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Application of ETS-10 microporous titanosilicate as support of Ru nanoparticles for hydrogen production

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ABSTRACT

Supported ruthenium catalysts have been shown to be effective for the dry reforming of methane. Besides, ETS-10 titanosilicate has properties able to disperse Ru species. In this work, microporous ETS-10 titanosilicate was synthesized by hydrothermal synthesis employing anatase as Ti source. Ru was incorporated using three different methods: by incipient wetness impregnation (RuH), by ion exchange (RuI) and by adding Ru to the gel synthesis (RuG). The species present in the solids were characterized by XRD, N_2 adsorption, ICP, SEM, TEM, EDX, TGA, TPR, UV–vis and XPS.

RuH and RuI catalysts were found to be active and stable for the dry reforming of methane. These results show the potential application of ETS-10 as support of Ru catalysts for the production of hydrogen.

1. Introduction

The simultaneous incorporation of octahedral Ti $[TiO_6]^{2-}$ and tetrahedral Si $[SiO_4]$ microporous materials has led to the appearance of a new family of microporous crystalline titanosilicates, materials mainly inspired in similar compounds found in nature, which has generated great interest from the viewpoint of catalytic processes and ion exchange. ETS-10 (Engelhard titanosilicate Structure 10), one of the main members in the family of titanosilicates, presents a structure similar to that of inorganic microporous zeolites [1]. In fact, the topological similarities between ETS-10 and β zeolite (aluminosilicate three-dimensional channels with micropores of 0.71 nm × 0.73 nm) are remarkable. Titanosilicate Ti atoms are octahedrally connected to four Si and two Ti atoms through oxygen bonds, giving rise to a three-dimensional structure with a significant degree of disorder [2]. The disordered material can be described by two ordered polymorphs, arranged in layers. The porous structure consisting of rings of 12, 7, 5 and 3 members has a three-dimensional pore system whose minimum diameter is defined by the 12-member rings, with a micropore size of 0.49 nm × 0.76 nm. A network of tetrahedral SiO_4 and octahedral TiO_6 is associated with a charge of −2 compensated by cations mainly located in areas adjacent to the Ti chains and 12- and 7-member rings. The stoichiometry of ETS-10 is given by $M_2TiSi_5O_{13}{\cdot}4H_2O$ where M: Na^+ and K^+ are compensation cations. Cation density is high, roughly equivalent to that of a zeolite with a Si/Al = 2.5, for example Y zeolite.

This titanosilicate has some advantages over other similar materials, such as the possibility of synthesis based on different sources of Ti and the presence of a pure phase which can be obtained in the absence of a structuring agent. Additionally, by functionalizing its structure, it is possible to modify its catalytic properties and adsorption isomorphic substitution, or its high ion exchange capacity, hydrophilicity and basicity.

Few studies have employed ETS-10 as catalyst support. However, some encouraging results are related to the activity and selectivity of the titanosilicate. Anderson and coworkers [3] have synthesized Pt/ETS-10 for n-hexane reforming reporting that these solids exhibit very high selectivity. In addition, Santamaría and coworkers [4] have used Pt/ETS-10 catalysts for the selective oxidation of CO in the presence of H_2, CO_2 and H_2O.

Bueno and co-workers [5] used similar materials (NaY and mordenite) as supports for ruthenium catalysts for the dry reforming reaction. These authors reported a H_2/CO ratio close to 1, indicating that the RWGS reaction was minimized. The dry reforming of methane is important from the environmental viewpoint since these two gases contribute to the green-house effect. In addition, the use of synthesis gas as feedstock for fuel cells and for the Fischer–Tropsch reaction has brought about an increasing interest in methane reforming reactions. One of the main problems for the preparation of effective reforming catalysts is the deactivation

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