

Mesoporous carbon materials as promising catalysts for oxidative dehydrogenation of alkanes

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Industrial synthesis of alkenes

From the beginning of the twentieth century, a systematic growth of demand for high volume products of chemical industry has been observed [1]. A rapid economic development of Asian (especially China, India and Middle East) as well as African countries suggests that during the next decades a further growth of such production should be expected [2]. It is worth to note that a majority of thousands of available chemicals is produced from a small group of tens of base chemicals. Among them, alkenes (e.g. ethylene, propylene, butadiene), being the most important monomers in the plastics industry, play a very important role. Ethylene with a global production capacity exceeding 150 mln t/year is a leading feedstock.

Olefins are mainly produced by the thermal cracking of relatively low reactive alkanes present in natural gas (North America, Middle East) and in crude oil (Europe, Japan) [1]. In this process, water vapour is used as an agent, which lowers partial pressure of reagents and supplies a heat energy needed for the endothermic conversion. This fact significantly restricts the economic efficiency of this technology and unfavourably affects the cost of final chemical products. For example, in the synthesis of acrylonitrile about 67% of the overall cost of its production is related to the propylene synthesis, which is the main feedstock [3]. An additional disadvantage of the cracking process is low selectivity to desired products, which is a typical feature of reactions carried out without any catalyst. Despite the continuous efforts aiming to reduce the energy requirement of the thermal cracking process, it still consumes 40% of global energy used by the petrochemical industry [4].

A technology giving higher selectivities is the catalytic cracking. In terms of contribution to the total world alkenes production, this process is placed on the second position. In the catalytic cracking plants designed for the production of light olefins, Y zeolite with an addition of shape selective ZSM-5 zeolite is commonly used. In this case, the narrow-pore ZSM-5 zeolite restricts obtaining of branched products and increases the selectivity to light alkenes. Both Y and ZSM-5 zeolites exhibit high thermal stability and resistance to work in continuously repeated reaction-regeneration cycles. Despite its numerous advantages, the catalytic cracking is still one of the most environment polluting processes in the petrochemical industry due to the emission of SO_x and NO_x during the frequently repeated catalyst regeneration [1].

Some technologies based on the dehydrogenation of light paraffins, e.g. UOP Oleflex and Catofin, are known to be used for the synthesis of propylene or iso-butylene over Al₂O₃ catalyst doped with Pt, Cr, or Pt-Sn. Nevertheless, the contribution of olefins obtained by this method in their total world production is still negligible. The selective, catalytic dehydrogenation is nowadays

applied as a main method of the production of heavier alkenes, like styrene. For the synthesis of this important monomer, the catalyst based on iron(III) oxide doped with potassium and chromium is used. However, the endothermic reaction of dehydrogenation exhibits some drawbacks, analogous to the thermal cracking [5].

Disadvantages of the aforementioned principal technologies of olefin production as well as tendency to a sustainable development and growing efficiency of the production cause that in the nearest future the implementation of fundamental changes in the high volume production of alkenes seem to be inevitable. From this point of view, the oxidative dehydrogenation (ODH) of alkanes is one of the most promising alternatives. In contrast to the majority of presently applied methods, ODH exhibits an exothermic heat effect and a lack of thermodynamic limitations. Consequently, it allows to achieve substantial conversions of paraffins at lower temperatures, with high selectivity to the desirable products. The technology based on the oxidative dehydrogenation was independently implemented to the industrial production of butadiene by Phillips Petroleum Company (*O-X-D*) and Petro-Tex (*Oxo-D*) [6–8]. Oxygen present in the introduced air is an oxidizing agent in both cases and plays a complex role including: (i) initiation of the oxidative dehydrogenation through the elimination of the hydrogen atom from the alkane molecule, (ii) oxidation of hydrogen produced in the simultaneous reaction of direct dehydrogenation and (iii) internal regeneration of the catalyst. In the *O-X-D* technology the conversion of *n*-butane achieves 80% with the selectivity to butadiene of ca. 90%, while in the *Oxo-D* one these parameters reach 70 and 96%, respectively.

A kind of substitute of the oxidative dehydrogenation is a method of alkenes production combining the direct dehydrogenation with the subsequent oxidation of the produced hydrogen, which has been already implemented in the chemical industry. An example of such approach is the *STAR* technology (*S*Team *A*ctive *R*eforming), developed by ThyssenKrupp Industrial Solutions and used for the production of propylene. This solution is based on using of a multi-tubular reactor, in which the direct dehydrogenation takes place. Subsequently, in an adiabatic reactor connected in series, the oxidation of the produced hydrogen occurs with the simultaneous evolving of heat and a shift in the reaction equilibrium towards the products, which increases the overall conversion of propane [9]. In this part of the plant, a mixed zinc-calcium-aluminum oxide catalyst doped with noble metals, which is stable at high temperatures and in the presence of water vapour and oxygen, is used.

The comparison of the two described technologies is presented in Figure 1. It should be noticed that the *STAR* technology actually does not use the oxidative variant of the ODH reaction on the dehydrogenation catalyst, but it is just based on the effect of shifting the equilibrium of the standard dehydrogenation reaction to the products. The implementation of the forthcoming solutions based on the ODH reaction to the industrial practice depends on the development of adequately active, selective and stable catalysts. As an example, the studies dedicated to obtain the catalyst for the

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ODH of ethylbenzene, which involve two main pathways, can be considered. The first approach is focused on the synthesis of active oxide catalysts, of which vanadium-magnesium mixed oxide turned out to be the most promising material [10–13]. The second trend is based on the design of catalysts with acidic properties (including carbon materials), whereby the superficial carbon layer, created as a surface deposit at the beginning of the reaction, acts as the catalytically active phase [14–19]. Due to the promising results of many research, the application of carbon materials in the ODH of ethylbenzene is the object of in-depth investigation.

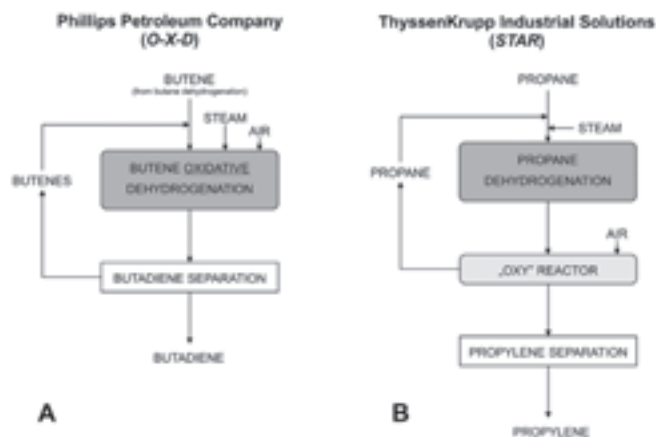


Fig. 1. Schematic diagrams of O-X-D technology (Phillips Petroleum Company) (A) and STAR (ThyssenKrupp Industrial Solutions) (B) [6, 9]

Mesoporous carbon materials

Originally, microporous carbon materials (mostly activated carbons) were considered as the promising catalysts of the ODH reaction due to highly developed specific surface area and appropriate chemical composition of the surface [20]. It should be noted that these catalysts do not contain metals, thus they are environmentally friendly and their application is highly desirable [21]. The activated carbon was used the first time as the catalyst in the ODH of ethylbenzene by Alkhazov et al. in 1978. The authors observed that the reaction occurs over carbon materials at the temperatures lower by 150°C than in the presence of oxide catalysts [19, 22]. Thereafter, other microporous carbon materials were tested in the ODH reaction [16, 19, 23–31]. An example of the application of carbon structures different than activated carbon, namely activated carbon nanofibers, was presented by Pereira et al. [28]. They showed that the catalytic activity depended on the diameters of pores present in the material. The intensification of the carbon deposition within pores was observed below the limit value of 1.2 nm. As a result, the fast catalyst deactivation was noticed. On the other hand, Keller and co-workers used for the same reaction so-called onion-like carbons, which exhibit multi-layer spherical structure. The authors proved that this carbon material showed the higher catalytic activity in comparison to other carbon materials, like graphite or carbon nanofibers. The observed effect was probably related to the optimal distribution of superficial oxygen-containing functional groups [26].

Despite many advantages, microporous carbons have a few troubling drawbacks, including: (i) diffusion limitations which occur during migration of substrate molecules to active sites localized on the internal surface of catalyst and (ii) foregoing deposition of carbonaceous deposit on the material surface during the reaction, which results in the gradual clogging of narrow pores and as a consequence, in the decrease in the catalytic activity [28, 32]. An effective solution of this problem might be to use materials, which have pore diameters out of commonly accepted range of microporosity. It can be assumed that within mesochannels with diameters > 2 nm, the migration of reactants is facilitated, and the process can proceed in the kinetic-controlled regime [20]. In such case, the efficiency of the catalyst depends only

on the character and concentration of the superficial active sites [33]. The surface analysis of the mesoporous carbon materials showed that generally they do not differ from the typical activated carbons. In both cases, the presence of surface heteroatoms (mostly oxygen), is determined by irregular edges of the graphene layers in the turbostratic (pseudographitic) structure of carbon material. Figure 2 illustrates types of oxygen-containing functional groups detected on the surface of mesoporous carbon materials by TPD and XPS analyses [34]. Mainly carbonyl, quinone, carboxylic, phenol, lactone and anhydride entities were identified. These results are consistent with a model of surface chemistry of activated carbons discussed in the literature [19, 35, 36].

Due to the described advantages of mesoporous carbon materials, which do not limit their application only to the ODH processes, new synthesis methods have been still developed. The most common pathways are based on: (a) a deep physical or physical-chemical activation of previously pyrolyzed carbon precursor (e.g. coal, wood, polymers) [37] or (b) catalytic activation with metals and/or metal oxides [38], (c) carbonization of aerogels [39], (d) structural nanoreplication by hard- [40, 41] or (e) soft-templating technique [42]. The methods a)-c) lead to obtaining mesoporous carbon materials with a broad pore size distribution and substantial contribution of micropores, whereas the methods d) and e) allow to control better pore diameters [43]. However, both of them require to use the properly selected shape-forming template in order to obtain the planned spatial structure of carbon material. For the soft-templating method, the templates are usually organics molecules, which undergo self-assembly together with the carbon precursor by hydrogen bonds and hydrophobic-hydrophilic interactions. In the case of hard-templating, silica gels with an unordered spatial structure as well as silica mesoporous sieves (e.g. SBA- or MCM-type) are usually used as the structure-controlling agents. The materials produced by this method exhibit the precisely defined three-dimensional pore structure. Because of many parameters of the synthesis, which affect the properties of final carbon material, the soft-templating technique is rarely used in contrast to the hard-templating one. In the latter approach, a rigid, porous structure significantly determines the ordering of synthesized carbon replica, which is in fact a negative of the utilized template. The idea of the hard-templating synthesis of mesoporous carbon replicas is based on the deposition of a carbon precursor within pores of the template. Subsequently, the obtained composite is carbonized at high temperatures (usually above 700°C) in the inert atmosphere in order to pyrolytic decomposition of the carbon precursor which fills the template pores. As a result, the majority of non-carbon elements are eliminated from the carbon precursor in the form of volatile gaseous products and the carbonaceous material with the turbostratic (pseudographitic) microstructure is generated inside the pores. The final stage of the synthesis is a removal of the template in order to expose the carbon material [40, 41].

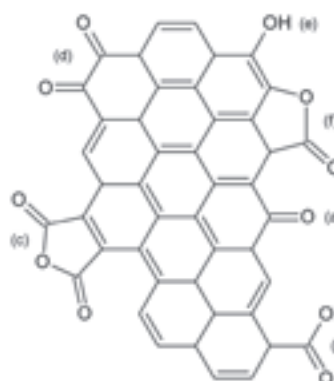


Fig. 2. Oxygen-containing functional groups identified on the surface of mesoporous carbon replicas: (a) carbonyl, (b) carboxylic, (c) anhydride, (d) quinone, (e) hydroxyl, (f) lactone

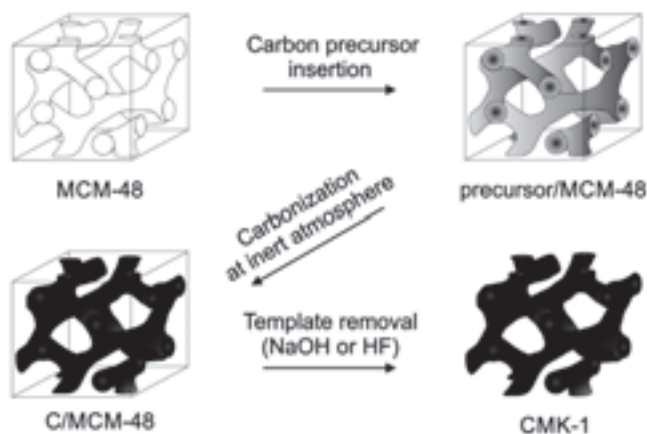


Fig. 3. Scheme of the synthesis of CMK-1 mesoporous carbon replica

The substantial increase of interest in the synthesis of ordered mesoporous replicas took place after 1999, when Ryoo et al. presented the successful synthesis of CMK-1 mesoporous carbon material with the regular structure, based on nanoreplication of MCM-48 sieve (cf. Fig. 3) [41]. Afterward, other mesoporous carbon replicas were prepared, however, the family of CMK-type materials (*Carbon Mesoporous by KAIST – Korea Advanced Institute of Science and Technology*) should be indicated as the most important [44]. The classification of this group of materials, including templates used for the synthesis, is summarized in Table 1.

Oxidative dehydrogenation of alkanes over carbon mesoporous catalysts

Until now, unordered and ordered mesoporous carbon materials were tested as catalysts mostly in the oxidative dehydrogenation of propane, isobutane and ethylbenzene. In the case of ODH of propane, Liu and co-workers studied the catalytic activity of mesoporous carbon monoliths synthesized using resorcin as a carbon precursor and Pluronic F127 copolymer as a self-assembly agent [45]. The collected results showed that over the obtained carbon material, the conversion of propane at 400°C reached ca. 20%, both at the beginning of the reaction and after 50 h time-on-stream, with the selectivity to propene of ca. 25%. In the same reaction, Michorczyk et al. studied the catalytic activity of highly ordered CMK-3 carbon replica with the hexagonal structure [46]. At the temperature of 400°C, the CMK-3 catalysts exhibited slightly lower initial propane conversion (ca. 16%), but reached significantly higher selectivity to propene (ca. 55%). Similar investigations were carried out for the ODH of ethylbenzene. Almost a decade after the first synthesis of the hexagonally ordered mesoporous carbon sieve by Ryoo et al., Su and co-workers used this material as the catalyst for the ODH of ethylbenzene [47]. The conversion of ethylbenzene after 5 hours time-on-stream at the temperature of 400°C reached 69%, with the selectivity to styrene equal to 76%. Utgenannt et al. used for the same reaction unordered mesoporous carbon materials obtained by nanoreplication of mesoporous silica gel [49]. Over the most active sample, the conversion of ethylbenzene after 5 h of reaction carried out at 350°C reached ca. 16% with the selectivity to styrene as high as 98%. Schwartz and co-workers showed that in the ODH of isobutene, mesoporous graphite-like carbons allowed to achieve the relatively low conversion of isobutene, giving the high selectivity to isobutylene (>70%) at the same time [48]. Moreover, the uncommon stability of catalyst operation was observed during 15 hours time-on-stream, which revealed its limited susceptibility to burning at relatively high temperature of 400°C as for the carbonaceous material.

The described examples of the application of various types of mesoporous carbon materials as the catalysts for the ODH processes reveal that the presence of wide pores within the material positively

influences the catalytic activity. It should however be stressed that the type of spatial ordering of mesoporous carbon materials might also play an important role. The family of CMK-type carbon replicas can be considered as an example (cf. Tab. 1). Figure 4 shows the preliminary results of the studies carried out in the Organic Technology Research Group at the Faculty of Chemistry of Jagiellonian University. The catalytic activity of the CMK-1 and CMK-3 carbon replicas was investigated in the ODH of ethylbenzene [34, 40]. Both materials were synthesized using the same carbon precursor, i.e. sucrose, however, the higher initial conversion of ethylbenzene was detected in the presence of the CMK-1 replica. In contrast to the hexagonally arranged CMK-3 replica, the CMK-1 material exhibits the regular structure. It can therefore be assumed that the CMK-1 replica enhances the accessibility of the reagent molecules to the active sites distributed inside the pores, as well as reduces the negative effect of a deposition of carbonaceous deposit, because of shorter residence time of the styrene molecules within the pore system of this material.

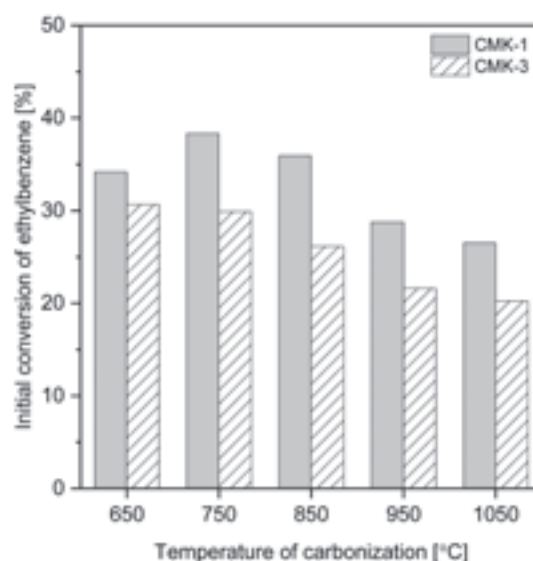


Fig. 4. Comparison of the initial conversion of ethylbenzene in the ODH reaction carried out at 350°C over CMK-1 and CMK-3 carbon replicas

Table 1

Classification of CMK-type carbon replicas – symmetry and silica templates used for the synthesis [44]

Replica	Hard template	Replica symmetry
Materials obtained by complete filling of the pores of template		
CMK-1	MCM-48	regular, Ia132
CMK-2	SBA-1	regular, Pm3n
CMK-3	SBA-15	hexagonal 2D, p6mm
CMK-4	MCM-48, FDU-5	regular, Ia3d
CMK-6	SBA-16	regular, Im3m
CMK-8	KIT-6	regular, Ia3d
Materials obtained by deposition of carbon film inside the pores of template		
CMK-5	SBA-15	hexagonal 2D, p6mm
CMK-7	SBA-16	regular, Im3m
CMK-9	KIT-6	regular, Ia3d

Factors affecting the activity of the carbon surface in the oxidative dehydrogenation of alkanes

The surface properties of mesoporous carbon materials (e.g. specific surface area, degree of graphitization, content of oxygen functional groups and the presence of heteroatoms) are an important factor influencing their catalytic activity in the ODH reactions. The effect of surface area on the catalytic activity in the ODH of ethylbenzene

was studied by Utgenannt et al. [49]. For the mesoporous carbon materials with the same chemical surface character and different surface areas, almost linear correlation between the initial conversion of ethylbenzene and the specific surface area of carbon material was observed. A doubling of the catalyst specific surface area resulted in twice as high initial catalytic activity.

The advanced studies on the influence of the degree of graphitization of mesoporous carbon materials synthesized using spherical silica gel on the catalytic activity in the ODH of ethylbenzene were performed by Walter et al. [50]. It was displayed that the catalytic activity was inversely proportional to the degree of graphitization of carbon material. This effect was explained by the decrease in the concentration of superficial oxygen-containing functional groups (e.g. carbonyl), which are considered as the active sites of ODH reaction. These moieties are formed easier on the surface containing the high amount of small graphite crystallites/domains, with high reactive layer edges, which are usually present in the carbon materials with the low degree of graphitization. Therefore, the degree of graphitization is strongly related to the ability of oxygen entities generation on the surface of mesoporous carbon materials.

Janus et al. studied the catalytic performance of chemically activated CMK-3 type mesoporous carbon replicas in the ODH of ethylbenzene [51]. These materials were activated in the solutions of 30% H_2O_2 or 65% HNO_3 in order to generate higher amounts of superficial oxygen-containing groups, which was confirmed by the XPS analysis. The influence of performed modification on the initial conversion of ethylbenzene is depicted in Figure 5. The results show that the increase in the content of superficial carbonyl groups entailed the increase of the initial conversion of ethylbenzene. It should be stressed that during the reaction, the surface composition changes continuously. Furthermore, due to the gradual formation of carbonaceous deposit, the decrease in the catalytic activity to the similar level was observed, regardless of the initial surface composition. Xie et al. also investigated the catalytic activity of mesoporous carbon materials taking into consideration the surface composition, but in the ODH of isobutane [52]. It was found that probably not only carbonyl functional groups are responsible for the catalytic activity in the ODH reaction. The authors suggested that a further investigation of the role of dissociatively adsorbed oxygen atoms is essential. This kind of oxygen atoms adsorbs on the layer edges and structure defects. The number of them can vary during the reaction and significantly contributes to the total catalytic activity.

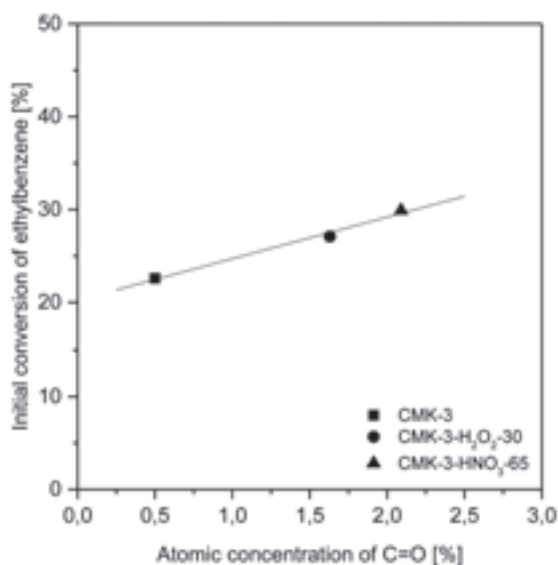


Fig. 5. Relationship between initial conversion of ethylbenzene and the concentration of superficial carbonyl groups for CMK-3 material [51]

The presence of superficial heteroatoms is also the factor affecting the catalytic activity of mesoporous carbon materials. Schwartz and co-workers examined the influence of modification of mesoporous carbon surface with phosphorus on the catalytic activity in the ODH of isobutane [48]. The obtained results revealed that the addition of phosphorus did not alter the nature of active sites of ODH reaction, but only modify their accessibility. Regardless of the amount of incorporated modifier, negligible changes of activation energies of ODH reaction were determined for all samples, which confirmed the foregoing hypothesis. The consequence of this kind of surface activation was the increase in the selectivity to isobutylene as well as the inhibition of total oxidation products (CO_x) formation. Nevertheless, the selectivity increase was not proportional to the amount of inserted phosphorus. Such tendency could be caused by blocking of carbonyl active sites at higher concentrations of phosphoric acid used as a source of this element.

The presented examples of the factors which can modify the activity of carbon surface in the oxidative dehydrogenation of alkanes, are certainly not the only possibilities that should be taken into account during the studies on the catalytic activity of mesoporous carbon materials. Due to the complexity of the structure of this kind of materials, the aforementioned factors should be considered not separately, but together, since the final catalytic activity in the ODH reaction depends on their combination. The outcomes of the studies on the catalytic activity of various mesoporous carbon materials in the ODH of ethylbenzene seem to be a good example [49–51]. Doubling of the specific surface area resulted in about 100% higher initial conversion of ethylbenzene. On the other hand, the increase of the content of carbonyl groups on the material surface from 0.50 to 2.09 wt.%, improved the initial conversion by only ca. 38%. A similar benefit was observed for two marginal graphitization degrees of mesoporous carbon materials. The graphical comparison of discussed activity changes is presented in the form of histogram in Figure 6. The area presented in the graph might indicate the field of appropriate combination of three considered parameters, in order to obtain the best possible final effect in terms of the catalytic activity.

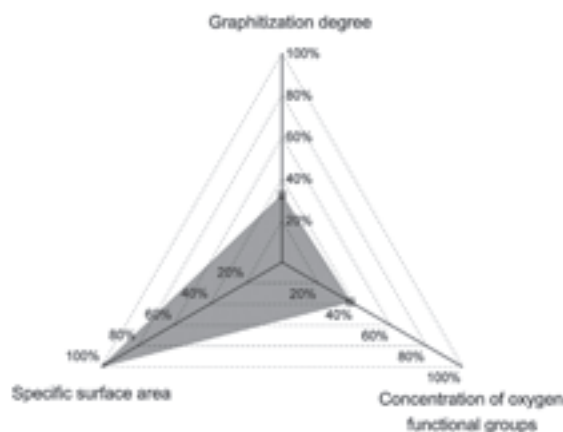


Fig. 6. Percentage influence of selected factors on the alteration of initial conversion of ethylbenzene in the ODH reaction over various mesoporous carbon catalysts

Summary and conclusions

Mesoporous carbon materials represent a promising group of materials, which can become attractive catalysts for the oxidative dehydrogenation of alkanes exchanging the currently applied, energy consuming and environmentally harmful technologies of olefins production. The preliminary results shown in the scientific literature reveal that these materials have great application potential, which depends on the surface properties, including surface area,

accessibility of pores, surface chemical composition as well as degree of graphitization. In order to obtain the sufficient activity and selectivity of carbon materials, the proper selection of all these parameters is necessary. It gives an opportunity to further investigations, with a hope of developing the industrial carbon catalyst.

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Literature

- Moulijn J. A., Makkee M., Van Diepen A. E.: *Chemical Process Technology*, John Wiley & Sons Ltd 2013, 99.
- Valencia R. C.: *The Future of the Chemical Industry by 2050*, Wiley-VCH Verlag GmbH & Co. KGaA 2013, 21–27.
- Brazdil J. F.: Strategies for the selective catalytic oxidation of alkanes. *Topics in Catalysis* 2006, **38**, 4, 289–294.
- Yoshimura Y., Kijima N., Hayakawa T., Murata K., Suzuki K., Mizukami F., Matano K., Konishi T., Oikawa T., Saito M., Shiojima T., Shiozawa K., Wakui K., Sawada G., Sato K., Matsuo S., Yamaoka N.: Catalytic cracking of naphtha to light olefins, *Catalysis Surveys from Japan* 2000, **4**, 2, 157–167.
- Cavani F., Trifirò F.: Alternative processes for the production of styrene. *Applied Catalysis A: General* 1995, **133**, 219–239.
- Totten G. E.: *Fluid and Lubricants Handbook: Technology, Properties, Performance and Testing*, ASTM International 2003, 190–192.
- Weissermel K., Arpe H.-J.: *Industrial Organic Chemistry*, John Wiley & Sons Ltd 2008, 109–112.
- Schulze J., Homann M.: *C4-Hydrocarbons and Derivatives: Resources, Production, Marketing*, Springer Science & Business Media, 2012, 71.
- HYPERLINK “<http://www.thyssenkrupp-industrial-solutions.com/products-solutions/chemical-industry/gas-technologies/star-process/overview.html>” www.thyssenkrupp-industrial-solutions.com data dostępu 04.03.2016.
- Hanuza J., Jezowska-Trzebiatowska B., Oganowski W.: Structure of the active layer and catalytic mechanism of the V_2O_5/MgO catalysts in the oxidative dehydrogenation of ethylbenzene to styrene. *Journal of Molecular Catalysis* 1985, **29**, 109–143.
- Shakhnovich G. V., Belomestnykh I. P., Nekrasov N. V., Kostyukovsky M. M., Kipermana S. L.: Kinetics of ethylbenzene oxidative dehydrogenation to styrene over a vanadia/magnesia catalyst. *Applied Catalysis* 1984, **12**, 23–34.
- Oganowski W., Hanuza J., Kępiński L.: Catalytic properties of $Mg_3(VO_4)_2$ -MgO system in oxidative dehydrogenation of ethylbenzene. *Applied Catalysis A: General* 1998, **171**, 1, 145–154.
- Raveendran Shiju N., Anilkumar M., Gokhale S. P., Seshagiri Rao B., Satyanarayana C. V. V.: Oxidative dehydrogenation of ethylbenzene using nitrous oxide over vanadia–magnesia catalysts. *Catalysis Science & Technology* 2011, **1**, 1262–1270.
- Emig G., Hofmann H.: Action of zirconium phosphate as a catalyst for the oxydehydrogenation of ethylbenzene to styrene. *Journal of Catalysis* 1983, **84**, 1, 15–26.
- Cadus L. E., Arrua L. A., Gorrioz O. F., Rivarola J. B.: Action of activated coke as a catalyst: oxydehydrogenation of ethylbenzene to styrene. *Industrial & Engineering Chemistry Research* 1988, **27**, 12, 2241–2246.
- Pereira M. F. R., Órfão J. J. M., Figueiredo J. L.: Oxidative dehydrogenation of ethylbenzene on activated carbon catalysts. I. Influence of surface chemical groups. *Applied Catalysis A: General* 1999, **184**, 1, 153–160.
- Figueiredo J. L., Pereira M. F. R.: The role of surface chemistry in catalysis with carbons. *Catalysis Today* 2010, **150**, 1–2, 2–7.
- Vrieland G. E., Menon P. G.: Nature of the catalytically active carbonaceous sites for the oxydehydrogenation of ethylbenzene to styrene: A brief review. *Applied Catalysis* 1991, **77**, 1, 1–8.
- Serp P., Figueiredo J. L.: *Carbon Materials for Catalysis*, John Wiley & Sons, 2009, 180–186.
- McNaught A. D., Wilkinson A.: *IUPAC. Compendium of Chemical Terminology*, 2nd ed. (the “Gold Book”). Blackwell Scientific Publications 1997.
- Anastas, P. T.; Warner, J. C.: *Green Chemistry: Theory and Practice*, Oxford University Press, 1998, 30.
- Alkhozov T. G., Lisovskii A. E., Ismailov Y. A., Kozharov A. I.: Oxidative dehydrogenation of ethylbenzene on activated carbons. I. General characteristics of the process. *Kinetics and Catalysis* 1978, **19**, 3, 611–614.
- Pereira M. F. R., Órfão J. J. M., Figueiredo J. L.: Oxidative dehydrogenation of ethylbenzene on activated carbon catalysts. 2. Kinetic modelling. *Applied Catalysis A: General* 2001, **196**, 1, 43–54.
- Pereira M. F. R., Órfão J. J. M., Figueiredo J. L.: Oxidative dehydrogenation of ethylbenzene on activated carbon catalysts. 3. Catalyst deactivation. *Applied Catalysis A: General* 2001, **218**, 307–318.
- Zhang J., Su D. S., Zhang A. H., Wang D., Schlögl R., Hébert C.: Nanocarbon as Robust Catalyst: Mechanistic Insight into Carbon-Mediated Catalysis. *Angewandte Chemie International Edition* 2007, **46**, 7319–7323.
- Keller N., Maksimova N. I., Roddatis V. V., Schur M., Mestl G., Butenko Y. V., Kuznetsov V. L., Schlögl R.: The Catalytic Use of Onion-Like Carbon Materials for Styrene Synthesis by Oxidative Dehydrogenation of Ethylbenzene. *Angewandte Chemie International Edition* 2002, **41**, 11, 1185–1188.
- Zhang J., Liu X., Blume R., Zhang A., Schlögl R., Su D. S.: Surface-Modified Carbon Nanotubes Catalyze Oxidative Dehydrogenation of n-Butane. *Science* 2008, **322**, 73–77.
- Pereira M. F. R., Órfão J. J. M., Figueiredo J. L.: Oxidative dehydrogenation of ethylbenzene on activated carbon fibers. *Carbon* 2002, **40**, 2393–2401.
- Delgado J. J., Vieira R., Rebmann G., Su D. S., Keller N., Ledoux M. J., Schlögl R.: Supported carbon nanofibers for the fixed-bed synthesis of styrene. *Carbon* 2006, **44**, 809–812.
- Pereira M. F. R., Figueiredo J. L., Órfão J. J. M., Serp P., Kalck P., Kihn Y.: Catalytic activity of carbon nanotubes in the oxidative dehydrogenation of ethylbenzene. *Carbon* 2004, **42**, 2807–2813.
- Su D. S., Maksimova N., Delgado J. J., Keller N., Mestl G., Ledoux M. J., Schlögl R.: Nanocarbons in selective oxidative dehydrogenation reaction. *Catalysis Today* 2005, **102–103**, 110–114.
- Kane M. S., Kao L. C., Mariwala R. K., Hilscher D. F., Foley H. C.: Effect of Porosity of Carbogenic Molecular Sieve Catalysts on Ethylbenzene Oxidative Dehydrogenation. *Industrial & Engineering Chemistry Research* 1996, **35**, 3319–3331.
- Pereira M. F. R., Órfão J. J. M., Figueiredo J. L.: Influence of the textural properties of an activated carbon catalyst on the oxidative dehydrogenation of ethylbenzene. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 2004, **241**, 165–171.
- Jarczewski S., Drozdek M., Wach A., Dudek B., Kuśtrowski P., Casco M. E., Rodríguez-Reinoso F.: Oxidative Dehydrogenation of Ethylbenzene Over Poly(furfuryl alcohol)-Derived CMK-1 Carbon Replica. *Catalysis Letters* 2016, DOI 10.1007/s1056-016-1748-z.
- Rodríguez-Reinoso F.: The role of carbon materials in heterogeneous catalysis. *Carbon* 1998, **36**(3), 159–175.
- Figueiredo J. L., Pereira M. F. R.: The role of surface chemistry in catalysis with carbons. *Catalysis Today* 2010, **150**, 2–7.
- Hu Z., Srinivasan M. P., Ni Y.: Preparation of Mesoporous High-Surface-Area Activated Carbon. *Advanced Materials* 2000, **12**, 1, 62–65.
- Oya A., Yoshida S., Alcaniz-Monge J., Linares-Solano A.: Formation of mesopores in phenolic resin-derived carbon fiber by catalytic activation using cobalt. *Carbon* 1995, **33**, 8, 1085–1090.
- Tamon H., Ishizaka H., Yamamoto Y., Suzuki T.: Preparation of mesoporous carbon by freeze drying. *Carbon* 1999, **37**, 2049–2055.
- Niebrzydowska P., Janus R., Kuśtrowski P., Jarczewski S., Wach A., Silvestre-Albero A., Rodríguez-Reinoso F.: A simplified route to the synthesis of CMK-3 replica based on precipitation polycondensation of furfuryl alcohol in SBA-15 pore system. *Carbon* 2013, **64**, 252–261.
- Ryoo R., Joo S. H., Jun S.: Synthesis of Highly Ordered Carbon Molecular Sieves via Template-Mediated Structural Transformation. *Journal of Physical Chemistry B* 1999, **103**, 37, 7743–7746.
- Liang C., Dai S.: Synthesis of Mesoporous Carbon Materials via Enhanced Hydrogen-Bonding Interaction. *Journal of American Chemical Society* 2006, **128**, 5316–5317.
- Liang C., Li Z., Dai S.: Mesoporous Carbon Materials: Synthesis and Modification. *Angewandte Chemie International Edition* 2008, **47**, 3696–3717.
- Niebrzydowska P., Kuśtrowski P.: Adsorbenty i katalizatory. *Wydawnictwo Uniwersytet Rzeszowski* 2012, 93–109.

45. Liu L., Deng Q-F, Agula B., Ren T-Z., Liu Y-P, Zhaorigetu B., Yuan Z-Y.: Synthesis of ordered mesoporous carbon materials and their catalytic performance in dehydrogenation of propane to propylene. *Catalysis Today* 2012, 186, 35–41.
46. Michorczyk P., Kuśtrowski P., Niebrzydowska P., Wach A.: Catalytic performance of sucrose-derived CMK-3 in oxidative dehydrogenation of propane to propene. *Applied Catalysis A: General* 2012, 445–446, 321–328.
47. Su D. S., Delgado J. J., Liu X., Wang D., Schlögl R., Wang L., Zhang Z., Shan Z., Xiao F-S.: Highly Ordered Mesoporous Carbon as Catalyst for Oxidative Dehydrogenation of Ethylbenzene to Styrene. *Chemistry – An Asian Journal* 2009, 4, 1108–1113.
48. Schwartz V., Xie H., Meyer III H. M., Overbury S. H., Liang C.: Oxidative dehydrogenation of isobutane on phosphorous-modified graphitic mesoporous carbon. *Carbon* 2011, 49, 659–668.
49. Utgenannt S., Hansen F., Klepel O., Jarczewski S., Wach A., Kuśtrowski P.: Control of porosity and composition of carbon based catalysts prepared by template assisted routes. *Catalysis Today* 2015, 249, 38–44.
50. Walter R., Klepel O., Erlen T., Bron M., Niebrzydowska P., Wach A., Kuśtrowski P.: First Steps on the Way to a Modular Concept for the Preparation of Carbon Based Catalysts. *Catalysis Letters* 2013, 143, 642–650.
51. Janus P., Janus R., Kuśtrowski P., Jarczewski S., Wach A., Solvestre-Albero A. M., Rodríguez-Reinoso F.: Chemically activated poly(furfuryl alcohol)-derived CMK-3 carbon catalysts for the oxidative dehydrogenation of ethylbenzene. *Catalysis Today* 2014, 235, 201–209.
52. Xie H., Wu Z., Overbury S. H., Liang C., Schwartz V.: Investigation of the selective sites on graphitic carbons for oxidative dehydrogenation of isobutane. *Journal of Catalysis* 2009, 267, 158–166.

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Aktualności z firm

News from the Companies

Dokończenie ze strony 303

Pełny skład Zarządu Grupy LOTOS

Rada Nadzorcza Grupy LOTOS SA zdecydowała o rozstrzygnięciu konkursu na członków Zarządu gdańskiego koncernu. Do składu Zarządu wchodzi: Pan Robert Pietryszyn, Pan Mateusz Bonca, Pan Marcin Jastrzębski oraz Pan Przemysław Marchlewicz.

13 maja br. zakończył się rozpoczęty wcześniej konkurs na członków Zarządu Grupy LOTOS SA. Rada Nadzorcza spółki przeanalizowała kilkadziesiąt ofert i po przeprowadzonych rozmowach z wybraną grupą kandydatów zdecydowała o powołaniu do składu Zarządu nowych członków. Są to: Pan Robert Pietryszyn, który objął od 13 maja br. funkcję Prezesa Zarządu; Pan Mateusz Bonca, który obejmie od 1 czerwca br. funkcję Wiceprezesa Zarządu ds. Strategii i Rozwoju; Pan Marcin Jastrzębski, który objął od 13 maja br. funkcję Wiceprezesa Zarządu ds. Operacyjnych; Pan Przemysław Marchlewicz, który obejmie od 17 maja br. funkcję Wiceprezesa Zarządu ds. Korporacyjnych.

W Zarządzie Grupy LOTOS SA zasiadają również: Pan Maciej Szozda, Wiceprezes Zarządu ds. Produkcji i Handlu; Pan Mariusz Machajewski Wiceprezes Zarządu ds. Ekonomiczno-Finansowych.

Pan Robert Pietryszyn ukończył prawo na Uniwersytecie Wrocławskim, Master of Business Administration (MBA) oraz Menedżerskie Studia Podyplomowe Zarządzania firmą na Akademii Ekonomicznej we Wrocławiu. Posiada doświadczenie w pracach rad nadzorczych spółek giełdowych, takich jak Grupa LOTOS SA (przewodniczący), RUCH SA (przewodniczący) oraz Polcolorit SA, Prezes Zarządu spółki Wrocław 2012, gdzie odpowiadał za procesy inwestycyjne, handlowe oraz był odpowiedzialny za projekt UEFA Euro 2012 we Wrocławiu; w przeszłości związany z grupą kapitałowa KGHM SA oraz PKO BP SA oraz biznesem konsultingowym w zakresie bankowości inwestycyjnej i procesów IPO, członek zarządu PZU SA, gdzie odpowiadał m.in. za operacje międzynarodowe.

Pan Marcin Jastrzębski studiował na Uniwersytecie Warszawskim (Wydział Nauk Ekonomicznych), Wyższej Szkole Informatyki, Zarządza-

nia i Administracji (Wydział Nauk Społecznych i Administracji) w Warszawie oraz Uniwersytecie w Liverpoolu (Zarządzanie w sektorze ropy i gazu). Były Konsul Honorowy Gruzji w Polsce. W latach 1997 – 2006 oraz 2008 -2013 pracował w firmie Polkomtel SA r. jako Administrator systemów informatycznych, Zastępca Dyrektora Departamentu Strategii i Zarządzania IT, Dyrektor Departamentu Zarządzania Systemami Informatycznymi, Dyrektor Zarządzający IT oraz Dyrektor Centralnego Departamentu Zakupów. W latach 2006 – 2008 był Członkiem Zarządu ds. Strategii i Operacji PERN „Przyjaźń” SA W latach 2006 – 2010 był Prezesem Zarządu MPR Sarmatia. W latach 2013 – 2015 sprawował funkcję Prezesa Zarządu firmy Gazoprojekt SA W latach 1999 – 2007 zasiadał w radach nadzorczych spółek: WARS Sp. z o.o., RADPEC SA, PERN Przyjaźń SA, Naftoport sp. z o.o. Od dnia 12 kwietnia do 13 maja 2016 r. pełnił funkcję Członka Rady Nadzorczej Grupy LOTOS SA (abc)

(Inf. Grupa LOTOS. 13.05.2016)

Krzysztof Homenda nowym członkiem zarządu GA Puławy

25 maja br. Zarząd Grupy Azoty Puławy został poszerzony; Rada Nadzorcza Spółki powołała Pana Krzysztofa Homendę na stanowisko wiceprezesa Zarządu. Pan Krzysztof Homenda – nowy członek Zarządu – jest absolwentem Katolickiego Uniwersytetu Lubelskiego. Wykształcenie wzbogacił na uczelniach w Londynie, Helsinkach i Łodzi. Ma za sobą liczne kursy, seminaria i szkolenia z zakresu finansów, zarządzania projektami, restrukturyzacji i zarządzania ludźmi. Pan Krzysztof Homenda pracował ostatnio w Grupie Kapitałowej PEPEES SA, gdzie był m. in. członkiem Zarządu i Dyrektorem Finansowym. Wcześniej sprawował funkcje wiceprezesa Zarządu OT Logistics SA, Soda Polska CIECH i EXATEL S.A oraz członka Zarządu PF Jelfa SA. Od blisko 20 lat zasiadał w Radach Nadzorczych wielu Spółek, pełniąc często funkcję Przewodniczącego – m.in. Zachem SA, Polskie Towarzystwo Ubezpieczeń SA i PDH SA (abc)

(<http://www.pulawy.com>, 27. 05.2016)

Dokończenie na stronie 313