

Molecular Spectroscopy in Coke-free Carbon Catalysis

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Elemental carbon can catalyze the oxidative dehydrogenation (ODH) of ethylbenzene to styrene, as one of the most important monomers. Compared with the traditional polyvalent metal oxides, carbon-catalyzed ODH reaction is free of coking formation.[1, 2] Herein, we report a combination of molecular spectroscopy (IR, Raman) and electron microscopy (EELS, HRTEM) to identify the coke-free behavior in such a metal-free route.

Nanocarbons (carbon nanotubes, nanodiamonds) can stably catalyze the reaction over a long period of time.[1] After reaction, the used nanocarbons are clean and free of observable coke impurity (Fig. 1a-b), being approved by TPO/EELS results. As revealed in Fig. 1c, major characteristics of nanocarbon remained after a long-time of reaction. No signal corresponding to polymer coke can be found in the infrared spectroscopy of the used sample. To show the unique advantage of nanocarbon, we heated the nanocarbon in a diluted ethylbenzene flow without O₂. As showed in Fig. 1d, the relative ratio of D to G bands ($I_{(D)}/I_{(G)}$) remained almost unchanged, as a direct evidence for the coke-free nature of nanocarbon. Nanocarbon-mediated coke-free ODH represents a significant step to the "green" chemical industries.

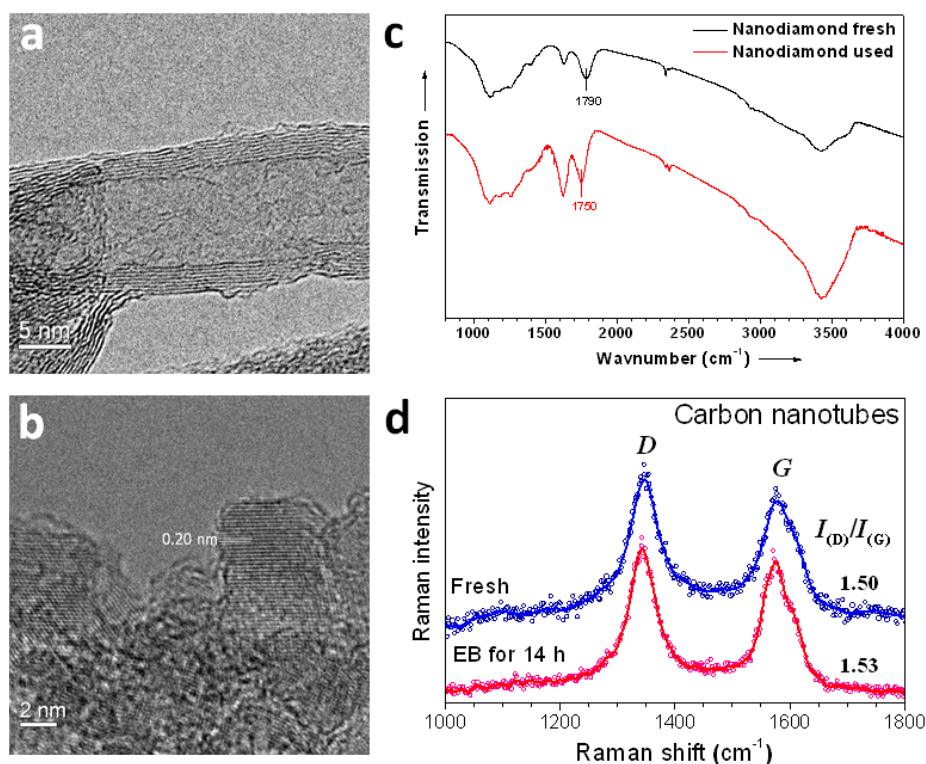


Figure 1: HRTEM images of carbon nanotubes (a) and nanodiamonds (b) after the ODH reaction (2.8% EB, O₂/EB=0.5, $SV_{\text{total}}=150,000 \text{ ml g}^{-1} \text{ h}^{-1}$, 723 K); (c) Infrared spectra of the used nanodiamonds; and, (d) Raman spectra of fresh and used nanotubes after contact with EB for 14 h at 823 K.

- [1] J. Zhang, D.S. Su, A.H. Zhang, D. Wang, R. Schlögl, C. Hébert, *Angew. Chem. Int. Ed.* 46 (2007) 7319-7323.
 [2] D.S. Su, X.W. Chen, X. Liu, J. Delgado, R. Schlögl, A. Gajovic, *Adv. Mater.* in press.