



Characterization of redox and acid properties of mesoporous Cr–TiO₂ and its efficient performance for oxidative dehydrogenation of propane

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ABSTRACT

Mesoporous Cr–TiO₂ materials with chromium content from 0.02 to 0.30 (Cr/Ti molar ratio) were synthesized using a nonionic Pluronic F127 surfactant, and the mesostructure was confirmed by BET, SAXS and TEM. The stability of the mesoporous structure under the atmospheres of propane oxidative dehydrogenation (PODH) and air was investigated. The variety in valence states and the distribution of Cr species on the surface were also evaluated by WXR, XPS, UV–vis and H₂-TPR methods. The acid properties including kinds, number and strength were measured by NH₃-TPD and IR-Py experiment. Propane oxidative dehydrogenation to propylene employed as a probe reaction suggested that the catalytic performance relates closely with the content of Cr, the easily reducible soluble Cr species, and the modification of the acid properties on the surface, while TiCr_{0.15} catalyst performs good conversion and selectivity, with a yield of propylene near 19%.

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1. Introduction

After the discovery of M41S silicate materials, the extension of the surfactant templating procedure to form non-silica mesoporous oxides has never been stopped, due to their various applications such as catalysis, sorption, chemical and biological separation, photonic and electronic devices and drug delivery [1,2]. Among these materials, TiO₂ is one of the most important metal oxides in heterogeneous catalysis because of its broad functionality, long-term stability and nontoxicity. High-quality mesoporous TiO₂ can now be easily and reproducibly prepared [3,4], but there are still some disadvantages such as the limited active sites on its surface and the aggregation of its mesostructure under high temperatures [5,6]. Thus, the incorporation of various heteroatoms into the mesoporous or nano-sized structure to embed a catalytic function is of tremendous interest [7–10].

Catalytic dehydrogenation represents a route to obtain olefins from low-cost alkanes, especially propane and ethane, and possesses both theoretical and industrial significance [11]. For propane dehydrogenation, vanadium and molybdenum catalysts have been extensively studied, while supported chromium catalysts also show competitive performance. The oxidation state of chromium, structure (amorphous or crystalline, chromate or dichromate) and the interaction of chromium with the support are the main factors that determine its catalytic performance. More interestingly, these factors could be controlled by varying the metallic content, the

precursor, the support characteristics and calcination conditions [12].

Catalysts using TiO₂ as the support have been extended to the PODH reaction as well [13–17]. Moreover, for chromium catalysts, TiO₂ even appears to be the most suitable support compared by the dispersion amount of chromium oxide on different supports and the catalytic performance in PODH [18].

However, despite having great potential, reports about the application of mesoporous Ti–Cr materials are still seldom. Mesoporous structure allows the reactants access additional active sites in the pores and has advantages in mass diffusion and transportation, as well as other unpredicted beneficial properties, which may improve catalytic activity.

In view of the above, it is quite interesting for us to synthesize mesoporous materials and test their catalytic performance in PODH reaction. In this work, we prepared a series of Ti–Cr oxide catalysts and studied the influence of Cr content on mesopores (surface area, pore volume and stability), surface properties (chromium valence distribution, reducibility, and acid property of the chromium species) and catalytic performance (propane conversion, yield to propylene) of these catalysts. Attempts have been made to correlate the PODH results with the composition of the catalysts and the nature of the active sites.

2. Experimental

2.1. Catalysts preparation

All catalysts are prepared by solvent evaporation induced self-assembly (EISA) method, similar to the procedure previously

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