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In situ oxidation for stabilization of Fe/MCM-41 catalyst prepared by metal organic chemical vapor deposition

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Abstract

Oxygen has been found to be a key factor in the process of metal organic chemical vapour deposition (MOCVD) to stabilize the iron catalyst supported on MCM-41, particularly in the acidic aqueous reaction. Such stabilization is achieved by *in situ* oxidation of iron, which intercalates oxygen atoms into the framework of both siliceous and ferric oxides by developing Fe–O–Si and Fe–O–Fe bonds, respectively. This stable Fe/MCM-41 catalyst shows an excellent mineralization efficiency of orange II of ~85% and an extremely low iron leaching concentration of ~0.17 mg/L. The catalyst maintains its excellent catalytic activity after multiple reaction runs under acidic aqueous medium.

Keywords: MOCVD; Intercalated oxygen; *In situ* oxidation; Stability; Low leaching

1. Introduction

Metal organic chemical vapor deposition (MOCVD) has been a mature technique for metal coating in the semiconductor industry for a few decades [1]. Recently, it has been used in the catalyst synthesis, especially for coating the catalytically active metal element onto porous solid support. Those catalysts synthesized by the MOCVD method are usually utilized in the gas-phase reaction but seldom applied in the liquid-phase reaction [2,3]. This is because there is a special issue to be considered for the liquid-phase reaction, that is, the leakage of the active metal element from the porous support. Such a leaching phenomenon is critically important when the catalytic materials are utilized in liquid-phase reaction, particularly in an acidic medium. The detachment of active metal content from the solid support to the treated liquid poses a gradual loss of catalytic activity [4,5]. Moreover, when this reaction is applied to wastewater treatment, the leached metal ion in turn becomes a secondary pollutant which is toxic to marine animals [6–8]. To date, it is rarely found in the literature on the issue of catalyst stability in the liquid-phase reaction. Metal catalysts like platinum [9], palladium [10], rhodium [11], and titanium oxide [12] supported on porous substrates have been tried by other researchers and used in the acidic or wild operating conditions (high pressure and temperature process like wet air oxidation). Since these noble metal catalyst have relative by higher stability due to their inertness to the acidic condition, the catalyst leaching is not a big issue. However, transition metals such as iron [13] and copper [14], which are well-known and much cheaper catalysts for wastewater treatment by Fenton's reaction or catalytic wet oxidation, always encountered a significant leaching problem which has puzzled the scientists for a long time. Improving the heterogeneous catalyst stability in acidic liquid-phase reaction through a proper catalyst preparation process remains a big challenge.

In this study, therefore, an investigation on the stabilization of metal catalyst supported on MCM-41 is conducted. Heterogeneous photo-Fenton's reaction will be used as a model reaction to test the catalyst's activity and stability.

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The role of oxygen during the MOCVD process on the enhancement of binding metal element onto the solid substrate will be studied. The catalytic performance, durability, and stability of such prepared metal catalyst will also be demonstrated.

2. Experimental

Iron catalyst supported on MCM-41 substrate was synthesized via a MOCVD technique by using ferric acetylacetonate (Fe(acac)$_3$) and MCM-41 as iron source precursor and target substrate, respectively [15]. A total of 0.25 g Fe(acac)$_3$ was housed inside a tubular rotating reactor, sublimed under vacuum and transported to 1 g target substrate by means of an oxygen flow of 0.25 mL/s at a deposition temperature of 280 °C. For comparison, other catalytic materials were also prepared without the use of oxygen as carrier gas, which were either post treated by calcination in air at 550 °C with a heating rate of 1 K/min or by reduction in hydrogen at 550 °C. The prepared materials were first tested by the washing process in order to estimate the binding strength between the deposited metal element and MCM-41 substrate. The washing process is conducted as follows: a total of 1 g of the developed catalyst was washed into one liter of acidic solution (pH 3) under vigorous stirring for 6 h at ambient temperature. The washed materials were filtered and dried at 50 °C overnight. They were characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction spectroscopy (XRD) to determine its loading, surface concentration and crystallinity of the deposited iron catalyst on MCM-41, in which the iron loading is evaluated by dissolving the catalytic materials in concentrated HNO$_3$ and measuring the ferric ion concentration in the filtrate by the ICP analysis. They were finally evaluated in the photo-Fenton oxidation of a model organic pollutant, orange II. The catalyst's stability and catalytic performance were reflected by the leached metal ion concentration and the removal of total organic carbon (TOC) concentration of the treated orange II solution, respectively. The leached iron concentration was measured by ICP-AES and the TOC concentration was determined by a TOC analyzer.

3. Results and discussion

Fig. 1 shows the leaching phenomenon of the deposited iron catalyst from the MCM-41 substrate tested in the washing process. The leaching ratio is defined as the ratio of the leached iron amount to the total deposited iron amount. For convenience, catalysts prepared with oxygen, without oxygen but post treated with calcination at 550 °C, and without oxygen but post treated with hydrogen reduction at 550 °C were denoted as Fe/MCM-41-O$_2$, Fe/MCM-41-without O$_2$ (calcined at 550 °C), and Fe/M41-reduced (reduced at 550 °C), respectively. It is seen that Fe/MCM-41-O$_2$ (open circle line) loses only 10% of the deposited iron in total, while Fe/MCM-41-without O$_2$ (filled circle line) has a loss of 65%. It is even worse to see that the reduced Fe/MCM-41 (open square line) has a leaching ratio of around 75%. This clearly demonstrates that Fe/MCM-41-O$_2$ has a much higher leaching resistance in the acidic solution compared to Fe/MCM-41-without O$_2$. The reductive environment increases the leaching ratio, which destabilizes the deposited iron catalyst from the MCM-41 substrate. It is noted that, although Fe/MCM-41-without O$_2$ has been calcined under air in a thermotreatment, it still gives a high leaching ratio of iron which reveals its poor binding between the deposited iron and the substrate. Such a large discrepancy in the leached iron concentration implies that oxygen is essential for the metal binding. The possible reason is that the continuous supply of oxygen during the deposition can decompose the organometallic precursor in situ and subsequently the metal deposits on the substrate surface with a binding of Si–O–Fe. In addition, oxygen can oxidize the coated iron to form a framework of iron oxide layer by layer, which develops a strong chemical binding on the interface between the deposited iron and the MCM-41 substrate. Therefore, the usage of oxygen can significantly improve the catalyst stability by developing a stable bridge of Si–O–Fe between the metal and the substrate during the MOCVD process.

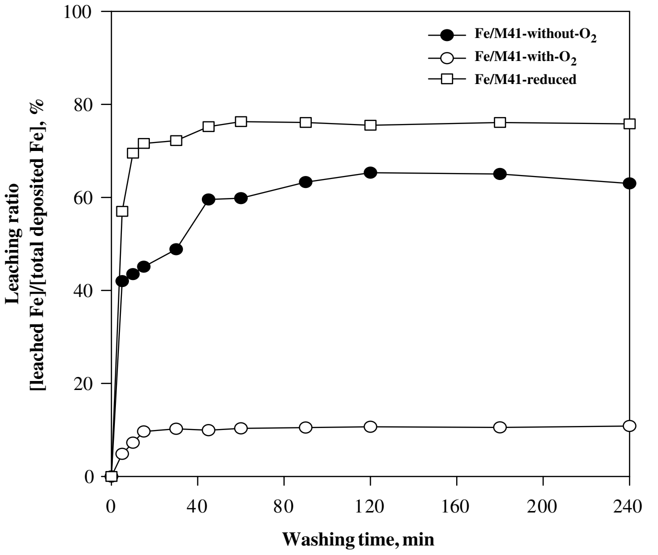

Fig. 1. Leaching ratio of the catalysts in the stability test. The washing process: 1 g of Fe/MCM-41 catalyst + 1 L of dilute HNO$_3$ solution of pH 3 under stirring for 6 h at ambient temperature.

To further investigate the stability of iron catalyst on the MCM-41 substrate, TEM-EDX analysis was conducted to examine the morphology of iron catalyst attached on the MCM-41 surface. The TEM images of the Fe/MCM-41 catalysts prepared without oxygen but post treated with reduction or calcination are shown in Fig. 2a and b, respectively. For the reduced Fe/MCM-41, as displayed in Fig. 2a, the reduced iron is found to be in the form of small black dots which are spherical iron nanoparticles. During