



Liquid phase hydrogenation of crotonaldehyde over copper incorporated in MCM-48

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ABSTRACT

A series of Cu/MCM-48 catalysts is studied for the liquid phase hydrogenation of crotonaldehyde. Copper is incorporated in MCM-48 following a classical hydrothermal synthesis or by wet impregnation of the MCM-48 precursor (before eliminating the directing agent) with Cu(AcAc)₂. The copper loading is in the 2–20 wt% range. Characterization results from TPR and XRD indicate that copper crystals supported on MCM-48 surface coexist with copper incorporated in the MCM-48 walls. The presence of Cu⁺ in MCM-48 is concluded from characterization with FTIR of adsorbed CO. This species would be the responsible for the relatively high selectivity of Cu/MCM-48. These catalysts show approximately 50% of selectivity against 7% of Cu/SiO₂ (both values measured at 10% of conversion).

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1. Introduction

Copper on MCM-41 has been widely employed as catalysts for different reactions [1–11]. On the contrary copper supported on MCM-48 has been much less studied, though this system should be preferred to the one supported on MCM-41 in the basis of the three dimensional structure of MCM-48. Probably this is due the fact that it is rather difficult to incorporate a high copper loading to the mesoporous structure of MCM-48 [12].

In a previous work [13] we have studied a series of copper catalysts employing MCM-48 as the support for the selective hydrogenation of cinnamaldehyde in liquid phase. Some of these samples were found to be more selective than copper supported on silica or alumina. It is well known that is very difficult to hydrogenate carbonyl bond in α , β -unsaturated compounds, due to kinetic and thermodynamic difficulties. In this context, our previous results encouraged us to further investigate on the catalytic properties of Cu/MCM-48 for selective hydrogenation reactions.

In the present work we study a series of Cu/MCM-48, for the liquid phase hydrogenation of crotonaldehyde. This α , β -unsaturated compound has been selected since it presents a low steric protection of the olefinic bond, then, hydrogenation of crotonaldehyde is still a big challenge for researchers.

The samples are studied by FTIR of adsorbed CO, XRD, TPR and BET. Finally, the samples are tested in the liquid phase hydrogenation of crotonaldehyde, in a Batch reactor. The catalytic patterns are discussed in the light of the characterization results.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of MCM-48

The silicon source was tetraethyl ortho-silicate (TEOS, Aldrich). The structure-directing agent was cetyltrimethylammonium bromide (CTAB, Aldrich). MCM-48 was prepared by hydrothermal synthesis, following the technique reported by Xu et al. [14]. 10 mL of TEOS were added to a solution of CTAB in water (8.8 g/79.2 mL). 10 mL of NaOH 2 M were added at 308 K. The mixture was stirred for half an hour. The gel was heated to 373 K for 72 h under static hydrothermal conditions in a steel/Teflon autoclave. The product was filtered, washed with water, and dried at room temperature. Finally the solid was heated up 673 K at 0.5 K min⁻¹ under N₂ flow, afterwards the flow was switched to chromatographic air, and the temperature was kept constant for 6 h.

2.1.2. Synthesis of Cu/MCM-48

Two series were prepared, one of them following a hydrothermal synthesis and another one by wet impregnation of MCM-48 with Cu(AcAc)₂.

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