Structural Transformation of Cu–Mg–Al Mixed Oxide Catalysts Derived from Hydrotalcites During Shift Reaction

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Abstract Cu–Mg–Al mixed oxide catalysts were prepared from calcination of hydrotalcite-like compounds. XRD patterns showed formation of CuO and MgO phases, where aluminum oxides are well dispersed. The Cu–Mg– Al catalysts exhibited high stability during 40 h with time on stream for the shift reaction at 250 °C, which can be related to the major presence of metallic copper, confirmed by in situ XRD reaction measurements, and no change of the mean crystallite size, suggesting high resistance to sintering. DRIFTS results confirmed the major presence of metallic Cu particles at the catalyst surface but also an insignificant amount of cationic copper species.

Keywords Cu–Mg–Al mixed oxide · Hydrotalcite · Shift reaction · In situ XRD · DRIFTS

1 Introduction

Hydrotalcite-like compounds (HTLCs) show interesting properties for application in catalysis because, after calcination, they form a homogeneous mixture of oxides with very small crystal size, stable against thermal treatments, which by reduction result in high dispersion of the metallic crystallites [1, 2]. We have recently reported the use of CuO/ZnO/Al₂O₃ catalysts prepared from hydrotalcites on

N. F. P. Ribeiro · M. Schmal (⊠) NUCAT/PEQ/COPPE/UFRJ, Centro de Tecnologia, Bloco G, sala 128, Rio de Janeiro, RJ CEP 21945-970, Brazil e-mail: schmal@peq.coppe.ufrj.br shift reaction [3]. On the other hand, Cu–Mg–Al mixed oxides derived from hydrotalcite precursors have been used as catalysts for various other reactions [4–8].

Shishido et al. [9] showed that addition of small amount of MgO to Cu/ZnO catalysts enhanced the activity for the shift reaction due to stabilization of copper cationic species by MgO. Yahiro et al. [10] reported that CuO/MgO/ Al_2O_3 catalysts prepared by conventional impregnation method have a very low activity for the shift reaction. To our knowledge, CuO/MgO/Al₂O₃ catalysts derived from hydrotalcites have not been reported in the literature for this reaction yet.

An important paper was presented by Chmielarz et al [11] analyzing the reduction of Cu–Mg–Al oxides (Mg/Al = 2.50, Cu/Mg = 0.23 and Cu/Al = 0.58) after different temperatures of calcination (600, 700, 800 and 900 °C). The sample calcined at 600 °C showed the reduction Cu^{2+} cations in CuO. For higher temperatures the profiles indicated the reduction of CuAl₂O₄ to CuAlO₂. The discussion based on TPR and ex situ XRD may not reproduce the reaction conditions of the shift reaction.

In the present work, we studied the structural transformation of CuO/MgO/Al₂O₃ catalysts prepared by calcination of hydrotalcite precursors during the shift reaction by in situ XRD and DRIFTS analyses, in order to elucidate the nature and dispersion of copper species present during the reaction.

2 Experimental

2.1 Catalyst Preparation

Hydrotalcite-like compounds (30CuMgHT and 42CuMgHT) were prepared by coprecipitation from aqueous

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