

Photo-Fenton oxidation of phenolic compounds catalyzed by iron-PILC



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HIGHLIGHTS

- 85–94% removal of chlorophenols was attained depending on the applied process.
- Mineralization degree is higher (50%) with photo-Fenton than with Fenton (~0%) process.
- Photo-Fenton process catalyzed with iron-PILC eliminates pH adjustment.
- Stoichiometric amount of H₂O₂ maximizes 4-Chlorophenol degradation.
- A relatively simple analytical method based on UV–VIS spectrophotometry was applied.

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ABSTRACT

This work aimed to examine an iron pillared inter-layered clay as catalyst of the photo-Fenton process to oxidize phenolic compounds. The effect of the number of chlorine atoms substituted onto the ring was also studied. The selected clay was bentonite and the phenolic compounds were phenol, 4-chlorophenol and 2,4,6-trichlorophenol. The catalyst was synthesized by ionic exchange and characterized by X-ray diffraction, N₂ physisorption, atomic absorption and X-ray photoelectron spectroscopy. In addition to the chlorine presence, the effect of other variables like initial concentration of H₂O₂ and catalyst loading was also evaluated. It was found that the highest 4-chlorophenol removal (94%) by degradation and mineralization is attained when using the stoichiometric amount of H₂O₂ and 0.8 kg/m³ of catalyst. It outstands the fact that no pH adjustment was required at any moment in the experiment. Regarding the presence of chlorine in the pollutant structure, it was concluded that it significantly favors the degradation of the phenolic compound.

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1. Introduction

According to the World Health Organization (WHO), approximately one quarter of global population lacks hygienic drinking water [1]. Actually, in developing countries water scarcity is already a severe problem. Unfortunately, the increase of human activities, for instance the production of goods as well as our daily routine, results in persistent fresh water pollution. Thus, the development of decontaminating technologies that transform existing refractory contaminants in innocuous end products, such as carbon dioxide, water and mineral acids at low concentrations, has become a subject of worldwide concern. In this context, advanced

oxidation processes (AOP), a class of chemical oxidation technologies, appear to be a promising field of study. These processes are characterized by the production by different means of unselective and highly oxidant species (hydroxyl radicals) that produce major changes in the chemical structure of the contaminants until their complete destruction [2]. As source of oxidant species, many AOP use H₂O₂ because this has been proven to be highly efficient regarding organic compounds mineralization. Besides, H₂O₂ is environmentally friendly since its self-decomposition yields to H₂O and O₂ [3]. The oxidant action of H₂O₂ is significantly improved by adding Fe²⁺. This mixture is known as Fenton's reagent. Among AOP Fenton's reagent has extensively been used due to its simplicity. Fenton's reagent in an acidic medium generates, via Reaction (1), hydroxyl radicals that subsequently attack organic matter [4,5]. At a proper value of pH (2.8), iron acts as a real catalyst because of the reduction of Fe³⁺ to Fe²⁺ via Reactions (2) and (3).

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The use of a natural Mexican zeolite as support of NiMoW sulphide hydrotreating catalysts

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ABSTRACT

In order to examine the influence of type of metal precursor on the hydrosulfurization (HDS) activity of synthesized samples, a series of ternary Ni–Mo–W catalysts supported on a natural Mexican zeolite (*clinoptilolite*) were prepared by sequential wet impregnation of the zeolite support with different thiosalts of W and Mo, and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The synthesized samples were characterized by N_2 adsorption–desorption isotherms at -196°C , X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX/SEM), high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) techniques. The catalysts activity was evaluated in the HDS of dibenzothiophene (DBT) reaction performed in a batch reactor at 350°C and 3.1 MPa of total hydrogen pressure. The activity tests demonstrated that the best catalyst was the NiMoW-H/zeo sample synthesized from ammonium thiosalts. The use of tetraalkylammonium thiometalates as metal precursors led to the decrease in the HDS activity. The most active catalyst in the HDS of DBT reaction showed the largest density of active phases on the support surface determined from HRTEM measurements.

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1. Introduction

Due to the new environmental regulations around the world concerning the decrease in the content of pollutants in fuels [1], the refining industry is under pressure to increase the efficiency of the hydrotreating process by developing new catalysts and/or modifying the actual process. The actual hydrotreating catalysts are generally based on Mo and W sulphides, commonly supported on alumina, and promoted with Co or Ni [2]. The new generation of catalysts, such as NEBULA[®], is based on a concept of bulk-like materials. This catalyst shows a four-fold greater HDS activity than that of the supported NiMo or NiW catalysts commercially available today [3]. The surface properties of bulk catalysts can be easily tuned by supporting them on different substrates, which allows the modification of the dispersion and coordination of the deposited active ingredient. Thus, the challenge is to develop supported systems, which could be more active than bulk-like systems.

Concerning the novel supports, zeolites with a unique crystal and pore structure have attracted wide interest in preparing highly dispersed supported metal sulfide catalysts because the dominant factor controlling both activity and selectivity is the dispersion of the active component. They also combine a large number of acid sites distributed through the network of channels and cavities, which provide bifunctional HDS catalysts. Moreover, there are studies demonstrating that the incorporation of a small amount of zeolites into metal sulphide catalysts supported on alumina led to significant improvement of activity due to the enhancement of the catalyst acidity [4–7]. In this sense, Shimada et al. [8] proposed that strong Brønsted centers might promote sulphur removal by enhancing hydrocracking of S–C bonds. As a consequence of the improvement in the catalyst acidity, more desired products (light hydrocarbons and gasolins) were formed and the catalyst resistance to poisoning by N- and S-containing compounds present in the feed was improved [9]. However, the Brønsted acidity of catalyst must be carefully controlled in order to balance the enhancement of activity induced by acidity and coke formation [10]. Contrary to synthesized zeolites, the use of natural zeolites as supports has been scarcely explored. Therefore, it appears desirable to study the potential use of natural zeolites such as a natural Mexican *clinoptilolite* as a support for HDS catalysts. *Clinoptilolite* has a cage-like structure consisting of SiO_4 and AlO_4 tetrahedral

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ESTUDIO DEL EFECTO DE DIFERENTES SOPORTES MIXTOS EN LA ACTIVIDAD CATALÍTICA Y LAS CARACTERÍSTICAS ESTRUCTURALES DE CATALIZADORES DE $\text{Bi}_2\text{Mo}_x\text{W}_{1-x}\text{O}_6$

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Palabras clave: actividad catalítica, oxidación de monóxido de carbón, óxidos mixtos, catalizadores soportados

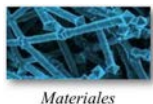
RESUMEN

Se preparó una serie de catalizadores de $\text{Bi}_2\text{Mo}_x\text{W}_{1-x}\text{O}_6$ soportados en $\text{Al}_2\text{O}_3\text{-SiO}_2$, $\text{SiO}_2\text{-TiO}_2$ y carbón activado (C^*). El propósito principal fue comparar el uso de diferentes soportes, así como también valorar el efecto de la temperatura de síntesis de los catalizadores en términos de su eficacia y de conversión en la reacción de oxidación de monóxido de carbono (CO) y en su temperatura de activación. La fase activa de los catalizadores, $\text{Bi}_2\text{Mo}_x\text{W}_{1-x}\text{O}_6$, se sintetizó a partir de los compuestos de alta pureza $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{W}_{12}\text{O}_{42}\cdot \text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$, empleando el método de co-precipitación química, y posteriormente soportada por el método de impregnación en $\text{Al}_2\text{O}_3\text{-SiO}_2$, $\text{SiO}_2\text{-TiO}_2$ ó C^* . Estos sistemas catalizador/soporte se caracterizaron mediante las técnicas de difracción de rayos X (XRD), microscopía electrónica de barrido (SEM) y área superficial (método BET). Con respecto a la actividad catalítica, el compuesto con mayor eficacia en la conversión de CO a CO_2 fue $\text{Bi}_2\text{Mo}_x\text{W}_{1-x}\text{O}_6/\text{C}^*$, que se preparó a 500 °C; se activó a 125 °C logrando una conversión de 90 %. Se concluye que existe un efecto de la temperatura de síntesis y del tipo de soporte que influye en los diferentes valores de actividad catalítica encontrados.

Key words: catalytic activity, carbon monoxide oxidation, mixed oxides, supported catalyst

ABSTRACT

A series of $\text{Bi}_2\text{Mo}_x\text{W}_{1-x}\text{O}_6$ catalysts supported on $\text{Al}_2\text{O}_3\text{-SiO}_2$, $\text{SiO}_2\text{-TiO}_2$ and activated carbon (C^*) were synthesized. The aim was to compare the different supports and calcination temperature of catalysts, studying their efficiency and activation temperature in the CO oxidation reaction. The catalysts active phase, $\text{Bi}_2\text{Mo}_x\text{W}_{1-x}\text{O}_6$, was made by means of chemical precipitation procedure starting from high purity $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{W}_{12}\text{O}_{42}\cdot \text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ compounds, which



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STUDY OF CONSTRAINED SINTERING OF POWDERS USED TO CRACKS REPARATION

ESTUDIO DEL SINTERIZADO RESTRINGIDO DE POLVOS UTILIZADO PARA REPARACIÓN DE FISURAS

²¹³ Derivation and application of the Stefan-Maxwell equations

(Desarrollo y aplicación de las ecuaciones de Stefan-Maxwell)
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Abstract

Sintering is a thermal treatment normally used to produce parts from different types of powders, and it is a phenomenon that has been studied since the 1950's. Mechanisms and diffusion paths for several materials have already been established. However, the use of sintering powders to repair fissures on solid materials has rarely been studied. The aim of this work is to study the solid state sintering of copper powders filling artificial grooves in a bar of solid copper. Sintering was carried out in an electrical furnace under H₂ and Ar (10-90 respectively) atmosphere at two different temperatures, 1000 and 1050°C. The powder used to fill the grooves was a spherical atomized copper powder with a wide particle size distribution, 0-63 µm. Sintering of particles was evaluated at the edge of the solid bar and at the center of the groove by scanning electron microscopy (SEM). It was observed that particles sintered well on the wall's surface at the site of the artificial groove. Greater densification reached by the smaller particles and higher sintering temperatures creates defects inside the groove. Those defects are the consequence of the constraints of sintering, and the necks developed during the thermal cycle could be broken by the higher stresses generated during densification.

Keywords: constrained sintering, copper, solid state sintering, defects evolution, cracks healing.

Resumen

El sinterizado libre es un tratamiento térmico usado para fabricar partes sólidas a partir de diferentes tipos de polvos. Este fenómeno se ha estudiado desde los años 50 y los mecanismos de difusión para diversos materiales son conocidos. Sin embargo, el sinterizado restringido ha recibido poca atención, a pesar de las aplicaciones que puede tener como la reparación de fisuras en materiales que no pueden ser soldados. El objetivo de este trabajo es estudiar el sinterizado restringido de polvos de cobre depositados al interior de una ranura creada artificialmente en barras sólidas de cobre. Se evaluó el efecto del tamaño de partícula y de la temperatura de sinterizado sobre la evolución microestructural. El sinterizado se llevó a cabo en un horno eléctrico a dos temperaturas, 1000 y 1500°C, bajo una atmosfera reductora de una mezcla de H₂ y Ar (10-90 respectivamente). Los polvos usados son esféricos y con dos distribuciones de tamaño de partícula, 0-40 y 40-63 µm. La evolución del sinterizado fue evaluada al borde de la barra sólida y al centro de la ranura mediante microscopia electrónica de barrido. Los resultados muestran que el método es capaz de reparar fisuras y que los contactos entre partículas y las paredes se desarrollan de manera satisfactoria. Sin embargo, se encontró que altas densificaciones generan esfuerzos suficientemente fuertes para romper los contactos creados entre partícula-pared y también entre partícula-partícula, generando defectos como grietas o delaminaciones al borde de la pared. Se encontró que el uso de partículas de menor tamaño es más perjudicial para la unión entre partículas y pared.

Palabras clave: sinterizado restringido, cobre, sinterizado en estado sólido, evolución de defectos, reparación de fisuras.

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