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Isothermal in situ reduction kinetics of $CoCl_2$–SiO_2 gels to Co–SiO_2 nanocomposites

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Abstract

In situ reduction kinetics of $CoCl_2$–SiO_2 gel to Co–SiO_2 nanocomposite in the 800–950°C range has been studied. The presence of nanosized metallic Co in the host matrix has been established from the X-ray diffraction patterns of the reduced gels. The metallic particle size has been found to be 17 and 23 nm when reduced at 850° and 950°C, respectively. Nucleation and growth type of mechanism remain operative during the course of the reduction. The activation energy is found to be in the range of 55–61 kJ/mol. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Nanocomposite; Sol–gel; In situ; Reduction; Kinetics; Mechanism

1. Introduction

The sol–gel technique has emerged as a versatile method for synthesizing a wide range of materials. Recently, preparation of glass–metal nanocomposite through this route has gained considerable momentum on account of the overall versatility and simplicity of the process [1–6]. In this method, glass–metal nanocomposites are synthesized by using a sol containing silicon tetraethoxide (TEOS) and a suitable metallic salt in ethyl alcohol, followed by subsequent conversion of sol to gel. The resulting gel is then subjected to reduction treatment at suitable temperatures by passing a mixture of nitrogen and hydrogen gas [2,3] or by generating hydrogen in situ [5,6]. The treatment leads to the evolution of metal islands of diameter ranging from five to 50 nm within the host SiO_2 matrix. The nanocomposites thus prepared exhibit remarkable electrical, magnetic and optical properties which raises the possibility of exploiting these new class of materials as substrates for semiconduction technology. However, the physical properties of these nanocomposites remain functions of shape, size, amount and distribution of the metallic species in the host matrix [7,8]. Again, the shape and size of these metallic islands are influenced, to a great extent, by the process control parameters. Although from the transmission electron micrograph, shape, size and distribution can be measured directly, the amount of metallic species present is assessed on the basis of the assumption that all the metal salt incorporated in the SiO_2 matrix is reduced to metal within the stipulated time of reduction. This is probably the main hindrance in preparing nanocomposites with uniform and reproducible physical properties. In reality also, the fore-

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going method does not help one to estimate the actual amount of metallic salt reduced at a particular instant of time during reduction and, therefore, fails to impart any knowledge on the mechanism(s) of reduction. Therefore, it is deeply felt that a study on the kinetics of reduction is essential from the view point of controlling the process parameters effectively to achieve a greater degree of control over the physical properties of the nanocomposites. Keeping the above-mentioned views in mind, the present paper deals with the in situ reduction kinetics of $CoCl_2$ in the SiO_2 gel matrix to Co–SiO_2 nanocomposites.

2. Experimental procedure

SiO_2 gels containing $CoCl_2$ and 1.5 times stoichiometric dextrose which when reduced would yield 5 wt% Co–SiO_2 nanocomposites were prepared from TEOS, C_2H_5OH and $CoCl_2$ solution with C_2H_5OH : - TEOS ratio of 4 : 1. The preparation technique has been described elsewhere [6]. The gels were heat-treated at 800°, 850°, 900° and 950°C, respectively, under nitrogen gas atmosphere at a flow rate of 5 cc/s. The heat treatments were carried out in an electrical heating furnace. The desired temperature was maintained by a PID controller with an accuracy of ± 1°C. The gel samples were placed in a porcelain boat, one at a time, and introduced into the constant heating zone of the furnace for heat treatment. The HCl vapour generated during the course of the heat treatment is absorbed in known volume of double-distilled water. The pH values of the resulting HCl solution were recorded as a function of heat-treatment time. The pH values of the solution yield $[H^+]$ in the solution from which the fraction of $CoCl_2$ reduced within the SiO_2 gel matrix were calculated.

3. Results and discussion

Figs. 1 and 2 are the representative characteristic X-ray diffraction (XRD) patterns of $CoCl_2$–SiO_2 gels, reduced at 850° and 950°C. The interplanar spacings (d_{hkl}) were computed from the XRD patterns. It is observed that the computed (d_{hkl}) values match reasonably well with the ASTM standard (d_{hkl}) values [9] of Co which confirms the presence of metallic Co in the SiO_2 gel matrix. The average particle size of the reduced metal is calculated from the XRD pattern with the help of the following equation: $t=0.9\lambda/B\cos\theta_B$, where t is the particle size, λ the monochromatic X-ray wavelength, B the width of diffraction curve in radians at an intensity equal to half the maximum intensity and θ_B the Bragg angle in degrees [10].

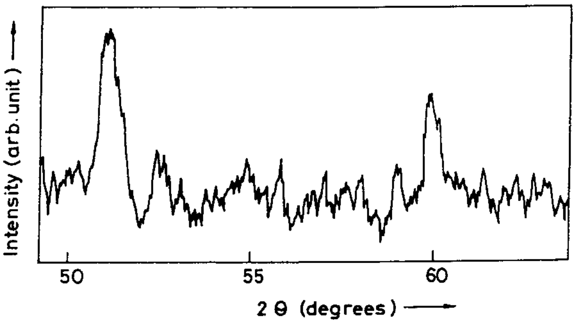

Fig. 1. Characteristic XRD patterns of $CoCl_2$–SiO_2 gels reduced at 850°C.

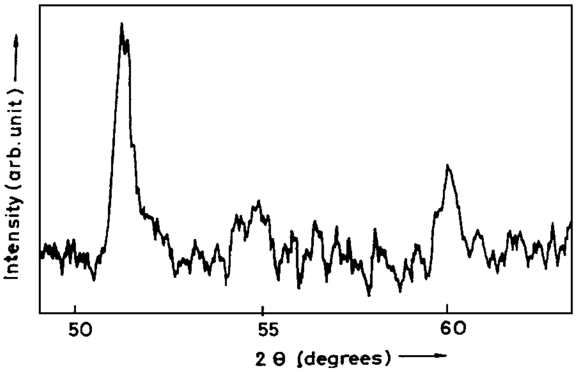

Fig. 2. Characteristic XRD patterns of $CoCl_2$–SiO_2 gels reduced at 950°C.

The average particle size has been found to be 17 and 23 nm, respectively, for temperatures of 850° and 950°C. Therefore, assignment of the term nanocomposite to the reduced gels seems to be reasonable and appropriate. The size of the metallic particles has been found to increase with increase in reduction temperature. This is attributed to the effect of grain coarsening with increase in temperature.

Fig. 3 depicts the fractional conversion (α) vs. time (t) plot of the Co–SiO_2 nanocomposites. It is evident from the figure that a maximum reduction occurs within the first 5 min. This can be attributed to the

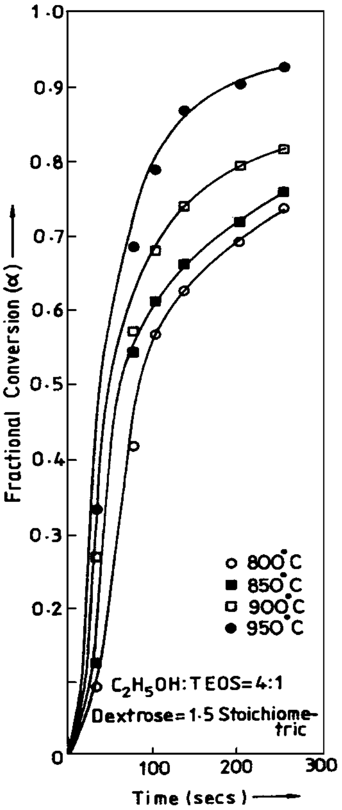

Fig. 3. Fractional conversion vs. time plot of Co–SiO_2 nanocomposites.

in situ generation of H_2 at the reaction sites. At the latter period, the reduction rate falls due to the fact that water vapour is only made available from the polycondensation reaction of SiO_2 gels [11]. As the rate of polycondensation reaction is slow, availability of water vapour is restricted, a fact that tends to slow down the generation of H_2 gas via the water–gas reaction. This causes the conversion rate to drop.

4. Identification of mechanism(s)

To ascertain the appropriate mechanism(s) which remain operative during the course of the reduction, the experimental data on time-dependent fractional conversion have been analyzed by taking recourse to the reduced time plots [12]. The analysis is as follows. The general equation for all the mechanism(s) is written as

$$g(\alpha) = kt \tag{1}$$

where $g(\alpha)$ is an appropriate function of α, k the specific rate constant and t the time.

For $\alpha = n$,

$$g(n) = kt_n \tag{2}$$

Where t_n is the time required for fractional conversion of n. Dividing Eq. (1) by Eq. (2), we obtain

$$\frac{g(\alpha)}{g(n)} = \frac{t}{t_n} \equiv \theta \tag{3}$$

where θ is the reduced time. Eq. (3) is independent of k, the reaction rate constant, which is the temperature-dependent term in kinetics. Therefore, for the same mechanism operative over the entire range of temperature, the computed α vs. θ plot from experimental data will coincide with the theoretically computed α vs. θ plot for the mechanism. By comparing the computed α vs. θ plot from experimental data with the theoretically computed α vs. θ plot for the mechanisms, it is possible to find out the mechanism which actually remains operative.

The reduced time plot shown in Fig. 4 reveals that the nucleation and growth(NG2)-type of mechanism is operative. The validity of the above-mentioned mechan-

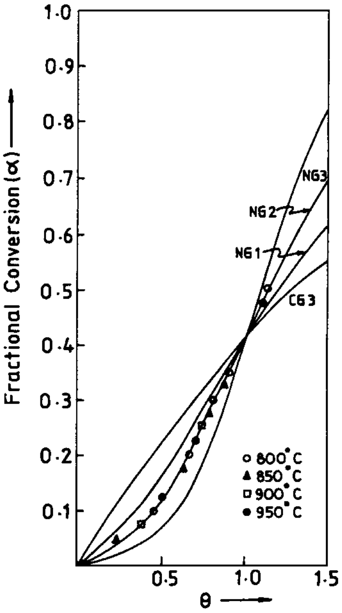

Fig. 4. Reduced time plot.

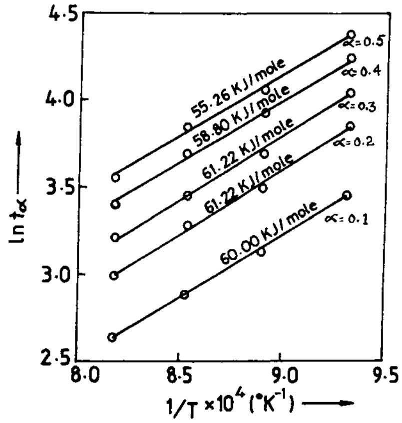

Fig. 5. Plots of ln t_α vs. 1/T at different levels of α.

ism can be established by considering the fact that equilibrium vapour pressure of $CoCl_2$ rises sharply with increase in temperature in the 800–950°C range [13]. Therefore, in the experimental temperature range, it is highly probable that the in situ generated H_2 will reduce $CoCl_2$ in the vapour state. Since, the melting point [13] of Co is very high (1480°C), solid particles will precipitate out from the vapour phase by nucleation and growth process. However, conversion of $CoCl_2$ to metallic Co in the gaseous state will decrease the vapour pressure of $CoCl_2$. Therefore, with the progress of the reduction, $CoCl_2$ will vaporise continuously to maintain an equilibrium vapour pressure. As the reduction in the gaseous phase is much faster than the gas–solid or gas–liquid reaction, the former, i.e. nucleation and growth of Co from the vapour state, will predominate and control the kinetics of reduction. It is for this reason that the nucleation-and-growth type of mechanism (NG2) is logical and physically viable.

The activation energies at different levels of α for $CoCl_2$–SiO_2 gel reductions has been calculated by the differential method [14]. The slope of the ln t_α vs. 1/T plots (see Fig. 5) multiplied by the universal gas constant, R, yields the activation energy at different levels of α. The computed activation energy has been found to be in the range of 55–61 KJ/mol.

5. Conclusion

The following conclusions are drawn from the present investigation

1. The in situ reduction of $CoCl_2$–SiO_2 gel to Co–SiO_2 nanocomposite progresses at a rapid rate and a maximum conversion occurs within the first 5 min of the reaction.
2. The particle size of Co in the SiO_2 matrix has been found to be 17 and 23 nm for the gels reduced at 850° and 950°C.
3. Co–SiO_2 nanocomposites exhibit grain coarsening with increase in temperature.
4. During the course of reduction, nucleation and growth type of mechanism remain operative.
5. The activation energy for the reduction process has been found to be in the range of 55–61 KJ/mol.

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