

Preparation of 1D Ag/Mn₃O₄ Catalyst for the Selective Oxidation of Styrene

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1. Introduction

Direct functionalization of hydrocarbons by catalytic oxidation of C-H bonds to form oxygenated products under mild conditions is a major challenge, since this path serve as the key to the formation of value-added oxygenated chemicals and pharmaceuticals [1]. Among many oxidation reactions, catalytic oxidation of styrene is one of the most notable examples since the reaction gives valuable oxygenated compounds, which can serve as precursors for many chemical products like styrene oxide, acetophenone and benzaldehyde, and even benzoic acid [2]. Styrene oxide (SO), which is an important intermediate for large variety of fine chemicals such as perfumes and drugs etc. The heterogeneous epoxidation of olefins by silver-based catalysts is an important process in chemical technologies [3], and the catalytic properties of AgNPs in oxidation reactions strongly depend on the particles' size and stability and the nature of the support. Here we prepared ultrasmall Ag nanoparticles supported on Mn₃O₄ nanorods using cationic surfactant cetrimonium bromide (CTAB) in hydrothermal process. Herein, we also report a styrene conversion of 55% with a styrene-oxide selectivity of 97% at mild reaction temperature (90 °C) over our so prepared 1D Ag/ Mn₃O₄ nanorods (Ag NPs are 2-5nm in range).

2. Material and Methods:

Anhydrous manganese chloride, silver nitrate, cetrimonium bromide (CTAB, 99%), solution of hydrazine monohydrate, styrene were purchased from Sigma Aldrich. Absolute ethanol (AR ACS for Analysis) from Fisher Scientific was bought. NH₃ solution was bought from Acros Organics. Deionized water (HPLC grade) was used in the synthesis.

3. Significant Results and Discussion

The 1D Ag-Mn rod-like nanocomposite was synthesized following our own preparation method [3] and was characterized by XRD, XPS, SEM, TEM, STEM-mapping, Raman, FTIR, TGA-DTG, BET surface area and ICP-AES. The XRD diffractogram confirmed the presence of Hausmannite-type tetragonal Mn₃O₄ with specific group I4₁/amd [JCPDS 24-0734]. HRTEM image displayed that the catalyst is composed of tiny silver nanoparticles of ~2-5 nm and are thoroughly dispersed on Mn₃O₄ nanorods (Figure 1a). The corresponding TEM histogram of showed that the supported Ag nanoparticles with sizes between 2.5-6.5 nm. The interplanar spacing of the lattice fringe distance of 0.28 nm indicates the (103) lattice spacing of Mn₃O₄ which was distinguished from of 0.23 nm corresponding to (111) plane of metallic Ag (Figure 1b).

The styrene oxidation reaction was carried out in a Parr-Bomb reactor, with molecular oxygen as oxidant. At room temperature (35 °C), the poor conversion of styrene conversion was noticed. At higher temperatures (>90° C) although conversion of styrene increased, selectivity to SO was noticed to be sharply dropping due to the formation of mainly benzaldehyde. To maintain the higher selectivity of SO, we tried to carry out the reactions at moderate temperature (at 90° C), where we also expected the satisfied conversion of styrene (55% conversion). Maintaining all the optimum conditions, when the reaction was allowed to run for hours, we noticed that, although the conversion of styrene increased with time, but SO selectivity gradually went decreasing due to the formation benzaldehyde and other by-products.

Notably, commercial Ag₂O, Mn₃O₄, and even metallic Ag catalyst did not show any activity. Conventional catalyst prepared by impregnation method also showed negligible activity. The reason can be attributed to the comparatively smaller size of Ag (supported) nanoparticles catalyst possess comparatively high specific surface area which corresponds to higher dispersion of the catalyst that leads to the availability of more exposed surface

active sites, where the catalytic reaction takes place. The poor catalytic activity of the impregnated catalyst may be attributed to their irregular shape and larger particles size which limits the accessibility of the catalyst towards the reacting substrates.

The efficiency of a heterogeneous catalyst is evaluated in terms of its recyclability and stability. The reusability of the Ag/Mn₃O₄ catalyst was studied without any regeneration. After each run, the catalyst was filtered during hot condition and repeatedly washed with acetonitrile and acetone and dried overnight at 100 °C and used as such. We observed that the catalyst showed negligible change in its activity. The amount of Ag and Mn present in the catalyst after 5 reuse was almost same as the fresh catalyst (estimated by ICP-AES) confirming the true heterogeneity of the catalyst.

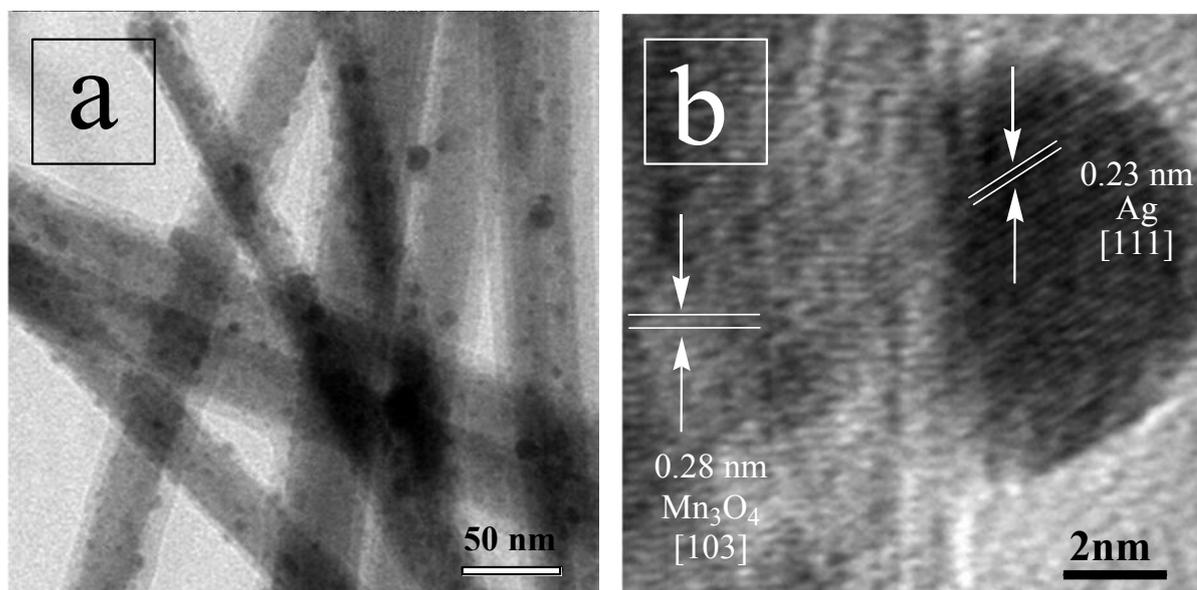


Fig. 1. HRTEM of the Ag/Mn₃O₄ catalyst (a-b) at higher magnifications.

4. Conclusions:

In conclusion, we reported a facile preparation of ultrasmall Ag nanoparticles supported on Mn₃O₄ spinel with a unique one-dimensional structure. This preparation-method could easily be scaled up due to its simplicity. Moreover the high thermal stability and reusability of the catalyst and its excellent ability in oxidation of styrene to SO using O₂ as oxidant and may be a potential alternative path of the conventional process.

References

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