



# Catalytic performance of sucrose-derived CMK-3 in oxidative dehydrogenation of propane to propene

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## ABSTRACT

CMK-3 carbon replica was synthesized by carbonization of sucrose introduced to the pore system of a SBA-15 hard template followed by dissolving SiO<sub>2</sub> with HF. The material with a stable hexagonal structure and an expanded surface area ( $S_{\text{BET}} = 1287 \text{ m}^2/\text{g}$ ) was obtained. TG measurements showed that CMK-3 type mesoporous carbon started to be intensively oxidized by molecular O<sub>2</sub> above 723 K. This carbon sample was tested as a catalyst of dehydrogenation of propane to propene under oxidative (O<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> = 0.25, 0.50 and 1.00) and non-oxidative (O<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> = 0.00) conditions in the temperature range from 573 to 873 K. The propene yield increased with rise in the reaction temperature, however above 573 K the formation of side-products (C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub> and H<sub>2</sub>) was observed. Moreover, coke was deposited on the catalyst surface. A decrease in the mass of a catalyst bed after the catalytic runs suggested the participation of oxygen in burning of deposited and bulk coke. The surface composition of a spent catalyst was investigated by XPS and TPD analysis. The changes in the concentration of oxygen functional groups, caused by the catalytic reaction, were observed regardless of a reaction temperature and feed composition.

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## 1. Introduction

Carbons with the surface exhibiting various electronic properties can act as catalysts of the processes occurring in the presence of metal conductors (e.g. hydrogenation), semiconductors (e.g. oxidation) and insulators (e.g. polymerization or halogenation) [1]. Exclusive catalytic activity of carbons can be enhanced by the controlled formation of their mesoporosity and nanosized particles. Ordered mesoporous carbons (OMCs), carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have high surface area with a large number of sites, which are active in various catalytic processes.

In 1999, Ryoo et al. [2] described a pioneer synthesis of highly ordered mesoporous carbon (CMK-1) belonging to a wide group of materials designated as CMK-n (Carbon Mesostructured by KAIST [3]). Nevertheless, CMK-3 developed by Jun et al. [4] has been the most intensively studied. This material is prepared using SBA-15 mesoporous silica as a hard template and therefore shows the highly-ordered hexagonal arrangement of carbon rods interconnected by carbon bridges (*p6mm* symmetry) [5].

The typical synthesis of a carbon replica includes: (1) preparation of mesoporous silica; (2) deposition of a carbon source (e.g. sucrose, poly(furfuryl alcohol), polyacrylonitrile, benzene, propylene, acenaphthene) in the channels of a hard template by

impregnation or chemical vapor deposition; (3) carbonization of an organic precursor in the obtained composite; (4) removal of the silica template with a NaOH or HF solution [6,7]. The final material is characterized by high specific surface area, well defined size of pores and particular surface composition, which make it useful in industrial applications including adsorption and catalysis. Carbon replicas have been successfully used in cellulose hydrolysis [8], sorption of dyes [9], hydrogen storage [10] and as an anode material for lithium-ion batteries [11]. They have been also examined as promising catalysts in the conversion of saturated hydrocarbons into their unsaturated analogs, which are valuable feedstock in chemical industry [12].

Propene is one of the most important intermediates and monomers in different petrochemical and polymer processes. Nowadays, steam cracking, catalytic cracking and selective technologies like dehydrogenation of propane, metathesis and methanol based processes (MTO or MTP) are the primary propene sources. However, a strong demand for propene leads to the optimization of the commercial technology as well as to a growing interest in developing new processes for the C<sub>3</sub>H<sub>6</sub> production.

Selective oxidative dehydrogenation of propane to propene in the presence of various hydrogen acceptors (e.g. O<sub>2</sub>, N<sub>2</sub>O or CO<sub>2</sub>) has been the subject of investigations for many years [13–17]. Among proposed solutions the oxidative dehydrogenation (ODH) of propane with oxygen is the most extensively studied. In contrast to the nonoxidative pathway of propene obtaining, ODH of propane has no thermodynamic limitations and is a highly exothermic

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