Applied Catalysis A: General 445–446 (2012) 14–25

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Citral hydrogenation on high surface area mesoporous TiO_2–SiO_2 supported Pt nanocomposites: Effect of titanium loading and reduction temperature on the catalytic performances

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ARTICLE INFO

Article history:
Received 10 April 2012
Received in revised form 12 July 2012
Accepted 18 July 2012
Available online 27 July 2012

Keywords:
Titania
Silica
Platinum
Mesoporous materials
Citral hydrogenation
Nanocomposites

ABSTRACT

Platinum-based catalysts supported on TiO_2-modified mesostructured silica were prepared using the direct co-condensation of silica and titania precursors to synthesize the mixed-oxide support. The physico-chemical properties of the Pt/*x*Ti-SBA15 samples with various *x*Ti contents (in mol%) were further evaluated using several techniques, including elemental analysis, X-ray diffraction, N_2-physisorption, H_2-chemisorption, transmission electronic microscopy and the probe reaction of cyclohexane dehydrogenation to evaluate the metal–support interaction (SMSI effect). All the Pt/*x*Ti-SBA15 samples display high specific surface areas (650–820 $m^2\ g^{-1}$) and high mesopore volumes (0.44–0.68 $cm^3\ g^{-1}$), with the formation of TiO_2 anatase nanoparticles since the low titanium content, *i.e.* 2 mol%. The hexagonal organized pore structure of SBA silica is also strongly altered by the titanium adding, but mixed oxides so obtained present very particular morphology with maintaining of high surface areas.

The catalytic performances of the Pt/*x*Ti-SBA15 catalysts were estimated for the citral hydrogenation performed at 70 °C under hydrogen pressure (7 MPa), and discussed in terms of activity and unsaturated alcohols (UA: nerol and geraniol) selectivity. A synergetic effect on the UA selectivity was obtained on the Pt/*x*Ti-SBA15 catalysts, compared to both Pt/SBA15 and Pt/TiO_2 P25 reference samples (reduction temperature = 300 °C), and was explained by the specific role of the reducible TiO_2 species, which under the nano-anatase form generate a strong metal–support interaction (SMSI effect) with platinum after reduction at 300 °C. The formation of partially reduced support species was finally modulated by varying the reduction temperature of the catalysts. It is then possible to achieve high selectivity after reduction at 350 °C, while maintaining high conversions.

1. Introduction

The modification of the catalytic properties (*i.e.* activity and selectivity) of porous materials, notably by the incorporation of the transition metals, attracts much interest of scientifics. In this context, MCM-41 material was largely studied because of its controllable pore size with a narrow pore size distribution, its high thermal and hydrothermal stability. Many routes to achieve the synthesis of catalysts containing transition metals in the MCM-41 inorganic walls were proposed [1–3]. MCM-41 has also allowed making the link between crystalline zeolites and amorphous silica in terms of pore size and pore distribution [4,5]. SBA15 materials, *i.e.* silica with hexagonal mesoporous structure similar to MCM-41, were extensively studied since their first synthesis from a copolymer triblock as structuring agent under conditions of strong acidity ($pH \leq 1$) [6]. Their high specific surface, high pore volume and adjustable pore size (from 2 nm to more than 20 nm) allow considering this support as ideal for the preparation of well dispersed heterogeneous catalysts, the control of the pore structure being also a great advantage to evaluate the effect of the textural parameters on the catalytic properties [7–11]. In addition, a largely higher thermal and hydrothermal stability is reported for the SBA-15 structure than for the MCM-41 due to the formation of wider walls [6]. Many efforts were then done to introduce heteroatoms in this structure in order to modify surface acidity (such as in the case of Al [12]), or to generate redox surface sites (examples of Ti [13–16] and V [17]). The titanium introduction into these mesoporous materials was performed either by direct incorporation of Ti during the synthesis or by post-synthesis [18,19]. Even if the complete Ti-atom incorporation by direct synthesis becomes difficult since the low degree of substitution [20], with a loss in pore structure periodicity, the

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http://dx.doi.org/10.1016/j.apcata.2012.07.023