

## Mesoporous Carbon-Based Rhodium Catalysts for Benzene Hydrogenation

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### Abstract

Two different carbons, namely CAS-P-500 and CRH-P-500, were prepared from apricot stones and rice husk by H<sub>3</sub>PO<sub>4</sub>-activation at 500°C and H<sub>3</sub>PO<sub>4</sub>/precursor (wt/wt) impregnation ratio of 2:1 followed by water washing and desilication by NaOH solution respectively. Elemental analyses of both samples using X-ray fluorescence spectroscopy and VARIO ELEMENTAR III elemental analyzer detected up to 1% of remained phosphorus and about 88% of carbon. SEM characterization and nitrogen adsorption data revealed that highly mesoporous materials were obtained. According to BJH scheme calculations, N<sub>2</sub> BET-surface area and pore volume for CAS-P-500 reached the values of 2030 m<sup>2</sup>/g and 1.64 cm<sup>3</sup>/g, while for CRH-P-500: 1690 m<sup>2</sup>/g and 1.95 cm<sup>3</sup>/g respectively. Activated carbons CAS-P-500 and CRH-P-500 were used as catalyst supports for the conversion of small amounts of benzene into cyclohexane to obtain cleaner gasoline. According to Euro-3 standards, gasoline should contain less than 1% of benzene, since the incomplete combustion of gasoline, which contains benzene, leads to formation of benzopyrene- a powerful carcinogen in exhaust gases. The activity of rhodium catalysts based on the CAS-P-500 and CRH-P-500 allow complete conversion of benzene into cyclohexane at 40 atm and 80°C temperature and is comparable to those of based on conventional carbons: “Sibunit”, etc.

### Introduction

According to Euro-3 standards, gasoline should contain less than 1% of benzene, since the incomplete combustion of gasoline, which contains benzene, leads to formation of benzopyrene- a powerful carcinogen in exhaust gases. It was shown previously [1, 2] that the best metal for complete selective hydrogenation of benzene in a variety of media is rhodium, which has been distributed on different supports, the most suitable of which is proven to be activated carbon. The aim of this work is to test some newly developed carbons obtained from renewable materials, e.g.: vegetable wastes such as rice husk (RH) and apricot stones (AS), via H<sub>3</sub>PO<sub>4</sub>-activation for suitability of being used as supports for Rh-catalysts in benzene hydrogenation processes.

### Experimental

70% phosphoric acid ( $\rho \approx 1.54 \text{ g/cm}^3$ ) was admixed to appropriate amount of RH or 1-2 mm fraction of AS to make H<sub>3</sub>PO<sub>4</sub>/precursor (wt/wt) impregnation ratio of 2:1. The mixtures were transferred into alumina crucibles, precarbonized in an oven at 200°C for 12 hours, loosely covered with stoppers and activated at 500°C during 1 hour (AS) and 2 hours (RH) in a vertical cylindrical furnace equipped with chromel/alumel thermocouple at the temperature ramp rate of ca. 5°C/min. Carbonized apricot stones (CAS-P-500) were continuously washed with hot distilled water till neutral pH. To obtain carbonized rice husk (CRH-P-500), the residue underwent additional neutralization to Na<sub>2</sub>HPO<sub>4</sub> with the equivalent amount of concentrated NaOH followed by desilication in 0.5M NaOH and washing with hot distilled water till neutral pH according to the technique [3]. Samples were dried in hot air oven at 110±5°C.

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Product yields: 44% for CAS-P-500 and 30% for CRH-P-500. To analyze the textural characteristics of carbonized materials low-temperature (77 K) nitrogen adsorption-desorption isotherms were recorded using "ASAP-2400" Analyzer (Micromeritics Instrument Corp., Norcross, GA, USA), upon preliminary training of the samples at 150°C & residual pressure of 0.001 mm Hg. The measurements for isotherms were conducted at 77 K within range of relative pressures from 0.005 to 0.991. The desired concentrations for methylene blue (MB) adsorption studies and calibration solutions for spectrophotometric evaluation were obtained by successive dilution of aqueous MB stock solution (4000 mg/L). Each time a 50 mL glass-stoppered flask with 0.10 g activated carbon and twenty-five milliliters of a dye solution added was placed on a magnetic stirrer at room temperature for 20 min. Then the absorbance of supernatant solution was estimated to determine the residual concentration. MB adsorption was calculated from the mass balance equation:  $q_e = \frac{(C_0 - C_e) \cdot V}{m}$ , where  $C_0$  and  $C_e$  are the initial and

equilibrium dye concentrations,  $V$  is the volume of liquid phase and  $m$  - mass of adsorbent. Obtained adsorption isotherm data were plotted in the linear Langmuir-isotherm model [4]:  $\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}}$

where  $q_{\max}$  is the monolayer capacity and  $K_L$  is a constant related to adsorption free energy. Analyses of mineral part of the sample were performed using X-ray fluorescent spectroscopy on VRA-30 analyzer with Cr-anode X-ray tube. Carbon and hydrogen contents were determined by use of elemental analyzer "VARIO ELEMENTAR III". The morphology of activated carbons was studied by scanning electron microscopy (SEM) using a QUANTA 3D 200i microscope (FEI, USA) with accelerating voltage of 30 kV. The catalysts were prepared by wet impregnation of the carbon supports with aqueous  $\text{RhCl}_3$  solutions to achieve Rh concentration - 3 wt % [5]. Hydrogenation of benzene was carried out at 40 atm and 80°C in a special autoclave under isobaric-isothermic conditions. The reaction products were monitored using Chrome-5 type gas-liquid chromatograph.

## Results and Discussion

Phosphoric acid is a known porogen letting the carbonization reactions to occur at much lower temperatures (due to acidic catalysis causing dehydration) compared to simple pyrolysis which is

governed mostly by radical mechanisms, causing tar formation due to disproportionation reactions. The use of it thus is to provide both higher yields (less volatiles and tar) and high surface area, as well as to functionalize carbon surface with phosphate groups (C–O–P-bonding) via phosphorylation of cellulose OH-groups.

According to "VARIO ELEMENTAR III" analyzer results, CAS-P-500 and CRH-P-500 have C-content - 88.51% and 87.96%, while H-content- 1.68% and 1.92% respectively. These results are indicative of sufficient carbonization degree. X-ray fluorescent spectroscopy results showed that phosphorus content of CAS-P-500 is near 1 % and the ash elemental content - ca. 0.02 %. For the sample CRH-P-500, elemental content was as follows: P - 0.895%, Si- less than 0.04%, and other ash elements - 0.065%. These data signify both sufficient purity and presence of the acidic (phosphate, verified by IR-spectroscopy results) functional groups which are contributing to rhodium immobilization on carbon surface.

The standard calculations for isotherms were performed by Barret-Joyner-Halenda method, with the admission of postulated model for cylindrical pores, the calculation of total pore surface area  $S_{\Sigma}$  and micropore surface area  $S_{\mu}$  by BET-method, total pore volume  $V_{\Sigma}$  and micropore volume  $V_{\mu}$ ; average pore diameter  $D_{\text{pore}}$ . According to these results shown in Table 1, the largest portion of pores of both samples CAS-P-500 and CRH-P-500 is accounted for mesopores.

High values of MB-monolayer capacity (Table 1) of CRH-P-500 and CAS-P-500 samples also suggest high mesoporosity, since the MB molecule is accessible to the pores with diameters larger than 1.5 nm [6].

**Table 1**

MB-monolayer capacity of activated carbons and their textural properties according to  $\text{N}_2$  adsorption

| Sample    | Max. MB-sorption capacity, mg/g | $S_{\Sigma}$ m <sup>2</sup> /g | $V_{\Sigma}$ cm <sup>3</sup> /g | $D_{\text{pore}}$ , nm |
|-----------|---------------------------------|--------------------------------|---------------------------------|------------------------|
| CRH-P-500 | 562                             | 1690                           | 1.95                            | 4.4                    |
| CAS-P-500 | 893                             | 2030                           | 1.64                            | 3.2                    |

SEM images of the CRH-P-500 and CAS-P-500 are shown on Fig 1a-d. It can be observed at a higher resolution (Fig 1b, d) that the morphology of surface CRH-P-500 and CAS-P-500 samples is characterized by porous structure having nanoscale elements (pores).

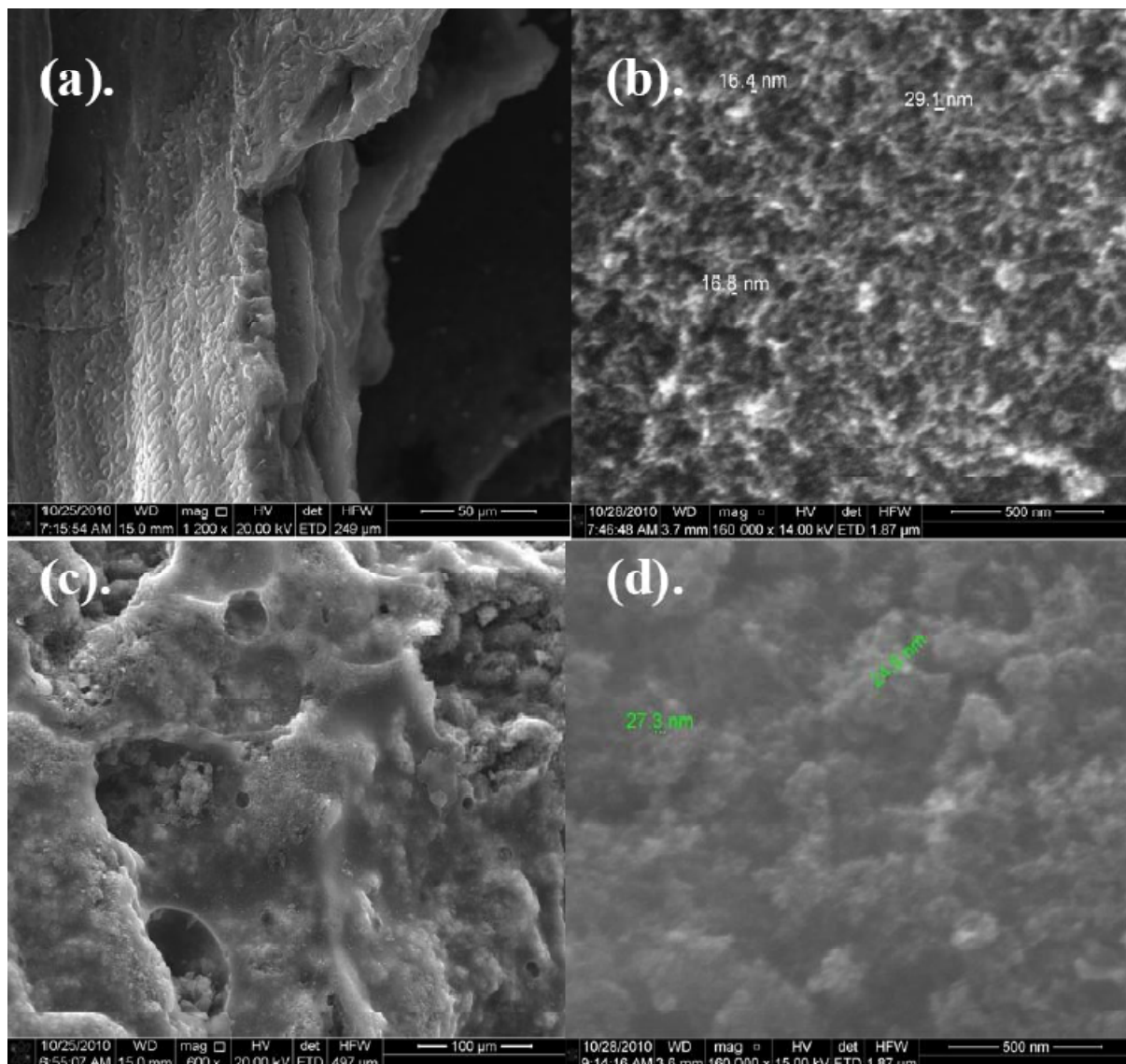


Fig. 1. SEM images of CRH-P-500 (a, b) and CAS - P-500(c, d) magnification: (a) –  $\times 1\,200$ ; (c) –  $\times 600$ ; (b) and (d) –  $\times 160\,000$

Conversion curves of benzene hydrogenation on Rh-catalysts based on CRH-P-500 and CAS-P-500, as well as based on commercially available “Sibunit”, fruit stones activated carbon (FSAC) and birch activated carbon (BAC) are shown in Fig. 2. The activity of the catalysts based on CRH-P-500 and CAS-P-500 is higher than of that based on FSAC, and only slightly less than of those based on BAC and Sibunit (in benzene hydrogenation processes). Selectivity of benzene hydrogenation on the catalysts based on CRH-P-500 and CAS-P-500 is much higher than of that based on “Sibunit” and is comparable to that based on BAC, when compared to hydrogenation of benzene homologues: toluene, xylene and cumene.

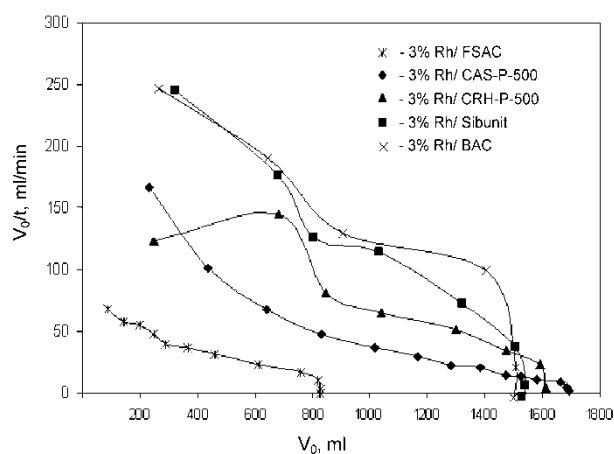


Fig. 2. Conversion curves of benzene hydrogenation: V - volume of hydrogen, V/t - hydrogenation reaction rate

## Conclusions

New highly mesoporous carbons were made by means of chemical activation using phosphoric acid at 500°C from vegetable row materials, e.g.: rice husk and apricot stones. In the case of RH, upon carbonization, an additional method of desilication with 0.5M NaOH solution was applied. SEM-investigation together with low-temperature adsorption studies, as well as methylene blue sorption studies revealed both high surface area and mesoporosity of obtained carbons making them suitable to be employed in catalytic processes. Elemental analyses of the carbons showed sufficient degree of carbonization and functionalization of their surface with phosphate groups. Since both high mesoporosity and presence of acidic functional groups contribute to rhodium catalysts activity, the obtained CAS-P-500 and CRH-P-500 were tested as catalyst supports for benzene hydrogenation to obtain cleaner gasoline. The activity of rhodium catalysts based on the CAS-P-500 and CRH-P-500 allow complete conversion of benzene into cyclohexane, is comparable to those of based on conventional carbons "Sibunit" and exceed the latter in selectivity.

## References

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