



## Mount-Etna-Lava-Supported Nanocarbons for Oxidative Dehydrogenation Reactions

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Efficient use of natural resources is a challenge to science and technology, especially in view of environmental protection, sustainable use of energy, and maintaining the climate. The natural resources are not only, in the common sense, crude oil, natural gas, useful minerals or water resources, and forest. There is also a lot of stone, rocks, clay, or biomass of which the application potential still needs to be explored. Huge efforts have been made to produce energy or hydrocarbon from biomass.[1] Another challenge is to explore the use of the “useless” natural materials directly in the emergin nanoscience and nanotechnology. For instance, the presence of iron oxide particles in the porous structure of Etna lava makes this material potential catalysts to synthesize carbon nanotubes (CNTs) or carbon nanofibers (CNFs).[2] As shown in Figure 1a, the CNTs/CNFs can be immobilized on the lava stones. The electron microscopy images in Figure 1b and c show a CNT with a catalytic particle in the tip that promotes the growth of CNTs. The production is highly efficient: On the laboratory scale, without any chemical pretreatment of the crushed lava stone, 1.05 g of nanocarbons can be immobilized on 0.2 g lava.

The immobilization of CNTs/CNFs on minerals without preparation of the catalyst is highly motivating, because owing to their loose form as “soot” CNTs/CNFs are unsuitable for many applications, for example, in catalysis or drinking water purification. CNTs and CNFs are reported to be highly active catalysts for chemical reactions.[3,4] However, technical problems such as hot spots or pressure drops in a reactor induce the loss of catalytic performance.[5] This can be avoided by immobilization of the nanocarbons onto the support. Operations of compaction can destroy or at least inhibit the access of the reactant medium in the nanostructures.[6] In this work, we explore the application of the novel lava–CNF composites in catalysis. As test reactions we choose the oxidative dehydrogenation of hydrocarbons (ODH), that is, the production of butadiene from 1-butene, and styrene from ethylbenzene. The latter reaction is one of the ten largest chemical industrial processes in the world.

The thermal stability of lava–CNF composites was tested in a thermo-gravimetric (TG) experiment with 5% O<sub>2</sub> in N<sub>2</sub>. The results, shown in Figure S1 (Supporting Information), reveal the good stability of lava–CNF composites up to about 550 °C. At higher temperatures the nanocarbon starts to burn, and its burning-off temperature lies at 650 °C. The lava stone remains unchanged in this temperature region, as observed in a separate TG experiment of pure lava stone revealing a weight loss of less than 0.6%. Differential TG shows different weight loss rates in the temperature region of 570 and 670 °C. This could be attributed to the abundance of defects in the synthesized nanocarbons and the coexistence of CNFs and CNTs in the composite. The defects in CNTs/CNFs are active sites in the ODH reactions to anchor oxygen-containing functional groups.[3,4] Owing to the different exposure of the prismatic and basal plane of graphene layers in these two kinds of nanocarbon, different combustion rates can be expected.

The catalytic performances of the lava–CNF catalyst in the ODH of 1-butene to butadiene and ethylbenzene to styrene are shown in Figure 2. The lava–CNFs catalyst is active for the two tested reactions. For the 1-butene to butadiene reaction, a conversion of 1-butene as high as 65% is observed at the beginning of the reaction. This conversion increases and stabilizes at about 80% after about 10 h. A stable butadiene yield higher than 50% is obtained after the activation period. For the styrene production from ethylbenzene, the conversion rate of ethylbenzene stabilizes at about 30% after a short deactivation period at the beginning of the reaction (Fig. 2b). A high selectivity to styrene of more than 85% is achieved, giving a styrene yield of about 25%.

Table 1 summarizes the reaction rates of 1-butene to butadiene over lava–CNT composites compared with those of unsupported loose CNTs from Applied Science (USA) and from Bayer (Germany), respectively. The pure lava does not exhibit any significant reactivity in the tested reaction. As we can see, the reaction rate is much faster when CNTs supported on lava are used to catalyze the reaction in comparison to when loose CNTs are used, indicating the advantage of immobilized CNTs for catalysis. Similarly, the reaction rate for ethylbenzene to styrene over immobilized CNTs is also higher than when only loose CNTs are used (Table 2). In addition, the obtained reaction rate for this reaction is also higher than those of the catalysts reported in the literature.[7]

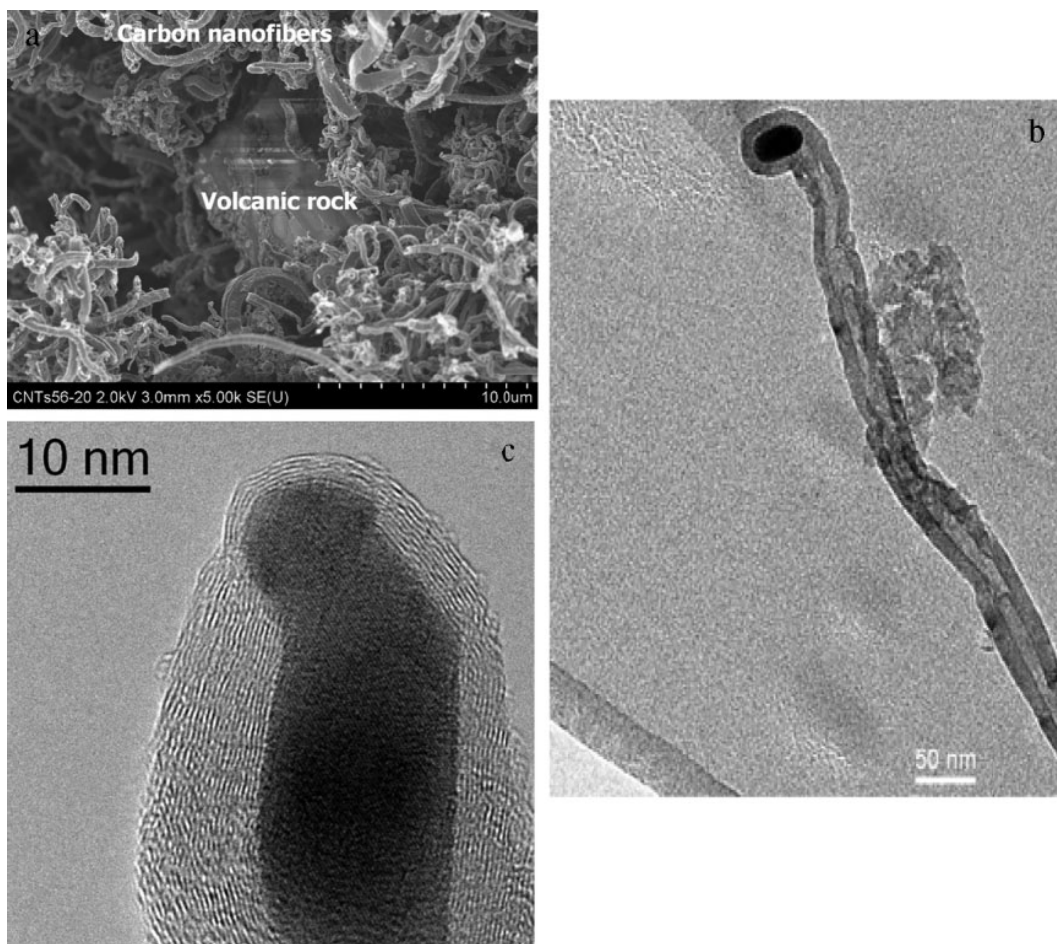


Figure 1. a) Scanning electron microscopy image of a lava–CNF composite, showing CNT/CNFs grown on igneous rocks. b) Transmission electron microscopy (TEM) image of a CNT with a catalytic particle in the tip. c) High-resolution TEM image, showing a catalytic particle that promotes the growth of the nanotube.

The high-resolution electron microscopy images in Figure 3 show the typical microstructure of CNFs on lava stone before and after reaction. The CNFs consist of declined carbon layers in a graphitic structure with a tubular morphology. After reaction, the main structure and morphology of the CNTs remain unchanged, indicating the high stability of the catalyst. A slightly disordered surface structure on the CNFs after reaction was observed, which may result from the carbon deposition during the reactions.

Raman spectra of pure lava and lava–CNF catalysts before and after reaction are shown in Figure 4a. Owing to its complex structure the Raman spectrum of pure lava contains numerous bands superimposed on an intensive fluorescent background (Fig. 4a, trace a). After immobilization of the CNFs on the lava support, the fluorescence background vanished and band characteristic to carbon[8,9] and CNTs[10] are observed (Fig. 4a, trace b) at  $1344\text{ cm}^{-1}$  (D band),  $1584\text{ cm}^{-1}$  (G band),  $2688\text{ cm}^{-1}$  (2D; overtone of D band),  $2928\text{ cm}^{-1}$  (G+D; combination of G and D bands), and  $3168\text{ cm}^{-1}$  (2G; overtone of G band). After the ODH reaction, all the major Raman features of lava–CNF composites remain (Fig. 4a, traces c and d). A slight shoulder at  $1612\text{ cm}^{-1}$ , known as a D' band,[10] appeared (Fig. 4b). The D' band is typical for disordered carbon.[8,9] This is in good agreement with the findings from high-resolution transmission electron microscopy (HRTEM). The Raman studies indicate that, besides the slight carbon deposition, the

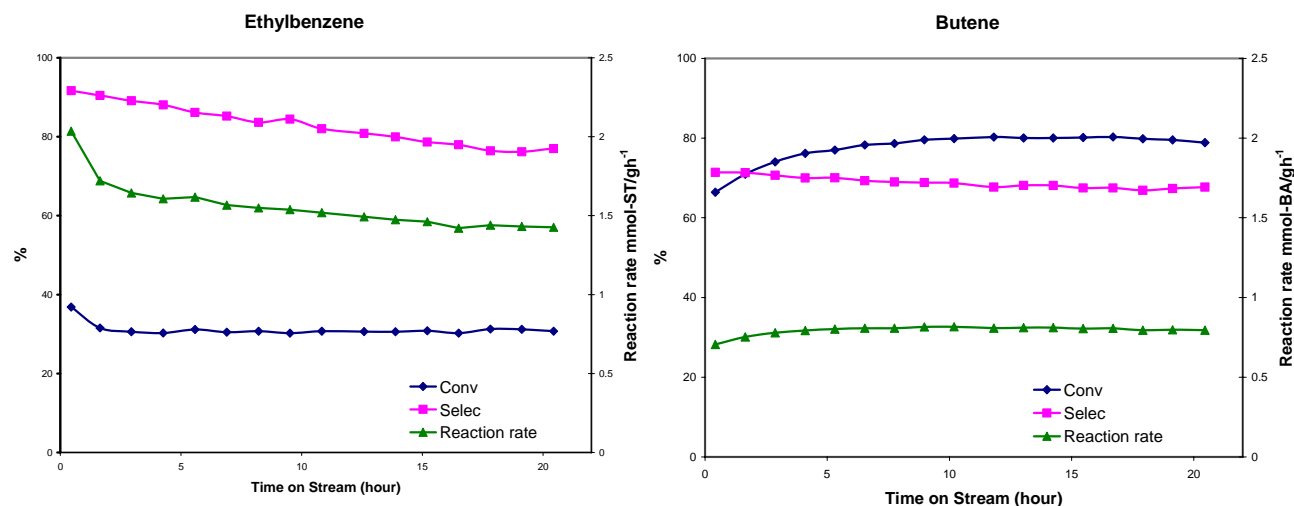


Figure 2. a) Conversion, selectivity and reaction rate for ODH reactions of 1-butene to butadiene, and b) ethylbenzene to styrene.

lava-CNFs are stable catalysts for the tested reactions. The carbon 1s X-ray photoelectron spectroscopy (XPS) spectra of lava-CNF catalysts before and after reaction are reproduced in Figure 4c. The high stability of lava-CNF catalysts during the reaction is well reflected in the spectrum, showing no significant changes in appearance. The slight broadening of the C 1s peak after reaction corresponds to a very small amount of disordered carbon, in good agreement with the observation in Raman spectra.

**Table 1. Catalytic activities comparison of different catalysts in the oxidative dehydrogenation of 1-butene (BU) to butadiene (BA).**

Catalyst	O/BU molar ratio	SV [a] [mL g <sup>-1</sup> h <sup>-1</sup> ]	T[°C]	BU conversion[%]	BA selectivity [%]	Reaction rate [mmol-BAg <sup>-1</sup> h <sup>-1</sup> ]
Lava-CNT	4:1	5000	400	79	66	0.79
CNT-I [b]	4:1	5000	400	72	59	0.64
CNT-II [c]	4:1	5000	400	34	13	0.06
Lava	4:1	5000	400	0.7	45	0.0004

[a] Space velocity. [b] CNT-I: multiwalled CNTs from Applied Science. [c] CNT-II: multiwalled CNTs from Bayer Materials.

**Table 2. Catalytic activities comparison of different catalysts in the oxidative dehydrogenation of ethylbenzene (EB) to styrene (ST).**

Catalyst	O/EB molar ratio	SV [a] [mL g <sup>-1</sup> h <sup>-1</sup> ]	T[°C]	EB conversion[%]	ST selectivity[%]	Reaction rate [mmol-STg <sup>-1</sup> h <sup>-1</sup> ]
Lava-CNT	5:1	5000	400	31	78	1.46
CNT-I [b]	5:1	5000	400	29	71	1.24
Sepiolite [c]	2:1	3636	440	37	96	0.29
AlPO <sub>4</sub> [c]	2:1	3636	440	44	99	0.35

[a] SV, space velocity. [b] CNT-I: multiwalled CNTs from Applied Science. [c] See Ref. [8].

**Table 3. Composition of starting lava material used for the CNT/CNF growth. XRF: X-ray fluorescence.**

	Elemental composition [at %]								
	O	Na	Mg	Al	Si	P	Ca	Ti	Fe
EDX	61.7	3.9	1.5	7.1	18.4	0.2	1.9	0.5	3.4
XRF	59.5	3.1	2.2	8.6	17.9	0.1	4.2	0.53	3.4
XRF [a]	60.7	2.4	2.6	7.9	17.8	0.01	4.0	0.44	3.1

[a] Data from a previous study of lavas erupted from Mount Etna, for comparison [12].

We demonstrate here examples of the promising use of a huge, inexpensive natural resource in nanomaterials synthesis and in catalysis for production of butadiene and styrene. The key message of the present work is the use of iron oxide particles existing abundantly in minerals as natural catalysts for CNT growth without any prior treatment of the lavas and the use of lava-CNF composites as catalyst, also without any prior treatment. A good and stable performance of the synthesized composite in catalytic

reactions is demonstrated. Because iron exists in a large number of minerals, clays, and soils and even in plants, we may open a new era for the cheaper production of immobilized CNTs and extend the application potential of CNTs, owing to the low costs, into other areas such as catalysis.

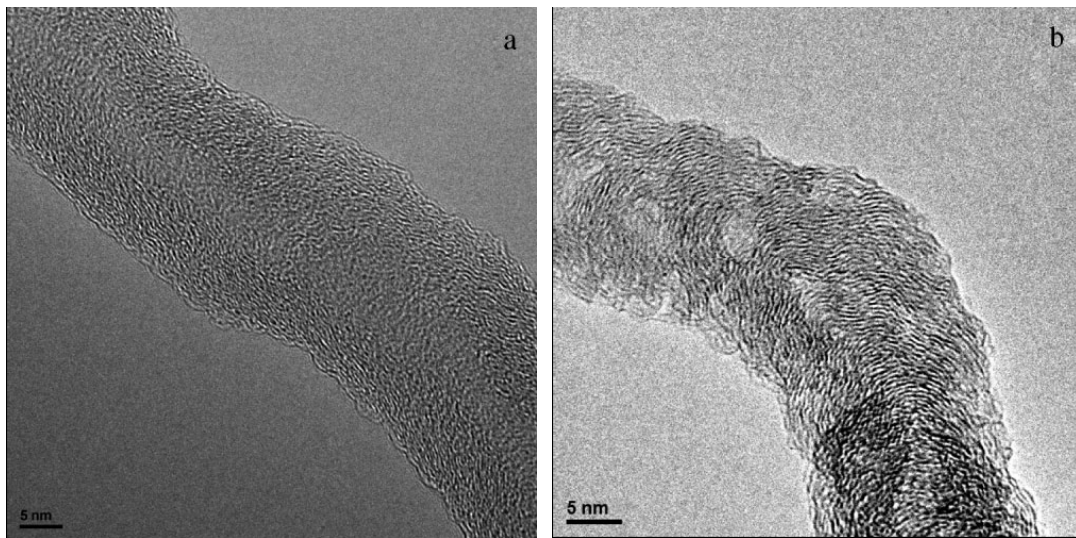


Figure 3. High-resolution TEM images of CNFs before (a) and after (b) ODH of ethylbenzene to styrene reaction.

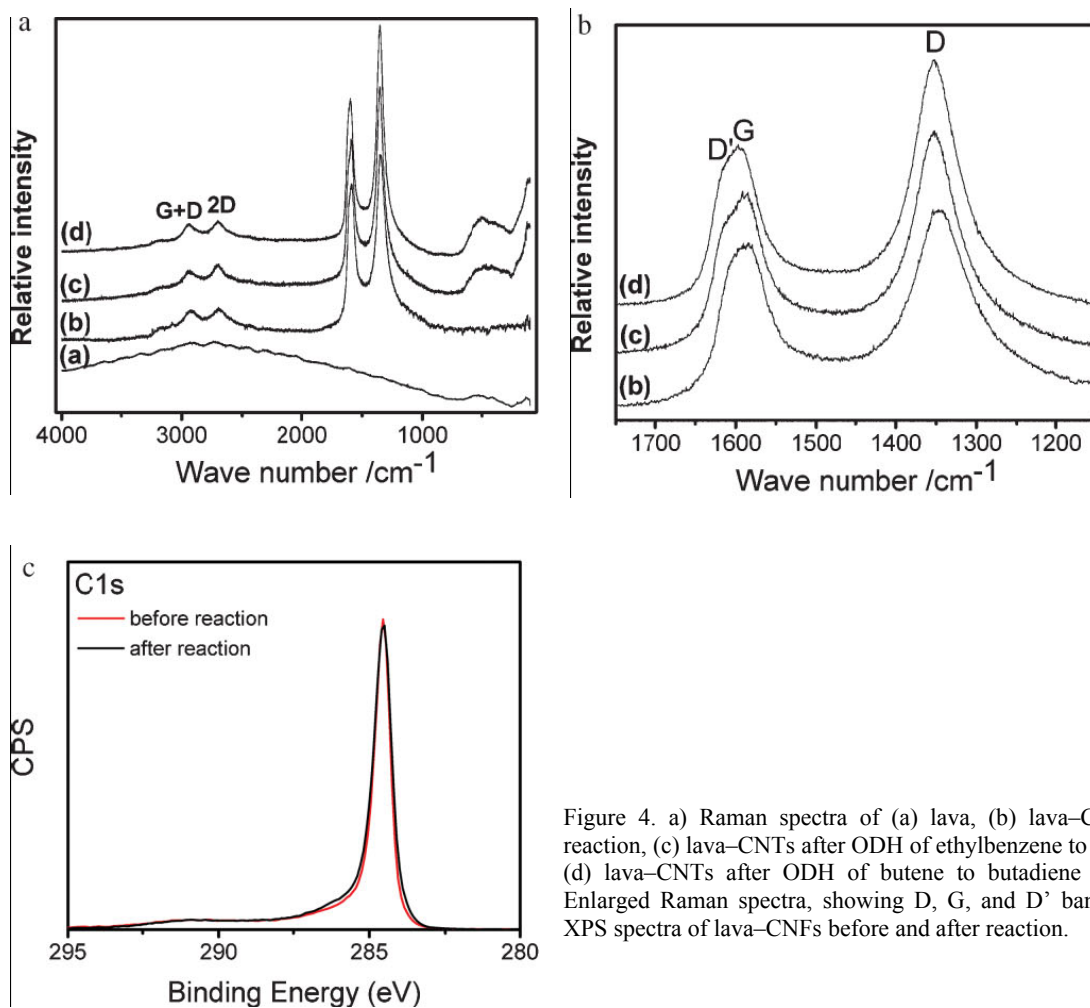


Figure 4. a) Raman spectra of (a) lava, (b) lava-CNFs before reaction, (c) lava-CNTs after ODH of ethylbenzene to styrene, and (d) lava-CNTs after ODH of butene to butadiene reaction. b) Enlarged Raman spectra, showing D, G, and D' bands. c) C 1s XPS spectra of lava-CNFs before and after reaction.

## Experimental

The Mount Etna lava used in the present work was collected on the north flank of Etna on November 23, 2003. It is a slightly evolved form of an alkaline series (trachybasalts and alkali basalts) exhibiting a porphyritic texture with abundant phenocrysts of plagioclase and fewer clinopyroxenes and olivines [11]. The chemical composition of the lava is given in Table 3. For the chemical vapor deposition (CVD) growth, the crushed powder (200 mg) was put into a vertical quartz reactor and reduced in H<sub>2</sub> at a flow rate (100 mL min<sup>-1</sup>, 700 °C, 2 h). A mixture of ethylene and H<sub>2</sub> (total flow rate 200 mL min<sup>-1</sup>, 50 vol % C<sub>2</sub>H<sub>4</sub>) was introduced into the reactor for 2 h. The temperature of the lava powder was kept at 700 °C. The CNTs/CNFs were grown by well-known decomposition of ethylene on metal particles, as is shown in Figure 1b and c. Energy-dispersive X-ray (EDX) analysis reveals that only iron carbides are found in the CNTs/CNFs, indicating that iron particles are the active catalytic particles in the CVD process (Supporting Information Figure S2). The obtained lava–CNF composites exhibit a Brunauer–Emmett–Teller (BET) specific surface area of 109 m<sup>2</sup> g<sup>-1</sup> while the specific surface area of the lava stone is only 0.02 m<sup>2</sup> g<sup>-1</sup>. For TG measurements, the procedure is as follows: The TG/DSC data were acquired using a Netzsch-STA 449 Instrument with Al<sub>2</sub>O<sub>3</sub> crucibles. The samples were evacuated and the sample chamber was refilled with 5% O<sub>2</sub> in N<sub>2</sub>, which was maintained at a total flow rate (100 mL min<sup>-1</sup>). A heating rate of 5 K min<sup>-1</sup> was used.

The 1-butene-to-butadiene reaction was carried out in a continuous flow fixed bed reactor equipped with a quartz tube holding 180 mg of catalyst. The feed consisted of mixtures of 1-butene, oxygen, and helium. The feed and product streams were analyzed on-line by a Micro GC (Varian CP-4900) for the simultaneous analysis of the different compounds. The ODH ethylbenzene-to-styrene reaction was performed in the same kind reactor at 673 K. The ethylbenzene concentration in the stream was 2.7 vol %. The O/EB ratio was 5 vol% and the total flow was 5 mL min<sup>-1</sup>. The morphology of the catalytic materials was observed by SEM in a Hitachi S-4000 FEG microscope operating at a 15 kV voltage. TEM investigations were performed on a Philips CM 200 LaB6 electron microscope and a Philips CM 200 FEG microscope, both operating at 200 kV. Raman spectroscopy was performed using a Jobin Yvon T64000 system working in micro Raman, single mode, with Coherent Innova 400 argon ion laser operating at 514.5 nm for excitation.

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