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Fe-exchanged zeolites as materials for catalytic wet peroxide oxidation. Degradation of *Rodamine G* dye

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ABSTRACT

The effect of surface acidity, nature, and dispersion of iron species, controlled by the catalyst preparation techniques and parent zeolite Si/Al ratio, on the catalytic wet peroxide oxidation of *Rodamine G* dye over the Fe-ZSM-5 materials has been studied.

Fe-ZSM-5 and Fe-USY have been prepared using two techniques: improved aqueous ion exchange (IE) and conventional aqueous ion exchange (CE). The former procedure causes some rearrangement of the coordination sphere of four-fold coordinated Al^{3+}, accompanied by formation of a small amount of octahedrally coordinated non-framework aluminium species. In case of Fe-ZSM-5(IE), iron is predominantly present in the form of well-dispersed Fe^{2+} ions, while Fe-ZSM-5(CE) and Fe-USY(CE) contain small aggregated oligonuclear $(FeO)_n$ clusters formed by Fe^{3+}. In both cases, iron species are mainly located inside the zeolite pore system. The contribution of the zeolite is a controlling factor in enhancing the *Rhodamine G* dye degradation activity of the Fe-ZSM-5 catalysts, which is influenced by the specific procedure used for preparation of these materials.

The catalytic wet peroxide oxidation (CWPO) behaviours of the materials prepared *via* the (IE) and (CE) procedures differ due to different nature of the iron species involved. The non-framework Al^{3+} species present in both the Fe-exchanged ZSM-5 and USY zeolites may participate in formation of the active sites responsible for CWPO of *Rhodamine G* dye over these catalysts.

At near ambient temperature (323 K), quasi-neutral pH (4.9), short reaction time (around 150 min), catalyst concentration of $1.0\,g\,L^{-1}$, and H_2O_2 addition rate of $41.2–82.3\,mmol\,h^{-1}$, the (IE)-prepared Fe-ZSM-5 catalyst enables the total degradation of the dye, accompanied by removal of *ca.* 80% of TOC without notable leaching of the Fe ions.

1. Introduction

Disposal of wastewater streams containing toxic pollutants has emerged as a topic of growing concern in the last decade [1]. Dyeing and finishing industry, which uses annually more than 9.5 million cubic meter of water per textile plant [2], is the source of considerable water consumption and contamination. This results in the discharge of large quantities of wastewater containing different dyes into the environment. Deep oxidation of these compounds in their aqueous solutions offers an opportunity of direct removal of these chemicals or transformation into non-toxic products to be eliminated by a biological treatment [2]. However, efficiency of the classical oxidation processes for removal from wastewater is still limited. For this reason, new advanced oxidation techniques, including the catalytic wet oxidation, are considered as quite promising. They use hydrogen peroxide for the dye degradation under ambient or near ambient conditions [2–4] to make the oxidation processes attractive for industrial application. Furthermore, H_2O_2 is widely applied as a pretreating reagent in dyeing. Evidently, this provides additional economical benefits for the application of H_2O_2 in the textile plants.

The Fenton's reagent ($Fe^{2+}/Fe^{3+}/H_2O_2$) [5,6] is one of the most common homogeneous oxidative catalytic systems, which is being utilised for discoloration and degradation of dyes [2,7]. However, this approach involves removal of the precipitated catalyst from the treated water, which significantly increases the overall costs of such processes. These drawbacks can be overcome using heterogeneous catalysts, among them recoverable and reusable iron-containing

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zeolites [2]. They can be prepared by impregnation, ion exchange, sublimation of a suitable iron precursor, and by steaming isomorphously Fe-substituted materials [8–11]. All these procedures affect catalytic properties of the resulting materials. For instance, we have recently shown that Fe-exchanged zeolites, when prepared using in situ obtained ferrous solution, are more active and selective catalysts for benzene hydroxylation to phenol than those prepared *via* the conventional ion exchange [12].

Herein, we report the catalytic performance of Fe-containing zeolites with different crystal and porous structures, Si/Al ratios, and iron loadings towards catalytic wet peroxide oxidation of *Rhodamine G* (cationic basic dye), along with their physicochemical characterisation. An attempt has also been made to evaluate the impact of the preparation procedure of the materials on their catalytic properties.

2. Experimental

2.1. Catalyst preparation

The cationic basic dye, *Rhodamine 6G* (~95%), was obtained from Sigma. The 35% hydrogen peroxide solution (pure grade) from Merck was used for CWPO.

Iron-containing samples were prepared from commercially available zeolites: NH_4-ZSM-5 (Si/Al ratio = 20, 40, 110, Akzo-Nobel), regular Y (Si/Al = 2.54, Akzo-Nobel), and ultrastable Y (USY). The latter zeolite was derived from NH_4-Y by steaming in an 100% steam atmosphere at 873 K for 4 h [13]. In order to remove extra-framework Al^{3+} species resulting from steaming, a portion of the USY sample was treated at 298 K four times with 0.1 M NH_4F for 10 min [14]. The solid was separated by centrifugation, thoroughly washed with deionised water, and dried at 383 K overnight.

The first-series catalysts were prepared by the improved ion exchange (IE) as described by Long and Yang [15]. According to this procedure, the Fe^{2+} ions formed in the reaction between metal iron and a dilute HCl solution replace cations in the zeolite ion-exchange sites. Typically, 2 g of zeolite was suspended at room temperature without stirring in a 200 ml aqueous solution of 0.1 M HCl, which contained also 0.73 g of iron powder (Fluka). The reaction mixture was kept at 298 K for 3 days in flowing Ar (20 ml min^{-1}), then the solid was recovered by filtration, washed with dry ethanol to preserve Fe^{2+} species, and vacuum-dried at 373 K. The catalysts were placed in the sealed containers and stored in desiccator.

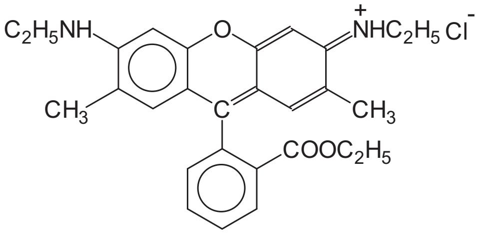
The second-series catalysts were prepared through the conventional ion exchange (CE), following the procedure by Neamtu et al. [2]. The zeolite samples were exchanged three times with an excess of 0.1 M $Fe(NO_3)_3$ for 6 h at 353 K, thoroughly washed with distilled water, recovered by filtration, and dried in an oven at 383 K overnight.

2.2. Catalyst characterisation

X-ray powder diffraction (XRD) patterns were acquired using a Rigaku diffractometer. Typically, an XRD pattern was recorded at the 2Θ range of 5–50° using CuK_α radiation (λ = 1.54178 Å) with the 1° (2Θ) scan per minute.

Infrared (IR) spectra of powdered samples were recorded between 1400 and 200 cm^{-1} at the optical resolution of *ca.* 3 cm^{-1} with a SPECORD M80 (Carl Zeiss Jena) and Perkin–Elmer 2000 spectrometers by the KBr technique (the sample concentration was about 1.5 wt.%; a pure KBr disc was utilised as reference).

UV–visible diffuse reflectance spectra (UV–VIS DRS) were recorded in air at room temperature at the 190–800 nm range using a Shimadzu UV 2401 spectrometer. $BaSO_4$ was used as reference.



Scheme 1.

Solid-state ^{27}Al magic-angle spinning NMR spectra were acquired using a Bruker DMX spectrometer. The instrument was equipped with a 4-mm MAS probe head and the sample rotation speed was 12.5 kHz at the magnetic field of 11.7 T. The Al resonance frequency at this field is 130 MHz. ^{27}Al chemical shifts were referenced to a saturated $Al(NO_3)_3$ solution and reported in ppm.

Nitrogen adsorption at 77 K was carried out in a Micromeritics ASAP 2000 apparatus. Prior to the adsorption, samples were evacuated at 623 K for 16 h.

2.3. Catalytic degradation of dye

Catalytic wet hydrogen peroxide oxidation of *Rodamine G* (see Scheme 1) was performed under isothermal conditions using a temperature-controlled glass reactor with a stirrer. The pH value of the reaction medium, measured with a pH-meter I-160 M (Belarus), was corrected for some experiments by adding small amounts of a diluted HNO_3 solution (pH 3.0) or aqueous ammonia (pH 6.0). 100 mg of a catalyst was introduced into 100 ml of an aqueous dye solution (100 mg L^{-1}), under continuous stirring, 15 min before the beginning of H_2O_2 (30%) addition. The concentration of *Rhodamine* G in the solution was analysed in order to check possible dye adsorption by the catalysts. This test confirms the absence of noticeable adsorption at the initial stage of the experiments. Hydrogen peroxide was added continuously using a peristaltic pump at a constant flow rate of 2 ml h^{-1}. To maintain the amount of dissolved oxygen in the solution close to the saturation [4], the reaction was performed under the flow (1.5 L h^{-1}) of air bubbling directly through the reaction mixture.

A homogeneous Fenton catalyst was tested in a similar way by adding $Fe(NO_3)_3$ to the dye solution. The amount of iron in this test was equivalent to its maximum content in the 1 g of Fe-exchanged zeolites (0.30 mmol Fe^{3+}).

2.4. Analyses

Visible light absorbance at the wavelength characteristic of the reaction solution, *viz.* 540 nm, was recorded at regular intervals using a photocolorimeter KFK-3 (Zelenograd Optical Factory, Russia) to follow the progress of the dye discoloration. The content of TOC (total organic carbon) was measured using a Shimadzu 5050 TOC analyser. Before the determination of TOC, the reaction was stopped by increasing pH to 9–10 and adding a 10% Na_2SO_3 aqueous solution. The TOC abatement was found to be negligible in the absence of the catalyst and/or without addition of H_2O_2. Residual hydrogen peroxide was determined using the potassium iodide titration method [16].

The iron content in the catalysts and its quantity leached out after the oxidation reaction were determined by AAS (atomic absorption spectroscopy) and ICP-AES (inductively coupled plasma-atomic emission spectroscopy, Agilent Technologiestechniques). Ion-exchange chromatography, performed on a Tsvet 3006 (Russia) instrument equipped with an HIKS-1 column and operating in the suppressed conductivity detection mode, was used for the anion analysis. All the analyses were made in duplicate.