

Ultrathin mesoporous NiCo₂O₄ nanosheets as efficient and reusable catalyst for benzylic oxidation

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NiCo₂O₄ nanorods was synthesized according to previous research^{S1}. In a typical procedure, Ni(NO₃)₂·6H₂O (0.44 g, 1.5 mmol), Co(NO₃)₂·6H₂O (0.87 g, 3.0 mmol) and urea (3.24 g, 54 mmol) were dissolved in a mixture solution of distilled water (20 ml) and ethylene glycol (40 ml) to form a clear pink solution. Then, the solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and kept at 110 °C for 16 h. After cooling down, the product was washed with water and ethanol several times, and dried at 50 °C for 12 h. The crystalline NiCo₂O₄ nanorods were obtained after annealing at 300 °C for 3 h. The typical morphology of NiCo₂O₄ nanorods was shown in Fig. S1. The NiCo₂O₄ nanorods are well dispersed with a diameter around 50 nm and a length extended to several hundred nanometers.

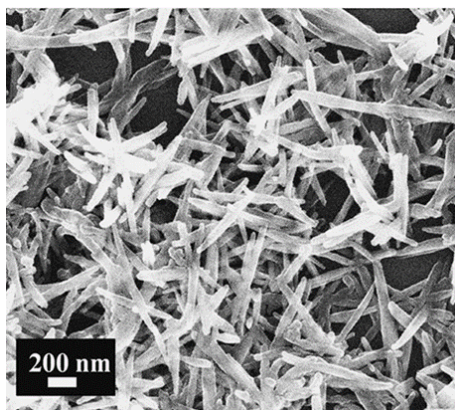


Fig. S1. SEM image of NiCo₂O₄ nanorods.

The Ni 2p spectrum (Fig. S2 a) is composed of two spin-orbit doublets and two shake-up satellites (identified as “Sat.”). Two kinds of nickel species have been detected and assigned to Ni²⁺ and Ni³⁺. Specifically, the fitting peaks at 854.1 and 871.9 eV are ascribed to Ni²⁺, while the peaks at 855.8 and 873.6 eV are assigned to Ni³⁺. The Co 2p spectrum (Fig. S2 b) is composed of two spin-orbit doublets characteristic of Co²⁺ and Co³⁺, including Co²⁺ at 780.8 and 795.8 eV, and Co³⁺ at 779.4 and 794.7 eV. The O 1s spectrum (Fig. S2 c) shows four oxygen contributions, denoted as O₁, O₂, O₃ and O₄, respectively. O₁ at 529.4 eV is associated with typical metal-oxygen bonds. O₂ (529.9 eV), O₃ (531.2 eV) and O₄ (532.6 eV) correspond to the oxygen in hydroxyl groups, the high number of defect sites with low oxygen coordination in the material with small particle size, the multiplicity of physi/chemisorbed water at and within the surface, respectively. These results show that the NiCo₂O₄ nanosheets contain Co²⁺, Co³⁺, Ni²⁺ and Ni³⁺ species, which is in well agreement with the results of literatures.^{S2,S3,S4}

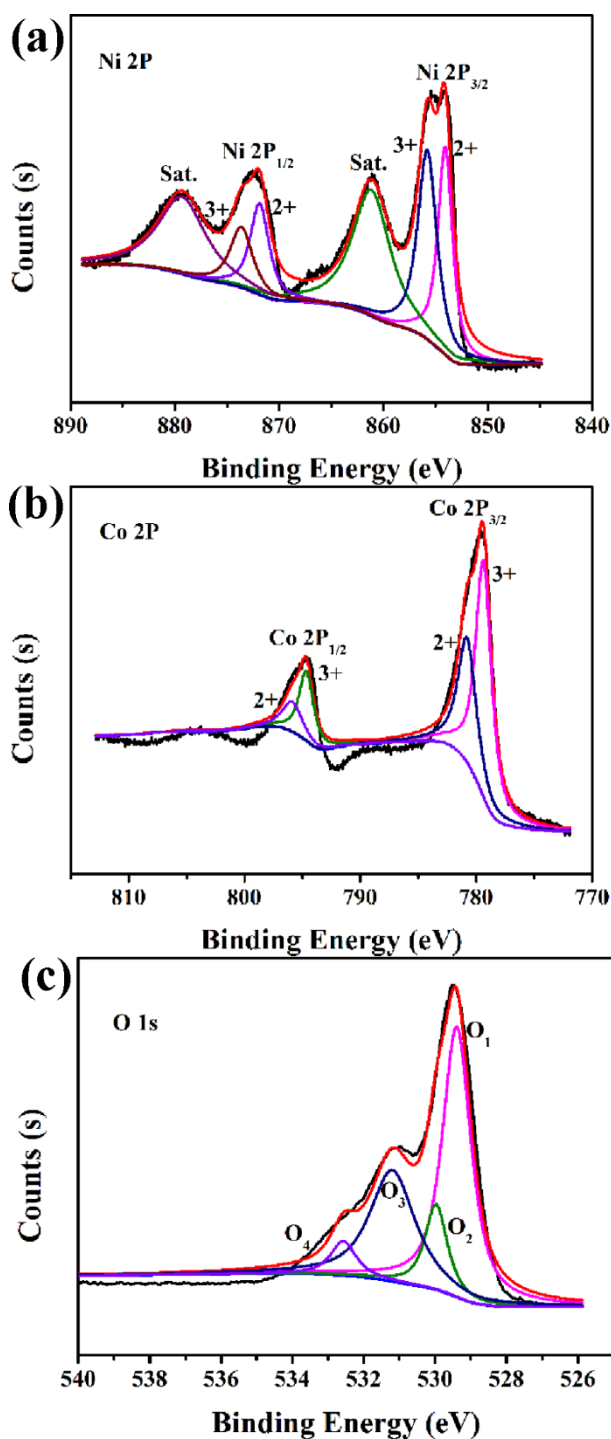


Fig. S2. XPS patterns of the NiCo₂O₄ nanosheets: a) the Ni 2p core levels; b) the Co 2p core levels and c) O 1s core level.

The fresh and recovered catalysts after reaction have been characterized by XRD, FTIR and SEM (Fig. S3). The powder XRD curves of the fresh and recovered catalyst (Fig. S3 a) reveal that the nanosheets remain spinel phases after catalytic reaction. FTIR spectra (Fig. S3 b) of the fresh and recovered catalyst show the same peaks. SEM images (Fig. S3 c) of the

recovered catalyst show that the assembled structure of the nanosheets is slightly collapsed, which possibly result in the slightly decreasing of the conversion and selectivity for the oxidation of 4,4'-difluorodiphenylmethane during the cycling experiment.

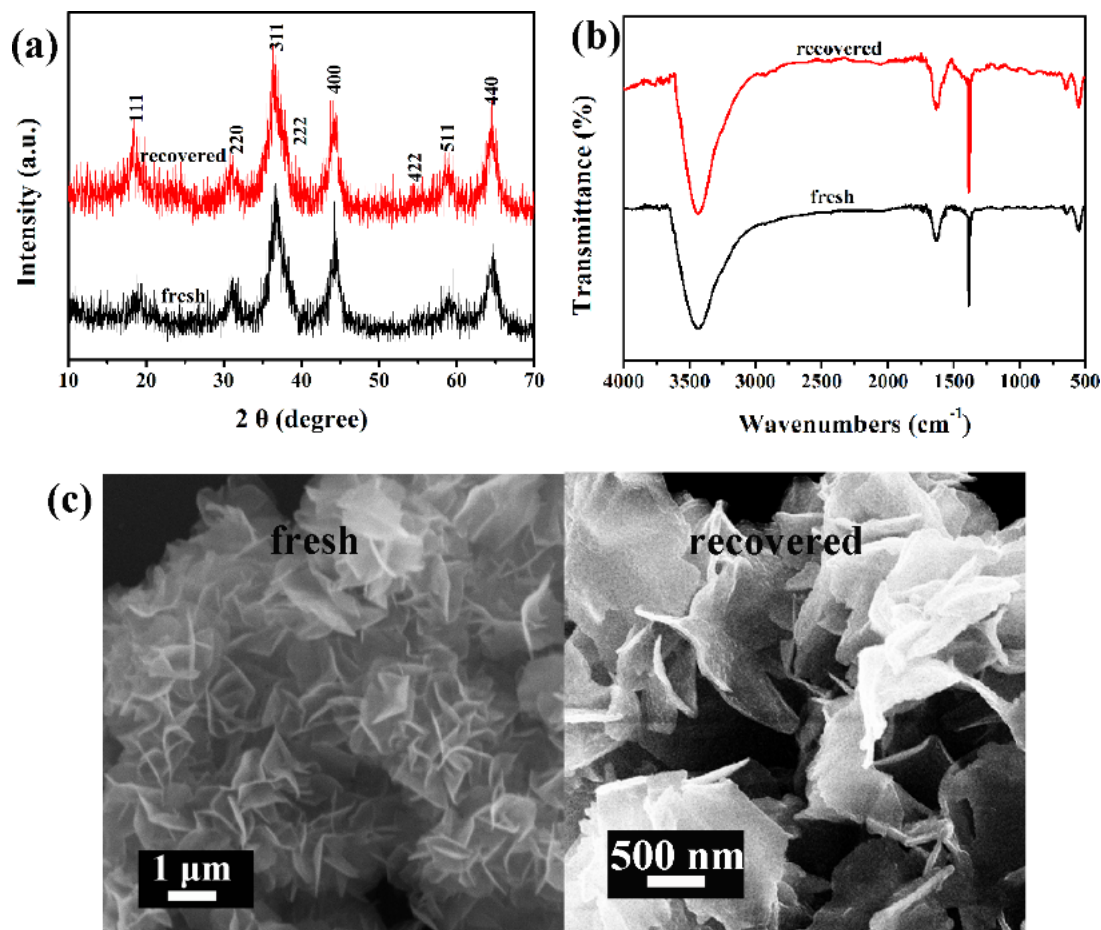


Fig. S3. (a) XRD pattern (b) FTIR spectra and (c) SEM images of the fresh and recovered NiCo_2O_4 nanosheets.

In order to investigate the change of NiCo_2O_4 nanosheets in benzylic oxidation, XPS spectra of the fresh and recovered NiCo_2O_4 nanosheets are provided (Fig. S4). The spectrum of Ni 2p has a shift toward high energy with the concomitant a low energy shift of O1s spectrum, indicating an increasing of Ni^{3+} moiety and oxygen-metal bonds. It may be because the benzylic oxidation proceeds rapidly in the presence of Ni^{2+} and produce more Ni^{3+} during the formation of $t\text{-BuO}\cdot$ radical.⁵⁵ The spectrum of Co 2p has no obvious change after reaction, which indicates the Co^{3+} and Co^{2+} moiety has a dynamic balance state during reaction. Therefore, the deactivation of NiCo_2O_4 nanosheets in benzylic oxidation might be attributed to the changes of oxidation state catalytically active sites, as well as the slightly collapsed of

assembled structure.

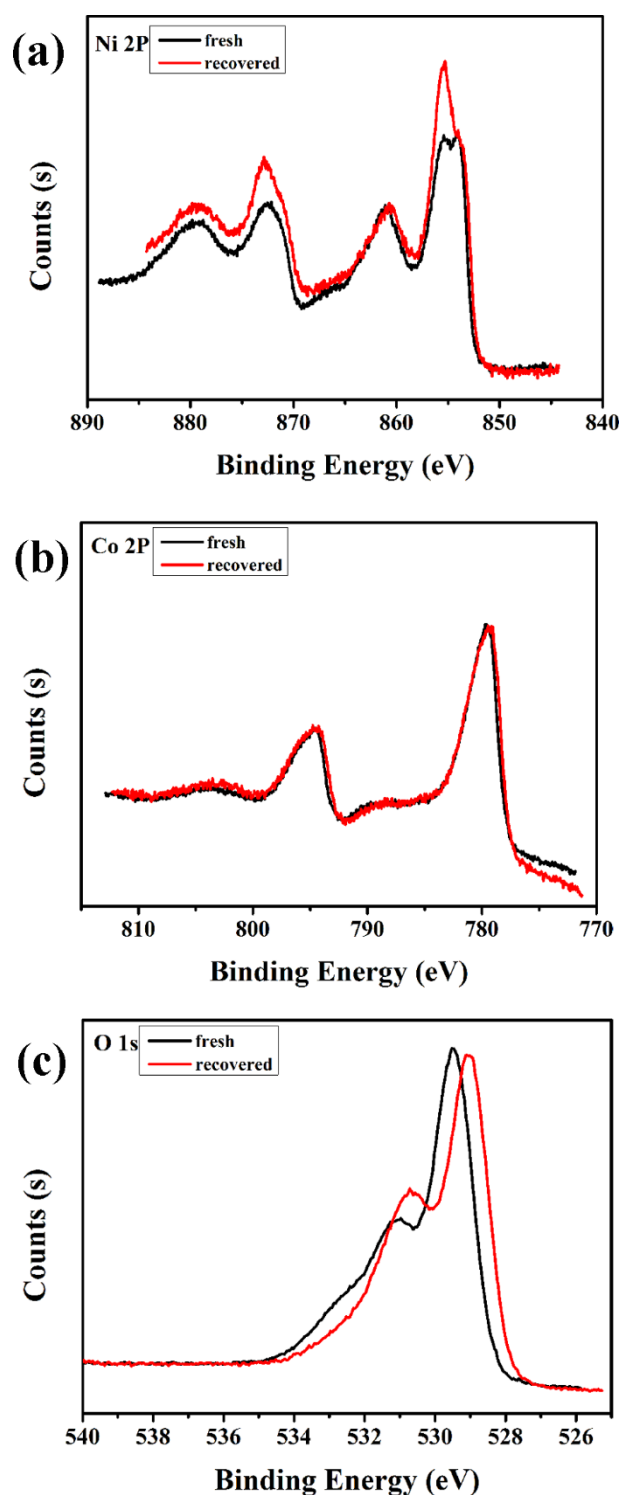
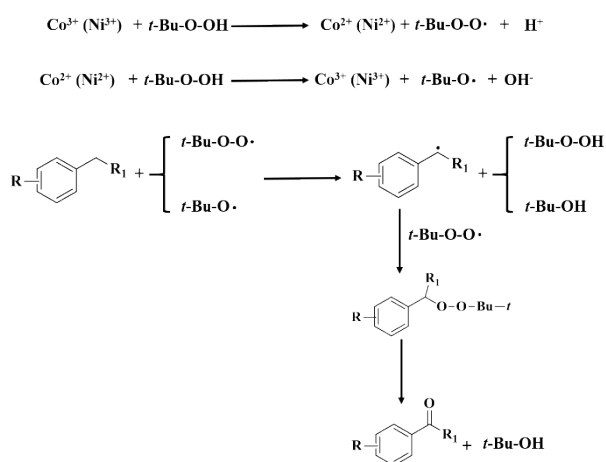


Fig. S4. XPS patterns of the fresh and recovered NiCo₂O₄ nanosheets: (a) the Ni 2p core levels, (b) the Co 2p core levels and (c) O 1s core level.

The speculated mechanism shown in Scheme S1 for benzylic oxidation by NiCo₂O₄ nanosheets catalyst was proposed based on related precedents.^{S6,S7} Firstly, TBHP is adsorbed into the pore of the NiCo₂O₄ nanosheets and coordinates with Co³⁺ (or Ni³⁺) ions and

generates *t*-BuOO· radical. Meanwhile, Co²⁺ (or Ni²⁺) also coordinates with TBHP and generates *t*-BuO· radical. Then, the *t*-BuOO· radical attacks the substrate and abstracts a hydrogen atom from the substrate, leading to a carbon-centered radical with the concomitant formation of TBHP. The *t*-BuO· radical also attacks the substrate and abstracts a hydrogen atom from the substrate, leading to a carbon-centered radical with the concomitant formation of *tert*-butyl alcohol. The carbon-centered radical continues to react with the *t*-BuOO· radical and form benzylic peroxide. Finally, the peroxide decomposes and produces the keto compound. Co³⁺/Co²⁺ or Ni³⁺/Ni²⁺ act as the active sites circularly during the catalytic cycle.



Scheme S1 Proposed mechanism for benzylic oxidation by NiCo₂O₄ nanosheets catalyst.

Reference

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