

Nano-flowered Ce@MOR hybrids with modulated acid properties for the vapor-phase dehydration of 1,3-butanediol into butadiene

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Abstract: A series of Ce@MOR hybrids based on CeO_x nanoparticles (1-2.5 nm) encapsulated in mordenite and exhibiting a genuine flower-like morphology were prepared by simple hydrothermal synthesis. The cerium content in the catalysts could be easily tuned by adjusting the Si : Al : Ce composition in the preformed gel, affecting the textural properties and the density of acid sites of the catalysts. The genesis of acid sites with medium strength induced by encapsulated CeO_x nanoparticles was directly correlated to the catalytic activity for the vapor-phase dehydration of 1,3-butanediol into butadiene.¹

Keywords: ceria, zeolite, acid modulator, dehydration, 1,3-butadiene, 1,3-butanediol

1. Introduction

1,3-Butadiene (BD) is a relevant industrial intermediate used for the production of synthetic rubbers and resins. Current BD production processes rely on naphtha cracking and on the catalytic oxidative dehydrogenation of *n*-butane and *n*-butene, which are all non-sustainable feedstocks. Butanediols (BDO) appear as competitive biobased substrates that can be derived from sugars and glycerol by fermentation. The dehydration of BDOs can lead to different products depending on the starting diol and on the catalyst used. In particular, BD was obtained at yields up to 60% at 473-573 K upon 1,3-BDO dehydration over HZSM-5 and Al-SBA enriched with Brønsted acid sites with medium strength.^{2,3} Herein, we report the preparation of a series of hybrids based on encapsulated CeO_x nanoparticles in MOR. The hybrids were denoted as Ce@MOR_X, while Ce-impregnated catalysts were denoted as Ce-MOR_X(IWI) (X = Si/Ce ratio). The different catalysts were tested in the vapor-phase dehydration reaction of 1,3-BDO to BD.

2. Experimental

The Ce@MOR_X hybrids were synthesized by one-pot hydrothermal synthesis at 453 K for 20 h using a pre-formed gel with a Si : Al : Ce atomic ratio of 1 : 0.08-0.11 : 0.005-0.05. In a typical synthesis, an aqueous solution of the Ce and Al precursors was prepared by dissolving 0.53 g of Ce(NO₃)₃ and 1.82 g of Al(NO₃)₃ in 5.5 mL of deionized water containing 0.64 M H₂SO₄ (pH = 0.19). A second aqueous solution was prepared by dissolving 12.5 g of sodium silicate in 10 mL of deionized water (pH=9-10) A third aqueous solution was prepared by dissolving 5.3 g of Na₂CO₃ in 34 mL of deionized water. The first and second solutions were added dropwise to the third solution and the as-formed gel was vigorously stirred for 2 h at room temperature. Then, the gel was sealed in a Teflon[®]-lined autoclave and subjected to hydrothermal synthesis at 180 °C for 20 h. The resulting white solid powder was filtered, washed with deionized water, activated, and calcined at 450 °C for 4 h under static air.

The Ce-MOR_X(IWI) catalysts were prepared by the IWI method on MOR previously synthesized by one-pot hydrothermal synthesis at 180 °C for 20 h using a pre-formed gel with a Si : Al molar composition of 1: 1. The as-synthesized MOR was soaked over aqueous solution of Ce(NO₃)₃ with a volume equaling the pore volume of MOR. After Ce-impregnation, the samples were calcined at 450 °C for 4 h under static air.

3. Results and discussion

The catalysts were further tested in the dehydration of 1,3-BDO to BD (Figure 1). The post-synthesized Ce-MOR₂₀₀(IWI) exhibited almost no change in both the 1,3-BDO conversion and the BD selectivity

compared to the parent MOR, the latter remaining at a value lower than 14%. Ce-MOR_50(IWI) displayed an increase in the conversion to a value >60%, but the BD selectivity remained almost unchanged. In contrast, the Ce@MOR_X hybrids exhibited a positive effect on both the conversion and the BD selectivity. Indeed, the BD selectivity reached a value up to 46% for Ce@MOR_50 at almost full conversion. The different Ce@MOR_X hybrids exhibited a stable performance during 8 h on stream.

The Ce@MOR_X hybrids exhibited a genuine flower-like morphology with a homogeneous distribution of CeO_x nanoparticles (1-2.5 nm) encapsulated in the zeolite framework (Figure 2A,B). This morphology contrasts with Ce-impregnated catalysts with CeO₂ nanoparticles mainly located at the external MOR surface. The acid loading in the hybrids decreased after Ce-incorporation, as confirmed by NH₃-TPD and ²⁹Si-MAS-NMR. The ratio of medium over strong acid sites increased from 0.73 for the parent MOR to >4.0 for Ce@MOR_50 (Figure 1C), as inferred from NH₃-TPD after deconvolution, while the Ce-impregnated catalysts displayed lower ratios (<2.5).

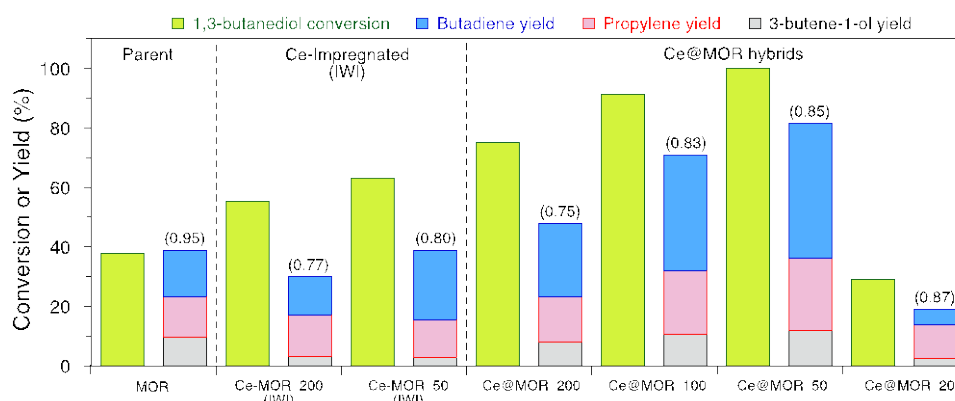


Figure 1. 1,3-BDO conversion and yield to main products over different Ce-modified H-MOR catalysts. Conditions: 300 °C, time on stream, 8 h; catalyst loading, 200 mg; 1,3-BDO flowrate, 2.8 mL/h; carrier N₂ flowrate, 60 mL(STP)/min; ambient pressure.

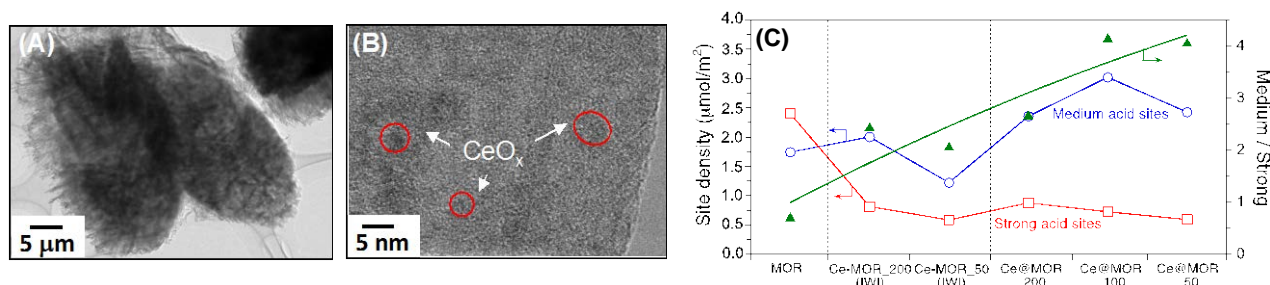


Figure 2. (A-B) SEM and TEM micrographs of Ce@MOR_50 (Si/Ce=50); (C) Density of medium and strong acid sites and corresponding ratio for Ce@MOR_X, virgin MOR and post-synthesized Ce-MOR_X(IWI).

4. Conclusions

Ce@MOR_X hybrids based on CeO_x nanoparticles encapsulated in mordenite and exhibiting a flower-like morphology were prepared by one-pot hydrothermal synthesis. The textural properties and density of acid sites of the hybrids could be simply tuned by adjusting the cerium content of the synthesis gel. The genesis of acid sites with medium strength was directly correlated to the catalytic activity for the vapor phase dehydration of 1,3-butanediol into butadiene. Ce@MOR_50 displayed a superior activity and selectivity compared to the parent mordenite and Ce-impregnated MOR due to a higher density of acid sites with medium strength induced by encapsulated CeO_x nanoparticles.

References

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