

## Electronic Supplementary Information

### Ordered mesoporous carbon catalyst for dehydrogenation of propane to propylene

Lei Liu, Qing-Fang Deng, Bao Agula, Xu Zhao, Tie-Zhen Ren and Zhong-Yong Yuan\*

#### *1. Experimental section*

##### *1.1. Synthesis*

The preparation of the ordered mesoporous carbon (OMC) materials was from the reference by a low-temperature autoclaving method based on organic-organic self-assembly [S1]. In a typical synthesis, 3.3 g of resorcinol and 2.5 g of F127 was dissolved in a mixture of 20 ml water and 20 ml ethanol. 0.2 g of 37% hydrochloric acid was then added to the above solution. After one hour of stirring, 2.5 g of 37% formaldehyde solution was added dropwise under tempestuously stirring. The reaction mixture was further vigorously stirred for another one hour and then transferred to a Teflon-lined autoclave and heated at 50 °C for 4 days. The obtained product was collected by filtration, washed with water and dried, and then carbonized at 600 °C for 6 h. The final product was denoted as OMC-1. While the molar ratio of formaldehyde to resorcinol is fixed at 2:1, autoclaving for 3 days, the synthesized carbon was denoted as OMC-2.

The CMK-3 ordered mesoporous carbon was synthesized using mesoporous silica of SBA-15 ( $S_{\text{BET}} = 648 \text{ m}^2\text{g}^{-1}$ ,  $D_{\text{BJH}} = 9.4 \text{ nm}$ ) as a hard template [S2]. Typically, mesoporous silica was impregnated with sucrose solution in the presence of sulfuric acid and dried at

80 °C and subsequently at 160 °C. Then the impregnation/drying step was repeated once. The obtained sample was carbonized under nitrogen atmosphere at 900 °C for 4 h. The resultant mesoporous carbons were obtained by stirring carbon/silica composition in HF acid (20 wt%) for 24 h to remove the silica frameworks, filtering, washing and drying at 100 °C overnight.

CNTs were prepared as the reference mentioned [S3]. The procedure was conducted in a horizontal quartz tube in a furnace. A ceramic boat containing Catalyst powder (Co/SiO<sub>2</sub>) was placed in the center of the quartz tube. When the furnace temperature was increased gradually to 700 °C, a mixed gas of N<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> was allowed to flow into the reaction tube. After the multiwall nanotubes (MWNT) growth for *ca.* 20 min, the specimen was cooled down to room temperature under ambient N<sub>2</sub>. The obtained powder of Co/SiO<sub>2</sub>/CNTs composite was treated with a HF aqueous solution and nitric acid at room temperature in order to extract the nanotubes by dissolution of SiO<sub>2</sub> and cobalt particles. The residues were then separated by filtration, washed with distilled water and dried at 100 °C.

### 1.2. Characterization

Transmission electron microscopy (TEM) measurements were performed on a Philips Tecnai F20 microscope at 200 kV. All samples subjected to TEM measurements were ultrasonically dispersed in ethanol and drop-cast onto copper grids covered with carbon film. Powder X-ray diffraction (XRD) pattern was recorded using a Rigaku D/max-2500 diffractometer, with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at a scanning rate of 0.01 °/s. Small angle X-ray scattering (SAXS) experiments were performed on a Bruker Nanostar small angle X-ray scattering system. Nitrogen adsorption and desorption isotherms were measured on a Quantachrome NOVA 2000e sorption analyzer at 77 K. Before measurements, the samples were degassed in a vacuum at 200 °C for at least 6 h. The

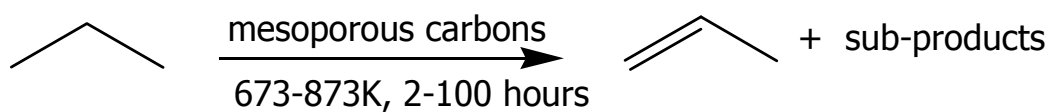
Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas ( $S_{\text{BET}}$ ), the pore size distributions were derived from the adsorption branches of isotherms using Non-Local Density functional theory (NLDFT) method, and the total pore volumes ( $V_{\text{total}}$ ) were estimated from the adsorbed amount at a relative pressure  $P/P_0$  of 0.980. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD (delay line detector) spectrometer equipped with a monochromatic Al K-X-ray source (1486.6 eV). All XPS spectra were recorded using an aperture slot of  $300\mu\text{m}\times 700\mu\text{m}$ , survey spectra were recorded with a pass energy of 160 eV, and high-resolution spectra with a pass energy of 40 eV. The temperature program desorption (TPD) profiles were obtained from CHEMBET-3000 with a custom built set-up, consisting of a U-shaped tubular micro-reactor, placed inside an electrical furnace. The mass flow rate of the helium carrier gas (20 mL/min) and the heating rate of the furnace (5 K/min) were controlled with appropriate units.

### 1.3. Catalytic testing

Catalytic tests were performed in a stainless steel, fixed-bed flow microreactor at atmospheric pressure, and the catalyst load was 400 mg. The gas reactant contained 5 vol% propane and a balance of nitrogen (total flow rate =  $40\text{ cm}^3/\text{min}$ ). The hydrocarbon reaction products were analyzed with an on-line gas chromatograph with a 6-m column of Porapak Q and a flame ionization detector (FID). Propane ( $\text{C}_3\text{H}_8$ ) conversion and selectivity to products have been calculated as follows:

$$\text{C}_3\text{H}_8 \text{ Conversion (mol \%)} = \frac{\text{moles of C}_3 \text{ reacted}}{\text{moles of C}_3 \text{ fed}} \times 100$$

$$\text{Selectivity (mol \%)} = \frac{\text{moles of product i formed}}{\text{moles of C}_3 \text{ reacted}} \times \left( \frac{N_i}{N_{\text{C}_3}} \right) \times 100$$

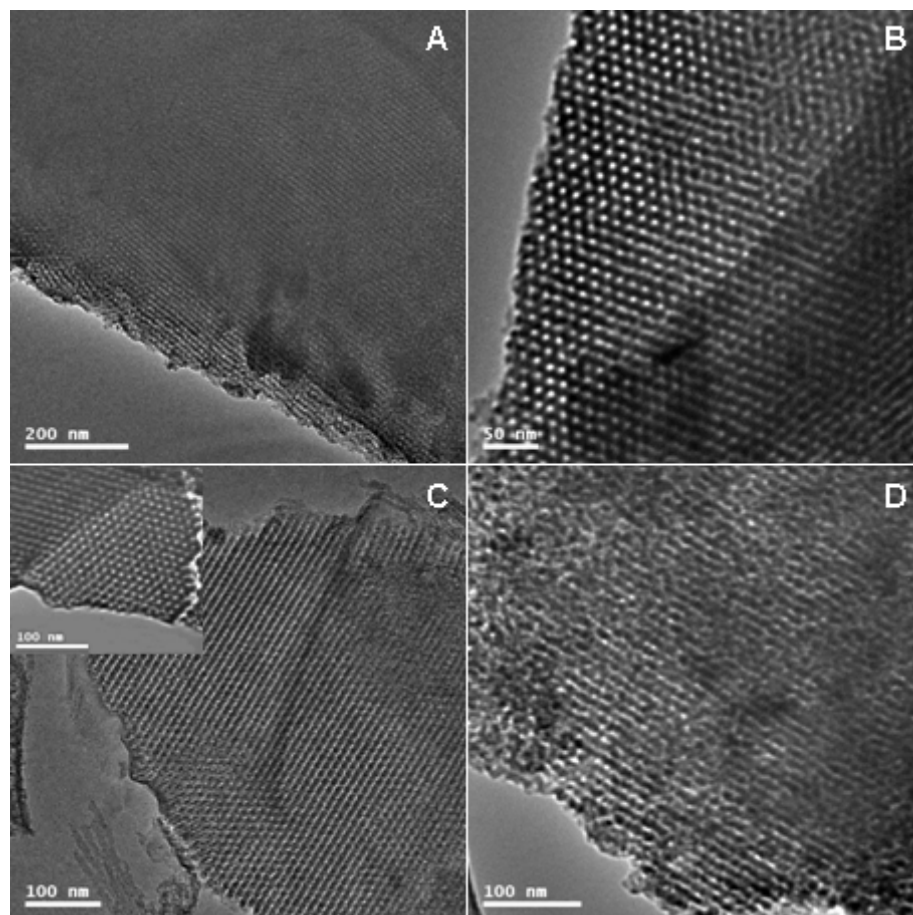


**Scheme 1.** Dehydrogenation of propane over mesoporous carbons.

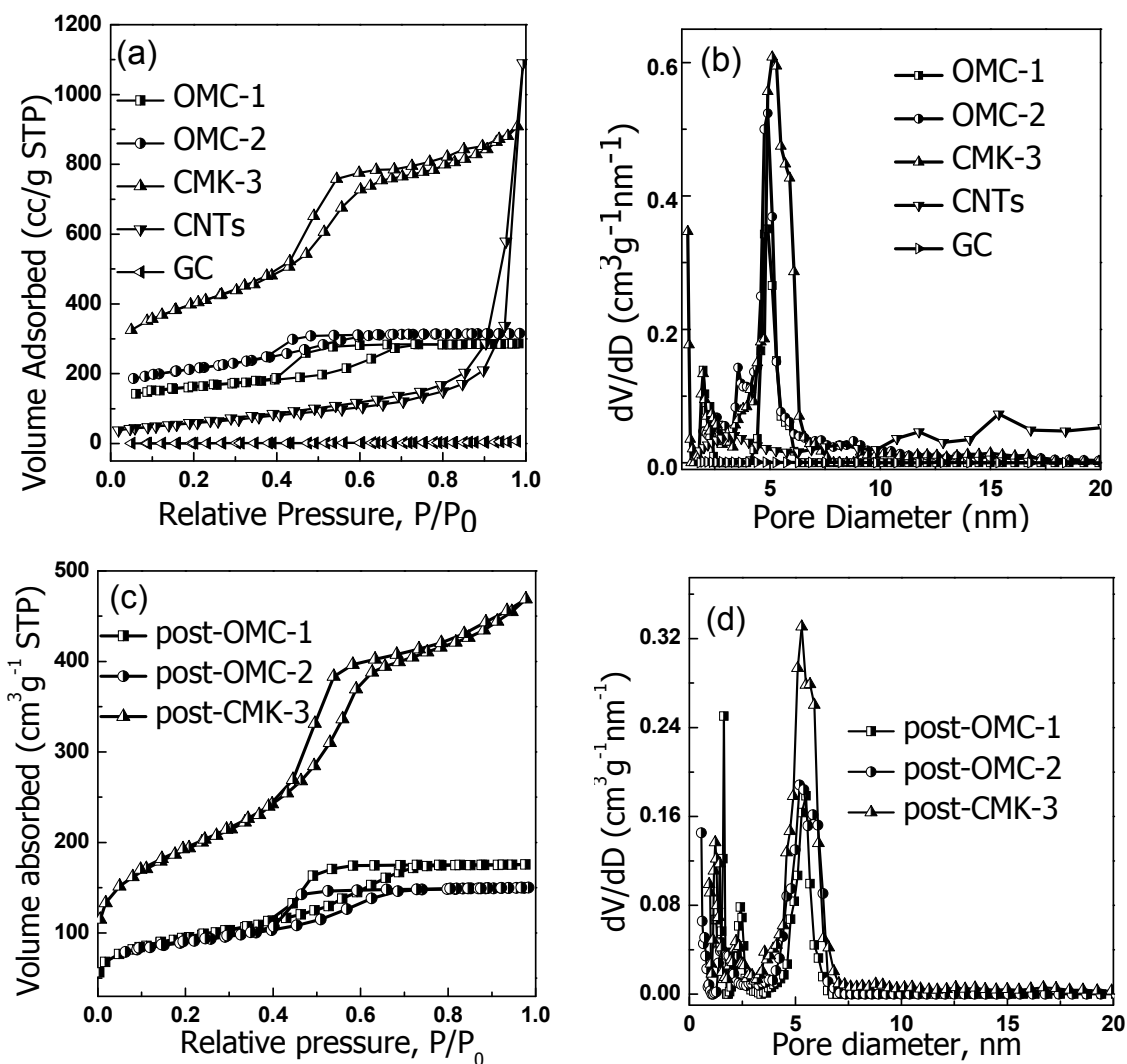
**Table S1.** Kinetic parameters for dehydrogenation of propane over mesoporous carbons<sup>a</sup>

Sampl	Dehydrogenation rate at 873 K <sup>b</sup>		Hydrogen yield	
	(mmol/g/h)	(mmol/m <sup>2</sup> /h) <sup>c</sup>	(mmol/g/h)	(mmol/m <sup>2</sup> /h) <sup>c</sup>
OMC-1	118	0.19	107	0.17
OMC-2	127	0.21	112	0.20
CMK-3	87	0.07	79	0.06
CNTs <sup>d</sup>	21.2	0.10	17.7	0.08
GC <sup>d</sup>	16.4	4.1	13.7	3.4

<sup>a</sup> Reaction conditions: 0.40 g, 873 K, 2% propane in nitrogen, 40 mLmin<sup>-1</sup>. <sup>b</sup> The dehydrogenation reaction rate was depicted as propylene formation. <sup>c</sup> Normalized by specific surface area of used sample in steady state. <sup>d</sup> The data showed is the initial reaction rate.

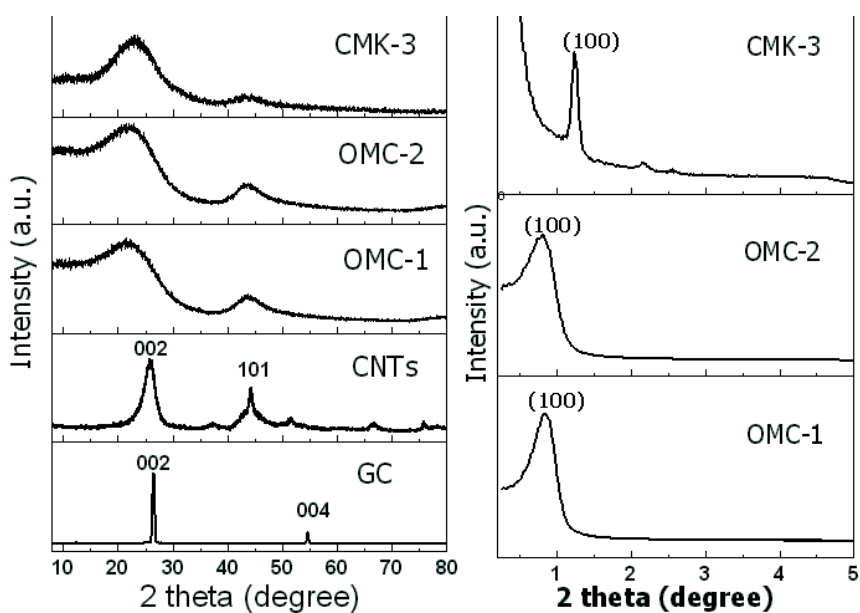


**Fig. S1.** Transmission electron microscopy (TEM) of the fresh carbon catalysts: (A, B) ordered mesoporous carbon OMC-1; (C) CMK-3; (D) mesoporous carbon OMC-2.



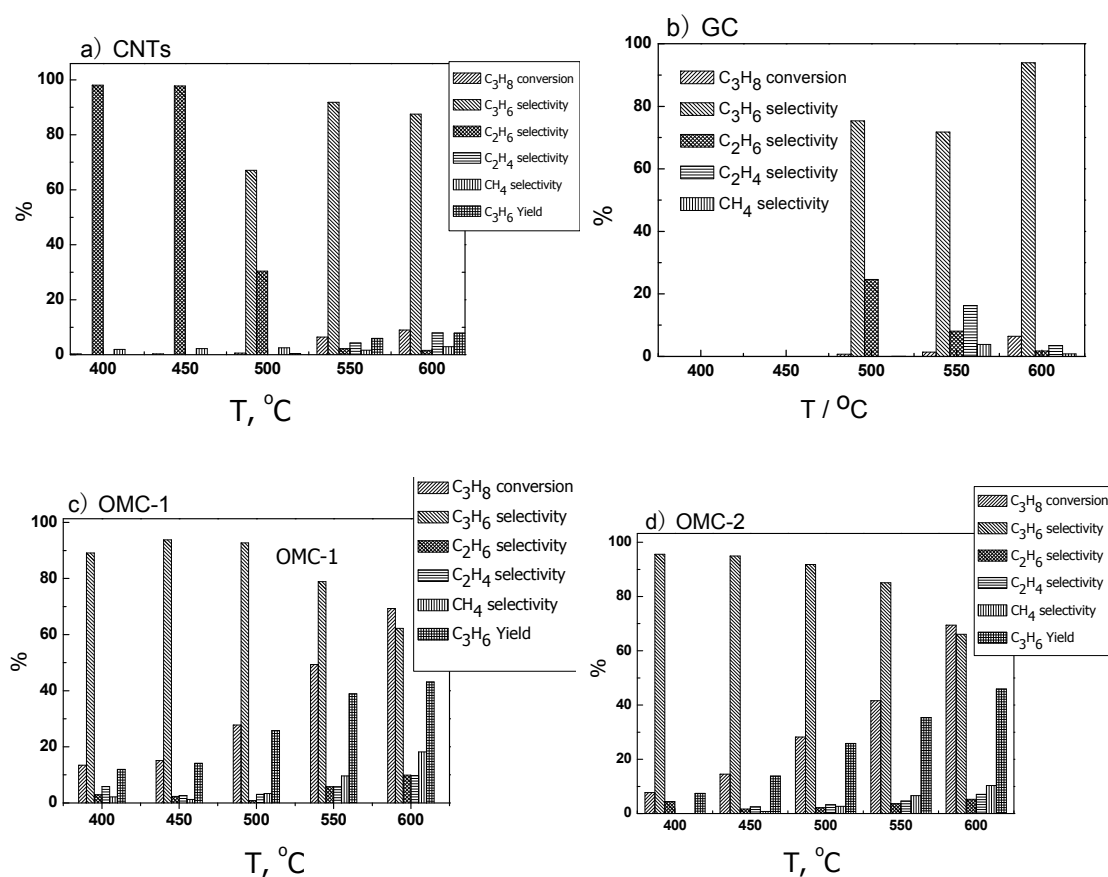
**Fig. S2.** Nitrogen sorption isotherms and the corresponding pore size distribution curves of different carbon catalysts before (a,b) and after (c,d) reaction.

Typical type-IV isotherms with a clear condensation step at  $P/P_0 = 0.5 - 0.7$  can be observed for samples OMC-1, OMC-2 and CMK-3, which is associated with the filling of mesopores due to capillary, with a narrow pore size distribution centered around 5 nm. Meanwhile, the large volume adsorbed at the lower  $P/P_0 = 0 - 0.1$  suggests the presence of microporosity of CMK-3 (Table 1). The capillary condensation of  $\text{N}_2$  molecules at high relative pressure  $P/P_0 = 0.9 - 1.0$  indicates the existence of pore system with small size and/or structural defects in the carbon walls of CNTs [S4], in accord with the broad pore size distribution ranging from 3 - 20 nm. Graphite carbon has a surface area as low as  $4 \text{ m}^2\text{g}^{-1}$ , indicating the absence of pores.



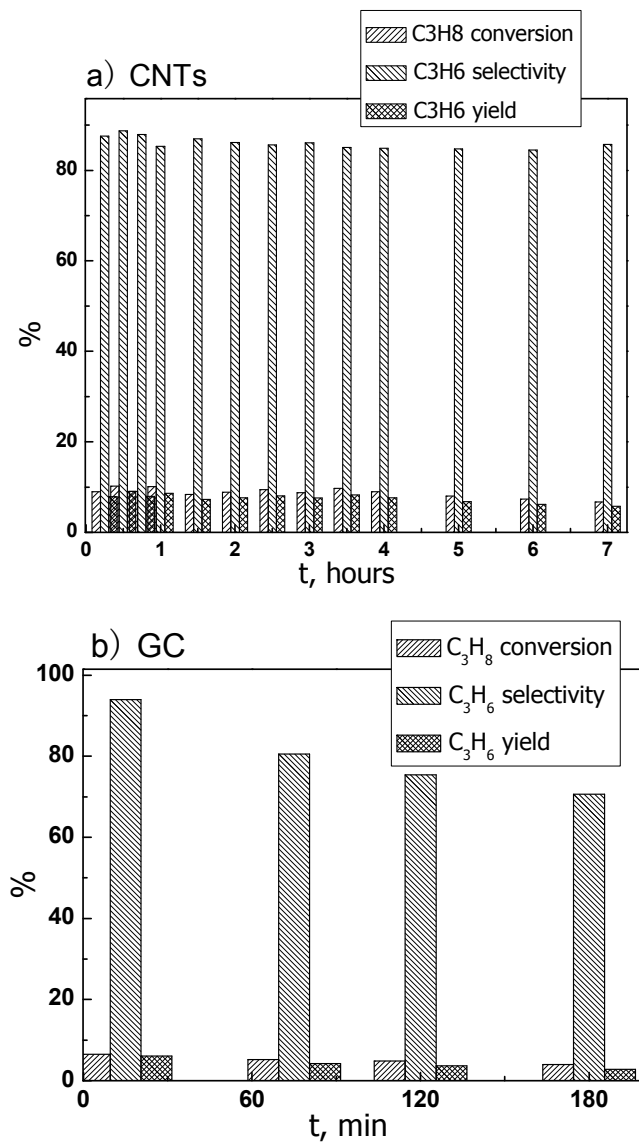
**Fig. S3.** Wide-angle XRD patterns (*left*) and the SAXS patterns (*right*) of different carbon catalysts.

From the wide angle XRD patterns, it can be clearly seen that GC exhibits two very sharp diffraction peaks at  $26.5^\circ$  ( $2\theta$ ) and  $54.5^\circ$  ( $2\theta$ ), which can be indexed to (002) and (004) reflection of the graphite lattice respectively (PDF 08-0415). CNTs represent a carbon with a high degree of graphitization, containing two intense diffraction peaks at  $2\theta$  value of  $26^\circ$  ( $2\theta$ ) and  $44.2^\circ$  ( $2\theta$ ), which can be assigned to (002) and (101) diffractions of the graphitic framework. In contrast, all the mesoporous carbon catalysts show two broad peaks at ca.  $24^\circ$  ( $2\theta$ ) and ca.  $44^\circ$  ( $2\theta$ ). These peaks are assigned to diffractions from the (002), (100) planes of graphite [S5], indicating the partially graphitic pore walls. In the low-angle reflections, a sharp and narrow diffraction peak is visible in all three mesoporous carbon samples, corresponding to the two-dimensional hexagonal periodicity of the pore systems, which is consistent with the TEM images.

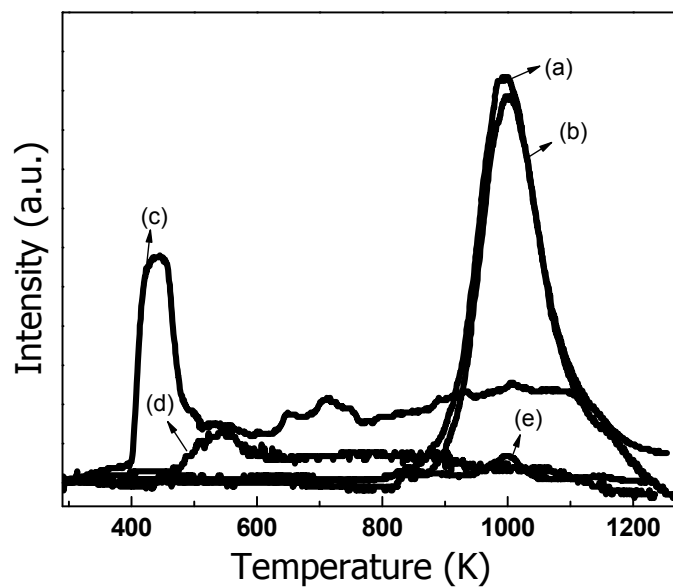


**Fig. S4.** Dependence of catalytic activity on the reaction temperature during the dehydrogenation of propane over nanostructured carbons, (a) CNTs, (b) GC, (c) OMC-1, (d) OMC-2. Although the higher selectivity to propylene occurred at higher temperature range, both carbon nanotubes and graphite carbon show poor catalytic activity. In contrast, the OMC-x can preferably catalyze the dehydrogenation reaction.

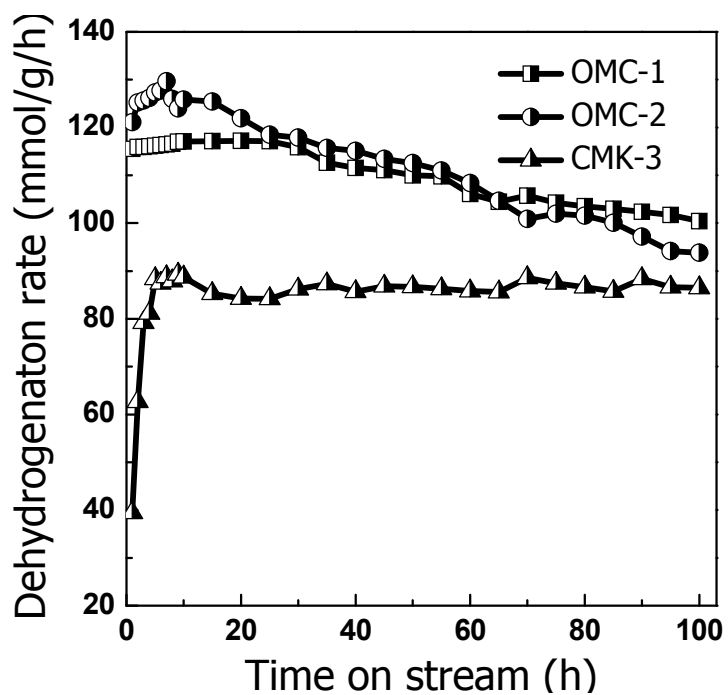




**Fig. S5.** Propane conversion, propylene selectivity and yield as a function of time on stream obtained at 873 K on a) CNTs and b) GC. Both carbon nanotubes and graphite carbon show poor stability.



**Fig. S6.** TPD profiles of different mesoporous carbons before reaction: (a) OMC-1, (b) OMC-2, (c) CMK-3, (d) CNTs, (e) GC.



**Fig. S7.** Reaction rates for the dehydrogenation of propane over different mesoporous carbons. Reaction conditions: 0.40 g, 873 K, 2% propane in nitrogen, 40 mL/min.

*References*

- [S1] L. Liu, F.Y. Wang, G.S. Shao, Z.Y. Yuan *Carbon* **2010**, *48*, 2089–2099.
- [S2] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* **2000**, *122*, 10712–10713.
- [S3] Z.J. Liu, Z.Y. Yuan, W.Z. Zhou, L.M. Peng, Z.D. Xu, *Phys. Chem. Chem. Phys.* **2001**, *3*, 2518–2521.
- [S4] H.P. Lin, S.T. Wong, C.Y. Mou, C.Y. Tang, *J. Phys. Chem. B* **2000**, *104*, 8967–8970.
- [S5] Y. Xia, R. Makaya, *Adv. Mater.* **2004**, *16*, 1553–1558.