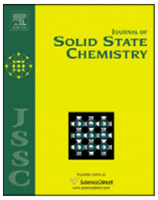
Journal of Solid State Chemistry 201 (2013) 222–228

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc



Structural and spectroscopic properties of high temperature prepared ZrO_2–TiO_2 mixed oxides

Chiara Gionco [a], Alfio Battiato [b], Ettore Vittone [b], Maria Cristina Paganini [a],*, Elio Giamello [a]

[a] Dipartimento di Chimica and NIS (Nanostructured Surfaces and Interfaces), Università degli Studi di Torino, Via Giuria 7, 10125 Torino, Italy
[b] Dipartimento di Fisica, Università degli Studi di Torino, Via Giuria 1, 10125 Torino, Italy

ARTICLE INFO

Article history:
Received 9 January 2013
Received in revised form
22 February 2013
Accepted 27 February 2013
Available online 13 March 2013

Keywords:
Mixed oxides
Oxygen depletion and reducibility
EPR
TiO_2
ZrO_2

ABSTRACT

ZrO_2–TiO_2 mixed oxides of various composition, with the molar fraction of TiO_2 ranging from 0.1% to 15%, have been prepared via sol-gel synthesis and then calcined at 1273 K to check both their thermal stability and physicochemical properties. These solids are usually employed in photocatalytic processes and as active phase supports in heterogeneous catalysis. As indicated by X-ray diffraction and Raman spectroscopy, solid solutions based on Ti ions diluted in the ZrO_2 matrix are formed in the whole range of Ti molar fraction examined. Materials with low Ti loading (0.1%–1%) are basically constituted by the monoclinic phase of ZrO_2 while the tetragonal phase becomes prevalent at 15% of TiO_2 molar fraction. The presence of Ti ions modify the electronic structure of the solid as revealed by investigation of the optical properties. The typical band gap transition of ZrO_2 undergoes, in fact, a red shift roughly proportional to the Ti loading which reach the remarkable value of 1.6 eV for the sample with 10% of molar Ti concentration. Comparing chemical analysis of the solids with XPS data it has been put into evidence that the titanium ions distribution into the solid is not uniform and the concentration of Ti^{4+} tend to be higher in subsurface layers than in the crystal bulk. The introduction of titanium ions in the structure increases the reducibility of the solid. Annealing under vacuum at various temperatures causes oxygen depletion with consequent reduction of the solid which shows up mainly in terms of formation of Ti^{3+} reduced centres which are characterized by a typical EPR signal. Ti^{3+} defects forms, as also forecast by theoretical modelling of the solid, as their energy is lower than that of other possible reduced defective centers. The reduced solids are able to transfer electrons to adsorbed oxygen molecules in mild condition resulting in the formation of surface superoxide anions ($O_2^{\bullet-}$) which are stabilized on surface Zr^{4+} or, alternatively, on Ti^{4+} ions according to the sample composition.

1. Introduction

Zirconium dioxide is a strategic material which attracted a great deal of interest in the past few decades because of the large range of applications in the fields of ceramic compounds, optical devices, gas sensors and catalysis [1]. There are three main polymorphs of pure ZrO_2 whose structures are respectively monoclinic (stable up to 1443 K), tetragonal (stable from 1443 K to 2643 K) and cubic (stable at high temperature from 2643 K up to the melting temperature at 2979 K) [2]. An additional metastable tetragonal phase (up to 650 °C) is also reported whose formation, in preparations involving moderate calcinations temperature of precursors aiming to obtain high surface area systems, has been attributed either to impurity effects or to crystallite size effects [1]. For several applications the use of tetragonal or cubic phases is required to avoid phase transformations caused by temperature. Stable tetragonal and cubic zirconia are obtained via doping with Y_2O_3 (t-ZrO_2) or CaO (c-ZrO_2) both causing the formation of anion vacancies in the system. High surface area ZrO_2 has low thermal stability and, when calcined at high temperatures, undergoes a phase transition from tetragonal to monoclinic accompanied by a drastic decrease in surface area. Therefore, several attempts have been made to improve the ZrO_2 thermal stability also by incorporation of isovalent ions like Ce and/or Ti [3–5] which, in principle, do not generate anion vacancies. ZrO_2–TiO_2 mixed oxides have been studied in recent years because they show both better thermal stability and modified surface acidity properties with respect to the bare ZrO_2 [4,6] and they are therefore used, like the parent material, as catalysts and catalyst supports for various catalytic reactions such as dehydrogenation [7,8] and isomerisation [9,10]. Several examples of photocatalytic applications of this mixed oxide are also available [11–16]. A relatively large number of studies have been thus devoted to the preparation of ZrO_2–TiO_2 mixed materials [17,18] under the form of powders or of thin films.

---

* Corresponding author. Fax: +39 011 6707855.
E-mail address: mariacristina.paganini@unito.it (M.C. Paganini).

0022-4596/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jssc.2013.02.040