Preferential dissolution of copper in CuMnOx: effect of the starting binary oxide to get new efficient γ-MnO_2-like catalysts

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Abstract: This work investigates the concept of preferential dissolution from CuMnOx by HNO_3 treatment to acquire novel γ-MnO_2 like polymorphs through Cu extraction. Two host CuMnOx oxides were tested: a crystallized $CuMn_2O_4$ spinel phase with a SSA of 47 m^2/g and an amorphous CuMnOx with a Mn/Cu atomic ratio of 4.8 (SSA: 166m^2/g). How the properties of the host oxides can affect the final γ-MnO_2-like properties were particularly studied. Finally these new γ-MnO_2-like oxides were evaluated for toluene oxidation.

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

1. Introduction

MnO_2 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-MnO_2 phases, for their part, have structures consisting of different three-dimensional packing of MnO_6 octahedra units. Among the different strategies of MnO_2 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 AMn_2O_4 compounds (A = Li)[1] and very recently from $LaMnO_3$[2,3]. Thus the treatment in diluted HNO_3 of a three-dimensionally ordered macroporous $LaMnO_3$ perovskite selectively removed La cations to get a novel γ-MnO_2-like material exhibiting improved catalytic properties in CO oxidation[2] and in total oxidation of toluene[3]. Herein, we investigate the possibility to extent the concept of selective dissolution to CuMnOx using HNO_3 treatment to acquire novel MnO_2 like polymorphs. This solid transformation is concomitantly based on the disproportionation ability of Mn^{3+} to give MnO_2 and Mn^{2+} as well as on the affinity of Cu^{2+} to complex with NO_3^- ligand. The first host structure is a crystallized $CuMn_2O_4$ spinel phase synthesized by-coprecipitation[4] exhibiting Cu^+/Cu^+ and Mn^{4+}/Mn^{3+} valences on its surface. The second precursor is a rather amorphous $CuMnO_x$ prepared by the redox-precipitation method[5] 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 $CuMn_2O_4$ ($CuMn_2O_4$-P4) was prepared using a co-precipitation method[5]. The amorphous CuMnOx (CuMnOx-R3) was prepared using the redox-precipitation method[6]. Typically 0.5 g of host oxide was immerged in 50 mL of an aqueous solution of HNO_3 (10M) and the suspension was stirred for 65h ($CuMn_2O_4$-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-$CuMn_2O_4$-P4 and AT-MnOx-R3 (AT: acid treated). The fresh acid treated materials were characterized by SEM/EDX, N_2 physisorption, XRD, H_2-TPR, XPS and ToF-SIMS analyses. The catalysts were tested for toluene oxidation in similar conditions as described elsewhere[6].

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 $CuMn_2O_4$-P4, respectively (Table 1). Thus a treatment of 65h for $CuMn_2O_4$-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.

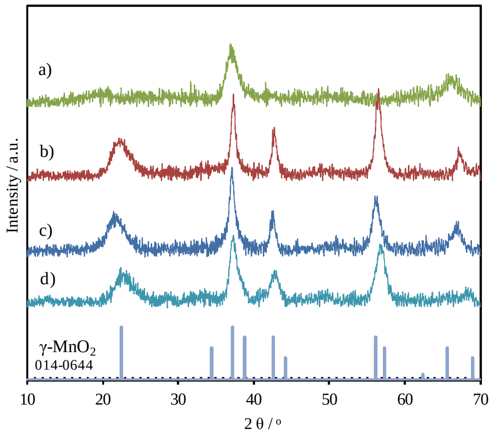

Figure 1. XRD of a) CuMnOx-R3, after b) acid-treatment, c) washing, d) calcination

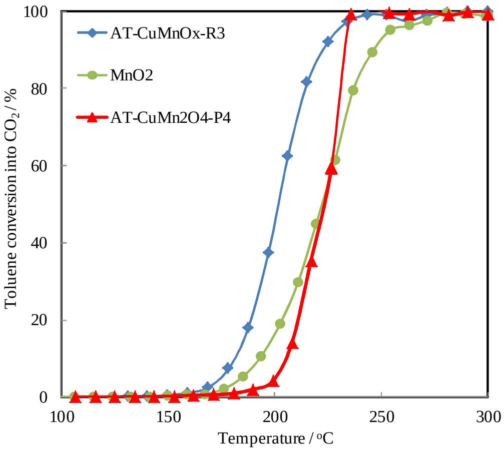

Figure 2. Light-off curves of catalysts.

The XRD patterns after acid treatment, washing and calcination presented in Fig.1 for CuMnOx-R3 evidence the formation of a γ-MnO_2-like oxide. Comparatively, when considering $CuMn_2O_4$-P4, a mixture of λ/γ-MnO_2 is highlighted after acid-treatment, the relative content of γ-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 γ-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 ($(T_{50})_{CO2}$ = 202°C) than the AT-$CuMn_2O_4$ sample ($(T_{50})_{CO2}$ = 202°C) and a reference α-MnO_2 ($(T_{50})_{CO2}$ = 223°C).

Table 1: Physico-chemical and catalytic data for the catalysts

	Cu/Mn[a]	SSA / $m^2.g^{-1}$	H_2 consumption / $mmol.g^{-1b}$	$(T_{50})CO_2$ /°C
$CuMn_2O_4$-P4	0.56	48	-	-
AT-$CuMn_2O_4$-P4	0.078	91	10.55	224
CuMnOx-R3	0.21	166	-	-
AT-CuMnOx-R3	0.019	105	10.63	202

a: molar ratio (EDX) ; b: From H_2-TPR

4. Conclusions

In summary, we report for the first time an easy method to synthesize new γ-MnO_2-like catalysts utilizing CuMnOx as starting hosts. This novel template free route to γ-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 γ-MnO_2-like oxides as possible efficient catalysts in different fields.

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