

Highly Hydrophilic Ti–Beta Zeolite with Ti–Rich Exterior as Efficient Catalyst for Cyclohexene Epoxidation

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Abstract: Nanocrystalline Ti–Beta zeolite with high hydrophilicity and a Ti-rich exterior was successfully prepared via a dissolution–recrystallization method. With the post-treatment of tetraethylammonium hydroxide (TEAOH) solution at elevated temperature, the Si and Ti species within the Ti–Beta matrix were partially dissolved and recrystallized on the outer surface of crystals, resulting in the Ti-rich exterior and higher hydrophilicity, which improved the accessibility of the active Ti sites and the enrichment of H₂O₂. Simultaneously, some of the closed Ti(OSi)₄ species were transformed to more active open Ti(OSi)₃OH or Ti(OSi)₂(H₂O)₂(OH)₂ species. The modified Ti–Beta zeolite exhibited greatly enhanced catalytic performance in the epoxidation of cyclohexene in comparison to the parent Ti–Beta.

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Keywords: Ti–Beta; Ti-rich exterior; hydrophilicity; cyclohexene epoxidation

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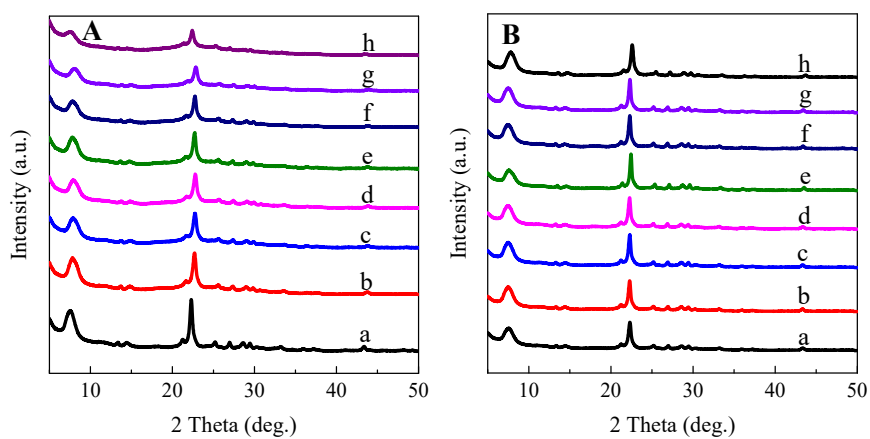


Figure S1. XRD patterns of Re-Ti-Beta-0.04 (A) and Re-Ti-Beta-0.20 (B) postsynthesized for a different crystallization time of 0 h (a), 1 h (b), 4 h (c), 8 h (d), 12 h (e), 16 h (f), 20 h (g), 24 h (h).

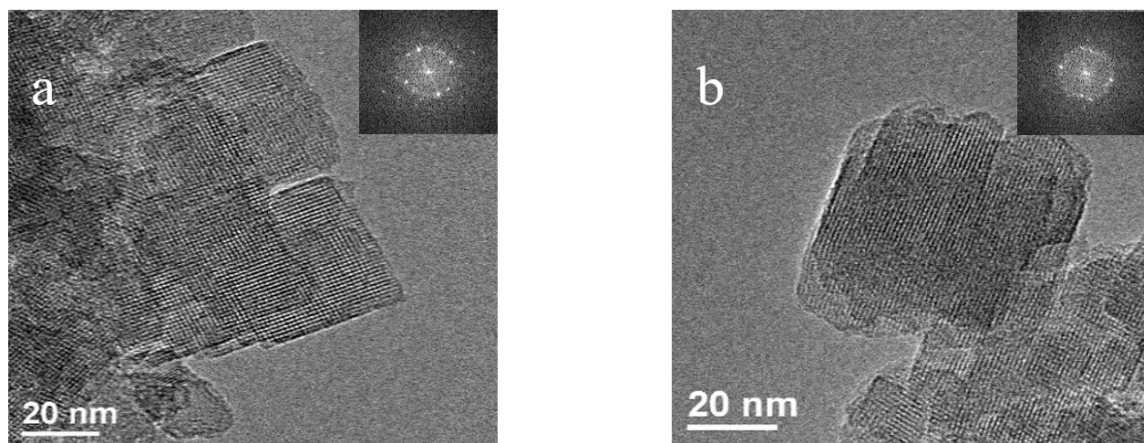


Figure S2. The TEM images of pristine Ti-Beta (a) and Re-Ti-Beta-0.20 (b).

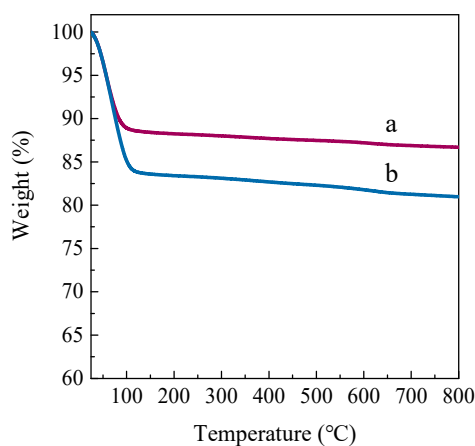


Figure S3. TG curves of Ti-Beta (a) and Re-Ti-Beta-0.20 (b) after adsorption of water vapor provided by saturated NH_4Cl solution at 293 K for 24 h.

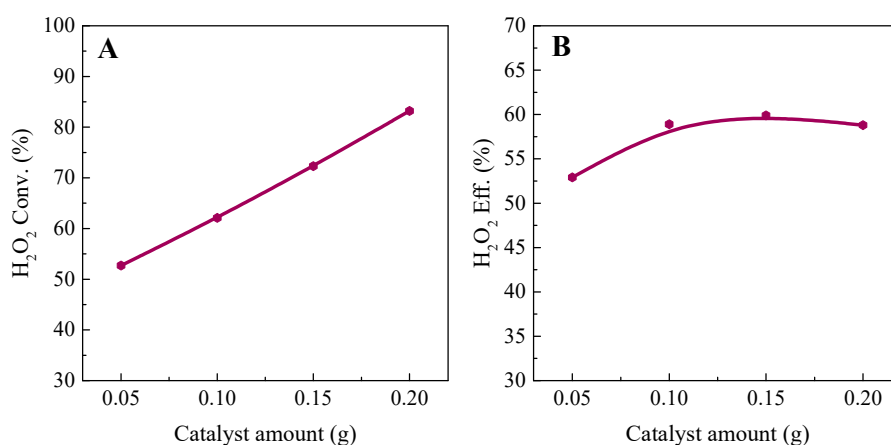


Figure S4. Dependence of H_2O_2 conversion (A) and H_2O_2 efficiency (B) on the amount of Re-Ti-Beta-0.20. Reaction conditions: CHE, 10 mmol; H_2O_2 (30 wt.%), 10 mmol; MeCN, 10 mL; temp., 333 K; time, 2 h.

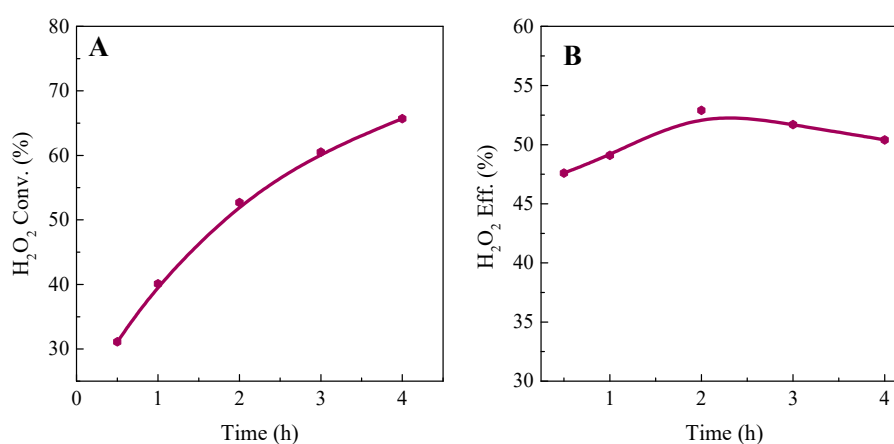


Figure S5. Dependence of H_2O_2 conversion (A) and H_2O_2 efficiency (B) on the reaction time over Re-Ti-Beta-0.20. Reaction conditions: catalyst, 50 mg; CHE, 10 mmol; H_2O_2 (30 wt.%), 10 mmol; MeCN, 10 mL; temp., 333 K.

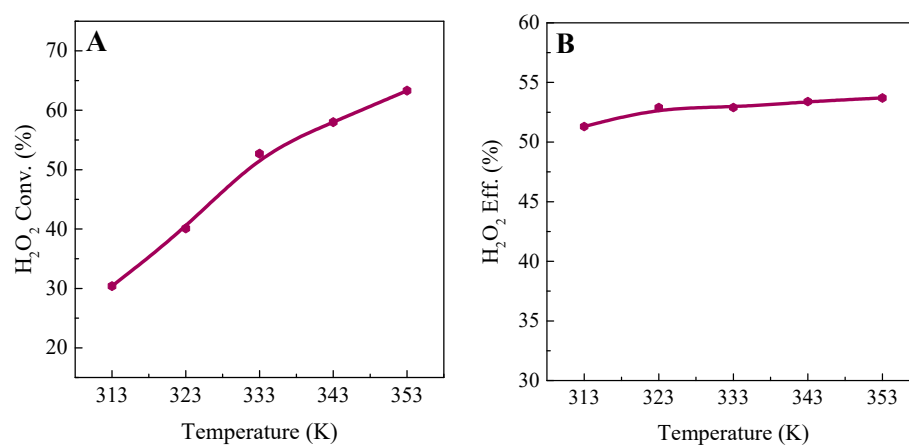


Figure S6. Dependence of H₂O₂ conversion (**A**) and H₂O₂ efficiency (**B**) at different reaction temperatures over Re-Ti-Beta-0.20. Reaction conditions: catalyst, 50 mg; CHE, 10 mmol; H₂O₂ (30 wt.%), 10 mmol; MeCN, 10 mL; time, 2 h.

Table S1. The average values of reaction rate constants (k) at different reaction temperatures of Ti-Beta and Re-Ti-Beta-0.20 in cyclohexene epoxidation.

Sample	Reaction rate constant (k) 10 ⁻⁵ (s ⁻¹)				apparent activation energies (Ea) (kJ mol ⁻¹)
	313 K	323 K	333 K	343 K	
Ti-Beta	2.17	3.75	5.57	7.80	35.35
Re-Ti-Beta-0.20	5.80	10.66	14.20	18.83	31.72