

Oxidation of Chloride to Chlorine by Ceric Ions Mediated by the Three Forms of Crystalline Carbon

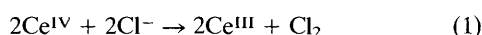
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C₆₀ is more effective than graphite or diamond as a redox catalyst for the oxidation of chloride to chlorine by ceric ions.

The intense interest in the new form of solid carbon, C₆₀, following its first production in macroscopic quantities in 1990, has led to a wide variety of investigations into its properties,¹ which often appear very different from those of the other crystalline forms,² diamond and graphite. One area which does not appear to have been investigated is the use of C₆₀ as a redox catalyst. This is not too surprising since, in redox catalysis, the role of the catalyst is usually as a simple conductor of electrons between the two redox couples, and diamond and C₆₀ are not highly conducting.³

The oxidation of chloride to chlorine by ceric ions, eqn. (1),



is a classic example of a thermodynamically feasible redox reaction (in 0.5 mol dm⁻³ H₂SO₄, $\Delta G = -15.4$ kJ mol⁻¹ of Cl₂) which requires a redox catalyst to proceed under ambient reaction conditions.⁴ Throughout most of the history of the chloralkali industry, graphite, or some related form of conducting carbon, has been used as the anode material⁵ and, in a previous study,⁶ we found that a variety of amorphous, conducting carbon blacks were able to act as catalysts for reaction (1). Although C₆₀ and diamond may not be highly conducting, they still may exhibit some redox catalytic activity. Thus, as an extension of our earlier work, we investigated the abilities of the three forms of crystalline carbon and an extra conductive, amorphous carbon black (ECB) to act as catalysts for reaction (1).

The kinetics of reaction (1), mediated by the different carbon redox catalysts (see Table 1), were studied spectrophotometrically by monitoring the change in absorbance at $\lambda = 430$ nm, due to a decrease in the concentration of the Ce^{IV} ions, as a function of time, at 30 °C. The reaction conditions were as follows: [NaCl] = 2 mol dm⁻³ in 0.5 mol dm⁻³ H₂SO₄, initial [Ce^{IV}] = 3.8×10^{-3} mol dm⁻³ and the recorded typical absorbance *versus* time profiles for: no catalyst, diamond, graphite, C₆₀ and ECB, are illustrated in Fig. 1. In all cases, the kinetics of catalysis gave an excellent fit to first-order kinetics with respect to [Ce^{IV}] over at least 2½ half-lives. The %Cl₂ yield for each catalyst was determined for reaction (1) using a triiodide trap flow system, which has been described fully elsewhere.⁶ All the carbon catalysts tested gave high, stoichiometric yields of chlorine (>90%). In the absence of

chloride ions, the carbon catalysts tested did not undergo oxidation, and were unable to mediate the oxidation of water, by Ce^{IV} ions.

The first-order rate constants, k_1 , for reaction (1), determined for the different carbon catalysts are listed in Table 1. Using this data, the specific first-order rate constant, *i.e.* k_1^* (units: s⁻¹ m⁻²), for each of the carbons tested was calculated *via* eqn. (2) where k_1 (blank) is the first-order rate constant for reaction (1) determined in the absence of catalyst (see Table 1), SA is the specific surface area of the carbon (units: m² g⁻¹), [cat.] is the concentration of the carbon catalyst used in the determination of k_1 (units: g m⁻³) and V is the volume of the reaction solution (units: m³); in our work $V = 2.5 \times 10^{-6}$ m³. One measure of SA for a carbon is its BET surface area and the latter, in combination with eqn. (2), has been used to calculate the k_1^* (BET) value for each of the different carbons listed in Table 1.

$$k_1^* = \{k_1 - k_1(\text{blank})\} / \{SA[\text{cat.}]V\} \quad (2)$$

From the different k_1^* (BET) values listed in Table 1, it would appear that C₆₀ is the most active of all the different carbons tested. This result is somewhat surprising, given that the higher electrical conductivity of ECB, compared with that of the other carbons, would be expected to make this material the superior redox carbon catalyst for reaction (1). However, the BET surface area is unlikely to provide a good measure of the specific surface area *in situ*; for example, the BET surface area for ECB of 1000 m² g⁻¹ is largely due to its porosity and a large fraction may be effectively unavailable for reaction due to poor exchange with the bulk reaction solution.

A more useful estimate for SA is the specific surface area of the carbon when it is dispersed in solution, $S(\text{disp.})$. If it is assumed, for each different carbon dispersion, that it is a monodisperse of spherical particles which do not appreciably scatter light and absorb all UV-VIS radiation incident upon them, then it can be shown⁷ that $S(\text{disp.})$ is related to the absorbance (in a 1 cm cell) of the dispersion at any

Table 1 Kinetic data and specific activities^a of the different carbons tested based on BET specific surface area, $S(\text{BET})$

Carbon type (supplier)	$S(\text{BET})/$ m ² g ⁻¹	[cat.]/ g m ⁻³	$10^4 k_1/$ s ⁻¹	k_1^* (BET)/ s ⁻¹ m ⁻²
Graphite (Aldrich)	55	2.6	0.47	0.039
		50	6.7	0.092
Diamond (Johnson Matthey)	20	7.1	0.36	0.0085
		37	0.56	0.012
C ₆₀ (MER) ^b	1.42	100	4.7	1.2
		250	9.4	1.0
ECB ^c (Degussa)	1000	10	48	0.19
None	—	0	0.33	—

^a k_1^* (BET) values were calculated using eqn. (2), with $SA = S(\text{BET})$.

^b Materials and Electrochemical Research Corporation. ^c Extra conductive black (tradename: Printex XE 2).

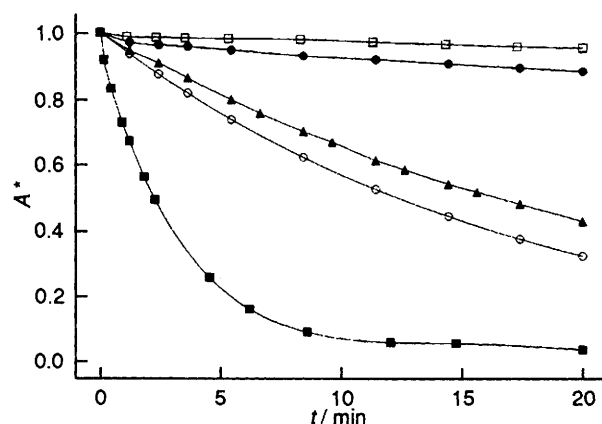


Fig. 1 Plots of the relative absorbance due to the Ce^{IV} ions, measured at 430 nm, (A^*) *versus* time recorded for the following carbon catalysts: (□) no catalyst, (●) diamond (0.037 g dm⁻³), (▲) graphite (0.050 g dm⁻³), (○) C₆₀ (0.250 g dm⁻³) and (■) carbon black (0.010 g dm⁻³). The initial reaction conditions were as follows: 2 mol dm⁻³ NaCl in 0.5 mol dm⁻³ H₂SO₄, [Ce^{IV}] = 3.8×10^{-3} mol dm⁻³, $T = 30$ °C.

wavelength, Abs., *via* eqn. (3), where ρ is the density of the carbon (units: g m^{-3}). Some support for applicability of eqn. (3) to carbon black dispersions is provided by the results of a previous study⁶ which showed, for a wide range of different carbon blacks, that at low-moderate concentrations the absorbance of the dispersion is directly proportional to its concentration, as predicted by eqn. (3). Table 2 lists the measured values for Abs. at 430 nm for the different carbon catalysts, along with the values for $S(\text{disp.})$, calculated using eqn. (3) and k_1^* (disp.), calculated using eqn. (2), with $SA = S(\text{disp.})$. From the different values for k_1^* (disp.), listed in Table 2, it appears that ECB is the most active of the carbons tested and that C_{60} is markedly the most active of the crystalline forms of carbon tested. This finding is the first reported example of C_{60} as a redox catalyst and, given its

relatively high activity, encourages further work into the catalytic and electrocatalytic properties of this material.

$$S(\text{disp.}) = -6\text{Abs.}/\rho \log(1 - \{3[\text{cat.}]/2\rho\}) \quad (3)$$

Previous work⁶ has demonstrated that the observed kinetics associated with reaction (1) catalysed by carbon blacks, such as ECB, can be readily rationalised using an electrochemical model of redox catalysis in which the Nernstian reduction of Ce^{IV} ions is coupled to the electrochemically irreversible oxidation of chloride to chlorine, *via* electron transfer through the micro-electrode carbon particles. Further work is in progress to elucidate the mechanistic details associated with the catalysis of reaction (1) by the particles of C_{60} and the other crystalline forms of carbon. The low electrical conductivities of the latter forms of carbon make it likely that the rate of electron transfer across the carbon particles will be an important factor in determining the overall rate of catalysis.

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Table 2 Specific activities^a of the different carbons tested based on specific surface area *in situ*

Carbon type (supplier)	Abs. (430 nm)	[cat.]/ g m^{-3}	ρ / g cm^{-3}	$S(\text{disp.})$ / 10^{-3} $\text{m}^2 \text{g}^{-1}$	k_1^* (disp.)/ $\text{s}^{-1} \text{m}^{-2}$
Graphite (Aldrich)	0.016 0.158	2.6 50	2.51	57 29	38 170
Diamond (Johnson Matthey)	0.030 0.170	7.1 37	3.21	40 42	4.2 5.9
C_{60} (MER)	0.032 0.164	100 250	1.70	3.0 6.0	580 240
ECB (Degussa)	0.170	10	1.85	160	1200

^a k_1^* (disp.) values were calculated using eqn. (2), with $SA = S(\text{disp.})$

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