Journal of Molecular Catalysis A: Chemical 418–419 (2016) 103–114

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Comparative study on the increased photoactivity of coupled and supported manganese-silver oxides onto a natural zeolite nano-particles

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ARTICLE INFO

Article history:
Received 29 December 2015
Received in revised form 17 March 2016
Accepted 23 March 2016
Available online 25 March 2016

Keywords:
Clinoptilolite nano particles
MnO-Ag_2O
Methylene blue
Heterogeneous photocatalysis

ABSTRACT

Supported MnO, Ag_2O and MnO-Ag_2O onto clinoptilolite nano-particles (NCP) were used for the photodecolorization of methylene blue (MB) aqueous solution. The catalysts were characterized by X-ray diffraction (XRD), diffuse reflection spectroscopy (DRS), transmission electron microscope (TEM), Brunauer–Emmett–Teller (BET) and Fourier transformation infra-red (FTIR). DRS results showed red shifts in band gap energies of the supported MnO-Ag_2O semiconductors with respect to the supported monocomponent one (MnO or Ag_2O). Also, in the coupled semiconductors Ag_2O-conduction band (CB) potential ($E^\circ = -1.3$ V) is enough negative to immigrate the photogenerated electrons from this level to MnO-CB level ($E^\circ = 0.1$ V). This significantly prevent from electron/hole recombination which caused to increase the photocatalytic activity. Due to more negative potential of Ag_2O-CB level than oxygen potential reduction, the photogenerated electrons in Ag_2O-CB can change oxygen molecules to superoxide radical and hydrogen peroxide. The produced H_2O_2 molecules can break to hydroxyl radicals during the irradiation process. In contrast, valence band (VB) potential of MnO ($E^\circ = 2.4$ V) is sufficient for oxidation of water molecules or OH anions to hydroxyl radicals. Adding sodium chloride and potassium bromated to the system caused to decrease the photocatalytic activity because these •OH scavengers produce other radicals such as •OCl ($E^\circ = 1.5$ V), •HOBr ($E^\circ = 2.4$ V) and •BrO_2 ($E^\circ = 1.2$ V) which have less oxidizing power the powerful •OH ($E^\circ = 2.8$ V). Photocatalytic results showed that the hybridized MnO-Ag_2O/NCP catalyst containing 10% MnO and 2.1% Ag_2O was more effective than the non-hybridized MnO/NCP and Ag_2O/NCP. The declororization process obeyed the first-order kinetics. Some photodecloriztion intermediates such as phenol and aniline were recognized by GC-Mass.

1. Introduction

Nowadays, due to increasing progresses in industrial technologies, especially textile, industrial effluents contain some variety pollutants such as dyes that pollute water and cause to significant damages to environment and life bodies. Hence, numerous methods have reported for treating textile dye wastewaters including various chemical, physical and biological processes [1]. Many of these reported methods have some drawbacks. For example, many organic substances are resistant to biological treatment and this method do not always give satisfactory results in the treatment of industrial wastewaters, or some physical methods such as adsorption move pollutants from one phase to another. Methylene blue (MB), as a resistant biodegradable compound, is a water soluble thiazin dye that has wide applications including: colouring paper, temporary hair colorant, dyeing cottons and wools. It can cause some harmful effects such as: heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [2]. In recent decades, the Advanced Oxidation Processes (AOPs) have been widely used for removing different organic pollutants since these methods are capable of converting organic pollutants into harmless products such as water and carbon dioxide, which is the final goal of AOP technology. On the other hand, catalytic oxidation reactions could mineralize of organic substances to environmental friendly compounds [1].

In heterogeneous photocatalysis, as one of the most successful AOP method for the destruction of contaminants existing in water

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http://dx.doi.org/10.1016/j.molcata.2016.03.034
1381-1169/

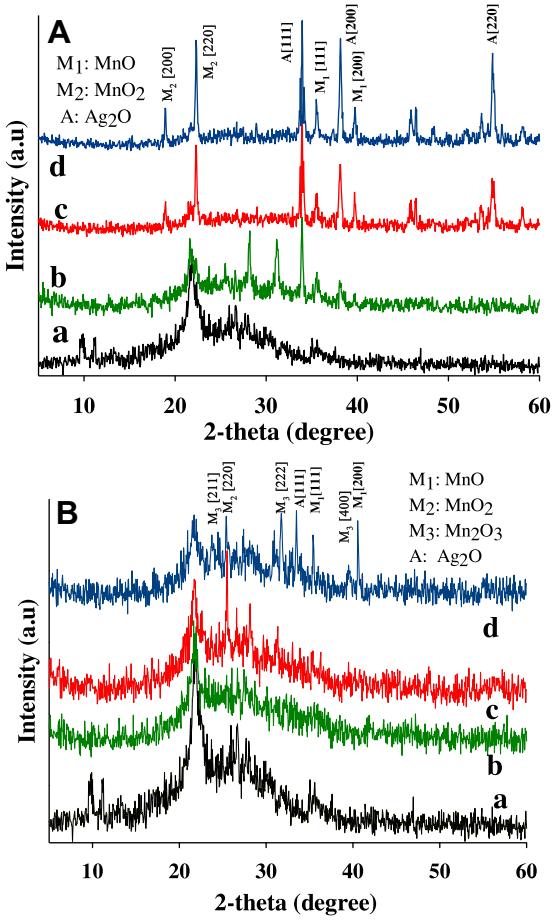

Fig. 1. XRD patterns of A) NCP (a), $MnO_{6.1\%}Ag_2O_{4.2\%}$/NCP (b), $MnO_{5.5\%}Ag_2O_{5.9\%}$/NCP (c), $MnO_{5.3\%}Ag_2O_{6.8\%}$/NCP (d); B) NCP(a), $MnO_{10.0\%}Ag_2O_{2.1\%}$/NCP (b), $MnO_{12.1\%}Ag_2O_{2.0\%}$/NCP (c), $MnO_{12.8\%}Ag_2O_{1.6\%}$/NCP (d).

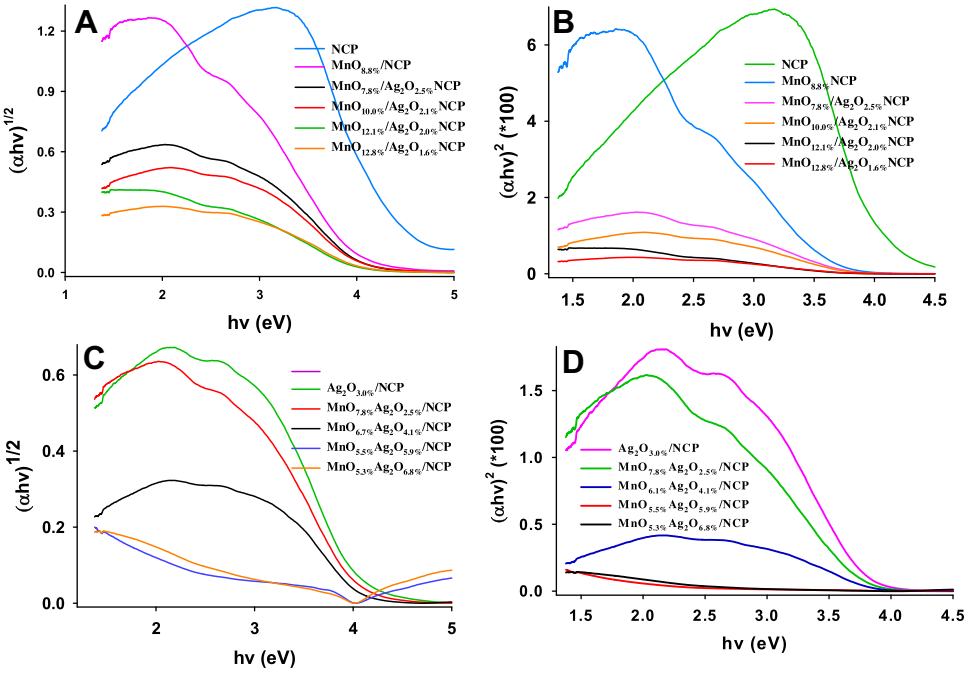

Fig. 2. Typical Tauc plots for allowed direct (n = 2) and indirect (n = 1/2) transitions of the used catalysts extracted from DRS spectra.