

Catalytic activity of CeO₂@TiO₂ for environmental protection

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Synthesis

The Ce(NO₃)₃·6H₂O and TiCl₄ (99.99%, Acros Organics) compounds were used as initial salts. All chemicals were purchased and used without further purification. Appropriate amount of cerium was dissolved in 500 mL distilled water containing of nitric acid (pH=2) to give total concentrations of metals of 0.04 M. After dissolution, polyvinylpyrrolidone (PVP 35000) was added (the proportion of PVP was 1 wt.% of the total mass of the mixture) and stirring was continued. Then, the co-precipitation was carried out by addition of aqueous ammonia at 30°C under stirring to reach pH 11. Ultrasonic processing (10 min, 35 kHz, 150 W, Sapphire UZV-4.0) was used during dissolution of salts in distilled water and after precipitation. The resulting precipitates were filtered, washed with distilled water-ethanol solution (H₂O/C₂H₅OH=9 vol.), dried at 150°C for 12 h, and calcined in static air by heating at a rate of 4°C/min from room temperature to 500°C and kept at 500°C for 1 h in a muffle furnace. The obtained ceria powder was further used as the core.

The synthesis of the core-shell structure was carried out as follows. First solution: PVP was dissolved in water, then ceria powder was sprinkled there and stirring was continued (at 30°C with ultrasonic treatment). Second solution: titanium chloride was dissolved in isopropanol under the same preparation conditions as the first solution. Next, the second solution was added to the first solution, stirring was continued for 5 h at 30°C (without ultrasonic treatment; the proportion of PVP was 1 wt.% of the total mass of the mixture), then the temperature was raised to 80°C, evaporating until a gel formed. Drying and calcination were carried out similarly to obtaining the ceria core. The content of titania (and hence the calculation of the initial titanium chloride) was chosen from the following considerations: since the particle size of ceria is about 15 nm, conventionally titania should have a shell nominal thickness of 0.5, 1, 2, 3, and 5 nm. For the calculation, the density of ceria (7.21 g/cm³) and titania (3.81 g/cm³, anatase phase, since at 500°C it is this phase that is generally formed) was chosen.

Table S1. Elemental analysis of the catalyst 1-Fe.

	Before, mg/kg	After, mg/kg	before/after, wt. %
Ce	660900	668100	CeO ₂ 81.2/82.1
Fe	20763	15649	Fe _x O _y 5.6/5.7 or Fe~4.1%
Ti	79000	73000	TiO ₂ 13.2/12.2

Table S2. Elemental analysis of the solution after methylene blue degradation of catalyst 1-Fe.

Cycle	Washing out the element, mg/l			Washing out the element, %		
	Ce	Ti	Fe	Ce	Ti	Fe
1	3.935	0.218	2.503	0.6	0.4	2.5
2	2.715	0.492	1.982	0.4	0.9	2.0
3	1.857	1.016	1.859	0.3	1.8	1.9
4	2.019	1.073	1.487	0.3	2.0	1.5

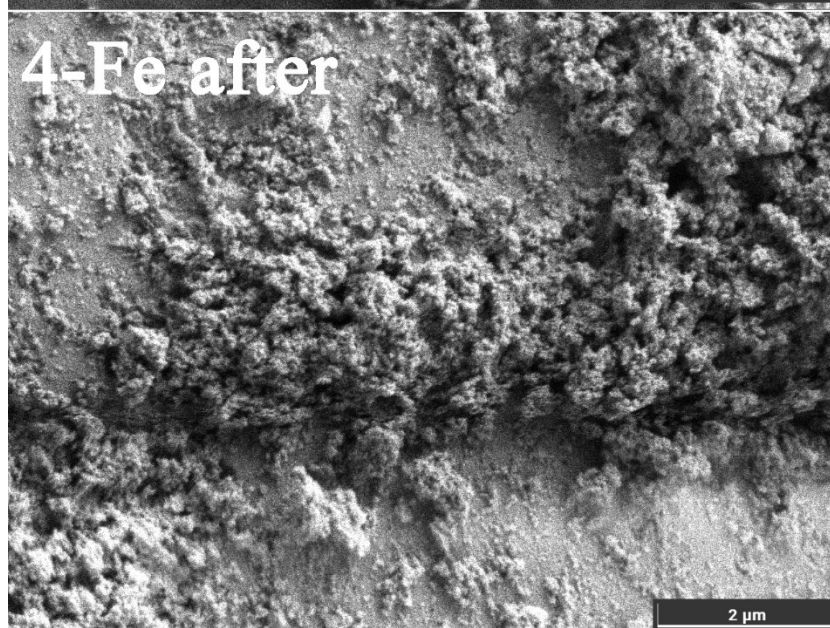
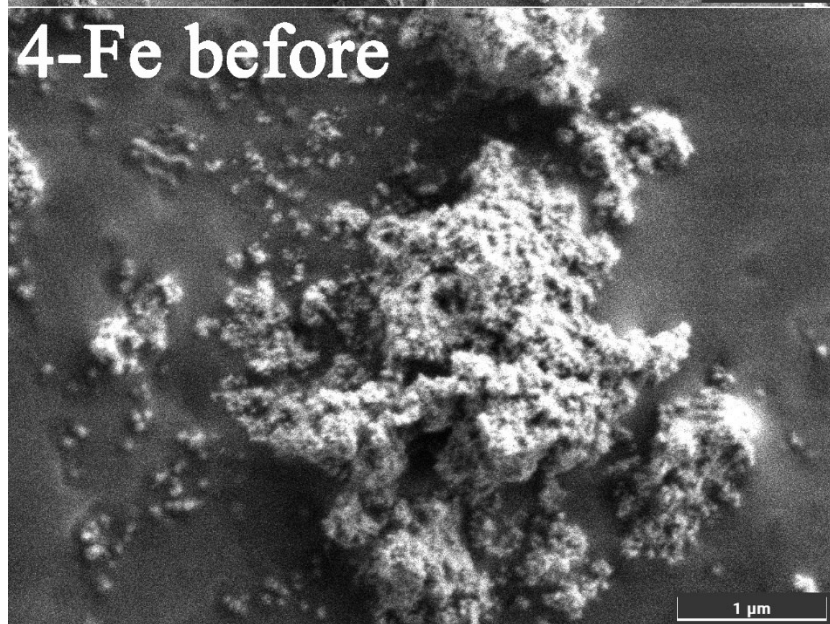
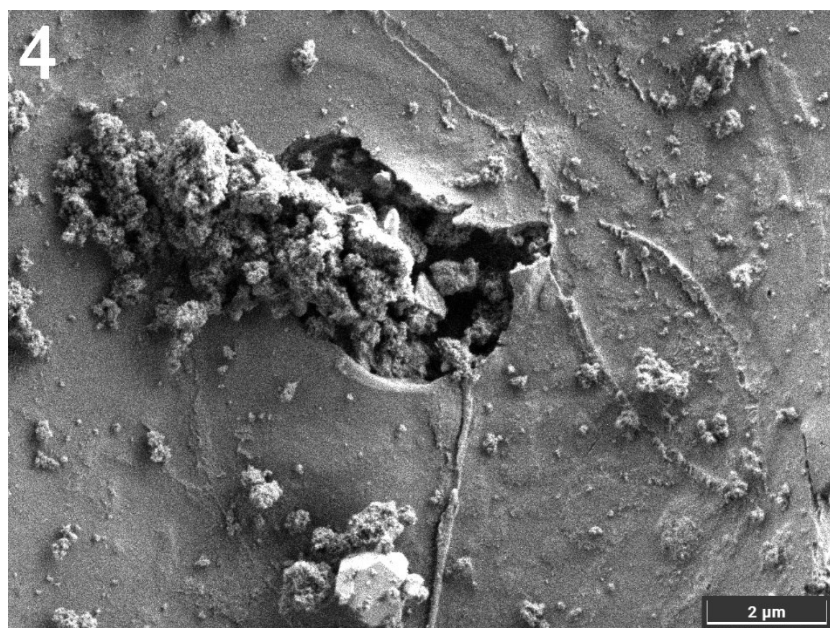


Figure S1. SEM microphotous of catalysts.

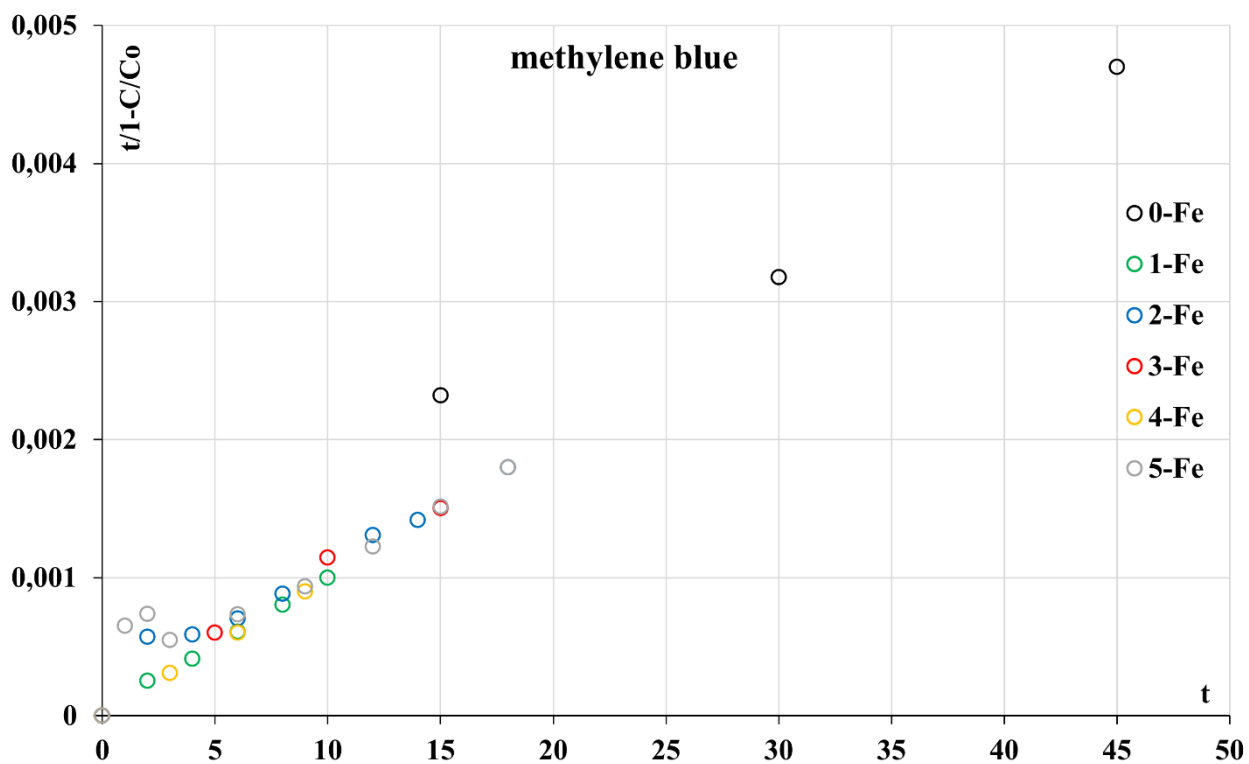


Figure S2. Linear fitting curve of the Behnajady-Modirshahla-Ghanbary kinetic model of methylene blue degradation.

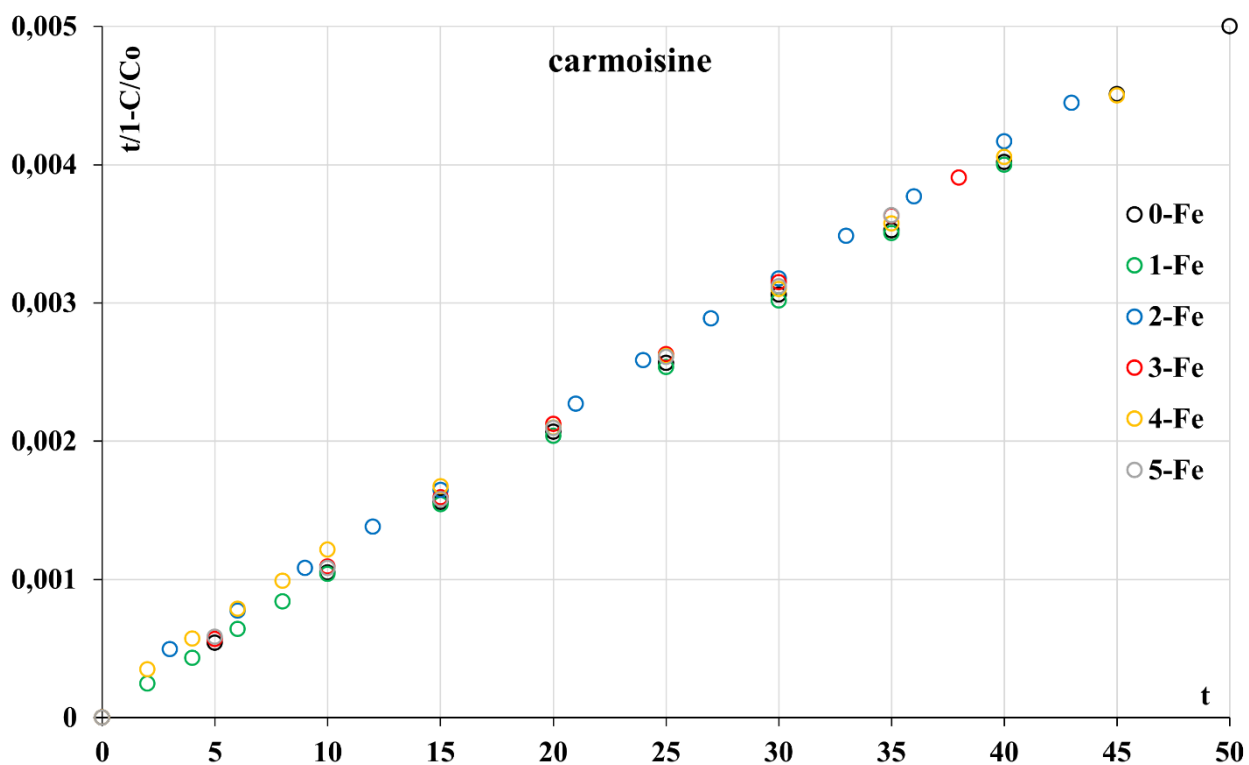


Figure S3. Linear fitting curve of the Behnajady-Modirshahla-Ghanbary kinetic model of carmoisine degradation.