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Abstract: This work investigates the concept of preferential dissolution from CuMnOx by HNO3 treatment to acquire novel γ-MnO2-like polymorphs through Cu extraction. Two host CuMnOx oxides were tested: a crystallized CuMn2O4 spinel phase with a SSA of 47 m²/g and an amorphous CuMnOx with a Mn/Cu atomic ratio of 4.8 (SSA: 166 m²/g). How the properties of the host oxides can affect the final γ-MnO2-like properties were particularly studied. Finally these new γ-MnO2-like oxides were evaluated for toluene oxidation.

Keywords: Acid treatment, Toluene, Total oxidation catalysis, Cu-Mn mixed oxides.

1. Introduction

MnO2 is one of the best promising candidates among transition metal oxides for catalytic oxidation due to its low cost, environmentally compatibility, multivalent and non-stoichiometric composition. The polymorphs λ-, β-, and γ-MnO2 phases, for their part, have structures consisting of different three-dimensional packing of MnO6 octahedra units. Among the different strategies of MnO2 preparation very little work has been reported on the cation selective dissolution in acid media starting from Mn based binary oxides apart those from normal spinel AMn2O4 compounds (A = Li)1 and very recently from LaMnO32,3. Thus the treatment in diluted HNO3 of a three-dimensionally ordered macroporous LaMnO3 perovskite selectively removed La cations to get a novel γ-MnO2-like material exhibiting improved catalytic properties in CO oxidation2 and in total oxidation of toluene3. Herein, we investigate the possibility to extent the concept of selective dissolution to CuMnOx using HNO3 treatment to acquire novel MnO2 like polymorphs. This solid transformation is concomitantly based on the disproportionation ability of Mn3+ to give MnO2 and Mn2+ as well as on the affinity of Cu2+ to complex with NO3- ligand. The first host structure is a crystallized CuMn2O4 spinel phase synthesized by-coprecipitation4 exhibiting Cu+/Cu2+ and Mn4+/Mn3+ valences on its surface. The second precursor is a rather amorphous CuMnOx, prepared by the redox-precipitation method5 exhibiting high SSA. The catalytic performances of the calcined acid treated catalysts were evaluated in total toluene oxidation and discussed in the light of the nature of host oxides.

2. Experimental

The spinel-type CuMn2O4 (CuMn2O4-P4) was prepared using a co-precipitation method5. The amorphous CuMnOx (CuMnOx-R3) was prepared using the redox-precipitation method6. Typically 0.5 g of host oxide was immerged in 50 mL of an aqueous solution of HNO3 (10M) and the suspension was stirred for 65h (CuMn2O4-P4) and 5h (CuMnOx-R3). After filtration and intense washing with deionized water and drying overnight at 100 °C the resulting powders were calcined at 300°C for 2h. The final samples were labelled AT-CuMn2O4-P4 and AT-CuMnOx-R3 (AT: acid treated). The fresh acid treated materials were characterized by SEM/EDX, N2 physisorption, XRD, H2-TPR, XPS and ToF-SIMS analyses. The catalysts were tested for toluene oxidation in similar conditions as described elsewhere6.

3. Results and discussion

The kinetic of Cu extraction is faster on the amorphous-like oxide host. Indeed after 5h of acid treatment, the Cu/Mn atomic ratio decreases by a factor of about 10 and 2 for CuMnOx-R3 and CuMn2O4-P4,
respectively (Table 1). Thus a treatment of 65h for CuMn$_2$O$_4$-P4 was carried out resulting into an increase of the efficiency of Cu removal as the Cu/Mn ratio decreases to 0.078. The efficiency of Cu extraction is also well monitored using XPS and ToF-SIMS measurements.

![Figure 1. XRD of a) CuMnOx-R3, after b) acid-treatment, c) washing, d) calcination](image1)

![Figure 2. Light-off curves of catalysts.](image2)

The XRD patterns after acid treatment, washing and calcination presented in Fig.1 for CuMnOx-R3 evidence the formation of a $\gamma$-MnO$_2$-like oxide. Comparatively, when considering CuMn$_2$O$_4$-P4, a mixture of $\lambda$/$/\gamma$-MnO$_2$ is highlighted after acid-treatment, the relative content of $\gamma$-MnO$_2$ increasing after washing to be the only detected crystallized phase after calcination. Upon Cu extraction, whatever the host oxide differences, the physico-chemical properties of the final $\gamma$-MnO$_2$-like oxides are not so different in terms low-temperature reducibility, SSA and oxygen mobility. Upon the removal of Cu cations, the obtained AT-CuMnOx-R3 sample showed a higher toluene oxidation catalytic activity ($T_{50}^{\text{CO}_2} = 202^\circ\text{C}$) than the AT-CuMn$_2$O$_4$ sample ($T_{50}^{\text{CO}_2} = 202^\circ\text{C}$) and a reference $\alpha$-MnO$_2$ ($T_{50}^{\text{CO}_2} = 223^\circ\text{C}$).

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<th>Table 1: Physico-chemical and catalytic data for the catalysts</th>
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<td>CuMn$_2$O$_4$-P4</td>
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a: molar ratio (EDX) ; b: From $\text{H}_2$-TPR

4. Conclusions

In summary, we report for the first time an easy method to synthesize new $\gamma$-MnO$_2$-like catalysts utilizing CuMnOx as starting hosts. This novel template free route to $\gamma$-MnO$_2$-like oxides, through the extension of the selective dissolution concept applied to these mixed oxides, opens new perspectives in the design of novel doped $\gamma$-MnO$_2$-like oxides as possible efficient catalysts in different fields.

References