CHEMOSPHERE

Chemosphere 61 (2005) 585–588

www.elsevier.com/locate/chemosphere

Short Communication

Dissolution studies on TiO_2 with organics

Amitava Mukherjee [a,1], Ashok M. Raichur [a,*,1], Jayant M. Modak [b]

[a] *Department of Metallurgy, Indian Institute of Science, Bangalore 560012, India*
[b] *Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India*

Received 2 July 2004; received in revised form 18 February 2005; accepted 25 February 2005

Abstract

In this work the effect of organic reducing reagents, namely, ascorbic acid, oxalic acid and L-cysteine on dissolution of commercial TiO_2 has been investigated. Kinetic studies showed that a maximum of about 45% of TiO_2 was dissolved by ascorbic acid in 4 h when oxide:acid molar ratio was kept at 1:2. The dissolution of TiO_2 increased with increase in ascorbic acid and oxalic acid concentration up to 0.15 M in 4 h (corresponding to molar ratio of oxide to acid of 1:3) and further addition did not affect the dissolution. Nearly 45% TiO_2 dissolution was obtained with ascorbic acid alone while oxalic acid yielded 40% dissolution. When oxalic acid was added along with ascorbic acid in equi-molar concentrations, dissolution of TiO_2 was enhanced to 60% in 2.5 h but when cysteine was added to ascorbic acid the dissolution was about 50% in just 1 h.

Keywords: Reductant; Ascorbic acid; Oxalic acid; Cysteine

1. Introduction

Titanium is extensively used in many applications including photocatalysts, gas sensors, paints and pigments and in ceramics. Recovery of Ti from spent TiO_2 products is important from both environmental and recycling/reuse perspective. In the recent past several attempts have been made to replace the classic pyrometallurgical process, namely the Kroll process, by electrodeposition of Ti from solutions containing Ti in ionic form. These processes had limitations in eliminating redox cycling of Ti and handling reactive products. Chen et al. (2000) reported an electrochemical method of reduction of solid TiO_2 in which oxygen is ionized, dissolved in a molten salt and discharged at the anode leaving pure titanium at the cathode. Jena et al. (1995) developed a combined pyro- and hydro-metallurgical method for recovery of Ti, V and Fe from titanomagnetite ore. Olanipekun (1999) reported that both temperature and concentration of HCl are important for dissolution of Ti and Fe from ilmenite. In another study, Van Dyke et al. (2002) showed that the temperature and acid to ilmenite molar ratio determine the dissolution of ilmenite.

Most studies on reductive dissolution of metal oxides by organics have concentrated on Mn and Fe oxides and Fe hydroxides. The reductive dissolution of manganese oxides in natural condition by microbial metabolites like oxalate and pyruvate was investigated extensively (Stone, 1987). Dissolution of Fe(III) (goethite, hematite and ferrihydrate) is another important natural geochemical process. Organics capable of reducing Mn(III, IV)

---

[*] Corresponding author. Tel.: +91 80 2293 3238; fax: +91 80 2360 0472.
E-mail address: amr@met.iisc.ernet.in (A.M. Raichur).

[1] Present address: Max Planck Institute for Colloids and Interfaces, Golm 14476, Germany.

0045-6535/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2005.02.059

oxides can reductively dissolve Fe(III) oxide also. Recent systematic studies on dissolution of Fe(III) and Mn(III, IV) oxides include those by Cornell et al. (1975), Stumm and Morgan (1981) and Stone and Morgan (1984). Most of these authors confirmed that dissolution reaction is facilitated under reducing conditions and is influenced by complex-forming organic ligands.

The objective of the present study was to investigate the reductive dissolution of TiO_2 by ascorbic acid and to determine the effect of adding other organics like oxalate and L-cysteine on the dissolution behavior.

2. Experimental

2.1. Materials

Commercial TiO_2 powder was procured from Merck Ltd (Mumbai, India). X-ray diffraction analysis (JEOL–JDX 8030 diffractometer) revealed an anatase phase while particle size analysis (Mastersizer, Malvern, UK) showed a D_{50} value of 0.38 μm. The TiO_2 powder was washed with double distilled water and dried prior to use. The organic acids were procured from Sisco Research Lab Pvt. Ltd., Mumbai, India. All experiments were performed with freshly prepared solutions using double distilled water.

2.2. Methods

Kinetic studies were conducted with ascorbic acid with an oxide:organic acid ratio of 1:2 (TiO_2 = 0.05 M and ascorbic acid = 0.10 M). When the effect of oxalic acid and cysteine along with ascorbic acid on dissolution kinetics was studied, the molar ratio was fixed at 1:1. The effect of organic acid concentration on dissolution was studied with ascorbic acid and oxalic acid separately. The organic acid concentration was varied from 0.05 M to 0.20 M and dissolution time was fixed at 4 h while the TiO_2 concentration was 0.05 M. During these experiments pH was not externally adjusted. The initial pH of the solutions was in a range of 2.8–3.0 depending on the ascorbic acid concentration in the solution. Addition of oxalic acid nor L-cysteine did not change the pH.

After adding the TiO_2 powder to the unamended and amended ascorbic acid solution, the mixture was allowed to react for different lengths of time with stirring. Dissolved Ti ($[Ti^{2+}]_{diss.}$) and solid titanium dioxide were distinguished by filtering the resultant solution with 0.2 μm pore size Millipore membrane filter. Before use each filter was rinsed once with 0.1 M HNO_3 and 3 times with 10 ml distilled water. After the filtration the residue was washed with 0.1 M HNO_3 to remove any adsorbed metal ions. The washings were added to the filtrate and the final volume calculated accordingly. Finally the filtrate was analyzed for dissolved Ti using an Inductively Coupled Plasma spectrometer. All the experiments were carried out in duplicate and the results could be reproduced with an error of less than 5%.

To investigate the effect of exposure to air on reduction of TiO_2 by ascorbic acid and oxalic acid, similar experiments were carried out under N_2 atmosphere. This was done by means of continuous N_2 purging in the solution for 30 min before adding TiO_2. After addition of solids, the shake flask was sealed using parafilm sheets and kept for mild stirring for required time periods of interaction.

For comparison purposes, we conducted some tests with TiO_2 in 50% HCl solution at 27 °C temperature for 4 h. At the end of the reaction the resultant solution was processed as described previously and analyzed.

3. Results and discussion

3.1. Dissolution studies with ascorbate

Fig. 1 illustrates the kinetics of TiO_2 dissolution by ascorbic acid. Dissolution increased until 2.5 h after which there was no significant increase. Nearly 45% of the oxide was dissolved at the end of 4 h. Fig. 2 shows the effect of increasing ascorbic acid concentration on dissolution of oxide. In a 4 h experiment with increasing concentration of ascorbic acid, oxide dissolution increased till 0.15 M concentration reaching a maximum of 45%. Further increase in acid did not affect dissolution significantly.

L-ascorbic acid, which is a well-known biological reducing agent (Pelizzetti et al., 1978) exhibiting a vicinal diol structure, can be oxidized to dehydroascorbic acid by TiO_2 according to the following reactions thereby getting dissolved in the process

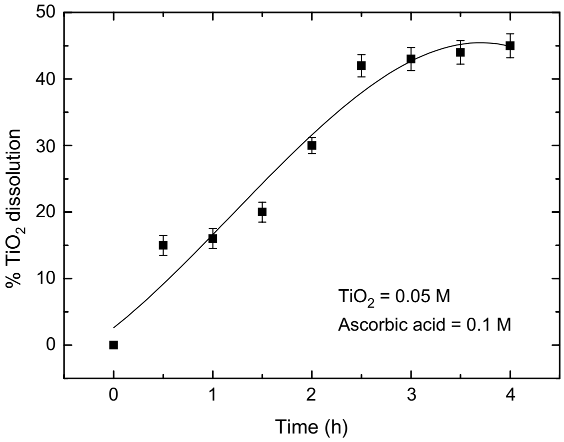

Fig. 1. Kinetics of TiO_2 dissolution by ascorbic acid.