



Oxidative dehydrogenation of ethylbenzene on nanocarbon: Kinetics and reaction mechanism



Wei Liu^{b,1}, Chao Wang^{a,1}, Dangsheng Su^b, Wei Qi^{b,*}

^a School of Medical Devices, Shenyang Pharmaceutical University, No. 103, Wenhua Road, Shenyang 110016, China

^b Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, No. 72, Wenhua Road, Shenyang 110016, China

ARTICLE INFO

Article history:

Received 4 September 2018

Revised 18 September 2018

Accepted 19 September 2018

Keywords:

Heterogeneous catalysis

Reaction kinetics

Oxidative dehydrogenation

TOF

Carbon catalysis

ABSTRACT

Active site titration, kinetic analysis, isotope and temperature programmed surface reaction experiments have been applied to reveal the nature of nanocarbon catalyzed alkane oxidative dehydrogenation reactions. The catalytic reaction involves the redox cycle of ketonic carbonyl-hydroxyl pairs on nanocarbon materials, during which the substrate of ethylbenzene (EB) dehydrogenates to product styrene, and the molecular oxygen re-oxidizes the catalysts yielding water. The rate equation based on the mechanistic interpretations of the catalytic reactions provides intrinsic rate or equilibrium constants, which have their specific physicochemical meanings and could be directly linked to the catalytic process. The proposed rate equation could also accurately describe the effects of reactant (EB or O₂) pressures and isotopomers (deuterated-EB or ¹⁸O₂) on rate data, and provide a quantitative analysis on the evolution and content of surface intermediates on carbon catalysts, which is a reliable descriptor of the intrinsic reactivity and essential to establish the structure-function relations for carbon catalyzed redox reactions.

© 2018 Elsevier Inc. All rights reserved.

1. Introduction

Nanocarbon materials, such as carbon nanotube (CNT), graphene and nanodiamond (ND) are potential alternatives to conventional metal-based catalysts for the dehydrogenation of alkanes to meet the strict requirements of renewable and sustainable chemistry [1–5]. Great achievements have been made in the field to design and fabricate high-performance nanocarbon catalysts with unique structure and functionality [1,6–9]. For example, it has been reported that the surface modified carbon nanotube materials exhibit obviously higher alkene yield than commercial V-MgO catalysts in n-butane oxidative dehydrogenation (ODH) reaction systems, indicating the advantages and potential applications of these new types of sustainable catalytic materials [10,11]. Very recently, the superiority of novel porous graphene, hierarchical carbon nanofibers/graphene composite containing nanodiamonds, carbon nitride encapsulated nanodiamond and mesoporous graphitic carbide-derived carbons in EB dehydrogenation reactions have also been reported [1,8,12,13]. Despite the rapid development in the field of novel carbon catalyst design and synthesis, the in depth understandings on the catalytic mechanism and a general regularity in structure-function relationships (identity and quan-

tity of active sites, elementary steps and rate-determining step (RDS), etc.) for carbon catalyzed reactions are still missing and are urgently needed in related fields for the rational design of non-metallic nanocarbon catalysts.

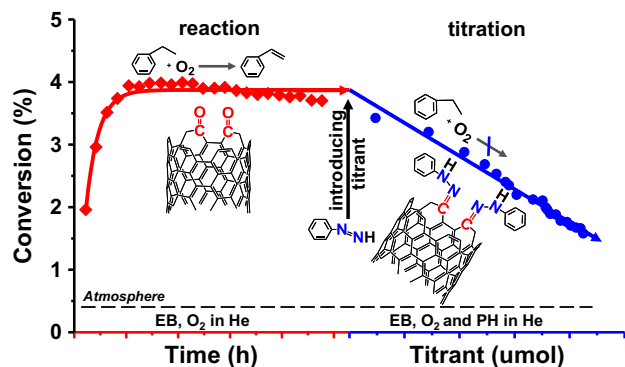
Alkane ODH to corresponding alkene is an extremely important industrial process, and it is also one of the reactions that has been studied earliest in the field of carbon catalysis [14,15]. The vital role of the surface ketonic carbonyl groups on nanocarbon for the catalytic process has been firstly demonstrated via *in situ* ambient pressure X-ray photoelectron spectroscopy (XPS) [10], chemical titration method [16], and conjugated polymers as model nanocarbon catalysts [17]. However, the detailed kinetic analysis and the quantitative description of the elementary steps for the catalytic reaction still remain a missing piece of the puzzle [16]. The main difficulty in the kinetic analysis for carbon catalysts is the measurement of intrinsic activity (turnover frequency, TOF), namely the accurate counting of the active sites under reaction conditions. The conventional spectroscopy-based techniques, such as XPS or temperature programmed desorption (TPD) etc., do not show enough accuracy for quantification of the active sites especially under reaction conditions [18–20] because of the complexity of the nanocarbon surface functionalities (hydroxy, carboxylic acid, lactone, and ketonic carbonyl groups etc.) [21–25].

Aimed at above problems, we have recently developed an *in situ* chemical titration process to quantify the active sites and the TOF

* Corresponding author.

E-mail address: wqi@imr.ac.cn (W. Qi).

¹ These authors contributed equally to this work.



Scheme 1. Schematic drawings of carbon catalyzed EB ODH reactions and subsequent titration process. EB conversion as a function of reaction time and titrant (PH) consumption, respectively.

for carbon catalysts in ethylbenzene (EB) ODH reactions [26]. As illustrated in Scheme 1, the titrant phenyl hydrazine (PH) is introduced into the reaction system when nanocarbon catalyzed EB ODH reaction reached steady state (the schematic drawings of the reaction/titration set up can be found in Fig. S1). The catalytic activity obviously dropped because of the selective reaction between PH and the ketonic carbonyl groups (forming hydrozones at a yield over 99%), and this phenomenon provides direct chemical evidence that ketonic carbonyl groups on nanocarbon are the active sites for EB ODH reactions [16]. In addition, the surface concentration of the active sites could be obtained through measuring the saturated consumption of the titrants, and the TOF for carbon catalysts could be calculated from the linear dependence of EB conversion rates on the consumption of titrants. It should be noted that the number of active sites obtained from this titration process does not necessarily equal to that on fresh catalysts [26]. It represents the number of active sites those are “working” under reaction conditions, and the TOF value reflects the intrinsic catalytic activity of nanocarbon catalysts [26]. Another key advantage of the proposed titration process is that it could realize TOF values for carbon catalytic process via one single measurement avoiding the related complex structural characterization processes for traditional quantitative methods (XPS or TPD etc.). This method provides sufficient basis for kinetic analysis of carbon catalytic process, and it is immediately applied in liquid phase [27] and biological reactions [28] after its invention. Here, we report the detailed kinetic and mechanistic studies on carbon catalyzed EB ODH reactions (heterogeneous) combining classic kinetic analysis, kinetic isotope effects (KIE) and single reactant surface reaction techniques. We hope present study could provide a promising strategy for quantitative description on carbon catalytic process at molecular level.

2. Experimental

2.1. Catalysts preparation

Pristine multiwall carbon nanotubes (pCNTs) is supplied by Shandong Dazhan Nano-materials Co., Ltd (China). The average diameter of pCNT is 20 ± 5 nm from TEM measurements. pCNTs were oxidized with HNO_3 prior to their applications in ethylbenzene (EB) oxidative dehydrogenation (ODH) reactions. In a typical oxidation process, 10 g pCNTs were refluxed with 1000 mL of concentrated HNO_3 (68%) at 120°C for 2 h. The precipitate was filtered out and washed with deionized water for several times until the pH of the filtrate reaches 7. The resulting precipitate was dried in vacuum at 120°C overnight to give black oxidized CNTs (CNTs).

2.2. Ethylbenzene oxidative dehydrogenation reactions

The reliability of the *in situ* titration set-up was carefully checked before kinetic tests [26]. EB ODH reactions were performed on nanocarbon catalysts (CNT, 200 mg) at 265°C using a tubular quartz flow reactor with a plug-flow. The reactant mixture contained EB (99.9%), O_2 (99.999%), and He (99.999%), and the molar flow rates of them were adjusted for the desired EB and O_2 pressures (0.05–16 kPa for EB, 0.25–16 kPa for O_2). The deuterated ethyl benzene used in the isotopic test is all H atoms deuterated EB (CAS: 25837-05-2) with 99% D abundance.

The concentrations of reactant and product were measured with gas chromatography (GC, Agilent 7890A) using a methyl silicone capillary column (HP-5, $25\text{ m} \times 0.32\text{ mm} \times 1.05\text{ }\mu\text{m}$) connected to a flame ionization detector and a Poropak Qpacked column (80–100 mesh, 12 ft. \times 1/8 in.) connected to a thermal conductivity detector.

2.3. Chemical titration of ketonic carbonyl groups on CNTs

The entire titration process includes two parts: the reaction stage and the titration stage. At the reaction stage, EB ODH reactions were performed on nanocarbon catalysts (CNT, 200 mg) at 265°C for about 5 h to reach steady state. The reactant mixture contained EB (99.9%), O_2 (99.999%), and He (99.999%), and the molar flow rates of them were adjusted for the desired EB and O_2 pressures (0.05–16 kPa for EB, 0.25–16 kPa for O_2). EB was introduced into the reaction system through a peristaltic pump with a syringe containing liquid ethylbenzene. The concentrations of reactant and product were measured with gas chromatography (Agilent 7890A) using a methyl silicone capillary column (HP-5, $25\text{ m} \times 0.32\text{ mm} \times 1.05\text{ }\mu\text{m}$) connected to a flame ionization detector and a Poropak Qpacked column (80–100 mesh, 12 ft. \times 1/8 in.) connected to a thermal conductivity detector.

The *in situ* titration process was performed when the reaction reached steady state. The inlet was switched to the syringe containing both EB and PH (content of PH at 2 wt%), and all the reaction conditions were kept the same as steady state reactions.

2.4. Structural characterizations

TEM measurements were performed on a FEI Tecnai T12 microscope with an accelerating voltage at 120 kV. N_2 physisorptions were measured on a Micrometrics ASAP 3020 instrument. Raman spectra were collected by a LabRam HR 800 excited with 532 nm laser.

3. Results and discussion

3.1. Kinetic measurements

The CNT catalysts used in current research were pretreated and oxidized (refluxing) with concentrated nitric acid, which means that all the accessible metal impurities would be removed during the treatment. ICP and TG result shows that the metal content of the treated CNT is below 0.2 wt%, confirming that the influence of metal impurities is negligible. As mentioned above, the full scale kinetic analysis on carbon catalytic systems is quite difficult to realize and is rarely reported because of the structural complexity of nanocarbon [6]. However, the combination of steady state activity measurements and active site chemical titration process could provide the TOF value for carbon catalysts [12]. EB ODH reaction is performed at 265°C to ensure the surface and structural stability of nanocarbon catalysts and the titration derivatives. XPS, Raman, TEM and N_2 adsorption characterizations (Figs. S2–S5) on the fresh

Download English Version:

<https://daneshyari.com/en/article/11009948>

Download Persian Version:

<https://daneshyari.com/article/11009948>

[Daneshyari.com](https://daneshyari.com)