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Influence of partial replacement of Cu by Fe on the CWO of phenol in the $Cu_{0.5-x}Fe_xZn_{0.5}Al_2O_4$ spinel catalysts

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Abstract

The activity and stability of the $Cu_{0.5-x}$ $Fe_xZn_{0.5}Al_2O_4$ spinel type catalysts prepared by sol–gel method were studied in the catalytic wet oxidation of phenol. All catalysts showed high catalytic activity and leach-proof ability. The loss of activity for the catalysts ($x \leqslant 0.25$) can be attributed to the elution of the active phase. The cation distribution of the spinel was calculated from XRD and it has been found that the amount of $Cu_{leached}$ ions in CWO reaction decreases with the fraction of Cu ions occupied in the octahedral sites decreasing.

Keywords: Catalytic wet oxidation; Phenol; Leaching; Carbonaceous deposits; Spinel; Cation distribution

1. Introduction

In recent years ,environmental concerns regarding water pollution problems have stimulated strong research activity efforts [1], catalytic wet oxidation (CWO) using heterogeneous catalysts is being developed as a powerful technique for the treatment of dilute aqueous waste streams contaminated by a variety of organic pollutants such as phenol [2]. A large variety of solid catalysts including supported and unsupported metal oxides have been tested in CWO [3–5]. Unfortunately, the threat of catalyst deactivation by carbonaceous deposits blocking the active sites emerged as a major drawback [6], another documented cause of active loss is leaching of the catalyst active compounds in hot acidic aqueous solutions [7]. Therefore, the main conclusion in several studies is that, new active and stable catalyst should be developed [8]. In some studies, the most refractive ceramic supports, such as CeO_2, TiO_2, ZrO_2 and ZnO have been introduced in order to get more stable catalysts [9,10] and alkali metals were used to reduce the undesirable carbonaceous deposits [6,11].

A commercial catalyst comprising 42 wt% CuO, 47 wt% ZnO and 10 wt% Al_2O_3 showed high catalytic activity of converting phenol to nontoxic compounds, but the formation of polymeric deposits on the catalyst surface [12] and dissolving of Cu, Zn and Al metals in acid or even neutral solution [7,13] reduced stability of the catalyst. In this paper, to enhance the catalytic stability to leaching, a new catalyst was prepared by regulating the content of Cu, Zn and Al in the commercial Cu–Zn–Al catalyst for forming the $Cu_{0.5}Zn_{0.5}Al_2O_4$ spinel structure, as spinel is highly resistant to dissolution in acidic fluids [14–16]. It was further proposed to substitute Cu by Fe in the spinel in an attempt to reduce the amount of Cu leached. The influence of the partial replacement on the structure of the catalyst and on CWO of phenol was studied.

2. Experimental

The $Cu_{0.5-x}Fe_xZn_{0.5}Al_2O_4$ spinel type catalysts ($x = 0$, 0.125, 0.25 and 0.375) were prepared by sol–gel method by mixing stoichiometric amounts of $Cu(NO_3)_2 \cdot 3H_2O$,

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$Zn(NO_3)_2 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and excess citric acid in distilled water. The solutions were heated up to 70 °C in order to remove water, then the resulted gels were kept at 110 °C for 15 h, the final catalysts were obtained by decomposition of the xerogels in air at 750 °C for 4 h.

Crystalline structure of the catalysts was analyzed with a Rigaku-D/max-γB diffractometer using Cu radiation. The X-ray was operated at 40 kV and 40 mA. Resulting patterns were indexed by comparison with standard XRD patterns.

The organic material deposited on the catalysts was investigated by TPO using an AUTOchem II 2920 instrument. Hundred mg of used catalyst was loaded and treated in 2 vol % O_2–He, 30 ml/min as the temperature was increased from ambient to 550 °C at 10 °C/min.

The CWO of phenol was carried out in a 250 ml autoclave reactor. The autoclave was first filled with 100 ml of 1.5 g/l phenol solution. Then, 0.2 g of powdered catalyst was added into the solution and the autoclave was closed. Oxygen was compressed into the autoclave with a pressure of 1.0 MPa at room temperature which was enough for the stoichiometric amount of phenol to be completely oxidized. The autoclave was heated to 150 °C with impeller stirring at a speed of 600 rpm for 2 h. Liquid samples were withdrawn after reaction. COD_{Cr} value of the solution was measured following standard determination techniques and concentration of leached Cu ions in the solution was analyzed by ICP-AES. Removal rate of COD was used as an index for catalytic properties.

3. Results and discussion

During the catalysts preparation, the ingredient Fe was first present as Fe^{2+}. As oxidation of Fe^{2+} to Fe^{3+} is very easy by oxygen in air, all Fe^{2+} may turn completely into Fe^{3+} upon calcinations [17]. In order to preserve the crystal electrical neutrality, a part of Cu^{2+} has to turn into Cu^{+}. Accordingly, the structure of $Cu_{0.5-x}Fe_xZn_{0.5}Al_2O_4$ spinel may be presented by the following formula:

$$[Cu_aZn_{0.5}Fe_bAl_c]^{tet}[Cu_{0.5-x-a}Fe_{x-b}Al_{2-c}]^{oct}O_4$$

In which Zn^{2+} are present in the tetrahedral sites [18], whereas the other ions are distributed in both the octahedral sites and the tetrahedral sites.

The X-ray diffraction patterns of $Cu_{0.5-x}Fe_xZn_{0.5}Al_2O_4$ spinel catalysts are shown in Fig. 1. XRD data show a single phase with the spinel structure for all catalysts, but diffraction intensities decrease with Fe content x increasing.

In order to check whether the structure was perfect, lattice parameters of the $Cu_{0.5-x}Fe_xZn_{0.5}Al_2O_4$ spinel were calculated and plotted against the Fe content x in Fig. 2, along with the theoretical line of Vegards'law [19]; which illustrates increase of the $Cu_{0.5-x}Fe_xZn_{0.5}Al_2O_4$ spinel lattice parameter with increase of the Fe concentration. It seems that a homogeneous solid solution was obtained in the range of Fe concentration $x \leqslant 0.25$ since the lattice parameter values observed were predicted by Vegard's law. However, at higher Fe concentration $x \geqslant 0.25$, the lattice parameter values deviate from Vegard's law. The reason for this may be that there are not enough Zn^{2+} and Cu^{2+} or Cu^{+} to react with Fe^{3+} and Al^{3+} at high Fe content and some amount of Fe^{3+} and Al^{3+} segregate forms patches of amorphous material [19].

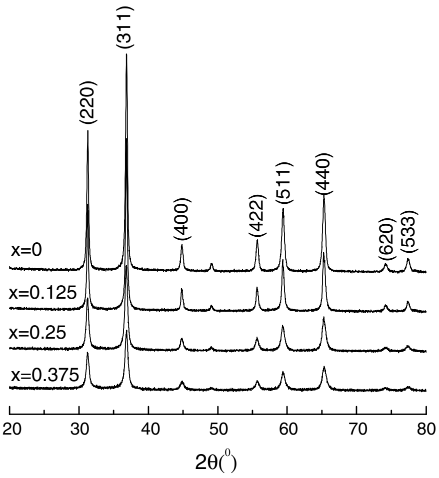

Fig. 1. XRD patterns of $Cu_{0.5-x}Fe_xZn_{0.5}Al_2O_4$ spinel.

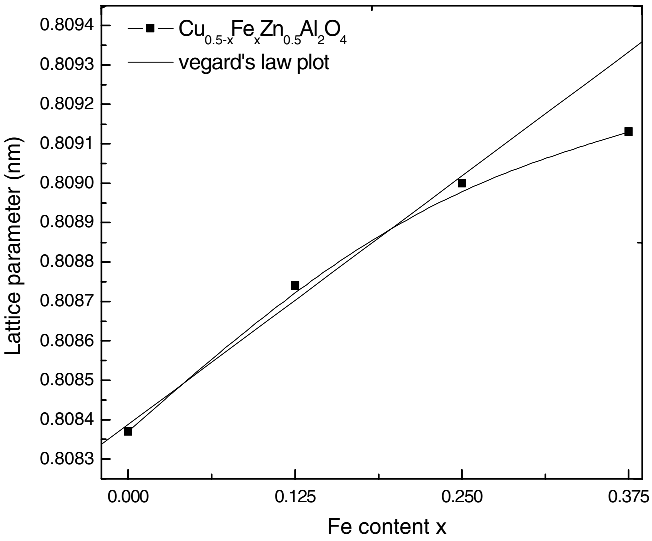

Fig. 2. Lattice parameter of $Cu_{0.5-x}Fe_xZn_{0.5}Al_2O_4$ spinel.

The effect of the substitution of Cu by Fe on the catalytic behavior during CWO reaction of phenol is given in Table 1 and Fig. 3.

Table 1
Catalytic behavior of $Cu_{0.5-x}Fe_xZn_{0.5}Al_2O_4$ in the phenol oxidation for the first reaction run

X	0	0.125	0.25	0.375	Blank
COD_{cr} removal (%)	82	84	90	93	15
$Cu_{leached}$ (ppm)	32.0	13.7	7.60	8.04	
$Cu_{leached}/Cu_{total}$ (%)	9.19	5.22	4.31	9.08	