Kinetics and mechanism of solid state reaction between CuWO₄-Li₂CO₃

Huma Naseer & Rafiuddin*
Department of Chemistry,
Physical Chemistry Division,
Aligarh Muslim University, Aligarh 202 002, India
Email: rafi_amu@yahoo.co.in

Received 20 January 2005; revised 28 September 2005

The kinetics and mechanism of CuWO₄-Li₂CO₃ solid state reaction have been studied, by the capillary method. The reaction follows the parabolic rate law, \( x^2 = kt \), where \( x \) is the thickness of the product layer at time \( t \) and \( k \) is parabolic rate constant. Mechanism of the reaction has been suggested on the basis of X-ray powder diffraction, chemical analysis, electrical conductivity and thermal measurements. The reaction is found to be diffusion controlled.

Tungstates have been investigated for various technological applications, and in particular, copper tungstate has received wide attention because of their applications as scintillation detectors, photoanodes and masers. The divalent transition metal tungstate, AWO₄ (A=Mn, Fe, Co, Ni, Zn and Cu) referred as NiWO₄, type tungstate, are members of a large family of structurally related compounds with small cation and crystallizes with wolframite structure. Many properties of CuWO₄ including dielectric, optical and transport properties, cell dimensions and electrochemical characteristics have been thoroughly investigated. The structure of CuWO₄ has been solved by Kihlborg and later by Vonklein and Forsyth et al. Solid state reactions involving Li₂CO₃ have also been studied in detail.

In the present investigation, we have studied the reaction between CuWO₄ and Li₂CO₃ in solid state, envisaging that the reaction products exhibit high electrical conductivity may be obtained. This study explains the kinetics and mechanism of solid state reaction between CuWO₄ and Li₂CO₃ using electrical conductivity measurements, visual technique and X-ray powder diffraction.

Experimental
Copper tungstate was prepared by precipitation from approximately 0.5 \( M \) aqueous \( \text{Na}_2\text{WO}_4 \) solution (E. Merck) and 0.5 \( M \) aqueous \( \text{CuNO}_3 \) solution (E. Merck) prepared in doubly distilled water. The precipitate was dried at 100°C for two days and the dried precipitate was powdered in a mortar. X-ray powder diffraction analysis of the powdered precipitate confirmed the formation of CuWO₄ (Fig. 1). Li₂CO₃ (AR grade) was used without further purification.

Electrical conductivity measurements
Pellets for the conductivity measurements were prepared by pouring the sample powders into a stainless steel die and pressing at a pressure of 4 tonnes with the help of a hydraulic pressure (Spectra Lab, model SL-89). Pellets were found to be of the same colour as the original powders. However, higher pressure caused uneven darkening in the pellets. All the samples were annealed at 200°C for 12 hours before measurements to eliminate any grain boundary effect.

The electrical conductivity measurements were performed by means of a two probe method. Pellets were mounted on copper plates to which leads were attached using two polished platinum electrodes. The copper leads were electrically insulated from the sample holder by Teflon sheets. This assembly was then placed inside a thermostat and the temperature was brought to the desired level and maintained for about 15 min to ensure attaining equilibrium. Electrical conductivity of the pellets was measured at different temperatures using Gen-Rad 1659 RLC Digibridge with the frequency range 100 Hz-10 KHz.
The mixtures were then stirred thoroughly, and CuWO₄ studied by capillary method by placing Li₂CO₃ over the CuWO₄ amount of gently with a glass rod to pack the powder and diameter which was sealed at one end. Weighed mixtures were taken in a double-walled calorimeter.

In an oven, the same amounts of CuWO₄ and Li₂CO₃ were used throughout to avoid the pressure effect. The progress of the reaction was followed by measuring total thickness of the product layer formed at the interface by a travelling microscope having the calibrated scale in the eyepiece. At 300°C, a black coloured product has developed immediately at the interface between CuWO₄ and Li₂CO₃ and this grew with time on the CuWO₄ side. The kinetics of the reaction was likewise studied at different temperatures.

Results and discussion

An equimolar mixture of CuWO₄ and Li₂CO₃ (both powdered above 300 mesh) did not show any change in the colour and electrical conductivity at room temperature. On raising the temperature to 300°C, the colour of the mixture changed to black with some increase in the electrical conductivity. However, at 400°C, a marked change in the electrical conductivity was observed (Figs 2 and 3), suggesting the formation of fast electrical conducting species. This mixture heated at 400°C was analysed by X-ray powder diffraction. The diffraction pattern (Fig. 1) shows the presence of Li₂WO₄ along with some unreacted CuWO₄ and Li₂CO₃. Electrical conductivity measurements were made at different temperatures with the pellets prepared from different molar ratio mixtures (1:1, 1:2 and 1:3) of powdered CuWO₄ and Li₂CO₃ at different temperatures. In all of these mixtures, substantial change in conductivity was observed at 400°C. This significant change in the electrical conductivity seems to be due to the formation of Li₂WO₄ obtained by the replacement of host Cu²⁺ ion by the small sized, highly conducting guest Li⁺ ion. Small sized Li⁺ ions percolate more readily into the framework of CuWO₄. The relatively small increase in conductivity in other ratios (1:2 and 1:3), is due to the blocking effect of Li₂CO₃ present in higher content. Thermal measurements with different molar ratio's of CuWO₄ and Li₂CO₃ show no remarkable change, indicating that the reaction does not occur at room temperature.

All these studies suggest that powdered CuWO₄ and Li₂CO₃ react completely in solid state at 400°C in an equimolar ratio giving Li₂WO₄ as the product. In other molar ratio's, the excess of either of the reactants remained unreacted, suggesting a simple exchange mechanism for the reaction in solid state.
Mechanism of lateral diffusion

In the solid state reactions, the reactants are not mixed on an atomic scale and thus must diffuse or penetrate into each other if the reaction is to start and propagate within the solid phase. There are two fundamental processes involved in a solid state reaction: the chemical reaction itself and the transport of matter to the reaction zone.

Soon after the placement of powdered CuWO₄ over powdered Li₂CO₃ in a glass capillary kept at 300°C, a black colour boundary formed at the interface and this grew with time on the CuWO₄ side.

The lateral diffusion reaction proceeded well with the formation of black layer on CuWO₄ and analysis of this black layer confirmed it to be Li₂WO₄. This suggests that Li₂CO₃ is the mobile species and reacts with CuWO₄ grain at the interface between CuWO₄ and Li₂CO₃ to give Li₂WO₄ as a product.

For CuWO₄ and Li₂CO₃ solid state reaction, lateral diffusion data for each isothermal reaction set fit best the parabolic rate equation (Fig. 4).

\[ x'' = kt \]  \hspace{1cm} \text{(4)}

where \( x'' \) is thickness of product layer at the interface at time \( t \), 'n' and 'k' are constants. In the temperature range of 300-400°C, 'n' attains a constant value of 2.20. The rate constant 'k' in each case follows Arrhenius equation and the activation energy for this reaction was found to be 184.96 kJ/mol.

The applicability of the parabolic rate equation for kinetic data suggests that CuWO₄ and Li₂CO₃ reaction in solid state is diffusion controlled. As the reaction proceeds, the thickness of the product layer increases and the reactant takes more time to diffuse through the product layer leading to a fall in the reaction rate.

Acknowledgement

We are thankful to Chairman, Department of Chemistry, Aligarh Muslim University, Aligarh, for providing necessary research facilities.

References