



Investigation of the selective sites on graphitic carbons for oxidative dehydrogenation of isobutane

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ABSTRACT

Reaction network analysis of the oxidative dehydrogenation (ODH) reaction of isobutane over model carbon catalysts with tailored open-edge graphitic structure and quinone-type oxygenated functionalities was used to identify the selective pathways for the formation of isobutene. Carbon-based materials have been widely used in catalysis, but the active sites are not well-understood due to the complexity of the carbon structure. Correct identification of these sites is essential for learning how to manipulate material structure to achieve high catalytic yields of the desired products. In this study, we created model catalysts with controllable surface concentration of oxygen based on graphitized mesoporous carbon (GMC). Our studies reveal that the ODH reaction of isobutane on carbon catalysts is a parallel-consecutive pathway with partial oxidative dehydrogenation for the formation of isobutene and deep oxidation pathway for the direct formation of CO and CO₂ from isobutane. These two pathways show different dependence on the quinone-type oxygen sites: the rate constant leading to the desired partial oxidation product does not show a strong correlation to the density of the oxygen sites, whereas the rate constant leading to the unselective CO_x products increases continuously with the density of oxygen sites.

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1. Introduction

Isobutene is the most versatile chemical intermediate among all C₄ olefins. The demand for isobutene has been increasing continuously over the years due to its importance as a monomer in the synthesis of various organic products for chemical and polymer industries. Conventional dehydrogenation route using metal catalysts for light olefin synthesis usually involves a high temperature endothermic process which has several disadvantages such as catalyst deactivation by coke formation and the consequent need for periodic catalyst regeneration [1]. Alternatively, oxidative dehydrogenation (ODH) reaction of paraffins to their corresponding olefins has received increasing attention since, as an exothermic process, ODH reaction requires much less energy consumption than dehydrogenation process which is commonly adopted in current industrial operations.

Most of the studies on ODH reactions have been done using transition metal oxide catalysts such as Mg–V–Sb-oxide, vanadium oxide, and manganese molybdate [1–3]. One of the major challenges of this kind of reaction is to be able to minimize the combustion side reactions leading to the undesired CO and CO₂ products while increasing the limited alkene selectivity achieved by these catalysts. The chemical complexity of the oxide catalysts

leading to their activity can also be detrimental to the elucidation of the active sites responsible for high selectivity.

Carbon-based catalysts have proven to be attractive alternatives to the conventional metal-based ones. Carbon materials have significant advantages due to their unparalleled flexibility as their physical and chemical properties can be tailored for specific needs. So far, activated carbon, carbon nanofibers, and carbon nanotubes have been reported to catalyze ODH reactions with high selectivity results. Delgado et al. [4] reported catalytic activity of carbon nanofibers immobilized on carbon felt support for the ODH reaction of ethyl benzene. Díaz Velásquez et al. [5] tested the surface-modified activated carbon for the isobutane ODH reaction, and considered the carbonyl/quinone groups on the surface as the active sites, where the isobutene yields were lower with lower concentrations of these groups. Due to the diverse nature of the structure and functionalities present in different carbon materials including the traditional activated carbons and the carbon nanotubes, the active sites of ODH reactions on carbon materials leading to the formation of the desired unsaturated products still have not been clarified. The precise mechanism of the ODH reaction over carbon surface remains controversial due to undetermined metal impurities as found in activated carbons and carbon nanotubes, dangling bonds, mixed sp² and sp³ hybridization, surface functional groups, and the defect/edge sites, which could all contribute to the reactivity with different selectivity.

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In order to identify the active sites of the ODH reaction on carbon catalysts, model compounds have been used to simplify the catalytic system and thereby leading to better understanding of the catalytic properties of carbon catalysts. A recent publication by Zhang et al. [6] used surface-modified carbon nanotubes as model catalysts and discovered that the nature of the surface oxygen species has a strong correlation with the selectivity of the catalysts: electrophilic oxygen species (converted from oxygen molecules on the defect/edge sites) led to unselective total combustion of *n*-butane and nucleophilic-oxygenated groups led to the preferential ODH reaction that formed butadiene. More recently, we demonstrated that the graphitized mesoporous carbon (GMC) with controllable openness of the graphite edge sites is an excellent model catalyst for the study of active sites in the ODH reaction on carbon catalysts [7]. The open graphitic edges in the GMC catalyst have been identified as the active sites for the ODH of isobutane. Interestingly, the initial existence of the oxygenated functional groups, mainly carbonyl groups, on the open graphitic edges of GMC catalyst shows no effect on its catalytic performance. The GMC catalysts with or without initial oxygen functional groups show negligible differences in the selectivity and reactivity. A plausible reason for this observation is that the open edge sites on the graphitic carbon are very active and the oxygenated functional groups are formed promptly when the reactant oxygen is introduced into the system. Indeed, oxygenated functional groups were observed after the ODH reaction even for the GMC catalyst without initially attached oxygenated groups. Although the edge sites are unambiguously the active sites for the ODH reaction, the role of the oxygenated functionalities that are either initially attached on the carbon catalysts surface or generated during the reaction has not been systematically studied on model catalysts. Revealing the role of these oxygenated functionalities in the ODH reaction is crucial for the fundamental understanding of the ODH reaction mechanism of hydrocarbons over carbon catalysts. Reaction kinetic analysis on carbon catalysts has been rarely studied, particularly on designed model catalysts. Therefore, a detailed kinetic study of the ODH reaction on model catalysts with intentionally generated functionalities will be valuable for gaining such a fundamental understanding of ODH reaction on carbon catalysts.

We report herein a detailed study on the reaction kinetics on carbon catalysts with tightly controlled surface functionality to gain insights on the reaction mechanism of ODH reactions. The GMC is an appealing model catalyst because of its simplicity in structure and surface functionality. In this study, we created synthetic carbon catalysts with controlled surface concentration of oxygenated functionalities based on GMC. These compounds have been investigated as model carbon catalysts for the ODH reaction of isobutane to reveal the reaction network at differential reaction conditions. We validate that the ODH reaction on carbon catalysts is a multistep parallel-sequential reaction path which has been thoroughly demonstrated over oxide catalysts [1,3,8,9]. Furthermore, the derived reaction rate constants for each step clarified the factors leading to superior selectivity to isobutene on these model carbon catalysts.

2. Experimental

2.1. Synthesis of model catalysts

Pluronic surfactant F127, phloroglucinol, hydrochloric acid (37 wt%), and formaldehyde (37 wt%) were obtained from Sigma-Aldrich, and anhydrous ethanol was purchased from Pharmco Aaper. The preparation of mesoporous carbon precursors was carried out following a procedure established by our group [7,10]. Briefly, F127 (50.4 g), phloroglucinol (25.2 g), and hydrochloric acid

37 wt% aqueous solution (10.0 g) were mixed in a round-bottomed flask and dissolved in 1300 ml of anhydrous ethanol. The resulting mixture was then heated with vigorous stirring until reflux. An aqueous solution of 26.0 g of formaldehyde 37 wt% was added to the reaction mixture. The heating and stirring were continued for additional 2 h. Orange-colored particles were collected after the reaction and were further pyrolyzed at 850 °C in a tube furnace (Thermolyne, model: 79300) in the presence of nitrogen. The resulting carbon materials were then treated in helium at 2600 °C in a graphite furnace (Thermal Technologies, model: 1000-2560-FP20) to reach the starting material of pristine graphitic mesoporous carbon denoted as sample SK0.

In our previous study we found out that our GMC pristine precursor can be homogeneously oxidized by air at 500 °C [7]. At this condition, we ensured the integrity of the graphitic structure while opening the fullerene-like cavities and creating open edges on its structure. Additionally, oxygen functional groups were created during the oxidation in air. In this study, the burn-off (B.O.) level, defined as the weight loss percentage after the oxygen treatment, and the amount of oxygenated groups were systematically varied by changing the duration of the oxidation treatment. The GMC samples prepared by this systematic approach were labeled as SK1, SK2, SK3, and SK4 corresponding to the oxidation treatment of 24 h, 30 h, 36 h, and 48 h, respectively.

2.2. Characterization of the physical structure of GMC catalysts

The nanometer-sized graphite crystals were characterized by Raman spectra, which were collected via fiber optics connected directly to the spectrographic stage of a triple spectrometer (Princeton Instruments Acton Trivista 555). Edge filter (Semrock) was used in front of the UV-Vis fiber optic bundle (Princeton Instruments) to block the laser irradiation. The 532 nm excitation was emitted from a solid state laser (Princeton Scientific, MSL 532-50) and the power was about 20 mW at the sample. The sample sat on a XY stage (Prior Scientific, OptiScan XY system) and translated in raster mode while collecting the spectrum in order to eliminate/minimize any laser damage of the samples. Cyclohexane solution was used as a standard for the calibration of the Raman shifts.

The porous structures of the model catalysts were characterized by physisorption. N₂ adsorption and desorption isotherms were measured in liquid N₂ at 77 K using an AUTOSORB-1C instrument (Quantachrome Corporation, USA). The samples were outgassed at 200 °C for 2 h prior to the isotherm measurement. The Brunauer–Emmett–Teller (BET) specific area, S_{BET} , was calculated from the relative pressure $0.05 < \frac{p}{p_0} < 0.3$ interval; and the total pore volume, V_{total} , at $\frac{p}{p_0} = 0.95$. The pore size distribution was calculated based on Barrett–Joyner–Halender (BJH) method using $0.05 < \frac{p}{p_0} < 0.94$ interval of the adsorption branch of the isotherm.

2.3. Probing surface functionalities

The surface-oxygenated functionalities before and after reaction were characterized by Temperature-Programmed Desorption (TPD) using a U-tube reactor (Altamira AMI-200) in flowing helium (20 ml/min) with a heating rate of 10 K/min from 298 K to 1300 K. The amounts of CO and CO₂ desorbed were quantified by a quadrupole mass spectrometer equipped with a 1 m long gas sampling capillary (Pfeiffer-Balzer Omnistar).

2.4. Catalytic measurements

The catalytic performance test for isobutane ODH reaction was carried out at atmospheric pressure in a packed bed stainless steel autoclave reactor (PID Eng & Tech, Spain). The feed consisted of iso-

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