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Catalysis and pollution abatement: the removal of hypochlorite from waste chlorine/caustic effluent

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Abstract

In the chlorine industry, waste chlorine/caustic effluents containing sodium hypochlorite are common and their discharge to the environment is strictly regulated. A technology has been developed for the selective decomposition of hypochlorite using a fixed bed, catalytic reaction. The insights gained into the chemical and physical mechanisms that determine the efficacy of the technology will be outlined.

Keywords: Pollution abatement; Waste chlorine; Caustic effluent; Hypochlorite

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1. Introduction

Balard, at the beginning of the last century, first discovered that silver oxide would decompose hypochlorite solutions [1] with the evolution of oxygen. Later work by Howell [2], Chirnoaga [3] and Lewis and Seemiller [4] has provided our understanding of the active metals, nickel, cobalt and copper, their promotion and the kinetics of the reaction. By the very nature of the substrate they were studying, hypochlorite solutions are only stable under neutral to alkaline conditions, the catalyst in the reaction (see below) was a suspended metal hydroxide.

$$2NaOCl \rightarrow 2NaCl + O_2$$

It was this type of system that was first transferred to the industrial arena where the technology was then generally referred to as the homogeneous catalytic decomposition of hypochlorite. The process is required because although sodium hypochlorite is a popular bleach and disinfecting agent, a considerable quantity of the material is produced by the chlorine users. The reason for this is both chlorine users and producers are required to prevent chlorine slippage to atmosphere and, to achieve their chlorine emission levels, they use caustic scrubbing. Then for this effluent, containing high concentrations of sodium hypochlorite, the homogeneous technology was well practised within the industry to meet the regulatory authorities discharge consent levels.

Apart from the difficulties of temperature and reaction rate control, that can to some extent be overcome by more sophisticated reactor design, there is one serious problem that is difficult to avoid. With this process the finely suspended metal hydroxide (usually nickel) is difficult to remove from the effluent and often ends up in the discharge. Hence the net result is only the replacement of one pollutant by another, as nickel, cobalt

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and copper are all toxic materials. A fixed bed catalytic system would provide a simple solution to this difficulty.

2. Experimental

The ESR spectra were recorded on a JEOL JES-REX2 spectrometer fitted with a ES-DVT2 variable temperature unit and linked to an ESPRIT 330 Data System. The X-band spectrometer was operated at 9.5 GHz and the samples were placed in a cylindrical cavity. The catalysts for the ESR and iron promotion experiments were prepared by slurry metal nitrate impregnation of a high purity magnesium oxide powder (from Aldrich Chemicals). The iron solutions used were atomic absorption grade, the nickel solutions were prepared from high purity nickel nitrate hexahydrate. The catalysts, after impregnation at room temperature, were air dried at 100°C and calcined at 450°C for 6 h. The final bulk active metal concentrations varied from 5000 to 20 000 ppm.

The experiments on the effect of bubbles on catalyst activity were carried out in a tubular, isothermal reactor (2.5 cm × 20 cm) with proprietary catalyst samples. Commercially available sodium hypochlorite was used throughout the work at concentrations between 2 and 10% w/v.

3. The mechanism of the reaction and activity promotion by the addition of Fe_2O_3

The early work had determined that the active base metals were nickel, cobalt and copper and of the precious metals, platinum, palladium and iridium could be used. The mechanism behind their activity has generally been considered to involve higher oxidation states of the metal [5]. However experimental evidence for a mechanism has been difficult to produce because of the analytical problems in determining the concentrations of these postulated oxidation states in situ. In the Katalco Research Group we have employed the technique of electron spin resonance (ESR) to allow in situ measurements of the oxidation states of nickel and with that demonstrate the unexpectedly complex nature of the catalysis.

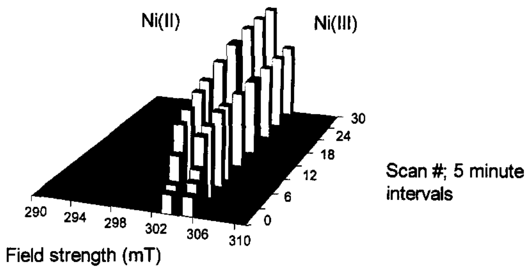

Fig. 1. The time resolved ESR signals of Ni(II) and Ni(III).

The time resolved detection of ESR active Ni(II) and Ni(III) is displayed in Fig. 1. The data documented in the figure reflects what is happening to the catalyst at the initial stage of the catalytic process.

The measurements show the increasing activation of the catalyst in the presence of sodium hypochlorite.

The Ni(II) signal arises from the loss of the ESR silent antiferromagnetic nickel oxide structure and it's replacement by a new ESR active NiO. Thus the reaction would appear to involve the production of a Ni(III) species and a new Ni(II) moiety, the result of the surface re-organisation that occurs through the catalytic cycle Ni(II) to Ni(III) to Ni(II). However for nickel there exists the possibility of a Ni(IV) oxidation state. As Ni(IV) is ESR silent the intervention of this species was examined by the addition of periodate, known to form stable complexes with Ni(IV) [6]. In the presence of periodate the time resolved increase in Ni(II)/Ni(III) shows a long delay before the gradual development of the signals (see Fig. 2). In this experiment sodium periodate solution has been added to the ESR cell

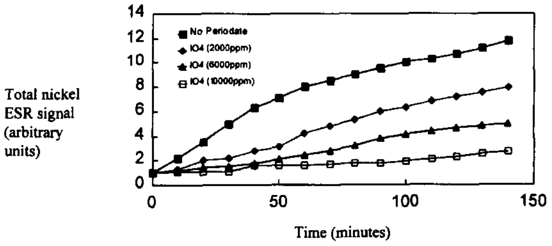

Fig. 2. Suppression of the nickel ESR signal with sodium periodate ($NaIO_4$).

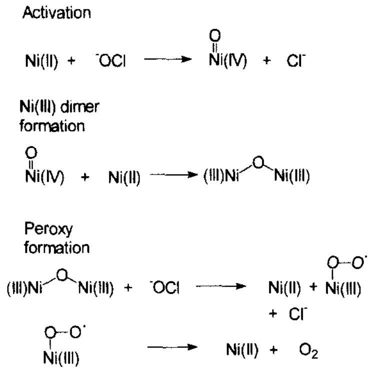

Fig. 3. A proposed reaction mechanism for the formation of Ni(IV), Ni(III) and Ni(II).

containing the catalyst and sodium hypochlorite. The 'no periodate' data was a duplicate of that observed in Fig. 1. The sum of the two nickel signals has then been recorded at increasing periodate concentrations. The figure shows that an induction period has been initiated that increased with increasing periodate concentration. There was an almost complete suppression of the initial rate of reaction at high periodate concentrations. However after that induction the rate of signal production was similar at all periodate levels.

This behaviour strongly suggests that Ni(IV) is the first formed intermediate in the catalytic cycle that can be represented by the reactions proposed in Fig. 3.

This mechanism accounts for the periodate inhibition of catalyst activity as eventually all the periodate added is complexed after which continued activation allows the catalytic reaction. From the amount of periodate required to suppress activity at a given time in the reaction an estimate of the Ni(IV) produced by oxidation can be obtained. This can be compared to the nickel(II) and nickel(III) levels measured by spin counting techniques. The above mechanism requires that the Ni(II)/Ni(III) total concentration should be equal to the Ni(IV) produced and estimates from the two independent measurements are very similar [7].

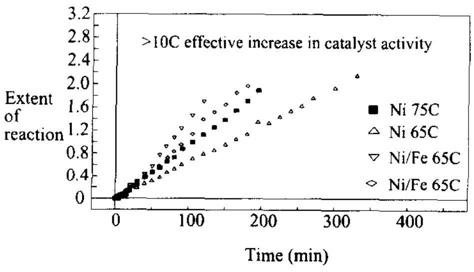

Fig. 4. Catalyst activity and promotion by iron.

The promotion by iron can be observed in Fig. 4.

The extent of reaction is determined from the timed measurement of the hypochlorite concentration in a well-stirred batch reactor at constant temperature. Then, at a fixed weight of catalyst in a standard volume of hypochlorite, the activities of different catalysts can be compared as the slope of the line is the rate constant for the reaction at that temperature. The two nickel catalysts containing different levels of iron, at 65°C, are significantly more active than a similar, undoped, nickel catalyst at 75°C. This promotion by iron reduces the catalyst volume required for a given hypochlorite destruction level and considerably improves the cost of treatment per volume of waste effluent.

The mechanism of the iron promotion would appear to be related to the substantial increase in the Ni(III) ESR signal that is observed experimentally. This can be understood by analogy with the predicted electronic structure of lanthanum strontium nickel oxides doped with iron [8]. This system shows strong Fe–O–Ni interactions capable of stabilising an unpaired electron on the nickel. Additionally the band gap between Ni(II) d^8 and Fe(III) d^5 is only ca. 0.5 eV making electron transfer reactions feasible. Therefore it is postulated that the presence of iron facilitates charge transfer between the Ni(II) and Ni(III) ions.

4. Reactor design and the effect of bubble rise

A Hydecat™ [1] reactor module, typically fabricated in titanium, operating at a typical range of inlet hypochlorite concentrations, will produce between 3–15 l of oxygen gas per l of effluent.

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[1] Hydecat™ is a trademark of ICI Chemicals and Polymers Ltd.

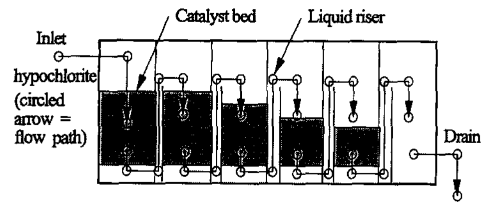

Fig. 5. A diagram of the flow path in the Hydecat$^{■}$ reactor.

Titanium is the material of construction of choice because the material is exceptionally inert to chemical attack. There are suitable plastics and other materials but they will suffer from hypochlorite related embrittlement and corrosion that will limit their operating temperature range and overall life.

The vent gas will consist of oxygen containing water vapour at its saturated vapour pressure. It is of interest to note that with this reaction the overall chlorine production process with Hydecat™ technology has succeeded in splitting water into oxygen and hydrogen. However, from the above gas rate, it is clear that the first requirement of the reactor is that this volume of gas can be removed from the liquid stream and vented to prevent major variations in the reactor voidage and possible gas blanketing of the catalyst. Significant gas blanketing of the catalytic material with oxygen bubbles would be a major concern has it would effectively suppress the reaction. The avoidance of any of these issues is achieved with a multiple bed, gravity driven design pictured (schematically) in Fig. 5.

The first two beds operate to allow rapid disengagement of the major fraction of the gas to be liberated. Hence the dimensions of these beds are determined by the requirement that the gas voidage at the liquid surface should be a small fraction of the total liquid surface. The volume of the beds will establish the amount of hypochlorite decomposed to oxygen and brine by fixing the residence time. The bed height and bed cross sectional area can then be adjusted to set the bubble voidage at the liquid surface to the design value. The subsequent bed heights are then calculated from the need to keep the hydrostatic head, after allowing for catalyst pellet resistance and bubble voidage density effects, below the height of the preceding bed.

Although the bubbles generated in the reactor are very small, the liquid superficial velocity is also low leading to a significant bubble slip velocity. These bubbles gradually coalesce to give a distribution of sizes throughout the reactor. Hence there is a steady state bubble voidage profile showing an increasing voidage from the bottom to the top of the bed. This bubble profile has been found to play a significant role in determining the experimentally measured activity of the catalyst. It could be expected that the bow/wake of a rising bubble would only create a dispersive influence on the flow pattern that would increase up the bed as the bubble voidage increased. However, unexpectedly, a very significant and discernible upward component to the flow was found. This can be best observed in a comparison of up and downflow reactors (see Fig. 6).

The activity of the catalyst was determined for various inlet hypochlorite concentrations. Under the conditions used variation in the inlet hypochlorite corresponded to a range of oxygen gas evolution rates. Inspection of Fig. 5 shows that the activity of the catalyst, as represented by a first order rate constant, for the downflow reactor shows only a slight change with varying inlet hypochlorite. However the upflow reactor, displays a marked decrease in activity at high oxygen gas evolution rates. In the upflow configuration the bubble rise results in hypochlorite transport to the exit of the reactor effectively by-passing the catalyst. Hence, unexpectedly, the Hydecat™ reactor contains a series of downflow beds for the

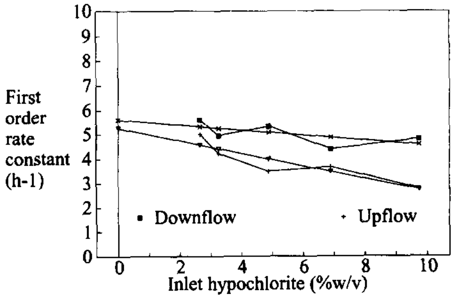

Fig. 6. The variation in catalyst activity with up and down flow reactors.

optimum performance of the catalytic process. These systems are now operating within ICI in the UK and at other installations world-wide. The applications include the simple disposal of hypochlorite produced as a consequence of protecting the environment from chlorine emissions during the actual manufacture of chlorine. The technology is also used to treat hypochlorite streams on plants producing such materials as chloro- and fluoro-hydrocarbons, chlorinated agrochemicals and chlorinated synthetic intermediates.

5. Conclusions

This paper has reviewed the chemical and physical processes that are at the centre of the technology. It has demonstrated that the effects, derived from these aspects of the catalytic reaction, must be considered together as they are both critical to the successful performance of the process.

Acknowledgements

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