Ibuprofen photodegradation under visible light promoted by Fe-doped nano CeO_2

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Significance and Relevance

The main novelty of the paper was the synthesis of an active catalyst for ibuprofen photodegradation under visible light irradiation. Reverse micelle synthesis fosters Fe doping of nanocrystalline CeO_2. From the synthesis, it was revealed that 2.5 mol % iron-doped ceria leads to high charge delocalization. Testing the synthesized catalysts, it was revealed that efficient visible-light photodegradation of ibuprofen was promoted using 2.5 mol % Fe-CeO_2. It was demonstrated that substitutional Fe favours the oxygen vacancies formation and ibuprofen adsorption.

Preferred and 2nd choice for the topic: Water treatment, Photocatalysis and photoelectrocatalytic approaches, solar energy utilization.
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Introduction and Motivations

Reverse micelle nanoreactors were successfully designed to synthesize small-sized ceria nanocrystals (3.5–4.2 nm) with a sizeable amount of substitutional iron. Undoped and doped CeO_2 catalysts with an iron content (0.50–10 mol %) compliant with the nominal value were prepared and tested for the first time for the removal of ibuprofen both in the dark and under UV or visible light irradiation. The effective inclusion and distribution of iron in the ceria lattice were ascertained through in-depth physicochemical characterization. In particular, X-ray diffraction suggested the formation of an F-type crystal structure, ruling out the formation of separate iron-containing crystalline phases. On the other hand, substitutional doping of CeO_2 with Fe atoms favoured the formation of Ce^{3+} defects and vacancy sites (VOs) with a maximum for the sample with 2.5 mol % iron (Fe2.5), as evidenced by X-ray photoelectron spectroscopy (XPS) measurements and Raman spectroscopy. UV–Vis spectroscopy showed that the optical properties were successfully modified by the presence of iron, which causes a gradual decrease in band gap as iron content increases. Nevertheless, it was found under dark conditions that adsorption capacity does not monotonically increase with iron content, revealing contrasting roles of surface characteristics. Indeed, catalytic experiments have identified a trade-off between adsorption and photodegradation, identifying Fe2.5 as the best-performing catalyst for ibuprofen removal under visible light irradiation. These results were discussed by considering the key properties of the catalysts as well as their different surface charge determined by ζ potential measurements. The best catalyst was tested through reuse experiments that proved its stability over 4 cycles.

Materials and Methods

In a typical synthesis, adapted from the literature[1], the oil/surfactant phase is prepared by dissolving 8.2 g of surfactant (Brij C10) in 100 mL of cyclohexane under stirring at room temperature. An aqueous solution is prepared by dissolving the proper amount of cerium and iron precursors in distillate water to achieve a final concentration of 0.5 M. The volume of the aqueous precursor solution has been selected to obtain a w0 value of 25 (w0 is defined as the water-surfactant molar ratio). The aqueous solution is slowly added dropwise to the oil phase to obtain appropriate water-in-oil (w/o) micelles. The optimized protocol involves alternating the additions of water and the co-surfactant. Finally, 5.4 mL of precipitating agent, ammonia solution, are slowly dripped. The mixture is stirred for 1.5 h at room temperature. The dried powder has been manually ground before being calcinated at

120 °C for 6 h. The amounts of cerium and iron were calculated to obtain a nominal composition expressed as a molar % of iron equal to 0 mol % (CeO_2), 0.5 mol % (Fe0.5), 2.5 mol % (Fe2.5), 5 mol% (Fe5) and 10 mol % (Fe10). The photodegradation experiments were conducted in a 1.5 L jacketed glass vessel, closed with a three-neck lid. The reactions were carried out using a co-axial lamp, connected to the reactor through the central neck of the lid. In particular, two different lamps were used: a lamp irradiating in the visible region (Sylvania T5, with a power of 4 W and a color temperature of 6500 K, solar emission spectrum, potential difference 220 V, and geometry 14 cm x 1.5 cm), or a lamp irradiating in the UV region (Toshiba FL4BLB, with a power of 4 W and emission at a wavelength of 365 nm, potential difference 220 V, and geometry 15 cm x 1.5 cm). ne neck of the lid was left free for collecting samples during the reaction, while the last neck is used for measuring the solution temperature through a dedicated thermocouple. The reaction temperature was controlled using an ultra-thermostat while the dispersion agitation was ensured by magnetic stirring. The airflow rate was set through an electronic gas flowmeter regulator (supplied by Bronkhorst).

Results and Discussion

Adsorption and photodegradation tests were conducted to investigate the performance of each synthesized catalyst. An attempt was made to justify the adsorption efficiency with the main properties of the catalysts. Except for the Fe10 sample, we do not observe any significant difference in terms of SSA and pore size. These findings lead us to speculate that the adsorption behaviour of IBU, except for Fe10, should not be determined by textural properties but could reflect differences in surface charge. For this reason, the ζ -potential values at the pH of ibuprofen solution (pH = 4.6), extrapolated from the ζ -potential curves, were plotted vs the maximum adsorption capacity (q_t=($C_{IBU,0}$-C_{IBU})/ρ_B), measured in dedicated experiments (Fig. 1A).

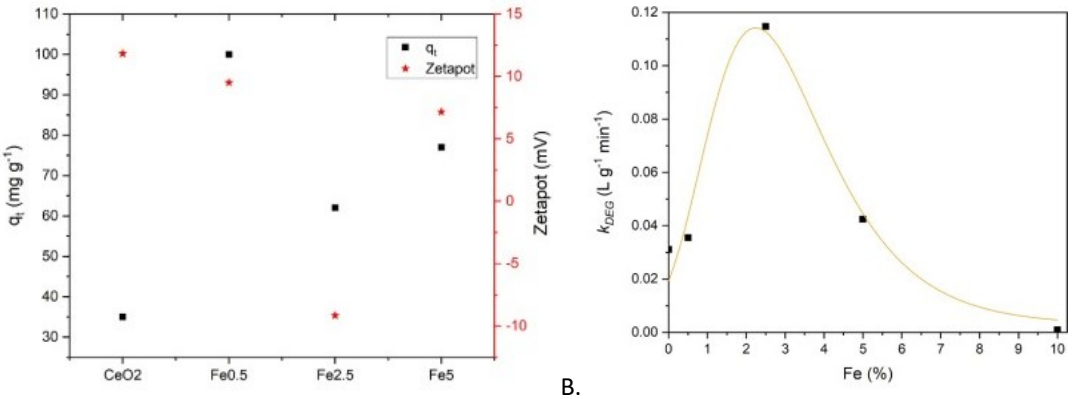

Figure 1 A. Potential (ζ) of the pristine and Fe-doped CeO_2 vs the adsorption capacity. b) Trend of the adsorption equilibrium constant. The present experimental conditions were adopted for each experiment: T = 30 °C, $C_{IBU,0}$ = 12.4 mg/L, ρ_B = 0.07 g/L, reaction time of 300 min. B. Plot of the degradation constant as a function of Fe loading.

The photodegradation experiments were conducted either in the presence of visible irradiation. The performance of the catalysts under visible irradiation is indeed promising for a scale-up process, considering the low lamp power and the used dosage of the catalysts. Fig. 1B clearly illustrates that Fe2.5 is the best performing photocatalyst as it shows the highest degradation constant.

In conclusion, meticulous synthesis strategies for the preparation of robust and efficient photocatalysts allowed an efficient removal of ibuprofen (an emerging contaminant) from waters, using visible light-activated photocatalytic processes.

References

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