The confinement by melt infiltration of manganese oxide nanoparticles in SBA-15, a promising route towards efficient catalysts for formaldehyde oxidation

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Abstract:
A solvent-free method based on the infiltration of hydrated manganese nitrate melts has been used to deposit the manganese species in the SBA-15 support. Different parameters, such as the presence or not of the triblock copolymer during the infiltration, the time of infiltration, the manganese content and the calcination temperature, have been studied in order to optimize the dispersion of manganese oxide species. The results of the redox and catalytic properties of the different catalysts in the formaldehyde oxidation are discussed with regard to their textural and structural characterizations.

Keywords: Melt Infiltration, Formaldehyde, Manganese Oxide, SBA-15, Volatile Organic Compounds

1. Introduction

Formaldehyde (HCHO) is a ubiquitous indoor pollutant with dramatic health effects. Among several technologies proposed for HCHO removal, catalytic complete oxidation is regarded as the most promising technology to convert this molecule into harmless species (H_2O, CO_2). Transition metals based catalysts are proposed to potentially replace noble metal based catalysts, the latter being very effective but costly. Among transition metals, manganese has a relatively low toxicity compared to other elements (Ni, Co, Cu). Moreover manganese oxide based catalysts have been found to be promising low-cost materials for low-temperature formaldehyde oxidation[1]. Activity of manganese containing catalyst is generally related to the capacity of the Mn (+III or +IV) cation to reduce and reoxidize upon reaction. However reducibility of high oxidation state Mn ions is strongly dependent on their local environment including the site symmetry, coordination number, structural disorder and also on their dispersion on a support. Solvent-free method is gaining importance as a tool for the synthesis of a wide variety of catalysts[2]. Melt infiltration, based on the infiltration of porous materials with the melt of a precursor, has been recently highlighted as an emerging technique for the preparation of Co, Ni and Fe based nanostructured materials[3]. This research reports for the first time the synthesis of MnO_x/SBA-15 nanocomposites using the melt infiltration method. These nanocomposites have been used as catalyst for the removal of formaldehyde in air.

2. Experimental

The SBA-15 support was prepared under classical acidic conditions, using triblock copolymer Pluronic as structure-directing agent and tetraethoxysilane as siliceous source. For the preparation of catalysts, infiltration of melt hydrated manganese nitrate ($Mn(NO_3)_2,4H_2O$) was adopt to introduce MnO_x nanoparticles in the support SBA-15. The powder SBA-15 is first grinded with the manganese nitrate. Then the mixture undergoes a thermal hydrotreatment in teflon tank (0 to 20 days) at temperature higher than the nitrate fusion point (38°C). Finally the obtained powder is activated under air. The evolution of textural (N_2-physisorption), morphological (TEM), structural (XRD and IR), surface (XPS) and redox (H_2-TPR) properties of the Mn-SBA-15 composites has been studied by varying different parameters such as manganese loading (5-30 %wt.), activation temperature (300-500°C), time of infiltration (0-20 days) using calcined SBA-15 (550°C) or native SBA-15 (uncalcined). The catalytic performances of the different MnO_x/SBA-15 nanocomposites were evaluated in the formaldehyde (100 ppm in 20% O_2/N_2) total oxidation.

3. Results and discussion

The infiltration of molten Mn nitrate salt into the calcined SBA-15 leads to the formation of β-MnO_2 pyrolusite phase after activation at 300°C or 500°C. The β-MnO_2 mean crystallite size is around 10 nm except for the sample loading with 30 wt% of Mn (18 nm). The specific surface area (SSA) decreases from 592 $m^2.g^{-1}$ (5 wt% Mn) to 402 $m^2.g^{-1}$ (30 wt% Mn), the calcined SBA-15 exhibiting a SSA of 786 $m^2.g^{-1}$. The N_2 physisorption isotherms are all of type IV and then confirm the preserving of mesoporosity upon Mn loading, infiltration time and activation temperature. Except for sample containing 30 wt% of Mn, hysteresis loops present a delay in the closure of the desorption branch and two maxima in the pore size distribution which can be explained by the partial blockage of the mesopores by MnO_2. 20 wt% Mn loading is found to be the optimum condition for the preparation of nanocomposite for HCHO oxidation, higher Mn content leading to a decrease in the catalytic activity. This result is consistent with the presence of large MnO_2 nanoparticles observed by TEM analysis at the external surface for the sample containing 30 wt% of Mn. In order to enhance the Mn dispersion, the optimization of the diffusion of the molten precursor into the support mesopores (to prevent the crystallization of the precursor outside the support) has been performed. Different periods of time of heat-treatment of the mixture $Mn(NO_3)_2$ (10 wt% Mn)-SBA15 (calcined at 500°C) have been achieved at 38°C varying from 2 days to 20 days. But contrary to that observed over Ni(10wt%)-SBA15 material[3], this diffusion seems not to be facilitated by a longer heat-treatment, since, whatever the time infiltration, similar structural, textural, redox and catalytic activity have been observed. Another way to improve the Mn dispersion has been studied through the use of uncalcined SBA15 containing the P123 copolymer during the melt infiltration. A significant improvement in Mn dispersion is detected (Figure 1) without formation of large nanoparticles outside the mesopores when keeping the polymer during the infiltration. In this condition, Mn_3O_4 hausmannite is formed owing to the presence of the polymer which probably reduces the manganese species during the activation process (Figure 2). Despite of lower Mn oxidation state, the catalytic activity in formaldehyde oxidation of such composite occurs at low temperature and is maintained during a long-term stability test (>140h).

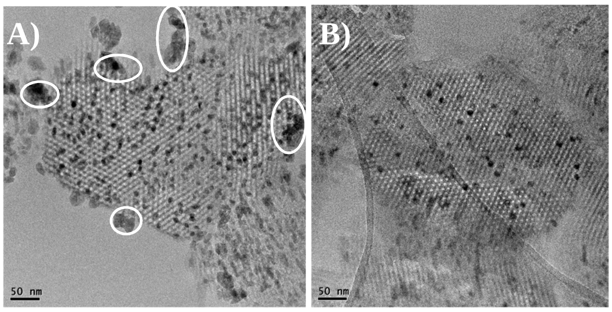

Figure 1 : TEM of Mn(20%)-SBA15 without (A) and with (B) P123 copolymer during melt infiltration

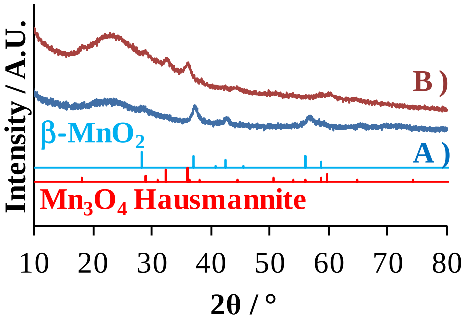

Figure 2 : XRD of Mn(20%)-SBA15 without (A) and with (B) P123 copolymer during melt infiltration

4. Conclusions

The confinement by melt infiltration (MI) of manganese oxide nanoparticles in SBA-15 has been explored to produce efficient nanocomposites for the total catalytic oxidation of formaldehyde. The diffusion of molten precursor is relatively fast and no additional heat treatment is needed to improve the Mn dispersion. The latter one can be enhanced using uncalcined SBA15 support during the MI. The catalytic performances (activity and stability) of such nanocomposites are related to their redox, morphological and textural properties.

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