

Heterogeneous catalysis on combustion synthesised SrZrO_3

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Strontium zirconate (SrZrO_3) has been synthesized by solution combustion synthesis method using mixture of fuels, such as glycine, urea and ammonium nitrate, and corresponding metal nitrates as oxidizer. It has been characterized by XRD, electrical conductivity, diffuse reflectance spectra, TGA and DTA analysis, surface area and powder density measurements. Surface area, measured by Brunquer-Emmett-Teller method, has a value of $15.34 \text{ m}^2 \text{ g}^{-1}$. Particle size is calculated using values of surface area and powder density, which has a value of 56 nm. The SrZrO_3 powders thus synthesised have been used as a catalyst for the decomposition of H_2O_2 at two different temperatures. Activation energy has been found to be 290 Cal.mol^{-1} , suggesting the occurrence of chemisorption.

Keywords: Catalyst, Solution combustion synthesis, Strontium zirconate, Surface area

Strontium zirconate (SrZrO_3) is currently gaining considerable attention in the field of heterogeneous catalysis^{1,2}. The performance of this material depends on starting powder purity, perfection of its crystal lattice and dimension of the crystal, which, in turn, depends on synthesis procedure and conditions. Conventional solid-state reaction between strontium carbonate and zirconium oxide (ZrO_2) requires high temperature (1200°C), intermittent grinding and prolonged duration of calcinations (48 h) (ref. 3) for the completion of diffusion-controlled reaction to form SrZrO_3 powder. Further, the SrZrO_3 powder thus obtained has undesirable powder characteristics such as inhomogeneity, presence of impurity, coarser powder with non-uniform size and its distribution. To eliminate these problems wet chemical methods viz. coprecipitation⁴⁻⁷, sol-gel^{8,9} and hydrothermal^{10,11} have been tried to generate active SrZrO_3 powder with required purity, stoichiometry, physical and chemical characteristics. However, some problems still persist in these methods¹²⁻¹⁴. To get rid of some of these problems, solution combustion synthesis method¹⁵⁻¹⁷ has been tried to obtain fine, pure and active stoichiometric SrZrO_3 crystalline powder. It has been used to produce wide variety of materials including catalysts and carriers characterized by high activity and selectivity and good physical, chemical and

mechanical properties¹⁸⁻²⁰. Many of these are cheaper, more efficient and can be used to replace traditionally processed catalysts used in the chemical industry²⁰.

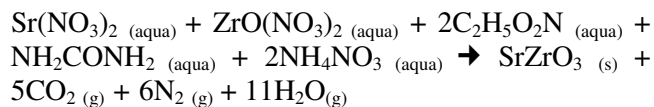
Literature survey reveals that combustion synthesised SrZrO_3 have not been used for heterogeneous catalysis. Present research work involves the study on synthesis, characterisation and catalytic property of strontium zirconate.

Experimental Procedure

The starting chemicals used in this study were zirconyl nitrate (Loba), strontium nitrate (BDH), ammonium nitrate (Merck), glycine (BDH), urea (Merck) and hydrogen peroxide (Merck). The stoichiometry of the metal nitrates and fuels was calculated based on total oxidizing and reducing valency of the oxidizer and fuels, which serve as numerical coefficient for stoichiometric balance so that the equivalence ratio (Φ_e) is unity²¹. The fuels, glycine, urea and ammonium nitrate were used in 2:1:2 molar proportions. The amount of oxidizers and fuels was taken in such a way that the desired product SrZrO_3 formed is 5 g. The mixture was dissolved in minimum quantity of water in a 250 mL capacity borosil make glass beaker. The beaker containing mixture was introduced into a muffle furnace maintained at 773 K. The mixture boils, froths, foams and ignite to burn, yielding voluminous and foamy SrZrO_3 . The theoretical equation for the formation of SrZrO_3 can be written as follows:

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The crystallinity and phase identification of the powder were determined by using Philips PW-1700 X-ray diffractometer with Ni filtered Cu K α radiations. Direct current (DC) resistivity of SrZrO₃ was measured as a function of temperature in the temperature range 650 -1000 K by standard two-probe method described elsewhere²². Reflectance spectra were scanned between 250 nm and 1000 nm wavelength range using Shimadzu UV- Visible spectrophotometer. DTA and TGA measurements were carried out on Mettler, Tolado, Switzerland in the temperature range 373 - 1173 K. Surface area measurement was done using nitrogen gas adsorption multipoint Brunquer-Emmett-Teller (BET) method and Micromeritics ASAP 2010 model, assuming a cross-sectional area of 0.162 nm² for nitrogen molecule. Powder density was measured using a pycnometer with xylene as the liquid medium. The diameter of the primary particle was calculated from the superficial area using following equation:

$$D_{\text{BET}} = 6/S_{\text{BET}} \cdot \rho \quad \dots (1)$$

where S_{BET} is the superficial area (m²g⁻¹) measured by BET analyses; ρ , the density of powder (g cm⁻³); and D_{BET} , the diameter of the produced particle.

The strontium zirconate thus synthesized was used as such without any modification as a catalyst for the decomposition of hydrogen peroxide. Very dilute H₂O₂ solution (5 cm³) (solution of H₂O₂ was prepared in such a way that after decomposition the total gas evolved is 50 cm³) was taken in a 100 cm³ capacity reaction vessel. To this vessel, 100 mg catalyst powder was added and then the vessel was connected to gas burette. Water reservoir of the gas burette was adjusted at 0 cm³. Then the pressure in the gas burette was adjusted to 1 atmosphere (by making the water level in gas burette and reservoir to stand at the same level). The contents in the reaction vessel were constantly stirred and the volume of the gas evolved was recorded at the intervals of 5 min (V_t), adjusting each time the pressure in the gas burette at 1 atmosphere. Without disconnecting the reaction vessel from the gas burette, the contents were heated in a boiling water bath so as to complete the decomposition of H₂O₂. When the gas ceases to evolve, the reaction vessel was cooled to the temperature of the experiment i.e. 308 K and final volume V_∞ was recorded. In order to determine the energy of activation the experiment was repeated at

another temperature, i.e. 318 K. The initial concentration at any time ' t ' is proportional to ($V_\infty - V_t$). A plot of log ($V_\infty - V_t$) against time ' t ' was plotted, the slope of which gives the value - $K/2.303$. The rate constant ' K ' was calculated using following relationship:

$$K = 2.303/t * \log V_\infty/(V_\infty - V_t) \quad \dots (2)$$

The energy of activation ' E ' (Cal.mole⁻¹) was obtained using the following equation:

$$\log K_2/K_1 = -E/2.303 R * [1/T_2 - 1/T_1] \quad \dots (3)$$

where E is the energy of activation; K_1 and K_2 , the specific rate constants at two temperatures T_1 and T_2 ; and R , the gas constant.

Results and Discussion

The solution combustion synthesis using glycine, urea and ammonium nitrate as fuels was found to be successful in producing crystalline, phase pure powder of SrZrO₃ at a temperature less than 773 K within 10 min time. Generally, suitable fuels react non-violently, produce non-toxic gases and acts as good complexant for metal cations²³⁻²⁴.

The XRD pattern of as synthesized SrZrO₃ is shown in Fig. 1. It is observed that only a single phase with orthorhombic structure has been formed and oxide is crystalline in nature. The powder XRD shows very sharp peaks, which can be attributed to high exothermicity of solution combustion process. The high exothermicity of process may be attributed to the presence of ammonium nitrate, which may act as a combustion aid as suggested by Segadaes *et al.*²⁵. Biamino *et al.*²⁶ observed that when ammonium nitrate is present in the reactants, the sample temperature, some time after ignition, increases more quickly and the combustion rapidly reaches the end. Thus, ammonium nitrate provides required temperature for the formation of pure SrZrO₃ and also hinders detrimental secondary reactions of thermal decomposition.

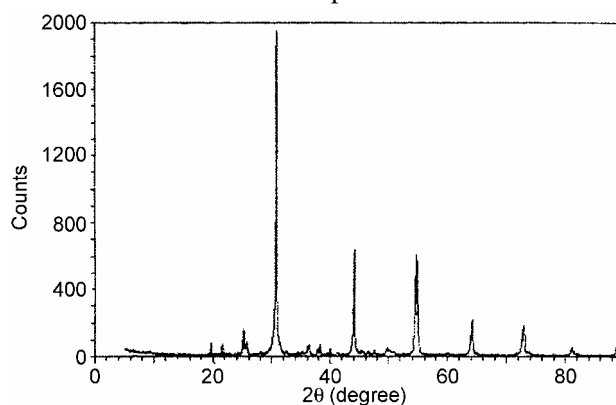


Fig. 1—XRD pattern of as synthesised SrZrO₃

Temperature dependence of the electrical conductivity is shown in Fig. 2. The plot of $\log \sigma$ against $1/T$ is linear showing that the well-known exponential law $\sigma = \sigma_0 \exp(-E_g/KT)$ is obeyed in the temperature range covered, indicating that strontium zirconate behaves as a semiconductor in the temperature range studied. The value of activation energy of SrZrO_3 is found to be 0.66 eV. The electrical transport in SrZrO_3 may be mixed ionic (protonic) type and electronic conduction²⁷⁻²⁹.

Diffuse reflectance spectra are an efficient tool for the determination of band gap of materials³⁰. It shows an absorption in the UV region. The band gap is found to be 3.42 eV. The difference in the values of the band gap determined from diffuse reflectance spectra and electrical conductivity measurements is attributed to different experimental conditions and the source of excitation of electron³¹. The absorption peak at lower wavelengths can be attributed to charge transfer process. In the oxide containing transition metals the absorption peaks due to charge transfer processes are observed at photon energy ≥ 3 eV(ref. 32).

TGA and DTA results of SrZrO_3 are shown in Fig. 3. It is observed from the thermogram that the compound is almost stable with very small weight loss (2.6%). The very small weight loss observed in the compound may be due to structural changes taking place in the compound. No thermal degradation is observed up to 865.5 K. DTA results of SrZrO_3 show four exothermic peaks. The exothermic peaks in the high temperature region can be attributed to the formation of different phases in the compound.

BET surface area is found to be $15.34 \text{ m}^2\text{g}^{-1}$. Powder density was calculated by pycnometer using xylene as liquid medium. The value of the same is found to be 6.89 g cm^{-3} . The average particle diameter obtained by

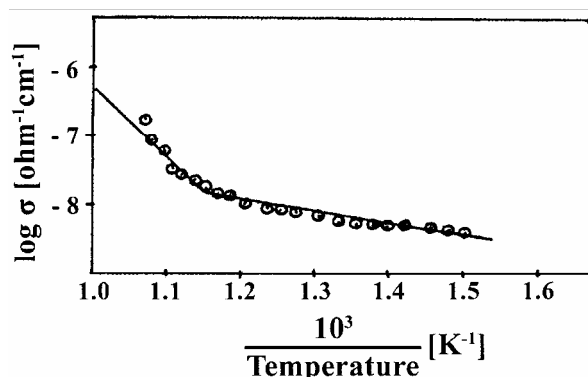
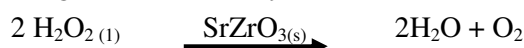


Fig. 2—Temperature dependence of the electrical conductivity of SrZrO_3

specific surface area measurement and density values is found to be 56 nm by using Eq. (1).

From the characterization of SrZrO_3 , it is observed that the material is stable having moderate surface area. It has been thought to use this material as a catalyst. The decomposition of hydrogen peroxide (H_2O_2) is studied using SrZrO_3 as a catalyst, as shown below:



This is an example of heterogeneous catalysis involving liquid reactants while catalyst is present in the solid form. The decomposition of H_2O_2 was studied at two different temperatures, namely 308 K and 318 K at time ranging from 0 min to 30 min in the intervals of 5 min. The results obtained are presented in Fig. 4 as a plot of $\log (V_\infty - V_t)$ versus time 't'. The

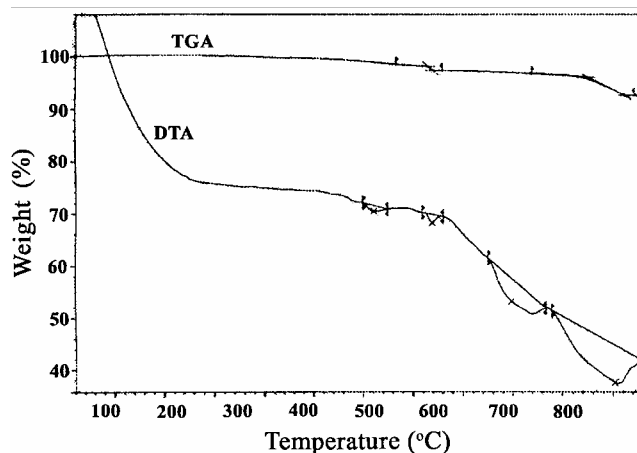


Fig. 3—TGA and DTA curve for SrZrO_3

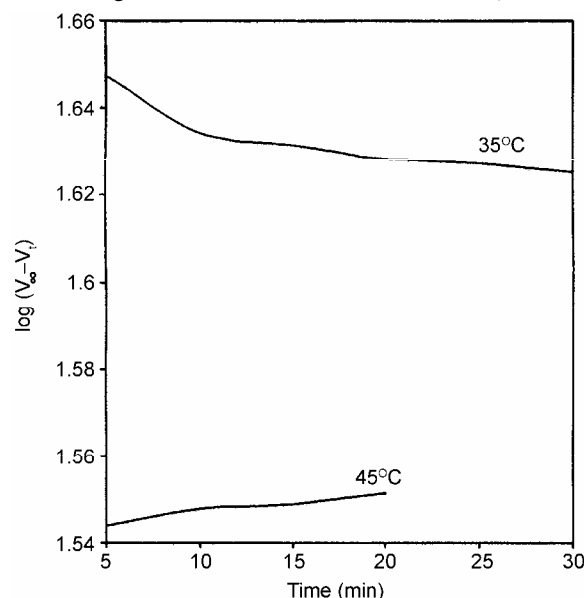


Fig. 4—A plot of $\log (V_\infty - V_t)$ versus time for catalytic activity of SrZrO_3

value of activation energy is found to be 290 Cals.mole⁻¹ as calculated using Eqs (2) and (3). High value of activation energy suggests that chemisorption is taking place with monolayer formation³³. The catalytic activity of the catalyst may be due to the presence of free valencies on its surface. These free valencies offer an opportunity to the reactant molecule to undergo chemical reaction on the surface of catalyst. With the decrease in size of the catalyst, the free surface area is increased, thereby increasing the free valencies or active spots, which are responsible for the adsorption of reactant molecule³⁴.

Conclusion

Solution combustion synthesis has produced a crystalline, phase pure, moderate surface area powder of SrZrO_3 at a temperature less than 773 K within 10 min of time, which shows the energy efficiency, and time saving nature of the method. The strontium zirconate thus produced has been successfully used as a catalyst in heterogeneous catalysis, wherein chemisorption is taking place with monolayer formation.

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