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Biomass-based nanoporous carbon as catalyst support for production of hydrogen by methanol degradation

I. Stoycheva[1], T. Tsoncheva[1], B. Tsyntsarski[1]*, B. Petrova[1], G.Georgiev[1],
A. Sarbu[2], A. Radu[2], T.Sandu[2]

[1] *Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 9, 1113 Sofia, Bulgaria*
[2] *National Research-Development Institute for Chemistry and Petrochemistry INCDCP-ICECHIM Bucharest, 202 Splaiul Independentei, 060021 Bucharest, Romania*

Dedicated to the 80th anniversary of Professor Lachezar Petrov, DSc,
Corresponding Member of the Bulgarian Academy of Sciences

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The present investigation deals with preparation of porous carbons based on of agricultural wastes as peach stones. The carbons obtained were modified with manganese and tested as catalysts in methanol decomposition for hydrogen production. Various physicochemical techniques, such as XRD, nitrogen physisorption, TPR, FTIR, and UV-Vis spectroscopy were used for characterization. Porous carbons produced from peach stones exposed a high surface area and well-developed porous structure with high amount of micropores and mesopores. Decomposition of added Mn salts caused reduction of the micropore and mesopore volume due to Mn particles located in the carbon pores. The resulting catalysts exhibited high catalytic activity and selectivity.

Keywords: biomass, nanoporous carbon, hydrogen, methanol, decomposition, catalysts

INTRODUCTION

In the last years, various alternative power sources have been developed and studied due to fast depletion of fossil fuel resources. Hydrogen is considered the fuel of the future; however, there are some problems related to production, storage, and application that have to be solved.

Being a steam reforming catalytic process, methanol decomposition is a reliable way to produce high purity hydrogen. The aim of the present investigation is by using agricultural waste such as peach stones to prepare nanoporous carbon with suitable texture and chemical surface properties as catalyst support for methanoldegradation.

Porous carbons are appropriate for use in heterogeneous catalysis because they satisfy most of desirable properties required for a proper support [1]. Porous carbon supports stable to chemicals and temperature can be prepared with different physical forms: granules, pellets, extrudates, cloth, and fibers. A significant advantage is the possibility to design largely porous carbon structure and internal surface by various methods[2].

Activated carbon (AC) exhibits a wide range of pore size, thus facilitating the access of the activephase during catalyst preparation and making possible high catalyst dispersions. Catalytic activity and adsorption capacity of carbons depend on porous structure and chemical nature of thesurface.

Active site distribution normally as edges of carbon sheets is also important. Catalytic activity can be changed by the presence of heteroatoms. Nitrogen increases activity whereas sulphur inhibits activity. Activity can also be influenced by the presence of acid or base surface oxide species.

Carbon-based catalysts are applied to many processes like oxidative dehydrogenation of hydrocarbons [3], dehydration and dehydrogenation of alcohols [4], NO_x reduction [5, 6], SO_x oxidation [7,8], ozonation [9], catalytic wet air oxidation [10,11], etc.

The aim of the current paper is the preparation of porous carbon using different agricultural wastes and preparation conditions. The materials obtained were modified with Mn active phase and tested as catalysts in methanol decomposition for hydrogen production.

EXPERIMENTAL

Peach stone based activated carbon (AC) was produced by carbonization (10 deg/min) at 450 ºC for 1 h and hydropyrolysis (10 deg/min) at 750 ºC for 45 min. Both carbonization and hydropyrolysis were performed using a stainless steel reactor placed in a tube furnace with 3 SiC heaters. Mn (8 wt%.) was added as manganese nitrate to activated carbon by incipient wetness impregnation. 0.5 g of activated carbon were heated at 60 ºC under vacuum for 30

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* To whom all correspondence should be sent:
E-mail:btsintsarski@orgchm.bas.bg

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min.

The impregnation was performed with manganese nitrate dissolved in 0.1 ml of methanol.

Nitrate decomposition was carried out in a flow of N_2 at 500 ºC for 2 h at a heating rate of 5 deg/min.

Texture characteristics were determined by N_2 adsorption at −196 °C by a Quantachrome NOVA 1200 apparatus. The amount of various acidic oxygen-containing functional groups was determined by Boehm's method using aqueous solutions of $NaHCO_3$, Na_2CO_3, NaOH, and C_2H_5ONa [12].

The amount of basic sites was verified by 0.05 N HCl [13]. Determination of pH values was made by boiling for 5 min in 100 ml H_2O, decantation, and cooling the solution to ambient temperature. XRD analysis was performed on a Bruker D8 Advance diffractometer with Cu K_α radiation and LynxEye detector. The average crystallite size was evaluated according to Scherrer equation. Temperature-programmed reduction/ thermo-gravimetric (TPR/TG) analysis was performed on a Setaram TG92 instrument in a flow of 50 vol % H_2 in Ar (100 cm^3/min) at a heating rate of 5 deg/min.

Methanol conversion was carried out in a fixed bed flow reactor (0.055 g of catalyst), argon being used as a carrier gas (50 cm^3/min). The methanol partial pressure was 1.57 kPa. The catalysts were tested under conditions of a temperature-programmed regime within the range of 80–500 ºC at a heating rate of 1 deg/min. On-line gas chromatographic analysis was performed on an HP apparatus equipped with flame ionization and thermal conductivity detector, using a PLOT Q column, an absolute calibration method, and a carbon-based material balance.

RESULTS AND DISCUSSION

The nitrogen isotherms (−196 ºC) of nanoporous carbon and Mn catalyst are shown in Fig. 1. The studied carbon sample shows a relatively narrow pore size distribution within the micropore range with a maximum at 1–2 nm, thus indicating that micro-porosity in this case is composed of pores of large dimensions. The ratio of calculated micropore to mesopore volumes also confirmed that the carbon obtained was highly microporous.Detailed porosity characteristics of the prepared samples are summarized in Table 1. Data show that after steam activation the sample displays an open structure of interconnected pores in a micro/mesoporous network. Isotherm similarity between parent and manganese loaded carbons clearly indicate absence of significant structural collapse of the supports during the modification procedure.

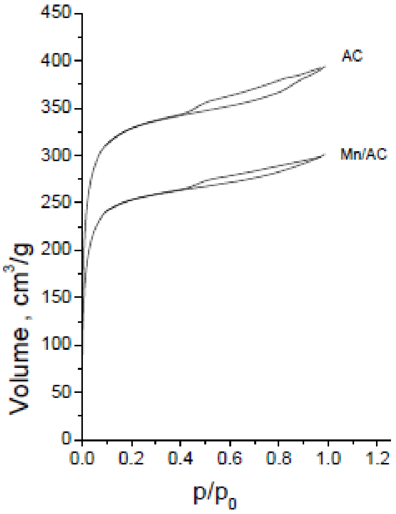

Fig. 1. Nitrogen physisorption (−196 ºC) isotherms of the activated carbon and manganese catalyst.

Table 1. Nitrogen physisorption data for parent AC and their manganese modifications

Sample	S_{BET}, m^2/g	S_{mi}, m^2/g	S_{ext}, m^2/g	V_t, cm^3/g	V_{mi} cm^3/g	V_{meso} cm^3/g
ACP	1258	1116	143	0.610	0.448	0.105
Mn/ACP	941	830	111	0.463	0.341	0.050

A decrease in BET surface area and pore volume after modification clearly reveals the deposition of the active phase into the porous structure of the support. A significant decrease observed in the microporous volume implies location of Mn particles exclusively into the micropores of the carbon supports.

Table 2 presents some chemical characteristics of the produced porous carbon. Presence of acidic (mainly carbonyl and hydroxyl) and basic groups was detected. The amount of carbonyl and lactonic groups is below detection limit obviously due to the high temperature treatment during preparation. The pH values indicate that the AC sample is characterized by relatively high basicity. This fact can be explained with the presence of basic groups on the carbon surface and considerably low amount of acidic surface groups.

Table 2. Chemical characteristics of the porous carbon.

Sample	pH	Acidic surface functional groups, mmol/g				Basic groups, mmol/g
		Carboxyl	Lactonic	Hydroxyl	Carbonyl	
AC	9.4	BDL	BDL	0.29	1.07	1.04

The FTIR spectra contain bands at 2925 and 1390 cm^{-1}, attributed to C-H stretching vibrations [5]. A broad band at 2835 cm^{-1} indicates vibrations of CH_3-O group. The band at 1690 cm^{-1} corresponds to C=O vibrations of lactonic, carboxyl, or ether groups [5].

The broad bands around 1525 and 1090 cm^{-1} are assigned to ring vibrations in a large aromatic skeleton typical of carbons [5]. The region of 1200–700 cm^{-1} contains various bands related to aromatic out-of-plane C-H bending [5]. The band at 1094 cm^{-1} could also be due to vibrations in ether C-O-C groups [5]. The observed changes in the bands at around 1690, 1525, and 1090 cm^{-1} for the Mn catalyst could be ascribed to interaction between Mn species with oxygen containing groups and aromatic ring. Increased absorption at around 800–500 cm^{-1} is probably due to δ-modes in Mn-O and Mn-O-C structures.

Fig. 2 displays the TPR-TG and TPR-DTG profiles for the manganese modified activated carbon. Generally, the reduction of MnO_2 and Mn_2O_3 in hydrogen takes place as a stepwise process with the formation of Mn_3O_4 in the inter-mediate step and further reduction to MnO [14] as follows: $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$.

In these three steps, the theoretical hydrogen consumption ratio is 3:1:2, respectively. Here, the main reduction effects with the manganese catalyst occur in the range 200–330 ºC and above 380 ºC. According to the literature [14], the low-temperature effect corresponds to manganese reduction in Mn^{3+}/Mn^{4+} state, while the high temperature effect is due to further reduction of Mn_3O_4 to MnO. TPR profile variations support data from the physicochemical analysis on differences in the state (phase composition, dispersion, location into the pores) of the loaded manganese species. XRD and UV-Vis data provide evidence for presence of MnO.

Fig. 3a shows the temperature dependence of methanol conversion over the Mn catalyst. CO, methane, and CO_2 were the only registered carbon-containing products, and the CO selectivity, which is directly related to the hydrogen release from methanol, is presented in Fig. 3b.

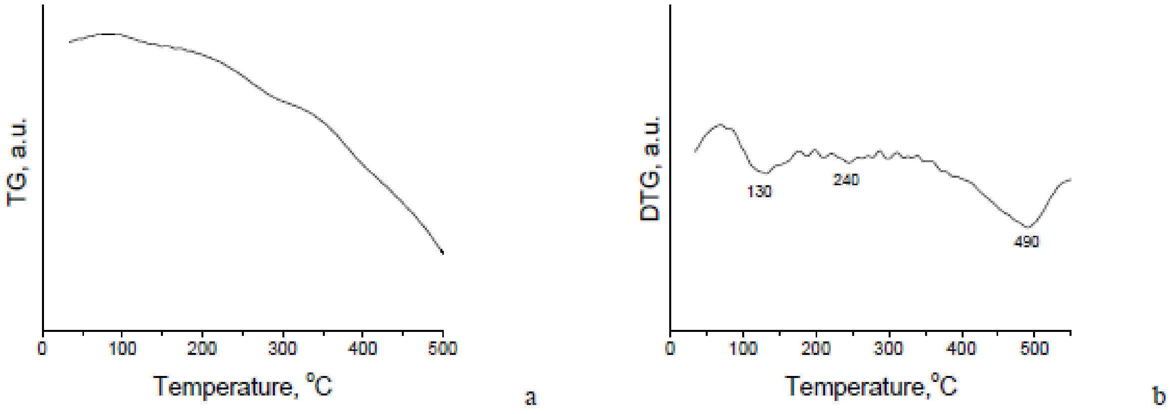

Fig. 2. TPR-TG (a) and TPR-DTG (b) profiles of manganese-modified activated carbon.

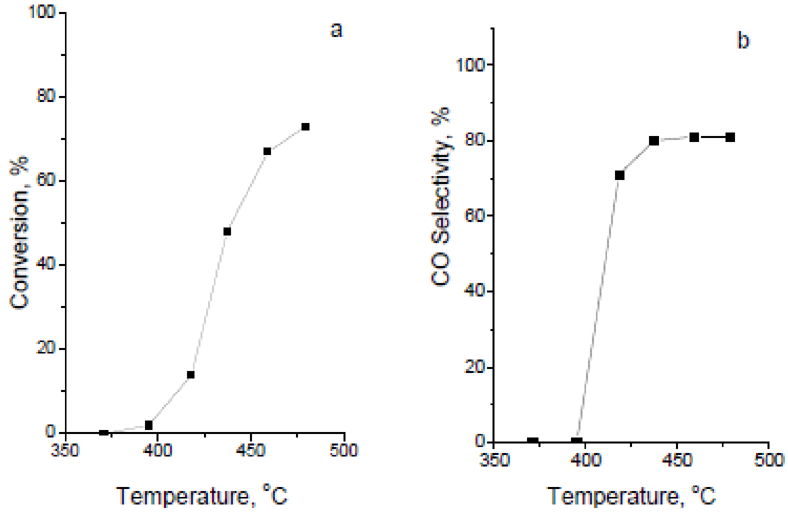

Fig. 3. Methanol conversion (a) and selectivity (b) towards CO of Mn catalyst.

The Mn catalyst was active above 400 ºC with a steep increase in the conversion up to 70% at 460°C. The selectivity to the main product (CO) remained high within 420–480 ºC.

CONCLUSIONS

Nanoporous carbons from peach stones possess a high surface area and well-developed porous structure with a high amount of micropores and mesopores. Modification treatment reduced the micropore and mesopore volumes due to the formation of Mn species into the pores. The catalyst based on biomass carbon exhibited a high catalytic activity and selectivity. The state of the manganese phase and its catalytic behavior is related to carbon structure and surfacefunctionality.

Taking into account N_2 physisorption, XRD, IR spectral and TPR results, we can assume that the catalytic activity is facilitated by the location of the manganese species into the mesopores of the carbon support. It seems that the catalytic selectivity is also influenced by the Mn oxidation state and the presence of Mn^{3+}/Mn^{4+} ions increases the ability for methanol decomposition to hydrogen and CO. It is not excluded that these species could be stabilized by some effects related to surface acidic groups.

Depending on composition and treatment conditions, the selected raw material allowed preparation of porous carbon with desired texture and chemical nature of the surface. This allowed us to study the characteristics of the porous carbon as a potential catalyst support. Mn catalyst samples were active over 400 °C showing a steep increase in the conversion up to 70% at 460 °C. Data show that the catalytic activity is favored by manganese species located into the mesopores of the carbon support.

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