# Photocatalytic Oxidation of Propan-2-ol by Semiconductor–Zeolite Composites

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The photocatalytic oxidation of liquid propan-2-ol to propanone has been investigated using semiconductorzeolite composites consisting of either CdS or TiO<sub>2</sub> in Y zeolite. CdS-based composites were prepared by cation exchange with Cd<sup>2+</sup> followed by sulfidation with either Na<sub>2</sub>S or H<sub>2</sub>S, whereas TiO<sub>2</sub>-based composite was prepared by Ti(OEt)<sub>4</sub> impregnation followed by hydrolysis and calcination. Rate measurements at 303 K were made to assess how the activity of CdS-based material depended on reaction conditions; differences from CdS supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are ascribed to smaller CdS particles and the higher adsorption potential of the zeolite matrix for O<sub>2</sub> and H<sub>2</sub>O. However, rate measurements under standard conditions over the temperature range 283–308 K yielded the same activation energies as for CdS and TiO<sub>2</sub> supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 53 ± 2 kJ mol<sup>-1</sup> for CdS-based catalysts and 21 ± 1 kJ mol<sup>-1</sup> for TiO<sub>2</sub>-based catalysts. It follows that the physico-chemical properties of the semiconductor control the activation energy, whereas the zeolite matrix is responsible for controlling semiconductor particle size during preparation and modifying the effective reaction conditions through adsorption.

Early work established CdS and platinised CdS to be photocatalysts for the dehydrogenation of aqueous propan-2-ol in the absence of oxygen.<sup>1,2</sup> Domen et al.<sup>1</sup> demonstrated the production of H<sub>2</sub> and propanone from propan-2-ol-water mixtures in both gas and liquid phases with UV-irradiated CdS. Since reaction did not proceed in the absence of  $H_2O$ , the authors suggested that H<sub>2</sub>O photodecomposition and propan-2-ol photo-oxidation were coupled reactions. Matsumura et al.<sup>2</sup> observed that photodehydrogenation with aqueous methanol, ethanol and propan-2-ol proceeded at similar rates on Pt/CdS irradiated with visible light. Further experiments showed that activity was favoured by buffering the reactant mixture to a pH above 10 and that bare CdS only possessed ca. 5% of the activity of Pt/CdS. The present authors have recently reported an investigation of the photocatalytic oxidation of liquid propan-2-ol on a number of CdS-based catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> using both visible and UV radiation.<sup>3</sup> With non-platinised catalysts, reaction proceeded only in the simultaneous presence of  $O_2$  and added H<sub>2</sub>O. However, with Pt/CdS-Al<sub>2</sub>O<sub>3</sub> these conditions gave a pronounced dark reaction, but photodehydrogenation could be followed when O2 was replaced by N2. The primary oxidant in the reaction was considered to be an 'OH radical generated by trapping a photohole at an adsorbed water molecule. An activation energy of  $53 \pm 2 \text{ kJ mol}^{-1}$ , common to all catalysts and insensitive to change of the reactant alcohol, was believed to be associated with 'OH generation. Differences between CdS-based catalysts and the more extensively studied TiO<sub>2</sub>-based catalysts<sup>4-11</sup> were emphasised in both experiment and discussion.

Cadmium sulfide can be synthesized within the pore systems of aluminosilicate zeolites by the interaction of  $Cd^{2+}$ , introduced by cation exchange, with either gaseous  $H_2S^{12-14}$ or aqueous  $Na_2S$ .<sup>14</sup> However, the size constraint imposed by the zeolite pore system yields CdS particles with dimensions comparable with those of the delocalised excitons initially generated by the absorption of UV–VIS radiation. Where this occurs the CdS exhibits a quantum size effect, in which the band-gap between valence and conduction bands increases as the particle size decreases. This is observed as a shift of the absorption band edge to shorter wavelengths, such that the CdS may be white rather than the orangeyellow as with bulk material. Herron and co-workers<sup>13</sup> have made a thorough study of the structure of the CdS clusters in Y zeolite. At low CdS loadings, discrete cubic (CdS)<sub>4</sub> clusters are located within the sodalite cages. At high CdS loading, the (CdS)<sub>4</sub> clusters interact, through the hexagonal prisms joining the sodalite units, to form a supercluster network with a concomitant shift of the absorption band edge to longer wavelengths. On exposure to water, liquid or vapour, the CdS clusters aggregate to form particles that are, from their spectroscopic properties, larger than the zeolite supercages.<sup>13,14</sup> It has been suggested that these particles are contained within a number of contiguous supercages without breakdown of the framework structure.<sup>14</sup> Such material was active for the photocatalytic evolution of H<sub>2</sub> from aqueous solutions containing S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> as sacrificial donors;<sup>14</sup> the specific activity of the CdS increased *ca.* 20 times when the CdS surface was modified with Pt or ZnS co-catalysts for H<sub>2</sub> evolution.

Clearly photocatalysis by semiconductor-zeolite composites warrants further investigation and we presently report on the photo-oxidation of liquid propan-2-ol on such material. The measurements are made with either CdS or TiO<sub>2</sub> in Y zeolite, where both the reactant and the propanone produced can access the supercage network, but not the sodalite cages. Having established the conditions necessary for sustained reaction, catalytic activities and activation energies are compared with those of CdS and TiO<sub>2</sub> supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The reaction mechanism for the composites is believed to be closely similar to that of the supported catalysts.<sup>3</sup>

## Experimental

## Preparation of CdS-Zeolite Composites

Cadmium-exchanged Y zeolite, CdY, was prepared by suspending 10 g of NaY zeolite, dry composition Na<sub>55</sub>(AlO<sub>2</sub>)<sub>55</sub>(SiO<sub>2</sub>)<sub>137</sub>, in 500 cm<sup>3</sup> of constantly stirred 0.06 mol dm<sup>-3</sup> Cd(NO<sub>3</sub>)<sub>2</sub> for 96 h at room temperature. The zeolite was then filtered off and washed with distilled water until the filtrate was free of Ca<sup>2+</sup> according to the dithiozone test. When the dried CdY zeolite was added to 125 cm<sup>3</sup> of 0.038 mol dm<sup>-3</sup> Na<sub>2</sub>S, the zeolite rapidly turned yellow and subsequently yielded a colourless filtrate. Following thorough washing and drying at 393 K the powder was stored over saturated NaCl solution. Photocatalysts made this way are designated CdS(x)/Y(Na<sub>2</sub>S), where x is the mass% CdS determined by atomic absorption spectroscopy. In a dry preparation of photocatalyst, CdY zeolite was dehydrated in a tubular silica vessel at 673 K in flowing dry  $N_2$  for 16 h, cooled to 373 K and  $H_2S$  at 1 atm passed for 1 h at this temperature. Following flushing off the excess of  $H_2S$  in  $N_2$ for 16 h, the vessel was cooled to room temperature. The pale grey product was stored in a vacuum desiccator over dehydrated 4A zeolite pellets. Photocatalysts made in this way are designated CdS(x)/Y(H\_2S). Use of a Phillips X'Pert X-ray diffractometer showed that for both types of material the zeolite had retained its framework structure and that the CdS particles possessed the zincblende structure following exposure to water vapour.

#### Preparation of TiO<sub>2</sub>-Zeolite Composites

Attempts to incorporate titanyl ions into NaY zeolite by cation exchange with aqueous  $K_2 TiO(C_2O_4)_2$  were unsuccessful. Although analysis of the product after calcination showed TiO<sub>2</sub> contents as high as 25 mass%, X-ray diffraction indicated almost complete breakdown of the zeolite framework structure. Furthermore, the product was not photocatalytically active, suggesting that any TiO<sub>2</sub> produced was encapsulated with an amorphous silica-alumina layer. Titanium alkoxides were subsequently used under conditions where either titanium isopropoxide or titanium ethoxide might be adsorbed within the pore system of dehydrated NaY zeolite. The introduction of water to hydrolyse the alkoxide to hydrous titania followed by calcination was expected to yield a TiO<sub>2</sub>-zeolite composite. The level of success achieved was critically dependent upon the low volatility of the alkoxides and the geometry of the bed of NaY zeolite used; in that an inhomogeneous product was frequently formed with an excess of  $TiO_2$  in those parts of the bed closest to the vapour phase. The final, and most successful, technique used a thinly spread layer of 10 g of NaY zeolite in a shallow Pyrex boat within a horizontal tubular reactor heated by an electric furnace. The zeolite was initially dehydrated at 673 K for 16 h in a 30 cm<sup>3</sup> min<sup>-1</sup> flow of pure He. After cooling the sample to room temperature, the He stream was laden with titanium ethoxide vapour from a saturator and this was passed over the zeolite until  $ca. 1 \text{ cm}^3$  had evaporated. Subsequently the adsorbed alkoxide was hydrolysed by passing the He through a water bubbler for 16 h. Finally the zeolite was calcined at 673 K for 16 h in a 30 cm<sup>3</sup>  $min^{-1}$  flow of air. The product, an off-white powder, was stored over saturated NaCl solution. X-Ray diffraction showed retention of the zeolite framework structure, but failed to detect peaks arising from TiO<sub>2</sub> in material produced by this method. Nevertheless, anatase was detected in the inhomogeneous material produced by other preparational methods. Photocatalysts made in this way are designated  $TiO_2(x)/Y$  where x is the mass%  $TiO_2$  determined spectrophotometrically.15

#### **Photocatalytic Activity Measurements**

The apparatus and analytical methods used to determine photocatalytic activities for carbonyl compound formation at precise temperatures in the range 283–308 K have been described.<sup>7</sup> Unless stated otherwise, 100 or 150 mg of photocatalyst was suspended in 20 cm<sup>3</sup> of pure alcohol by a motor-driven stirrer. Controlled atmospheres above the reaction mixture were achieved by flushing the reaction vessel for 1 h with a 30 cm<sup>3</sup> min<sup>-1</sup> flow of pure O<sub>2</sub>, pure N<sub>2</sub> or a metered mixture of both gases; these flows were maintained during subsequent photoreaction. The reaction mixture was normally irradiated using a Wotan Ultramed 400W UV lamp and an OX1 filter, giving a symmetrical band of UV centred at 366 nm. Uranyl oxalate actinometry at 298 K ( $\phi = 0.49$ )

showed that the unattenuated radiation entering the reaction vessel was  $2.6 \times 10^{-7}$  einstein s<sup>-1</sup>. In a preliminary experiment radiation from a Siemens-Ediswan 300W tungsten filament lamp of unknown intensity was used to determine whether CdS-zeolite composites were active in predominantly 'visible light'.

## **Results and Discussion**

#### **Preliminary Experiments**

A number of exploratory experiments were made using  $CdS(12.5)/Y(Na_2S)$  for the photocatalytic oxidation of propan-2-ol at 303 K. These showed that:

(a) The simultaneous presence of  $O_2$ , UV radiation and CdS, within the zeolite pore system, were necessary for sustained formation of propanone, there being no evidence for other products arising from further oxidation. (b) Linear reaction progress plots for propanone formation were observed over reaction times of 2 h. Furthermore, the propanone concentration remained constant after terminating irradiation, indicating that there were no diffusional effects and that the observed concentrations were in equilibrium with those within the zeolite pore system. (c) Photocatalytic activity with visible radiation, determined from the slope of reaction progress plots, was closely similar to that obtained with UV radiation. However, UV radiation was used in all further experiments so that comparisons could be made with TiO<sub>2</sub>-based catalysts which are inactive in visible radiation.

The TiO<sub>2</sub>-based catalyst, TiO<sub>2</sub>(3.0)/Y, was found to be active for propan-2-ol photo-oxidation at 303 K in the presence of O<sub>2</sub> and UV radiation.

#### **Dependence of Activity on Reaction Conditions**

It was anticipated that differences in environment between CdS within zeolite pores and on the surface of  $\gamma$ -alumina would be reflected in the dependence of activity on reaction conditions. CdS(12.5)/Y(Na<sub>2</sub>S) was selected as the photocatalyst in such studies since it was prepared using aqueous Na<sub>2</sub>S, as previously used in preparing CdS(14.5)/Al<sub>2</sub>O<sub>3</sub>.<sup>3</sup> All measurements were made at a reaction temperature of 303 K over a reaction time of 100 min.

Fig. 1 shows the reaction rate, calculated from the slopes of linear reaction progress plots, as a function of catalyst mass. The overall shape of the plot is similar to that obtained from  $CdS(14.5)/Al_2O_3$ , but a higher plateau of activity is achieved at a lower catalyst mass of *ca*. 100 mg. To conserve catalyst, this mass was used in further experiments.



Fig. 1 Effect of catalyst mass on reaction rate with CdS(12.5)/Y(Na\_2S) at 303 K. (---) Plot previously obtained <sup>3</sup> with CdS(14.5)/Al\_2O\_3.

A pronounced difference between CdS(12.5)/Y(Na<sub>2</sub>S) and CdS(14.5)/Al<sub>2</sub>O<sub>3</sub>, lies in the ability of the former to exhibit photocatalytic activity without the addition of water to the reaction mixture. This, together with a maximum activity at a much lower water content in a propan-2-ol-water reaction mixture, are shown in Fig. 2. We attribute the differences in behaviour to the preferential adsorption of considerable amounts of water in the micropore system of the Y zeolite, but not in the mesopores and macropores of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Reaction rates were determined as a function of the partial pressure of  $O_2$  above the reaction mixture, and are shown in Fig. 3. Clearly saturation is achieved with CdS(12.5)/Y(Na<sub>2</sub>S) at a pressure of 0.1 atm, whilst this was not achieved with CdS(14.5)/Al<sub>2</sub>O<sub>3</sub> at the highest experimental pressure of 1.0 atm.

The effect of radiation intensity entering the reaction vessel on reaction rate was determined using seven reduced intensities generated by neutral density filters. The reaction rate at full radiation intensity was reproduced when a partially silvered reaction vessel was used, indicating full absorption with no loss of activity through scattering by the photocatalyst particles. Fig. 4 shows that a plot of reaction rate against (relative intensity)<sup>0.5</sup> is linear and passes through the origin, whereas a direct plot against relative intensity exhibits pronounced curvature. In this respect CdS(12.5)/Y(Na<sub>2</sub>S) is the same as previously found for CdS(14.5)/Al<sub>2</sub>O<sub>3</sub>, <sup>3</sup> in that



Fig. 2 Effect of propan-2-ol mole fraction on reaction rate with CdS(12.5)/Y(Na<sub>2</sub>S) at 303 K. (---) Plot previously obtained<sup>3</sup> with CdS(14.5)/Al<sub>2</sub>O<sub>3</sub>.



Fig. 3 Effect of oxygen partial pressure on reaction rate with CdS(12.5)/Y(Na<sub>2</sub>S) at 303 K. (---) Plot previously obtained<sup>3</sup> with CdS(14.5)/Al<sub>2</sub>O<sub>3</sub>.



Fig. 4 Effect of UV radiation intensity on reaction rate with  $CdS(12.5)/Y(Na_2S)$  at 303 K

the loss of photoelectrons and photoholes through recombination exceeds their consumption in the surface processes of photocatalysis.<sup>16,17</sup> Calculated quantum yields of 0.027 at 100% intensity rising to 0.15 at 4% intensity are in accord with such a conclusion.

The differences between  $CdS(12.5)/Y(Na_2S)$  and  $CdS(14.5)/Al_2O_3$  can be ascribed to a higher adsorption potential for both oxygen and water within the CdS-zeolite composite. Furthermore, size constraints imposed by the zeolite pores on the CdS particles, even after agglomeration by water,<sup>14</sup> may yield smaller particles in which less photoelectron-photohole recombination occurs.

When the photocatalytic oxidation of propan-2-ol at 303 K was attempted using  $CdS(12.5)/Y(H_2S)$ , from which moisture had been rigorously excluded, no propanone formation was detected. However, when 0.3 cm<sup>3</sup> of water was added to the reaction mixture propanone formation became apparent and the colour of the catalyst changed from pale grey to yellow. Sufficient CdS(12.5)/Y(H<sub>2</sub>S) for a number of experiments was exposed to the water vapour above a saturated NaCl solution at room temperature. Rapid hydration occurred, as evidenced by the colour change to yellow, and the material was found to be photocatalytically active: the rate of propanone formation at 303 K was  $3.69 \times 10^{-7}$  mol  $dm^{-3}$  s<sup>-1</sup>. A further preparation, CdS(13.5)/Y(H<sub>2</sub>S), was more slowly hydrated by exposure to air in a lightly stoppered bottle, this material was appreciably lighter in colour, but possessed a higher activity at 303 K of  $4.90 \times 10^{-7}$  mol dm<sup>-3</sup> s<sup>-1</sup>. Presumably, the difference between these two catalysts arises from the size of the CdS particles, with slow hydration giving smaller more efficient particles.

## Effect of Temperature and Reactant Alcohol on Reaction Rate

The effect of temperature on the rate of propanone formation from propan-2-ol was studied on the three CdS-based and the single TiO<sub>2</sub>-based zeolite composites. Reaction rates determined at six temperature in the range 283–308 K gave excellent Arrhenius plots; activation energies, together with reaction rates, specific reaction rates and quantum yields  $\phi$  at 303 K are given in Table 1. To permit comparisons between different types of catalyst, corresponding published data<sup>3</sup> for

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Table 1 Reaction rates, quantum yields and activation energies for carbonyl compound formation on CdS- and TiO<sub>2</sub>-based cataysts

			reaction at 303 K			
catalyst	reactant	catalyst mass/mg	rate $/10^{-7} \text{ mol } \text{dm}^{-3} \text{ s}^{-1}$	$\phi$	specific rate <sup><i>a</i></sup> $/10^{-5}$ mol dm <sup>-3</sup> s <sup>-1</sup> g <sup>-1</sup>	$E_a$ /kJ mol <sup>-1</sup>
CdS(12.5)/Y(Na <sub>2</sub> S)	propan-2-ol	100	3.50	0.027	2.80	52 ± 2
( ) ( 2 )	methanol	100	3.33	0.026	2.66	$51 \pm 2$
	ethanol	100	3.49	0.027	2.79	$53 \pm 2$
$CdS(12.5)/Y(H_2S)^b$	propan-2-ol	100	3.69	0.029	2.95	$54 \pm 1$
CdS(13.5)/Y(H <sub>2</sub> S) <sup>c</sup>	propan-2-ol	100	4.90	0.038	3.63	$55 \pm 2$
$CdS(14.5)/Al_2O_3^{d}$	propan-2-ol <sup>e</sup>	150	2.67	0.021	1.23	$54 \pm 2$
TiO <sub>2</sub> (3.0)/Y	propan-2-ol	150	4.03	0.031	8.96	$21 \pm 1$
TiO <sub>2</sub> (8.7)Al <sub>2</sub> O <sub>3</sub> <sup>d</sup>	propan-2-ol	150	11.0	0.085	8.43	$21 \pm 1$
TiO <sub>2</sub> <sup>d</sup>	propan-2-ol	150	39.0	0.30	2.60	$19 \pm 1$

<sup>a</sup> Rate expressed per g of active constituent, CdS or TiO<sub>2</sub>. <sup>b</sup> Rapid hydration. <sup>c</sup> Slow hydration. <sup>d</sup> Ref. 3. <sup>e</sup> Water added to give  $X_{H,O} = 0.18$ .

alumina supported catalysts,  $CdS(14.5)/Al_2O_3$  and  $TiO_2(8.7)/Al_2O_3$ , and P25 anatase are also given in Table 1.

The photo-oxidation of methanol to methanal and ethanol to ethanal was successfully studied with  $Cd(12.5)/Y(Na_2S)$  over the range 283–308 K; the data obtained are presented in Table 1. However, attempts to study the same reactions with  $Cd(12.5)/Y(H_2S)$  and  $Cd(13.5)/Y(H_2S)$  were unsuccessful in that neither methanal, ethanal nor the corresponding carboxylic acids arising from further oxidation, could be detected in the liquid phase. We attribute this to the retention of polymeric aldehyde within the zeolite pore system, rather than a complete lack of reactivity. The Brønsted acidity responsible for the polymerisation is generated when the charge balancing  $Cd^{2+}$  ions react with  $H_2S$  to form CdS:

$$d^{2+} + 2O_z^- + H_2S \rightarrow CdS + 2O_zH$$

where subscript z denotes an oxygen atom in the zeolite framework.<sup>18</sup> Such strongly acidic  $O_zH$  groups are not formed during CdS preparation with aqueous Na<sub>2</sub>S, since two Na<sup>+</sup> replace the charge balancing Cd<sup>2+</sup> ions.

# **General Conclusions**

We have established that semiconductor-zeolite composites are active for the photocatalytic oxidation of alcohols. The data in Table 1 show that the activation energy depends upon the physico-chemical properties of photoactive constituent, CdS or  $TiO_2$ , and is unaffected by interaction with the matrix or support. No evidence has emerged against the earlier suggestions<sup>3,7</sup> that the activation energy is associated with photohole transport in CdS and photoelectron transport in  $TiO_2$ . We believe that the reaction mechanism with the composites is the same as that when the semiconductors are supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>3</sup> However, the inactivity of CdS(14.5)/Al<sub>2</sub>O<sub>3</sub> unless water was added to the reaction mixture,<sup>3</sup> was not observed with CdS(12.5)/Y(Na<sub>2</sub>S); this is ascribed to the retention of sufficient water within the zeolite pore system. Chemical synergism between photocatalyst and support appears to be restricted to the polymerisation and retention of the oxidation products of primary alcohols on  $Cd(12.5)/Y(H_2S)$  and  $Cd(13.5)/Y(H_2S)$ .

The quantum yields in Table 1 show that anatase predominates in utilizing incident UV radiation, whereas  $TiO_2(3.0)/Y$ possesses the highest specific activity for the semiconductor component. We suggest that high specific photoactivity, combined with the ability to enrich chemicals by adsorption, could lead to the use of  $TiO_2$ -Y zeolite composites in pollution control.

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