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Catalysis Today 66 (2001) 447–452

CATALYSIS TODAY

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Kinetics and mass transfer effects in the oxidation of ferrous sulfate over doped active carbon catalysts

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Abstract

Ferric sulfate is used in water purification. The oxidation of ferrous sulfate, $FeSO_4$, to ferric sulfate in acidic aqueous solutions of H_2SO_4 over finely dispersed active carbon particles was studied in a vigorously stirred batch reactor. Molecular oxygen was used as the oxidation agent and two kinds of catalysts were utilized: active carbon, doped active carbon. Both active carbon and doped active carbon catalysts enhanced the oxidation rate considerably.

Systematic kinetic experiments were carried out at the temperature and pressure ranges of 60–100°C and 4–10 bar, respectively. The results revealed that both non-catalytic and catalytic oxidation of Fe^{2+} take place simultaneously. The experimental data were fitted to rate equations, which were based on a plausible reaction mechanism: adsorption of dissolved oxygen on active carbon, electron transfer from Fe^{2+} ions to adsorbed oxygen and formation of surface hydroxyls. A comparison of the Fe^{2+} concentrations predicted by the kinetic model with the experimentally observed concentrations indicated that the mechanistic rate equations were able to describe the intrinsic oxidation kinetics of Fe^{2+} over pure active carbon and doped active carbon catalysts. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Kinetic and mass transfer effects; Active carbon; Doped active carbon; Catalytic and non-catalytic oxidation

1. Introduction

Ferric sulfate is used in wastewater purification as a coagulant, in concrete industry as an additive in cement and as a coating material in the production of video and audio cassettes. Ferric sulfate is obtained by oxidation of ferrous sulfate with molecular oxygen or air. The reaction formula is

$$4FeSO_4(aq) + O_2 + 2HSO_4{}^- + 2H_3O^+ \rightarrow 2Fe_2(SO_4)_3(aq) + 4H_2O$$

Other oxidizing agents, such as HNO_3, NO_2, $NaNO_2$ can be used, but their drawback is the production of stoichiometric amounts of nitrogen containing by-products. The conventional oxidation technology is based on the use of oxygen or air solely: the oxidation proceeds in large batchwise operating stirred tanks. The initial oxidation rate is high but it slows down rapidly and it becomes difficult to obtain high conversions (close to 100%) [1], which are required for an acceptable product quality. The oxidation can be forced to completion by adding a heterogeneous catalyst. An efficient one is active carbon, as demonstrated in our previous publication [2]. In the present paper, metal-doped active carbon is considered as a potential catalyst for the oxidation process. The purpose of the present work is to determine the kinetics and the mass transfer effects in the oxidation of ferrous sulfate in the absence and in the presence of doped active carbon catalysts.

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PII: S0920-5861(00)00651-9

Nomenclature

A	pre-exponential factor
b_n	parameters for estimating solvent vapor pressure correction
c	concentration
E	activation energy
k	rate constant
k', k''	lumped rate constants
K	equilibrium constant
K', K''	lumped equilibrium constants
p	partial pressure
P	total pressure
r, r'	reaction rates
R	gas constant
R^2	multiple correlation coefficient
T	absolute temperature
v'	stoichiometric number
w	weight fraction

Greek symbols

δ	vapour pressure correction
ρ_B	catalyst bulk density

Subscripts and superscripts

B	bulk, in bulk density (ρ_B)
c	concentration-based quantity
g	gas
L	liquid phase
nc	non-catalytic
vp	vapour
+/−	anion/cation
$*$	interfacial quantity

Abbreviations

O	oxygen (O_2 or surface oxygen O^*)
O^-	charged oxygen ion (O^{*-})
OH	surface hydroxyl (OH^*)
W	water (H_2O)
W^+	hydronium ion (H_3O^+)
$*$	surface site

2. Experimental

Isobaric and isothermal kinetic experiments were carried out in a pressurized autoclave (300 ml) at 4–10 bar and 60–100°C. The autoclave was equipped with a turbine impeller, the velocity of agitation exceeded 1000 rpm. The initial concentration of ferrous sulfate and sulfuric acid were 2–2.5 and 1.3 mol/dm^3, respectively. Oxygen was used as an oxidizing agent. Samples were withdrawn during the experiments and the Fe^{2+} contents of the samples were determined by redox-titration with cerium sulfate.

The kinetics of the active carbon catalyzed oxidation was studied by performing a series of tests at temperatures 60, 80 and 100°C and pressures 4, 7 and 10 bar. The carbon used in the tests was of fine quality and the average particle size was 14 μm. Internal diffusion resistance was not considered a limiting factor because of the very small particle sizes.

A complete oxidation series was done for doped active carbon in the same way as for the fineground active carbon. For the doped active carbon the average particle size was 18 μm. The amount of catalyst used in the oxidation was 1.2 wt.%.

3. Kinetics and catalysis

A reaction mechanism for the oxidation of ferrous sulfate over active carbon has been proposed in our previous paper [2]. The oxidation was presumed to proceed on the active carbon surface, where oxygen is dissociatively adsorbed. Fe^{2+} ions donate an electron to the adsorbed oxygen, which reacts with a hydronium ion forming a surface hydroxyl and releasing water. Two surface hydroxyls form water, leaving an oxygen-covered and a vacant site on the catalyst surface. The mechanism is summarized below:

Reaction step				Stoichiometric number (v')
I	$O_2 + 2^*$	$\rightleftharpoons$	$2O^*$	$\frac{1}{4}$
II	$Fe^{2+} + O^*$	$\rightleftharpoons$	$Fe^{3+} + O^{*-}$	1
III	$O^{*-} + H_3O^+$	$\rightleftharpoons$	$OH^* + H_2O$	1
IV	$2OH^*$	$\rightleftharpoons$	$H_2O^* + O^*$	$\frac{1}{2}$
V	H_2O^*	$\rightleftharpoons$	$H_2O + *$	$\frac{1}{2}$
	$Fe^{2+} + \frac{1}{4}O_2 + H_3O^+$	$\rightleftharpoons$	$Fe^{3+} + \frac{3}{2}H_2O$	

It was assumed [1] that step II alone is rate determining, whereas steps I and III–V are rapid enough for the quasi-equilibrium hypothesis to be applied. In order to reduce the number of adjustable parameters, the original model was simplified [2]. Some of the surface intermediates can be assumed to be more abundant than the others. When the concentrations of the surface hydroxyls and water are negligible compared to those of adsorbed oxygen and if oxygen and water are the dominating surface compounds and the concentration of water was assumed to be constant, a simplified rate expression was obtained:

$$r = \frac{(k'' c_O^{1/4}/c_{w^+})(c_{Fe^{2+}} c_O^{1/4} c_{w^+} - (c_{Fe^{3+}} c_w^{3/2}/K_C))}{K''_O c_O^{1/2} + 1} \approx k'' c_O^{1/2} c_{Fe^{2+}} \tag{1}$$

It is known that, in the presence of a catalyst Fe^{2+} can be completely oxidized to Fe^{3+} — thus a possible simplification of the rate equation is the irreversible case ($K_C \to \infty$), where the backward reaction terms are discarded. Also the denominator can be approximated to 1. These simplifications leave us with two parameters to fit. Factor k'' consists of a pre-exponential factor and an exponential term ($-E/RT$) that was estimated through an orthogonalized temperature variable ($1/x = 1/T - 1/T_{ref}$). The rate and mechanism of the non-catalytic gas–liquid reaction and the liquid-phase processes between Fe^{2+} ions and dissolved oxygen are treated in detail [1,2]. The essential results are summarized here.

The non-catalytic mechanism is assumed to proceed through the formation of an intermediate complex between dissolved oxygen and Fe ions and the cleavage of the O–O-bond of the complex. The addition of two Fe^{2+} ions to dissolved oxygen leads to a peroxide-type complex, which is rapidly decomposed. The successive addition of Fe^{2+} ions to oxygen is assumed to be rate determining. The mechanism is summarized to [1]

$$Fe^{2+} + O_2 \to Fe\text{–}O\text{–}O^{2+} \quad \text{(I)}$$

$$Fe^{2+} + Fe\text{–}O\text{–}O^{2+} \to Fe\text{–}O\text{–}O\text{–}Fe^{4+} \quad \text{(II)}$$

The remaining steps are combined to a quasi-equilibrium:

$$2Fe^{2+} + 4H_3O^+ + Fe\text{–}O\text{–}O\text{–}Fe^{4+} \rightleftharpoons 4Fe^{3+} + 6H_2O \quad \text{(III)}$$

The application of the steady-state hypothesis to steps I and II, i.e. $r_1 = r_2$, and the quasi-equilibrium hypothesis to step III give the rate expression for the non-catalytic process,

$$r' = \frac{k_{nc2} K_{nc1} c_{Fe}^2 c_O}{1 + k_{nc2}(K_{nc1}/k_{nc1}) c_{Fe}} \tag{2}$$

Kinetic parameters are listed in Tables 1 and 2.

Table 1
Parameters for the non-catalytic reaction (Eq. (5)) at $T_{ref} = 80°C$ [1]

$k_{nc2}K_{nc1}$	$21.6\,M^{-2}\,min^{-1}$
k_{nc1}	$36.8\,M\,min^{-1}$
E/R	4176 K

Table 2
Parameters for the intrinsic catalytic reactions (Eqs. (4) and (5)) at $T_{ref} = 80°C$

$A_{catalytic,active\ carbon}$	$0.00507\,M^{-0.5}\,min^{-1}$
$E_{catalytic,active\ carbon}/R$	4176 K, where $R^2 = 97.66\%$
$A_{catalytic,doped}$	$0.187\,M^{-0.5}\,min^{-1}$
$E_{catalytic,doped}/R$	2050 K, where $R^2 = 95.88\%$

4. Gas–liquid equilibria

The concentration of dissolved oxygen appears in the rate equations, which was estimated from the oxygen solubility data in water, as described by a temperature-dependent correlation [3]. For a mixture of electrolytes, the relation of Weisenberger and Schumpe [4] was used.

The mole fraction of oxygen at the gas–liquid interface was calculated from Henry's law and the interfacial liquid phase concentration $c^*_{O_2}$ was obtained from $c^*_O = x^*_{O_2} c_L$, where c_L is the total concentration of the liquid.

In order to obtain a reliable value of the partial pressure of oxygen (p_{O2}) and since the solvent has a notable vapor pressure at the highest experimental pressure, the measured total pressure (P) was corrected with the vapor pressure of the H_2O–H_2SO_4–$FeSO_4$ solution:

$$p_{O_2} = P - \delta P^{vp}_{H_2O} \tag{3}$$

where $P^{vp}_{H_2O}$ denotes the vapor pressure of water and δ a correction factor which depends on the solvent composition. The vapor pressure of water was calculated from a modified Antoine equation given by Reid et al. [5].

The correction factor (δ) is related to the weight fraction of sulfuric acid ($w_{H_2SO_4}$) in the solution. Based on data, published by Sippola [6], the following empirical correlation was developed:

$$\delta = 1 + b_1 w_{H_2SO_4} + b_2 w_{H_2SO_4}^2 \tag{4}$$

The values of the coefficients b_1 and b_2 are listed in [1].

Since the oxygen concentration was high in the gas phase, the gas-phase mass transfer resistance of oxygen was negligible, and the surface pressure $p_{O_2}^*$ was set to equal the bulk phase pressure of oxygen, p_{O_2}. Because of vigorous stirring, the liquid phase was assumed saturated with respect to oxygen, and the liquid-side mass transfer resistance of oxygen was taken to be negligible.

5. Kinetic results over doped active carbon catalysts

The oxidation rate is more sensitive on temperature than on pressure as shown in Fig. 1. The amount of active carbon catalyst used was 4.8 wt.%. The catalytic

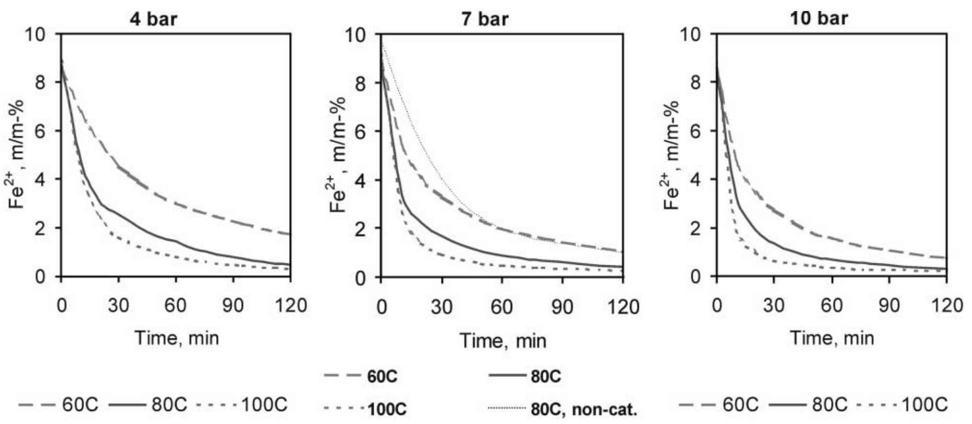

Fig. 1. Oxidation kinetics on fineground active carbon as catalyst.

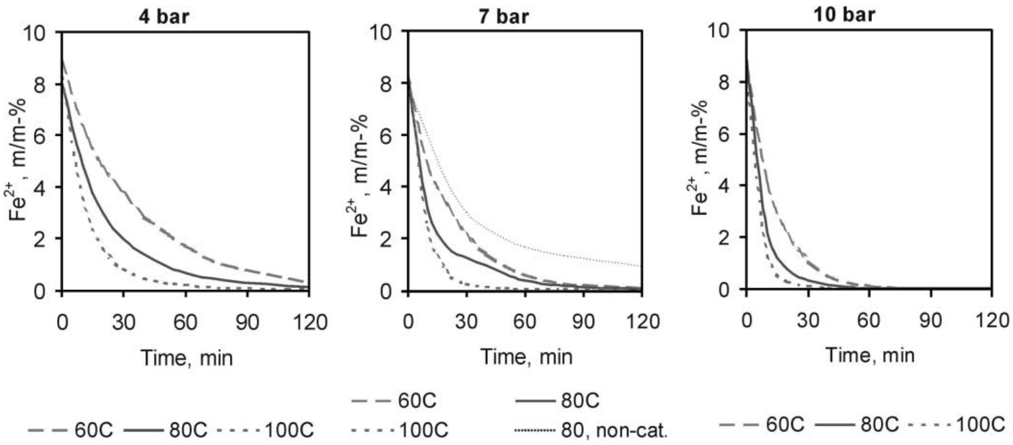

Fig. 2. Doped active carbon. Experimental kinetic curves at different temperatures and different pressures.

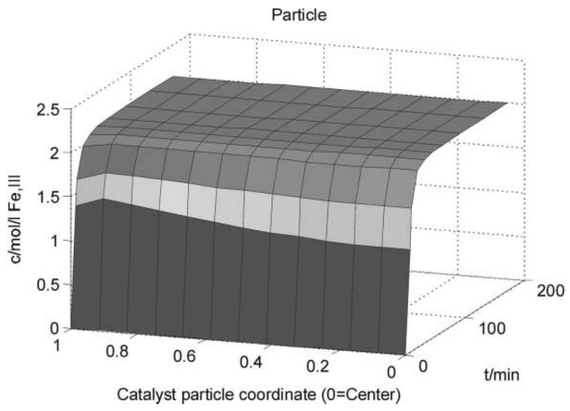

Fig. 3. Concentration of Fe^{3+} inside active carbon particle.

enhancement of the oxidation is most prominent at the beginning of the oxidation. Clearly, the best oxidation was achieved with doped active carbon, as presented in Fig. 2.

After determination of the non-catalytic and catalytic effects of active carbon in ferrous sulfate oxidation, the results obtained were compared to the experimental data. Further, the experimental data from oxidations with doped active carbon were fitted into the models. This finally lead to the conclusion that the effect on the doped active carbon in the oxidation of ferrous sulfate can be explained by Eq. (5):

$$r = r_{\text{non-catalytic}} + \rho_B\, r_{\text{catalytic, active carbon}} + \rho_B\, r_{\text{catalytic, doped}} \quad (5)$$

Typical kinetic curves are displayed in Figs. 1–3. As revealed by the figures, the presence of active carbon essentially enhances the oxidation velocity and the presence of a doping gives an additional improvement of the velocity. A comparison of experiments carried out with small and large particle sizes shows that the process was diffusion limited for the large particles. Rate equations based on plausible molecular mechanisms were derived for non-catalytic and catalytic oxidation. The parameters of the kinetic equations were determined with non-linear regression using the data obtained with small catalyst particles.

The role of mass transfer effects in the non-catalytic oxidation was elucidated with theoretical calculations of the Hatta number and the enhancement factor [1,2,7]. The calculations revealed that the enhancement factor is very close to 1, thus the film reaction was negligible.

The kinetic model was combined with the diffusion model for large catalyst particles. The parabolic partial differential equations describing simultaneous reaction and diffusion in porous catalyst particles were solved numerically and the simulations were compared with experimental data [7]. The reactor model, i.e. the system of ordinary differential equations (ODEs) was solved numerically during the course of parameter estimation. Software ODESSA [8] was used in the numerical solution. The kinetic parameters were estimated by minimizing the sum of residual squares (Q). A hybrid simplex-Levenberg–Marquardt algorithm [9] was used in the numerical minimization. The parameter estimation was carried out with Modest software [10].

The simulations also revealed the concentration gradients inside the catalyst particles confirming the presence of diffusion resistance of oxygen but also that of Fe^{2+} and Fe^{3+} ions (Fig. 3). The simulations convincingly showed that a realistic model for oxidation of ferrous sulfate over industrial-scale catalyst particles has to include both kinetic and diffusion effects. The effect of doping of active carbon was very prominent in the catalyst performance: by metal-doping, the reaction times for oxidation can be decreased considerably (∼50%) as revealed by comparison of Figs. 1 and 2.

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