Metal-Free Phenanthrenequinone Cyclotrimer as an Effective Heterogeneous Catalyst

Jian Zhang,[†] Xuan Wang,[‡] Qi Su,[‡] Linjie Zhi,*,[ll] Arne Thomas,[§] Xinliang Feng,[‡] Dang Sheng Su,*,[†] Robert Schlögl,*,[†] and Klaus Müllen*,[‡]

Fritz Haber Institute of the Max Planck Society, Berlin 14195, Germany, Max Planck Institute for Polymer Research, Mainz 55128, Germany, Max Planck Institute of Colloids and Interfaces, Golm 14476, Germany, and National Center for Nanoscience and Technology of China, Beijing 100190, China

Received June 8, 2009; E-mail: dangsheng@fhi-berlin.mpg.de; zhilj@nanoctr.cn; acsek@fhi-berlin.mpg.de; muellen@mpip-mainz.mpg.de

Since the invention and industrialization of the Haber−Bosch NH₃ process, almost all technical heterogeneous catalysts have been developed by empirical "trial-and-error" experiments. The enormous progress of surface science and theory provides fundaments for designing catalysts. A key challenge remains, however, the identification and realization of active sites for desired functions. Such sites are dynamical minority species in an "active matrix". They form through reaction of the active matrix with reactants and are capable of regenerating themselves in each catalytic cycle.

For styrene synthesis from ethylbenzene, the exothermic oxidative dehydrogenation (ODH) is an energy-saving candidate for an industrial process.[1] Carbon materials including cokes, pyrolyzed polyacrylonitrile, molecular sieves, activated carbons, and graphite are as efficient as metal catalysts.[2−5] Recent studies revealed that carbon nanomaterials with graphitic structure provide high activity over a long period of time due to the controlled homogeneity of the support structure and the chemical uniformity of the active sites.[6−8] On the basis of *ex situ* and quasi *in situ* characterizations, the structures of active sites have been proposed to consist of diketone- and/or ketone-like groups, which are initially generated during the synthesis and maintained in their oxidation states by contact with the reactant O₂.[9,10] Mechanistic investigations suggest that breaking C−H bonds may be kinetically limiting in the reaction sequences.[6] Styrene desorbs from the surface, while the produced hydrogen is oxidized to water. However, so far, there is still no direct evidence for the chemical structure of the active sites. We report herein the unique activity of a phenanthrenequinone based cyclotrimer with α-diketone subunits, serving as a model catalyst with excellent performance and as a molecular analogue to the carbon-based systems. A potential approach toward tailoring the active sites in a catalyst is thus demonstrated in the area of heterogeneous catalysis.

The macrocyclic trimer (MCT, **3**) was synthesized via a nickel(0)-mediated Yamamoto-type coupling reaction,[11,12] as depicted in Figure 1. After bromination under light illumination and subsequent recrystallization,[13] the commercially available phenanthrenequinone, **1**, was converted into the 3,6-dibromophenanthrenequinone, **2**, an orange needle-like crystal. Further Yamamoto coupling reaction of compound **2** and subsequent purification (see Supporting Information) produced the MCT oligomer as an insoluble powder with an overall yield of 84%. The poor solubility of the oligomer precluded direct structural verification by solution ¹H and ¹³C NMR. The macrocyclic structure was evidently confirmed by MALDI-TOF mass spectrometric characterization, while no obvious signal of other oligomers was detected (Figure S1).[14] The α-diketone structure was further supported by elemental

Scheme 1. Schematic Synthesis of the MCT Oligomer[a]
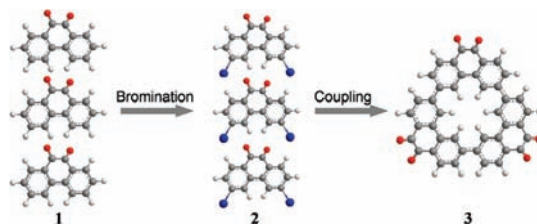
[a] Compounds: (1) phenanthrenequinone, **1**; (2) 3,6-dibromo-phenanthrenequinone, **2**; and (3) macrocyclic trimer of phenanthroquinone, MCT, **3**. Bromination: Br₂, nitrobenzene, 100 °C; Yamamoto coupling: bis(cyclooctadiene)nickel, cyclooctadiene, 2,2′-bipyridine, DMF, 75 °C.

analysis (Figure S2) and infrared spectra (data shown later). The high yield of MCT in the synthesis may arise from the intrinsic angle of the phenanthrenequinone unit, as well as from the poor solubility in common organic solvents serving as the driving force during the crystallization process. A similar analysis has been reported for the synthesis of the macrocyclic trimer of dialkyl substituted phenanthrene.[11,12] As the consequence of the macrocycle formation, the melting point of the compound increased above 410 °C after trimerization. Such a high melting point certainly benefits the application of MCT oligomer as a heterogeneous catalyst.

The performance of MCT oligomer was tested in a quartz microreactor under atmospheric pressure. Figure 1A shows the catalytic function of MCT at 350 °C along with the time-on-stream. The sample was immediately active and quickly reached a steady state, in which the reaction rate and styrene selectivity remained above 0.34 mmol g⁻¹ h⁻¹ and 86%, respectively. Increasing the O/C ratio from 2 to 5 enhanced the reaction rate to 0.44 mmol g⁻¹ h⁻¹ at constant styrene selectivity (83%). COₓ was the major byproduct. The time-independent carbon balance of 100 ± 4% indicated oxidative stability of the hydrocarbon catalyst. A comparison in performance between MCT and nonmolecular catalysts[15−22] is shown in Figure 1b, in which the activity was represented by the amount of styrene generated per square meter of BET surface area per hour (μmol m⁻² h⁻¹). MCT exhibits already at low temperature the highest activity of 84.5 μmol m⁻² h⁻¹, which is up to 47 times the activity of other catalysts including metal phosphates and oxides.

Kinetic parameters were derived in a differential reactor without mass and heat transport limitations (Figure S3). The reaction rate (R) displays (Figure 1c) a positive dependency on the partial pressures of ethylbenzene and O₂ (Pᵢ), revealing reaction orders of 0.39 and 0.25 for ethylbenzene and O₂, respectively. An activation energy (Eₐ) of 77.4 kJ mol⁻¹ was calculated from the slope of an Arrhenius plot (Figure 1d). All kinetic parameters are close to those determined from carbonaceous materials in previous studies,[6] confirming the similarity of both mechanism and structure of active

† Fritz Haber Institute of the Max Planck Society.
‡ Max Planck Institute for Polymer Research.
§ Max Planck Institute of Colloids and Interfaces.
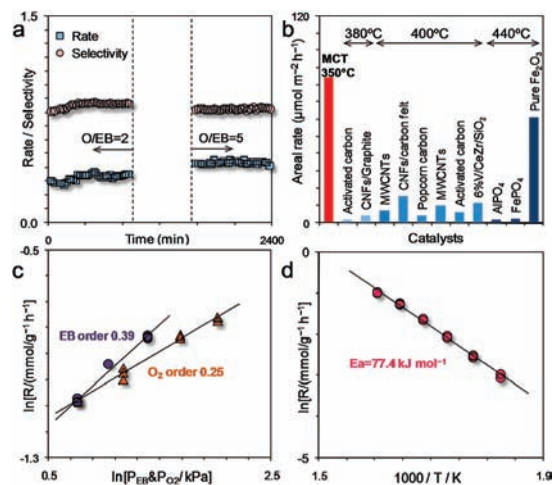ll National Center for Nanoscience and Technology of China.

Figure 1. (a) Reaction rate (mmol g^{-1} h^{-1}) and styrene selectivity on MCT oligomer. Conditions: 20 mg, 2.1%EB, O/EB = 2−5, 12.5 mL min^{-1}, 350 °C. (b) Comparison of activities with typical catalysts in literature. Dependencies of reaction rate on partial pressures of each reactant (c) and temperature (d).

sites (Table S1). Under the same conditions, MCT gives an areal rate 5−9 times those of the nanocarbons. The superior activity can be thus related to the abundance of diketone groups for styrene formation. The nonzero reaction orders for both reactants indicate the matched rates for the organic transformation and the oxidation of hydrogen in contrast to systems where lattice oxygen decouples the regeneration of the active site from the organic transformation.

The MCT sample after ODH reaction was studied by using nitrogen physisorption (BET surface area 5 m^2 g^{-1}), scanning electron microscopy (SEM) with EDX (only C, O, Figure S2), temperature-programmed oxidation/thermogravimetric analysis (TPO/TG), and transmission infrared spectroscopy. The solid-state MALDI-TOF mass spectrometric characterization on fresh and reacted samples shows that the molecular structure changed to a negligible degree (Figure S1). No obvious difference in the color of the substance can be found after reaction. TPO results reveal a weight loss less than 1% at the reaction temperature (Figure 2a) to indicate the oxidative stability of the molecule. The profiles of the produced CO$_2$ and H$_2$O (Figure 2b) show no additional features that could point to additional carbon structures from coke deposition or decomposition of the molecular catalyst. The peak profiles of
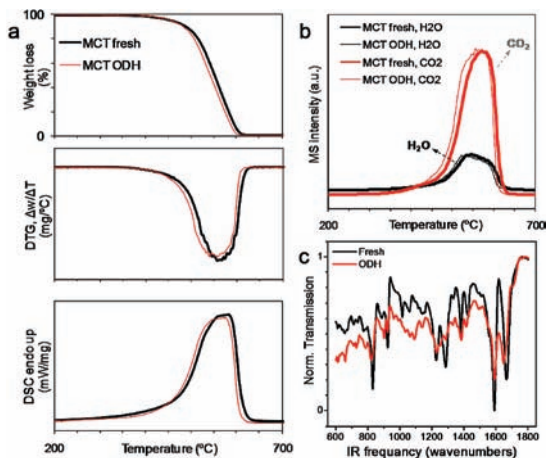

Figure 2. (a) TG/DTG/DSC profiles and (b) evolution of CO$_2$ and H$_2$O during TPO/TG of MCT samples before and after ODH reaction. Conditions: 10 mg, 21%O$_2$ in Ar, 100 mL min^{-1}, 5 K min^{-1}. (c) Infrared spectra of fresh MCT sample and the one after ODH.

TPO and related DSC signals remained unchanged, but the positions shifted slightly being consistent with a modification of crystallinity of the material during thermal stress in the reaction. The IR spectra (Figure 2d)[23,24] reveal retention of the terminating geometry (C=O bonds above 1550 cm^{-1} and C−H ones below 1000 cm^{-1}) and only slight modification of the crystal packing as felt sensitively[25] by the C−C stretch vibrations between 1000−1500 cm^{-1} in agreement with the thermal analysis data. A negligible change in long-range ordering is observed in the XRD patterns (Figure S4) of MCT before and after catalysis.

In summary, we have shown that MCT is a suitable model to study ODH catalysis under conditions being rather severe for a molecular catalyst. Its outstanding performance confirms the previous hypothesis that the carbon-catalyzed ODH process may be mediated by diketone- and/or ketone-like functional groups. Potential application is possible by supporting the molecular active component in submonolayer amounts.

Supporting Information Available: Synthesis, reaction, and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Cavani, F.; Trifirò, F. *Appl. Catal., A* **1995**, *133*, 219–239.
(2) Fiedorow, R.; Przystajko, W.; Sopa, M.; Lana, I. G. D. *J. Catal.* **1981**, *68*, 33–41.
(3) Emig, G.; Hofmann, H. *J. Catal.* **1983**, *84*, 15–26.
(4) Pereira, M. F. R.; Órfão, J. J. M.; Figueiredo, J. L. *Appl. Catal., A* **2001**, *218*, 307–318.
(5) Mestl, G.; Maksimova, N. I.; Keller, N.; Roddatis, V. V.; Schlögl, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2066–2068.
(6) Zhang, J.; Su, D. S.; Zhang, A. H.; Wang, D.; Schlögl, R.; Hébert, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 7319–7323.
(7) Zhang, J.; Liu, X.; Blume, R.; Zhang, A. H.; Schlögl, R.; Su, D. S. *Science* **2008**, *322*, 73–77.
(8) Resasco, D. E. *Nat. Nanotechnol.* **2008**, *3*, 708–709.
(9) Pereira, M. F. R.; Órfão, J. J. M.; Figueiredo, J. L. *Appl. Catal., A* **2001**, *184*, 153–160.
(10) Maciá-Agulló, J. A.; Cazorla-Amorós, D.; Linares-Solano, A.; Wild, U.; Su, D. S.; Schlögl, R. *Catal. Today* **2005**, *102−103*, 248–253.
(11) Yang, C.; Scheiber, H.; List, E. J. W.; Jacob, J.; Müllen, K. *Macromolecules* **2006**, *39*, 5213–5221.
(12) Staab, H. A.; Bräunling, H. *Tetrahedron Lett.* **1965**, *6*, 45–49.
(13) Bhatt, M. V. *Tetrahedron* **1964**, *20*, 803–821.
(14) Although the direct solution characterization of MCT was restricted, the functional soluble macrocycle derivatives through the condensation reaction of MCT with 1,2-diamino-4,5-dialkylbenzene were synthesized in good yields, enabling the NMR tests and thus indirectly proving its structure and purity. Takase, M.; Feng, X.; Müllen, K., unpublished.
(15) Reddy, B. M.; Lakshmanan, P.; Loridant, S.; Yamada, Y.; Kobayashi, T.; López-Cartes, C.; Rojas, T. C.; Fernández, A. *J. Phys. Chem. B* **2006**, *110*, 9140–9147.
(16) Bautista, F. M.; Campelo, J. M.; Luna, D.; Marinas, J. M.; Quirós, R. A.; Romero, A. A. *Appl. Catal., B* **2007**, *70*, 611–620.
(17) Yoo, J. S. *Appl. Catal., A* **1996**, *142*, 19–29.
(18) Wang, L. F.; Zhang, J.; Su, D. S.; Ji, Y. Y.; Cao, X. J.; Xiao, F.-S. *Chem. Mater.* **2007**, *19*, 2894–2897.
(19) Li, P.; Li, T.; Zhou, J.-H.; Sui, Z.-J.; Dai, Y.-C.; Yuan, W.-K.; Chen, D. *Microporous Mesoporous Mater.* **2006**, *95*, 1–7.
(20) Pereira, M. F. R.; Figueiredo, J. L.; Órfão, J. J. M.; Serp, P.; Kalck, P.; Kihn, Y. *Carbon* **2004**, *42*, 2807–2813.
(21) Delgado, J. J.; Su, D. S.; Rebmann, G.; Keller, N.; Gajovic, A.; Schlögl, R. *J. Catal.* **2006**, *244*, 126–129.
(22) Delgado, J. J.; Vieira, R.; Rebmann, G.; Su, D. S.; Keller, N.; Ledoux, M. J.; Schlögl, R. *Carbon* **2006**, *44*, 809–812.
(23) Crowley, P. J.; Haendler, H. M. *Inorg. Chem.* **1962**, *1*, 904–909.
(24) Floriani, C.; Henzi, R.; Calderazzo, F. *J. Chem. Soc., Dalton Trans.* **1972**, *23*, 2640–2642.
(25) Bauschlicher, C.W., Jr. *Chem. Phys.* **1998**, *233*, 29–34.

JA9046735