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ScienceDirect

Journal of Hazardous Materials 153 (2008) 364–371

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Photo-degradation of acid green dye over Co–ZSM-5 catalysts prepared by incipient wetness impregnation technique

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Received 18 March 2007; received in revised form 21 August 2007; accepted 22 August 2007
Available online 28 August 2007

Abstract

Co–ZSM-5 catalysts with different Co-loadings (2–30 wt.%) were prepared by incipient wetness impregnation method. The prepared solid catalysts were characterized by X-ray diffraction, FTIR, *in situ* FTIR of pyridine adsorption and surface area measurements. The XRD data presented disintegration in the zeolitic crystalline structure accompanied by an increase in particle size of the prepared solids. New phases, Co_3O_4 and Co_2SiO_4, were detected with increasing the Co-loading, which indicate the strong interaction of cobalt ions with the ZSM-5 zeolite. FTIR study proved the presence of Co ions in stabilized sites inside the ZSM-5 framework. The *in situ* FTIR of adsorbed pyridine determined the type and relative strength of acidity on the surface of the prepared solids. The acidity switched from B-acid sites to L-acid sites with impregnation of cobalt ions in ZSM-5 zeolite. The acidity decreased with increasing Co-loading, which might be due to the destruction of zeolite framework and presence of new phases such as cobalt silicate and cobalt oxide on the surface. The surface texture characteristics changed with the promotion of ZSM-5 by cobalt ions, since a decrease of surface area, mean pore radius and pore volume was observed.

The assessment of the catalytic activity was performed by the use of the photo-degradation of acid green (AG) dye as a probe reaction in presence of H_2O_2 as an oxidant. The pH value controlled the degradation rate since a gradual increase of AG degradation rate was observed with increasing pH value and the optimum H_2O_2 concentration was 61.6 mmol/l. It was found that, the AG degradation rate increased until an optimum value of Co-loading (*ca.* 10 wt.%), beyond which a monotonic decrease of reaction rate was recognized. The experimental data pointed to the importance of both the cobalt moieties and the zeolite framework structure in the AG degradation reaction.

Keywords: ZSM-5; Acid green dye; Cobalt oxide; Pyridine adsorption

1. Introduction

Zeolites modified with transition metal ions have received increasing attention as promising catalysts for a variety of important reactions [1]. Zeolites can serve as hosts to activate transition metal ions, offering a unique ligand system with multiple types of coordination for cations. In addition, the restricted pore size of zeolites could limit the growth or sintering of the nanoparticles of the cation even at high temperatures [2]. Generally the zeolite structure, the type, the location of the cation and the coordination are among factors that control catalytic activity. Among the transition metal ions cobalt showed high activity towards many reactions [3–6]. It was found that the presence of other cations such as Na^+ and $NH_4{}^+$ on the Co^{2+} sitting caused deformation, and an expected reconstruction of the Si–O–A1 bridges could occur. Consequently, the acidity of the samples and specifically the Lewis acid sites will be affected. It was reported in literature that increasing the Co-loading changed the activity and durability of the Co-promoted zeolites [7–9].

Wastewaters from the textile industry are characterized mainly by intense color resulting from considerable amounts of dyes such as acid green (AG). Effective removal of color from wastewater is a serious problem since even a small amount of dye is clearly apparent. The conventional methods used for color removal are ultra filtration, extraction, adsorption and oxidation with ozone and hydrogen peroxide. Heterogeneous photocatalysis is one of the most important efficient technologies used for removal of organic contaminants from wastewater. Photocatal-

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doi:10.1016/j.jhazmat.2007.08.060

ysis belongs to so-called advanced oxidation processes (AOP) [10]. AOP involves generation of a very reactive hydroxyl radical that aggressively attacks virtually all organic compounds. Photocatalytic processes are preferred due to several reasons such as: (i) complete mineralization; (ii) no waste disposal problems; (iii) no expensive oxidants needed; (iv) low costs; (v) only mild temperature and pressure are necessary [11]. Many dyes may be effectively decolorized using chemical oxidizing agents such as chlorine in the form of liquid or gas, ozone and H_2O_2 that is the most environmentally friendly oxidant [12].

The driving force of this work is to study the structural, acidic and photocatalytic properties of different loaded Co–ZSM-5 systems prepared by incipient wetness impregnation technique. Furthermore, the removal of an organic pollutant (namely acid green dye) will be tested to evaluate the relative photocatalytic activity of the prepared samples.

2. Experimental

2.1. Catalyst preparation

The impregnated Co–ZSM-5 samples were prepared by mixing calculated amount of ZSM-5 (CBr 8014, Lot no. 8014-08-D; Si/Al = 80) with an aqueous solution of cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$, ADWIC) to give 2, 5, 10, 20 and 30 wt.% of Co/ZSM-5. The volume of solution used was that necessary to completely wet the zeolite samples. The solution temperature was adapted at 80 °C for 3 h. After impregnation the water was allowed to evaporate. It followed drying at 110 °C. The obtained solid was then calcined at 550 °C in air for 6 h. The Co-promoted ZSM-5 prepared by impregnation will be referred to as *x*Co–Z, where *x* denotes to the Co-ratio and Z refers to ZSM-5.

2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns of various prepared samples were performed using a Philips diffractometer (PW 3710) with Ni-filtered copper radiation ($k = 1.5404$ Å) at 30 kV and scanning speed of $2\theta = 2.5$ °/min. The crystal size of the prepared materials was determined using the Scherrer equation [13]. The crystallinity of the prepared samples was calculated using the ratio of the sum of the areas of the most intense peaks for ZSM-5 samples ($2\theta = 23°$, 23.8° and 24.3°) to that the same peaks for the standard (ZSM-5 Mobil Chemicals) and multiplying by 100. The particle size of various zeolite samples was measured using a particle size analyzer (LB-500 HORIBA, Dynamic Light Scattering).

IR spectra were recorded in the solid state as KBr pellet on Bruker (Vector 22), single beam spectrometer at room temperature. For *in situ* FTIR spectra of pyridine adsorption, a self-supporting wafer of about 30 mg/cm^2 was placed in an *in situ* FTIR quartz cell equipped with $CaCl_2$ windows and a built-in furnace. As a typical experiment the sample was thermally treated at 300 °C for 1 h under a reduced pressure of 10^{-5} Torr prior to admitting 5 Torr of pyridine at room temperature. The samples were evacuated at room temperature (RT), 100 and 150 °C and cooled before recording the spectra at RT. In each sample, the pyridine free spectrum was subtracted from the recorded spectra to evaluate the spectral changes due to pyridine adsorption.

The nitrogen adsorption isotherms were measured at −196 °C using a conventional volumetric apparatus. The specific surface area was obtained using the BET method. The surface texture characteristics were obtained from both the BET isotherm and the V_{1-t} plots.

2.3. The catalytic activity

The evaluation of the photoactivity was carried out in a cylindrical Pyrex glass reactor. A magnetic stirrer was used continuously to guarantee the good mixing of the solution. Irradiation experiments were performed using a 6 W medium pressure Hg lamp (254 nm). Unless otherwise stated, the reaction was carried out at room temperature under the conditions of 0.15 g/l of the solid catalyst in 100 ml solution of 50 ppm AG dye, 61.6 mmol/l of H_2O_2 and the pH of the solution was initially adjusted at 8. Generally, (0.1 M) HCl and (0.1 M) NaOH were used to adjust the pH value in the beginning of all experiments including the effect of pH study. The degradation of AG dye was analyzed by UV–vis spectrophotometer (JASCO V-570 unit, serial no. 29635) in the range of 190–800 nm. The degradation was determined at the wavelength of maximum absorption (622 nm). Calibration plots based on Beer-Lambert's law were established relating the absorbance to the dye concentration to determine the dye concentration during the reaction (C). In agreement with previous literature [14,15], the degradation of AG dye fitted with pseudo-first order kinetics [$\ln(C/C^0) = -kt$] (where C° and C are the initial dye concentration and its concentration at time t, respectively, and (k, min^{-1}), is the reaction rate constant). The rate constant, k, was calculated from the slopes of the straight-line portion of the plots [$\ln(C/C^0)$ vs. time].

3. Results and discussions

3.1. XRD and particles size analysis

The X-ray diffraction (XRD) patterns of Co–Z samples are shown in Fig. 1. The parent ZSM-5 showed a pattern similar to the crystalline structure reported in the X-ray data file [PDF # 79-2401]. The diffraction patterns of Co–Z samples proved that the structure of ZSM-5 was noticed in 2, 5 and 10 wt.% of Co-loading, except for a decrease of the peaks intensity. Beyond 10 wt.% of Co-loading, a great loss of zeolite crystallinity was noticed and no diffraction lines assigned to ZSM-5 structure were detected. The patterns demonstrated the disintegration of ZSM-5 structure with increasing Co-loading which was accompanied by the appearance of new lines at $2\theta = 21.0°$, 31.8°, 36.0°, 38.6° and 47.8° which are assigned to Co_3O_4 [PDF # 09-0418] and other lines at $2\theta = 29.3$, 42.4° and 56.7° which are characteristic of cobalt silicate (Co_2SiO_4) [PDF # 15-0865]. The data in Table 1 presented a marked decrease of crystallinity to ≈68, 24 and 12% for 2, 5 and 10Co–Z samples, respectively, with respect to parent ZSM-5. The addition of various amounts of