

Behavior of Lewis and Brönsted surface acidity featured by Ag, Au, Ce, La, Fe, Mn, Pd, Pt, V and W decorated on protonated titanate nanotubes



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ABSTRACT

Ag, Au, Ce, La, Fe, Mn, Pd, Pt, V and W nanoparticles were decorated on the surface of titanate nanotubes obtained by hydrothermal treatment. Likewise, the titanate nanotubes with the incorporated active transition, precious and rare earth metals were characterized by XRD, HRTEM, and BET. FTIR-pyridine and UV–Vis were used in order to quantify the acid sites present in different metal catalysts, the main goal of this work.

Metal nanoparticles were incorporated *in-situ* on the surface of the titanate nanotubes by the hydrothermal treatment. The average sizes displayed by the metal nanoparticles were between 1 and 5 nm, finding highly uniform dispersion for all the metals. As a result of the metal incorporation, the acidity of each catalytic system was tuned specially, increasing the number of Brönsted and Lewis sites, which modified significantly the total surface acidity of the 1-D titanate nanotubes.

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1. Introduction

TiO₂-based nanostructures are of great interest in the field of catalysis due to special textural and morphological characteristics such as large surface area, mesoporosity, chemical stability, high ion exchange capacity, and band gap semiconductor properties [1,2]. Besides, titanate nanotubes obtained by the hydrothermal method have been used in photocatalysts, hydrogen sensing systems and solar cells [3,4]. On the other hand, titanate nanotubes without doping have been reported in the last decade, and in other cases, TiO₂ nanotubes doped with nitrogen can be obtained through nitration modification within the temperature interval of 500–700 °C [5]; in this sense, rhodamine B degradation has been attributed to the reduced band gap (E_g) displayed by TiO₂ nanotubes owing to interstitial N₂ doping [6]. Doped titanate nanotubes compared with un-doped titanate nanotubes have shown a narrow band gap that enhances the visible light adsorption capability, principally in photocatalysis [7,8]. There are different methods to

dope metals into TiO₂ nanotubes; metals such as Ag, Pt and Au have been added by photo or electro deposition [9–11]; other methods allow decoration via impregnation of metal oxide precursors such as CeO₂, V₂O₅ and WO₃ on the surface of TiO₂ nanotubes [12–14]. The metal active phases used to dope TiO₂ nanotubes as catalytic supports have been employed for specific purposes: Pt for cyclohexene hydrogenation–dehydrogenation, Au for water–gas shift reaction and Pd for CO oxidation [8,15,16].

Different methods have been employed to identify Brönsted and Lewis acid sites, for example, among the techniques that stand to determine the acidity by FTIR, basic probe molecules such as pyridine and Lutidine (2,6 dimethyl pyridine) allow the evaluation of Brönsted and Lewis sites, ammonia TPD helps to establish the amount and strength of acid sites. FTIR studies of surface OH groups and the adsorption of CO and CO₂ are useful to identify the nature of Lewis acid and basic sites in the TiO₂ structure. However, for the identification of Brönsted and Lewis acid sites, the FTIR spectroscopic analysis of adsorbed basic probes displays two great advantages: the *in-situ*-measuring conditions are very close to those of catalytic application and Brönsted and Lewis acid sites can be easily distinguished. Lewis and Brönsted acidities have been identified in

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this kind of structure due to the scrolling that suffers TiO_2 in the hydrothermal method. Kitano et al. [17] investigated protonated titanate nanotubes as solid acid catalysts in the Friedel–Crafts alkylation of toluene with benzyl chloride. In another study [18], the number of Lewis and Brønsted acid sites on the surface of TiO_2 nanotubes was increased by adding V_2O_5 and $\text{Ti}(\text{SO}_4)_2$.

In this work, the titanate nanotubes morphology with $\text{H}_2\text{Ti}_3\text{O}_7$ phase is reported, analyzing its band gap and surface acidity mainly by pyridine. Likewise, the addition of Ag, Au, Ce, La, Fe, Mn, Pd, Pt, V and W with identical loads on titanate nanotube supports was studied to contribute to the understanding of the effect of metallic decorated on the formation of surface Brønsted and Lewis acid sites and their total acidity.

2. Experimental

2.1. Preparation of titanate nanotubes

Titanate nanotubes were prepared by the hydrothermal method. 3.0 g of TiO_2 nanopowders obtained by the sol-gel method were dissolved in 60 mL of a 7 N NaOH aqueous solution; afterwards, the solution was mixed in a closed cylindrical Teflon-lined autoclave Parr reactor at 140 °C for 24 h, rotating the whole autoclave at 200 rpm. Thereafter, the solution was filtered with HCl until reaching a pH of two, and then, it was washed with abundant deionized water in order to reach a pH of 7. Finally, the material was dried under vacuum at 80 °C for 12 h. The catalysts were prepared *in situ* by the hydrothermal method in proper quantities of dihydrogen hexachloroplatinate (H_2PtCl_6), palladium chloride (PdCl_2), hydrogen tetrachloroaurate (III) hydrate ($\text{HAuCl}_4 \cdot \text{H}_2\text{O}$), ammonium metavanadate (NH_4VO_3), tungstic acid (H_2WO_4), silver nitrate (AgNO_3), lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), manganese (II) nitrate hydrate ($\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). After decorated with the aqueous metal salt solutions, the powder was dried again at 120 °C for 1 h and annealed in air (30 cm^3/min) at 300 °C for 4 h. The catalysts were labeled as NT followed by the X transition, precious and rare earth metals.

2.2. Characterization

X-ray diffraction (XRD) patterns of the samples packed in a glass holder were recorded at room temperature with a Cu $K\alpha$ 1.2 source (1.5418 Å) in a Siemens D-500 diffractometer having a theta–theta configuration and a graphite secondary-beam monochromator. The data were collected for scattering angles (2θ) ranging from 4° to 80° with a 0.02° step for 1 s per point. High resolution transmission electron microscopy (HRTEM) analyses of the samples were performed in a JEOL 2200FS microscope operating at 200 kV and equipped with a Schottky-type field emission gun and an ultrahigh resolution pole piece ($C_s = 0.5$ mm, point-to-point resolution, 0.190 nm). The samples were ground, suspended in isopropanol at room temperature and dispersed by ultrasonic stirring. Then, an aliquot of the solution was dropped on a 3 mm diameter lacey carbon copper grid.

Textural properties were determined in an ASAP-2000 analyzer from Micrometrics. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation by N_2 physisorption at 77 K. The pore size distribution was obtained by the Barrett–Joyner–Halenda (BJH) method from the desorption branch. A thermo-scientific evolution 600 UV–Vis spectrometer was used to record directly the diffuse reflectance spectra between 200 and 800 nm, using the reflectance spectra as a reference at room temperature. Pyridine spectra were recorded in a Nicolet 8700 spectrophotometer with a resolution of 4 cm^{-1} , accumulating 50 scans.

In the cell, all the samples were treated in vacuum at 400 °C for 1 h; pyridine was then admitted and adsorbed. Then, evacuations were performed from room temperature to 400 °C. The acidity per surface area unit for Lewis and Brønsted sites was calculated following the corresponding procedure [19].

3. Results and discussion

3.1. Characterization by XRD

The NT samples doped with Ag, Au, Ce, La, Fe, Mn, Pd, Pt, V and W were synthesized from the reaction between TiO_2 nanoparticles obtained by the sol-gel method and highly concentrated NaOH and analyzed by the XRD technique. Fig. 1(A) and (B) present the results obtained by XRD. It can be seen that the XRD patterns of the titanate nanotubes doped with Au, Pt, Pd, and Ag show the main diffraction peaks that are typical of the layered titanate nanotubes. Strong broad bands were found at around $2\theta = 9.7^\circ$, 24° , 28° , 32.2° , and 48.4° , which are attributed to the interlayer distance according to $\text{H}_2\text{Ti}_3\text{O}_7$ (from JCPDS = 036-0654). Likewise, in the NT-Au sample, diffraction peaks of Au (111), Au (200), Au (220) and (311) (from JCPDS = 004-0784) were detected in Fig. 1(A), demonstrating the formation of metallic Au. With regard to NT-Pt, NT-Pd and NT-Ag, diffraction

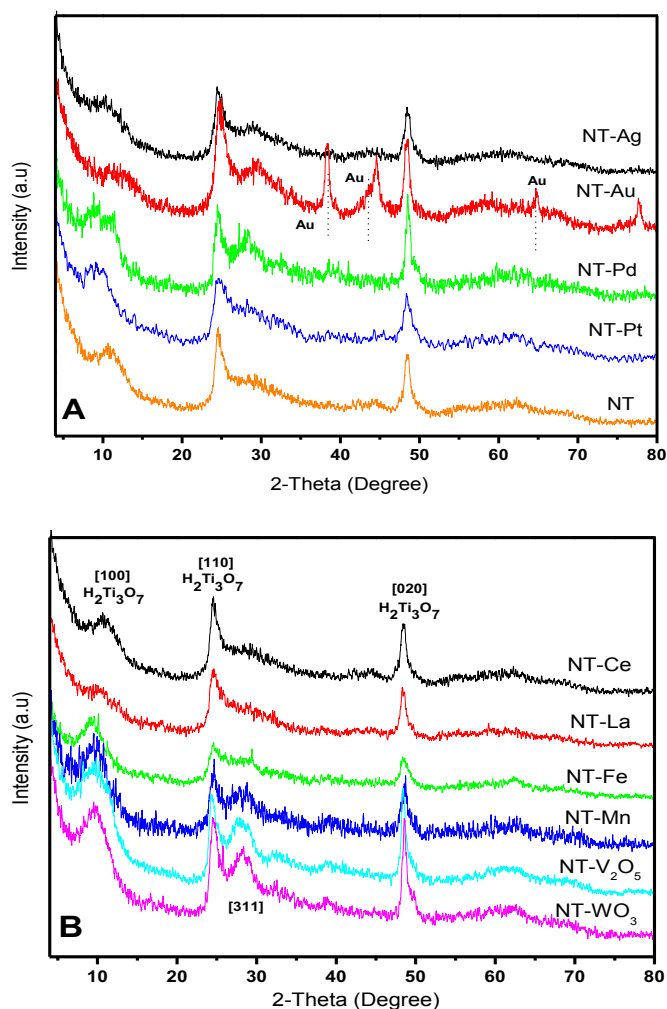


Fig. 1. (A) XRD diffraction patterns of nanotubes with silver, gold, palladium and platinum annealed at 300 °C. $\text{H}_2\text{Ti}_3\text{O}_7$ is the titanate acid phase and Au is gold. (B) XRD diffraction patterns of nanotubes with cerium, lanthanum, iron, manganese, vanadium and tungsten. $\text{H}_2\text{Ti}_3\text{O}_7$ is the titanate acid phase.

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