

Real-time *in situ* X-Ray Diffraction of Intercalation Reactions

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Real-time *in situ* energy dispersive X-ray powder diffraction techniques have been developed to monitor the intercalation of a guest species into a solid host; the time dependence of the extent of reaction (α) for the intercalation of cobaltocene CoCp_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) by SnS_2 has been experimentally determined and is consistent with a model involving nucleation followed by two-dimensional diffusion of the metallocene molecules into the host lattice.

The intercalation of inorganic, organic and organometallic molecules or ions into lamellar host lattices is now widely recognised.¹ These materials have been shown to exhibit some remarkable properties.¹⁻³ Our understanding of the mechanistic details of this class of reaction is, however, extremely limited, largely due to the technical difficulties in determining the kinetics of heterogeneous reactions involving solid-liquid or solid-gas reagents. For processes involving the structural modification of solids such as intercalation reactions, phase transitions and chemical modifications, solid-state chemists would ideally like to study the reaction using diffraction techniques; the primary problem with such diffraction experiments is the design of reaction vessels or window materials which allow transmission of the incident and diffracted beams. However, with the development of readily accessible synchrotron radiation sources and energy dispersive X-ray diffraction techniques these difficulties can now be overcome.⁴ In this communication we report the development of an experiment for monitoring the intercalation of guest molecules or ions into solid host lattices. We demonstrate the wide applicability of the technique by reporting the study of the kinetics of the intercalation of an oxygen-sensitive organometallic sandwich compound, cobaltocene CoCp_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), into the layered transition metal dichalcogenide SnS_2 .

At the heart of the experiment is a custom built diffraction cell which is designed to exploit the high flux white X-rays produced by the 2 GeV Synchrotron Radiation Source at Daresbury Laboratory, and in particular to take full advantage of the features of the energy-dispersive diffractometer on Station 9.7. The energy-dispersive mode allows us to measure a large energy window of the powder X-ray spectrum simultaneously at a single fixed detector angle; this means that the experimental cell need contain only small windows for the incident and diffracted X-ray beams. Furthermore, the use of X-rays at energies greater than 30 keV means that the beam is not significantly attenuated by the sample holder, or by solutions of reactants therein. As a consequence, high quality spectra can be collected from small sample sizes (*ca.* 200 mg of host) in very short acquisition times (*ca.* 10 s).

The apparatus is depicted in Fig. 1, and is designed to allow the rapid injection of accurate volumes of air-sensitive solutions into the reaction vessel, which is preloaded with the host material. The resulting suspension is stirred with a Teflon coated magnetic stirrer bar, and the X-ray beam passed through the suspension so that the diffraction pattern is recorded as the reaction proceeds. The temperature of the cell and the injection system can be accurately thermostatted in the range 10–150 °C.

We have been interested in the intercalation of metallocenes by layered metal dichalcogenides for many years and our extensive knowledge of the reaction of cobaltocene with the tin dichalcogenides led us to choose the intercalation of cobaltocene into the lamellar host lattice SnS_2 for initial study. In particular, $\text{SnS}_2(\text{CoCp}_2)_{0.3}$ is one of the best characterised molecular intercalation compounds.⁵ Fig. 2 shows the energy-dispersive X-ray powder diffraction spectra of SnS_2 as a function of time after the injection of an excess of CoCp_2 dissolved in dimethoxymethane. Even at room temp., the

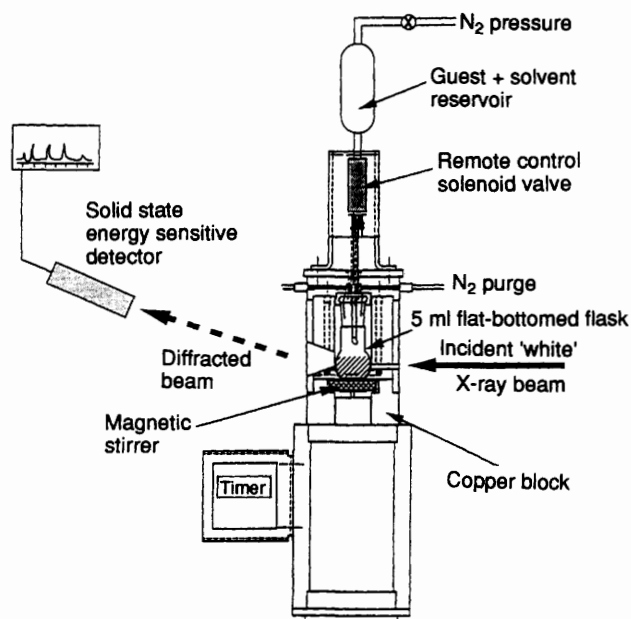


Fig. 1 Schematic of apparatus used on Station 9.7 at the Synchrotron Radiation Source, Daresbury. The heated holding tank (shaded) is equilibrated, by circulating hot oil, to the same temperature as the diffraction/reaction cell which consists of a Pyrex flask encased in a thick copper jacket. Accurate injections of a known concentration of solution are effected through the remotely triggered solenoid valve.

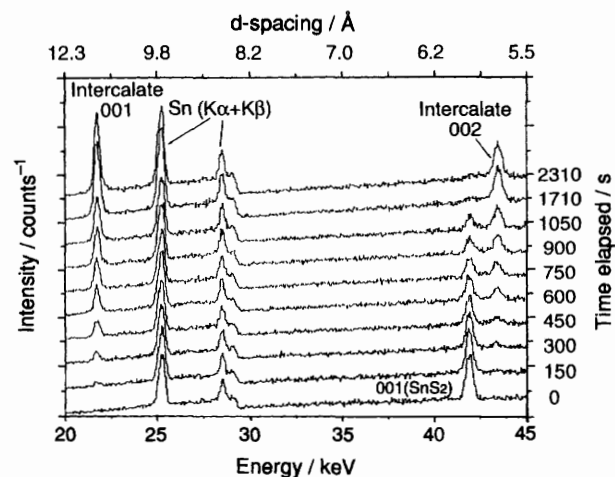


Fig. 2 Energy dispersive X-ray diffraction spectra of SnS_2 as a function of time after exposure to CoCp_2 in dimethoxyethane. Particle size of SnS_2 : 90–250 μm . Acquisition time per spectra was 30 s; SnS_2 (001-Bragg reflection), $\text{SnS}_2(\text{CoCp}_2)_{0.3}$ (001 and 002 Bragg reflections) occur at 5.8, 11.2 and 5.6 Å respectively.

speed of intercalation is remarkably fast. For SnS_2 crystals between 90–250 μm in diameter, the 001 and 002 Bragg reflections from the final stage-one product, $\text{SnS}_2\{\text{CoCp}_2\}_{0.3}$, are apparent after only 150 s. The series of spectra shown in Fig. 2 also show no new reflections attributable to intermediate phases, in contrast to earlier studies on the alkali-metal intercalates of metal dichalcogenides⁶ and graphite.⁷ Individual spectra collected during the reaction were normalised to the Sn-K α resonance at *ca.* 25 keV which will correct for any variation in the amount of sample in the beam during spectral acquisition. After normalisation the rate of disappearance of the host (SnS_2) is equal to the rate of appearance of the final product ($\text{SnS}_2\{\text{CoCp}_2\}_{0.3}$). Given the clean, self consistent kinetic behaviour of this system, a detailed analysis of the rate data was performed in order to elucidate a possible kinetic parameterisation for this reaction.

Fig. 3 shows a plot of the extent of reaction (α) vs. reduced time ($t/t_{0.5}$) for a series of reactions carried out in the range 10–60 °C. Preliminary screening of the data by the Sharp-Hancock method⁸ suggested a reaction mechanism of non-integral order intermediate between Avrami first and second

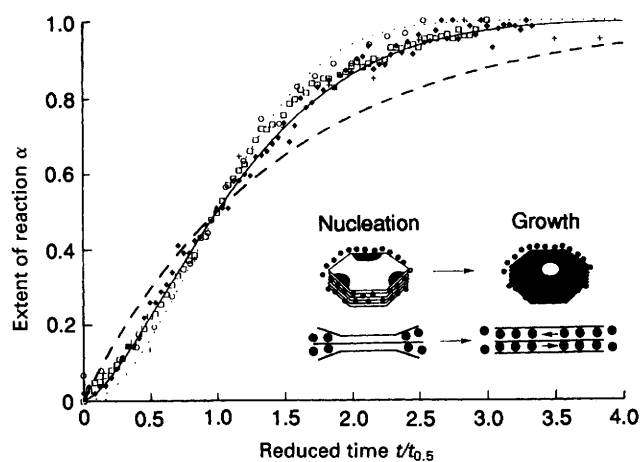


Fig. 3 Extent of reaction (α) vs. reduced time ($t/t_{0.5}$) plot of experimental data obtained for intercalation of CoCp_2 into SnS_2 (particle size: 90–250 μm) at several temperatures: (\square) 10, (\blacklozenge) 20, (\circ) 40, (\triangle) 50, ($+$) 60 °C. Also shown are theoretical curves obeying various rate expressions: (-----) Avrami 2nd order, $\alpha = 1 - e^{-(kt)^2}$; (—) First order, $\alpha = 1 - e^{-(kt)}$; (—) Deceleratory nuclei-growth, $\alpha = 1 - e^{-(kt)^{1.5}}$. *Inset:* Schematic representation of the nucleation and subsequent 2-D diffusion of Co(Cp)_2 into SnS_2 .

order kinetics.⁹ The data is best described by the rate expression for nuclei-growth reactions of non-integral order, $n = 1.5$.¹⁰ Assuming diffusion of the intercalant in the interlamellar space is a two-dimensional process, the results are suggestive of a deceleratory rate of nucleation, with diffusion-controlled growth of the product phase (Fig. 3). This contrasts with the phase-boundary control mechanism reported for lithium intercalation into the related metal dichalcogenides, 2H-TaS₂ and 1T-TaS₂, where the nucleation is rate-limiting.¹¹

Kinetic rate constants derived from least-squares fits to the expression, $\alpha = 1 - e^{-(kt)^{1.5}}$ at various temperatures for 2 different particle sizes can be fitted to an Arrhenius-type rate expression from which a pre-exponential factor of *ca.* 10^6 s^{-1} and an activation energy of $47 \pm 3 \text{ kJ mol}^{-1}$ can be calculated for this intercalation reaction. Activation energies have been determined for the formation of $\text{Li}_{0.2}\text{TiS}_2$ (33 kJ mol^{-1})¹¹ and $(\text{N}_2\text{H}_4)\text{TaS}_2$ (70 kJ mol^{-1}).¹¹

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