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Journal of Colloid and Interface Science 304 (2006) 283–291

Journal of Colloid and Interface Science

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A new glance at ruthenium sorption mechanism on hydroxy, carbonate, and fluor apatites: Analytical and structural studies

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Received 21 June 2006; accepted 31 July 2006

Abstract

The sorption mechanism of Ru^{3+} ions on hydroxy (HAp), carbonate (CO_3HAp), and fluor apatites (FAp) has been studied in detail. Ru apatites were obtained by reaction of the apatites with $RuCl_3$ in aqueous solution. The structure and composition of the ruthenium-modified apatites were studied by several techniques: elemental analysis, XRD, EXAFS, IR, NMR, SEM-EDS, TEM, and thermal analysis. The amount of Ru in the modified apatite varies from 7.8 to 10.5 wt% and is not related to the initial composition or the specific surface area of the apatite. The different characterization techniques show that in the Ru-modified apatites Ru is surrounded by six oxygen atoms and do not contain any chlorine. For Ru-HAp and Ru-CO_3HAp the new phase is amorphous whereas it is crystalline for FAp. The catalytic oxidation ability is higher for Ru-HAp and Ru-CO_3HAp compared to Ru-FAp apatite in the oxidation of benzylic alcohol.

Keywords: Ruthenium catalyst; Hydroxy apatite; Fluor apatite; Structure; Chemical composition; Catalytic activity

1. Introduction

Modified apatites, most notably hydroxy ($Ca_{10}(PO_4)_6(OH)_2$) and fluor apatites ($Ca_{10}(PO_4)_6F_2$), due to their ability to "include" different transition metal ions in the structure, attract increasing interest as mineral supports for catalysts in the field of "green" chemistry [1,2]. Two types of compounds can be obtained, resulting either from an ion exchange between calcium and a transition metal ion or by the formation of a new phase at the surface of the apatite. In this way, Ru^{3+}-containing hydroxy apatite (HAp) was found to be an effective and selective catalyst for several oxidative reactions: diels-alder, aldol reactions, and the racemization of configurationally stable chiral secondary alcohols. By comparison with other supported Ru catalysts, this modified apatite presents several advantages, e.g., simple usage, no leaching of Ru into the reaction media, and easy recovery of the catalyst after the reaction by simple filtration [2–11].

Different compositions and structures have been proposed for Ru-containing apatites. Yamaguchi et al. have claimed that monomeric Ru^{3+} species located on the surface of HAp are surrounded by one chloride and four oxygen atoms (provided by two PO_4 ions) and are weakly coordinated to an aqua ligand [3]. Wuyts et al. found that mononuclear Cl-free Ru^{3+} centers are mainly located at the outer rim of the apatite crystals as a result

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doi:10.1016/j.jcis.2006.07.079

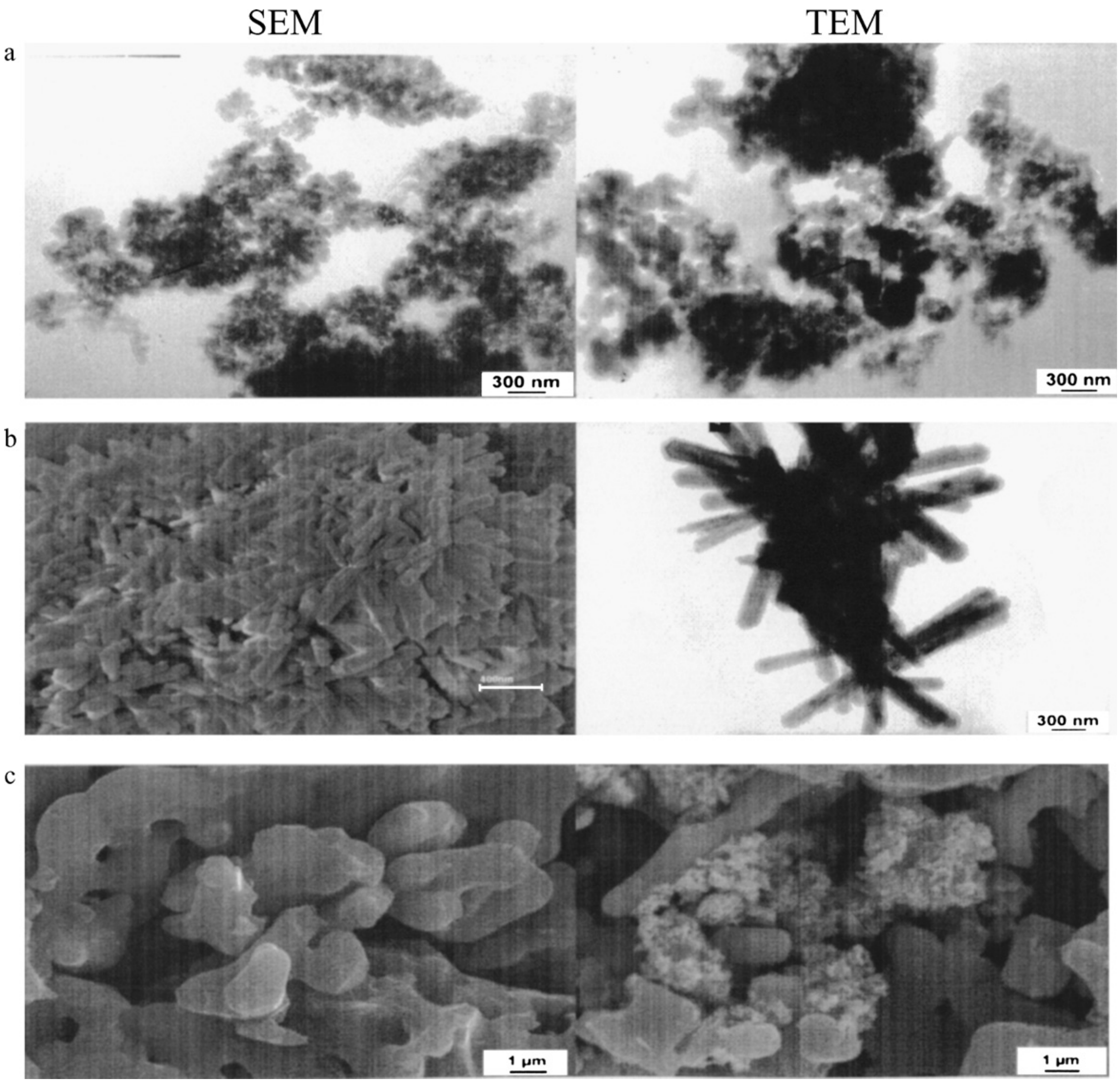

Fig. 1. SEM and TEM images of apatites before and after reaction with $RuCl_3$: (a) HAp_{110}, Ru-HAp_{110}; (b) HAp_{24}, Ru-HAp_{24}; (c) FAp_1, Ru-FAp_1.

of the exchange reaction: $Ca^{2+} \leftrightarrow Ru^{3+}OH^-$ [8]. Baiker and co-workers proposed that the first shell surrounding ruthenium on Ru-Co-hydroxy apatite consists of two hydroxy ligands and four oxygens bound to two phosphorous atoms whereas on RuHAp with low ruthenium concentration "it is assumed that the active sites are $Ru(OH)^+$ species stabilized by the phosphate O atoms and adsorbed (H-bonded) water" [10,11]. Therefore, it appears that the sorption mechanism of ruthenium is not clearly established. Taking into consideration that the sorption mechanism strongly depends on the composition of an apatite and on its specific surface area (SSA m^2/g hereafter denoted as Ap_{SSA}) we have systematically investigated the composition and structure of Ru-containing apatites as well as the Ru^{3+} sorption mechanism starting from different apatites.

2. Experimental and methods

2.1. Materials

In the present work hydroxy (HAp_{110}, HAp_{24}), fluor (FAp_1), and carbonate apatites (CO_3HAp_{26}) with different morphologies (Fig. 1), particle sizes (10–1000 nm), specific surface areas (1–110 $m^2\ g^{-1}$), and Ca/P molar ratios 1.68–1.95 (Table 1) were used.

2.2. Sorption experiment

The amount of 1.0 g of the apatite sample was added to 75 ml of a Ru^{3+} aqueous solution (concentration 1.34×10^{-2} M, initial pH 1.86) made from $RuCl_3 \cdot nH_2O$ (Ru 42.76%, Metals On-line, http://www.precmet.com.au). The resulting suspen-

Table 1
Chemical composition and specific surface area (SSA) of apatite samples

Apatite sample	P_2O_5 (%)	CaO (%)	CO_2 (%)	H_2O (%)	F (%)	Ca:P, mole ratio	SSA (m^2/g)
HAp_{110}	38.84	53.84	1.70	6.30	0	1.76	110.0
HAp_{24}	40.91	54.20	0.40	3.50	0	1.68	24.3
CO_2HAp_{26}	35.21	54.28	5.79	3.60	0	1.95	26.4
FAp_1	40.1	56.00	0	0	3.0	1.77	1.0

Note. Apatites were synthesized according to the literature methods [5,12,13].