ m}^2/\text{g}$), however the pore volumes are in the order SZ3 (0.70 cc/g) > SZ1 (0.40 cc/g) > SZ2 (0.35 cc/g). This can be explained by the fact that microwave radiation leads to good digestion of the reaction mixture resulting in a higher surface area [19].

Bulk density is an indicative of the strength of the material, and was contributed to by both silica and zirconia; however acidity was mainly due to the incorporation of the zirconium moiety in the samples.

3.5 Ammonia Desorption

The acidic characteristics of the $\text{SiO}_2\text{-ZrO}_2$ mixed oxides examined by NH_3 -TPD are shown in Table 1 and Figure 6. The results of the NH_3 -TPD profile showed that the peaks are obtained in two temperature regions i.e. a high

Figure 5. (a) Nitrogen adsorption/desorption isotherms (b) Pore size distribution

temperature (HT) region ($T > 400^\circ\text{C}$) and a low temperature (LT) region ($T < 400^\circ\text{C}$) and are due to the desorption of ammonia from strong acid sites and weak acid sites respectively [20-21].

The TPD profiles for all the samples (SZ1, SZ2, SZ3 and pure silica) were taken from 100–800°C (Figure 6). All the samples showed peaks between 100 and 500°C. The results demonstrate the presence of acid sites of different strengths in these solids. The desorption peaks of TPD profiles located at 100–200°C, 200–400°C and 400–650°C can be assigned to weak, moderate and strong acid sites, respectively [22-24].

Pure SiO_2 contained 0.35 mmol/g strong acid sites. While the $\text{SiO}_2\text{:ZrO}_2$ (SZ 1, SZ 2, and SZ 3) catalyst prepared in over study contained 0.67–1.68 mmol/g strong acid sites.

It was also observed that the ammonia desorption for the metal oxides, which indicates the total acidity of the metal oxide, varies with the synthesis route (Table-1). The peak above 500°C corresponded to the decomposition of strongly absorbed ammonia to nitrogen.

The BET surface area, pore volume (V_p), average pore diameter, average particle size, total acidity and bulk density of the structured oxides are given in Table-2.

4 Conclusion

Structured oxides of silica and zirconia ($\text{SiO}_2\text{-ZrO}_2$) have been prepared by three different methods. The results clearly indicate that the variations in the synthetic route also affected the characteristics of the oxides. All the prepared structured oxides (mixed oxides) were comprised of high surface areas, good pore volumes and acceptable

acidities and bulk densities, however, the microwave method showed an excellent increase in surface area, pore volume, pore size and acidity. In addition, the mixed oxides prepared by conventional methods (SZ1 and SZ2) were X-Ray amorphous, whereas the sample SZ3 prepared by the microwave synthesis route was crystalline in nature.

The NH_3 -TPD experiment shows that at a temperature of greater than 400°C ammonia was still chemisorbed indicating the presence of strong acid sites. Titration showed that pure SiO_2 contained 0.015 mmol/g strong acid sites. The $\text{SiO}_2\text{:ZrO}_2$ (SZ1, SZ2, SZ3) catalyst prepared contained 0.046–0.078 mmol/g strong acid sites.

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Figure 6. Ammonia desorption pattern of samples

Table 1: Acid sites in the samples

Sample	Acidity (mmol/g)			Total Acidity (mmol/g)
	100–200°C (Weak sites)	200–400°C (Moderate sites)	400–650°C (Strong sites)	
SZ1	0.03	0.1798	0.078	0.284
SZ2	0.02	0.175	0.030	0.225
SZ3	0.04	0.210	0.046	0.296
Pure Silica	0.011	0.084	0.015	0.111

Table 2: Characteristics of $\text{SiO}_2\text{-ZrO}_2$

Sample	S_A (m^2/g)	V_p (cc/g)	D_p (nm)	S_p (nm)	A_T (mmol/g)	D_B (g/cc)	Crystallinity
Pure SiO_2	578	1.7	10.0	11.0	0.111	0.2	Amorphous
SZ1	315	0.40	4.34	19.01	0.284	0.65	Amorphous
SZ2	324	0.35	3.67	18.50	0.225	0.69	Amorphous
SZ3	433	0.70	6.50	13.83	0.296	0.56	Crystalline

S_A : Surface area; V_p : Pore volume; D_p : Average pore diameter; S_p : Average particle size; A_T : Total acidity; D_B : Bulk density

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