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# Selective and efficient dimerization of isobutene over $H_3PO_4$/activated carbon catalysts

Anna Malaika, Paulina Rechnia-Gorący, Monika Kot, Mieczysław Kozłowski*

*Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland*

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## ABSTRACT

Dimerization of isobutene to branched $C_8$ olefins (precursors of high octane gasoline additives) was performed over eco-friendly activated carbon catalysts impregnated with phosphoric acid, under continuous gas phase operating conditions. A series of catalysts differing in phosphoric acid loading were prepared by incipient wetness impregnation and tested in the reaction carried out at various temperatures (100–260 °C), with the use of an isobutene/isobutane mixture at a molar ratio of 4:1 as a feedstock. The conversion and selectivity patterns obtained for a selected sample evolved visibly with the reaction temperature and the best results were obtained at 180 °C. The effect of phosphoric acid loading on the catalytic activity of the samples at this temperature was investigated and discussed. For the sake of comparison also other acidic activated carbons and the commercially available catalyst Amberlyst 15 were tested. The high $H_3PO_4$-loaded materials exhibited excellent catalytic performance in the process (high isobutene conversion, good selectivity to $C_8$ products and high catalyst stability) which was assigned to a combination of acidic and textural properties of the materials obtained.

## 1. Introduction

According to a special report published in 2016 by the International Energy Agency (IEA) [1], poor air quality is one of the most serious health threats the world faces today. The response to the worldwide increase in air pollution are increasingly restrictive clean air regulations concerning industry, energy and transport sectors. In particular, one of the greatest challenges that the governments have to tackle today is the problem of the environmental impact of transportation. Internal combustion engines generate air pollution, including nitrogen oxides, and particulate matter. They are also significant contributors to climate changes through $CO_2$ emission. Furthermore, in the nearest future the number of vehicles is predicted to increase regularly. Thus, it is expected that the high demand for efficient fuels which meet government regulations will successively drive the global fuel additives market.

One of the most widely used gasoline enhancers is methyl tert-butyl ether (MTBE). It should be noted, however, that it might be harmful to the environment. In the USA this compound caused the contamination of groundwater and because of that its application has been totally phased out there [2]. A promising alternative to MTBE might be 2,2,4-trimethylpentane (isooctane), which is a nonaromatic, high octane, low-sulfur, and low volatile fuel component [3]. The use of isooctane is preferred for several reasons, including environmental aspects, engine performance, as well as financial and practical motivations (easy and inexpensive retrofitting of the existing MTBE units) [4].

For large scale isooctane production two types of technologies are currently in operation: one is based on the direct alkylation of isobutane with butenes, the second one employs the reaction of dimerization of isobutene to diisobutenes (2,4,4-trimethylpent-1-ene and 2,4,4-trimethylpent-2-ene; DIBs) with subsequent well developed process of hydrogenation of the product formed (the so-called indirect alkylation) [5]. The first method uses strong mineral acids, such as HF or $H_2SO_4$, which raises great concerns about the environmental aspects of this technology (e.g., corrosion problems, waste disposal) [6,7]. In contrast to this, the dimerization reaction in the commercial indirect alkylation technology has been effectively carried out in the presence of solid acid catalysts, which, in general, are safer and easier to handle with, and fit perfectly into the concept of green chemistry. The other reasons why the reaction has gained considerable attention in recent years are: the use of surplus isobutene which appeared on the market after the MTBE phase out or, as mentioned above, the possibility of utilization of the existing MTBE production units [7–9].

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* Corresponding author.
*E-mail address:* mkozlow@amu.edu.pl (M. Kozłowski).

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The isobutene dimerization is a complex, highly exothermic process in which a sequence of parallel and consecutive reactions takes place. Because of that, besides the desired DIBs (diisobutenes) also high molecular weight by-products, such as $C_{12}$ and $C_{16}$ olefins (triisobutenes and tetraisobutenes, respectively) or even higher ($C_{20+}$), are formed [10]. These products lead to deterioration of the quality of the final blend, moreover, they are responsible for the catalyst deactivation and hence the reduction in the catalyst lifetime. To avoid these limitations, most industrial processes for isobutene dimerization operate at relatively low conversions (20–60%) [11].

Several papers on the improvement of the conventional isobutene dimerization have been published so far. Various solid acid catalysts, including ions-exchange resins [12–14], modified zeolites [15], sulfated titania [16,17], NiO-$W_2O_3$/$Al_2O_3$ [10], sulfated zirconia [18], and heteropolyacid catalysts [19], have been tested among others. Usually, the reaction was carried out in the liquid phase at relatively low temperatures, however, under elevated pressure. For this reason, the production units had to be equipped with additional systems, and rigorous safety precautions had to be taken.

Solid phosphoric acid systems (SPA) are attractive catalysts for industrial olefin oligomerization reactions. However, nowadays the only industrial process of isobutene dimerization that uses SPA as a catalyst is the InAlk technology (developed by UOP company), and this process is carried out in the liquid phase [20]. There are only scarce data on the use of carbon supported phosphoric acid materials as catalysts [21], and, to the best of our knowledge, such catalysts have never been tested in the gas-phase isobutene dimerization. Hence, in this study, the catalytic systems of this type were applied in the dimerization of isobutene carried out under normal pressure using gas – phase conditions.

## 2. Experimental section

### 2.1. Materials

The activated carbon was prepared from ash wood sawdust according to a slightly modified procedure presented in literature [22]. Briefly, the starting material was milled and sieved to obtain powder with particle sizes ≤ 2 mm. Then, the sample was impregnated with the 7% solution of calcium chloride at 85 °C for 7 h upon continuous stirring. The product obtained was dried overnight at 110 °C and then subjected to carbonization in nitrogen atmosphere at 800 °C (heating rate = 5 °C/min) for 1 h, followed by a 30 min activation with $CO_2$ at the same temperature. The initial carbon prepared in that way (AC) was demineralized with a 5% solution of HCl at boiling point for 1.5 h, washed with distilled water (until the neutral pH value was obtained) and dried overnight at 110 °C.

a) AC was subjected to different treatments as follows.*Incipient wetness impregnation*: AC was impregnated with phosphoric acid aqueous solutions of various concentrations at room temperature. After 24 h, the samples were dried at 110 °C for 12 h, and finally, at 200 °C for 4 h. The materials prepared were labelled as x% $H_3PO_4$/AC, where x is the phosphoric acid loading and it is equal to 0, 1, 5, 10, 20 or 40%.
b) *Phosphorylation:* the procedure proposed by Puziy et al. was applied for this purpose [23]. Briefly, AC was mixed with an aqueous solution of phosphoric acid at a 1.56 acid/precursor weight ratio and stirred at room temperature for 4 h (impregnation step). The impregnated sample was dried overnight at 190 °C and then heated in nitrogen flow (50 $dm^3$/min) at 800 °C for 30 min. After phosphorylation the carbon was washed with hot distilled water until the neutral pH was reached, filtered and dried overnight at 110 °C. The material obtained was labelled as AC-$PO_4$.
c) *Sulfonation*: 2.5 g of AC was mixed with 90 $cm^3$ of $H_2SO_4$ (95%) and heated at 140 °C for 5 h under argon flow upon continuous stirring. The mixture was then cooled to room temperature and the sample obtained was filtered, washed with hot distilled water and dried overnight at 110 °C. The carbon prepared was denoted as AC-$SO_3$H.

For the sake of comparison also the commercially available solid acid catalyst Amberlyst 15 was tested.

### 2.2. Characterization of the samples obtained

Textural properties of the samples were measured by $N_2$ adsorption/desorption at −196 °C, using an Autosorb IQ-Quantachrome apparatus. The apparent specific surface areas were determined by the Brunauer – Emmett – Teller equation, whereas the micropore volumes ($V_{micro}$) and external surface areas ($S_{ext}$) were assessed using the t-plot method [24]. The total pore volumes ($V_{tot}$) were calculated from the amount of $N_2$ adsorbed at a relative pressure close to unity and the mesopore volumes were estimated by the difference ($V_{meso} = V_{tot} - V_{micro}$). The pore size distribution was evaluated by the 2D-NLDFT method using the SAIEUS software by Micromeritics [25]. Quantitative elemental analysis CHNS was made with the use of an Elemental Analyzer Vario EL III. In order to determine the content of phosphorus in the AC-$PO_4$ sample, the material was analyzed by ICP-OES (inductively coupled plasma optical-emission spectrometry) method. The sample was mineralized with conc. nitric acid in a Mars 5 microwave oven (CEM Corporation, USA) and the determination of the P content was carried out using a Varian ICP-OES Vista MPX apparatus. Surface morphology of the samples was studied by scanning electron microscopy (SEM) using a ZEISS EVO 40 equipment. Total acidity of the activated carbon samples was determined by the potentiometric back-titration method using a Cerko Lab System titrator.

### 2.3. Catalytic tests

The catalysts obtained were investigated in the reaction of isobutene dimerization carried out in a flow reactor with fixed bed at 180 °C under atmospheric pressure for 210 min. The structures of the main products formed in the above process are presented in Fig. 1. For a selected sample also tests at 100 °C or 260 °C were conducted. Before each run, the catalyst (200 mg) was pretreated at 180 °C in the flow of He for 30 min. After the activation stage, an isobutene/isobutane mixture (molar ratio = 4:1, 20 $cm^3$/min) was fed into the reactor. Isobutane was used only as a diluent in the feed. Both gas as well as liquid post-reaction mixtures were analyzed every 10 or 30 min, respectively, by gas chromatography using a flame ionization detector (FID). A packed-type column Carbograph 2AP was applied for the analyses of gas post-reaction mixtures and a SE-30 packed column in the case of liquid ones. Isobutene conversions and selectivities to olefins were calculated using the equations presented in literature [19].

## 3. Results and discussion

### 3.1. Catalyst characterization

Data on textural parameters of the samples prepared are collected in Table 1. As can be seen, a combination of chemical and physical activation of the ash wood sawdust (activation of the $CaCl_2$-impregnated material followed by the activation stage with $CO_2$) led to the formation of activated carbon (AC) with relatively high surface area (above 600 $m^2$/g). At the same time, the material

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