The catalytic activity of phosphotungstic acid-carbon nanocomposites in the dehydration reaction of bioethanol

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Significant production volumes, ease of production, and low cost of bioethanol make it a valuable fuel additive and raw material for preparing important organic substances: diethyl ether, ethylene, ethylene oxide, propylene, butadiene, acetaldehyde, vinyl acetate, etc. Heteropolyacids are the most active catalysts for ethanol dehydration. They differ from other catalysts by significant acidity and high stability. Due to the low specific surface area, in the production of acid-based catalysts, heteropolyacids are usually loaded onto various carriers to increase their catalytic activity by increasing dispersion.

In this work, we investigated the activity and selectivity of nanocomposite catalysts. They were prepared by the incipient wetness impregnation. In a typical preparation, 1 g of the carbon material (activated carbon, carbon fibers, and carbon nanotubes or oxidized CM) was impregnated with 0.1 mmol water solution of phosphotungstic acid (PTA) $H_3PW_{12}O_{40}\bullet nH_2O$. These catalysts were examined in the gas-phase reaction of ethanol dehydration and characterized by different methods: SEM, adsorption of N_2, TG/DTG, TPD MS, and FTIR.

Bioethanol dehydration

A catalyst directs the reaction in such a way that desired products of the vapor phase dehydration, e.g., diethyl ether and ethylene, are selectively formed:

$$2\ C_2H_5OH \xrightarrow{cat,\ \Delta t} C_2H_5OC_2H_5 + H_2O$$

$$C_2H_5OH \xrightarrow{cat,\ \Delta t} C_2H_4 + H_2O$$

At below 160–180 °C, the reaction over a catalyst gives diethyl ether. Increasing the reaction temperature above 180 °C increases the rate of ethylene formation.

Characterization of phosphotungstic acid-carbon nanocomposites

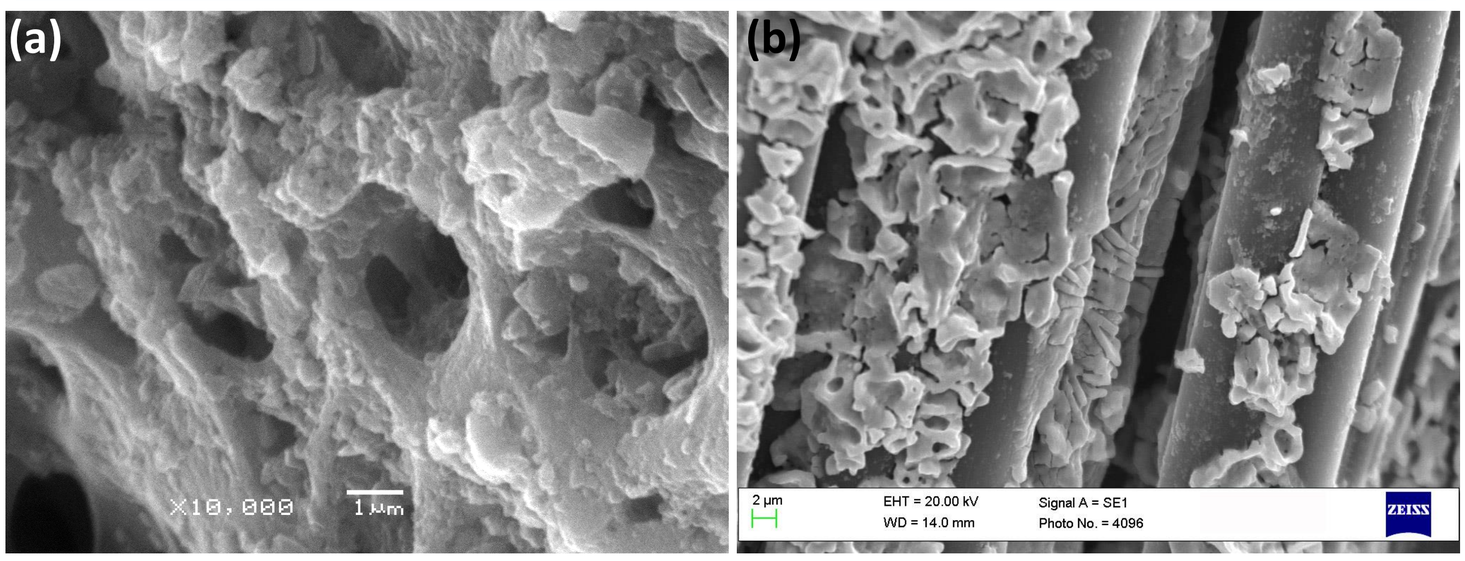

Fig. 1. Typical SEM micrographs of phosphotungstic acid-carbon nanocomposites : **a** – PTA-activated carbon, **b** – PTA-carbon fibers.

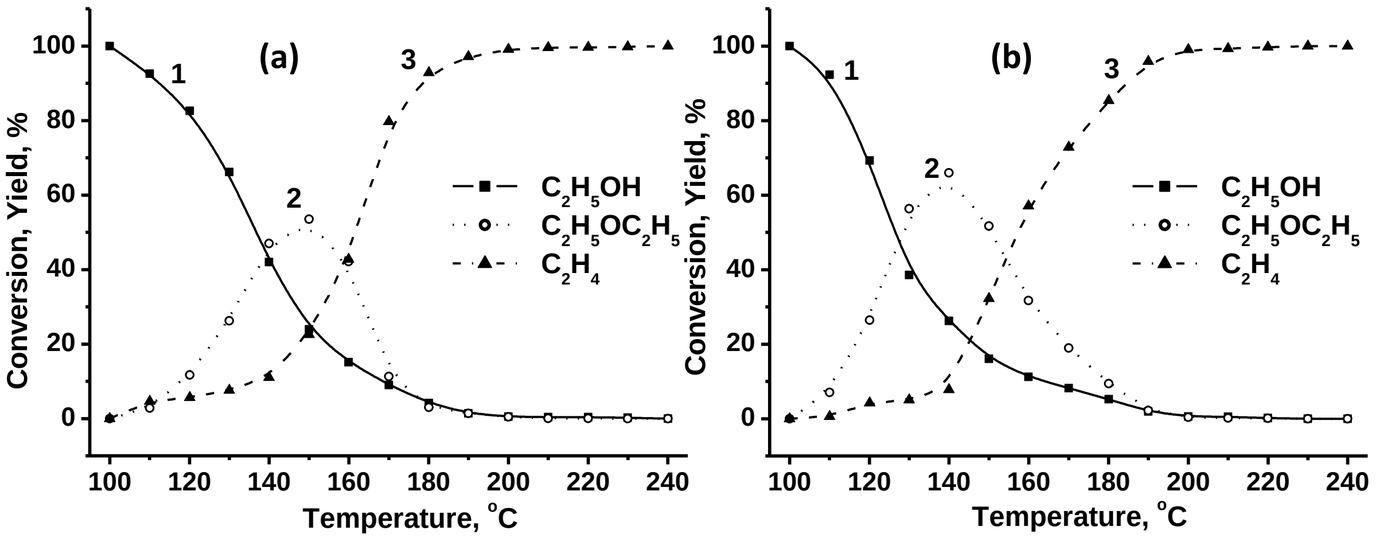

Fig. 2. Ethanol conversion (1) to diethyl ether (2) and ethylene (3) catalyzed by: **a** – PTA-AC, **b** – PTA-AC(OX).

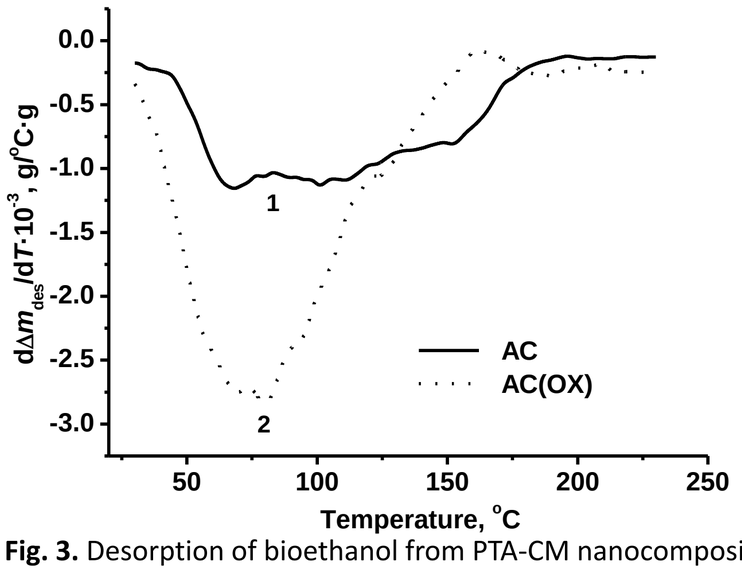

Fig. 3. Desorption of bioethanol from PTA-CM nanocomposites: 1 – PTA-AC, 2 – PTA-AC(OX).

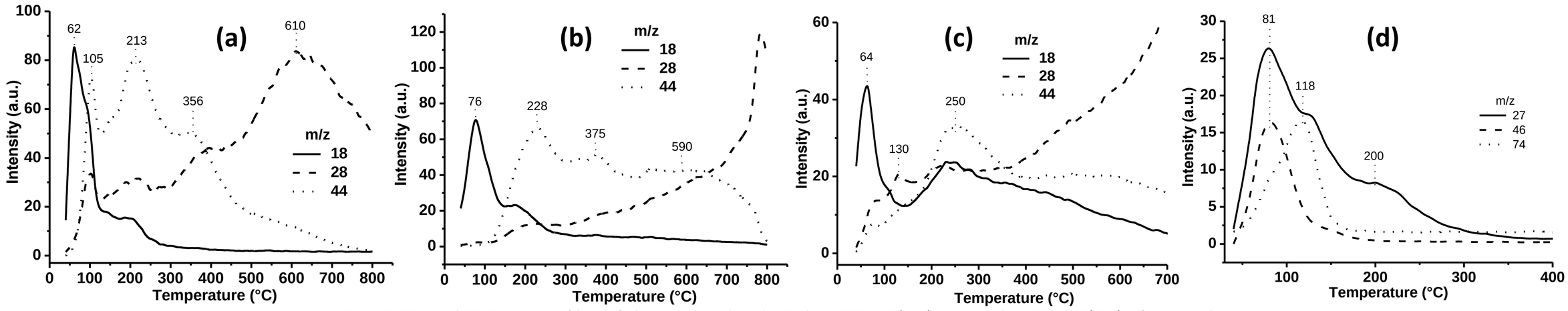

Fig. 4. Typical TPD MS profiles of the: **a** – oxidized AC, **b** – PTA-AC(OX), **c** and **d** – PTA-AC(OX) after catalysis (m/z: 18 – H_2O^+; 28 – CO^+; 44 – CO_2^+; 27 – $CH_2{=}CH^+$; 46 – $CH_3CH_2OH^+$; 74 – $CH_3CH_2OCH_2CH_3^+$).

Conclusions. It is shown the phosphotungstic acid-carbon nanocomposites can catalyze gas-phase reaction of ethanol dehydration to diethyl ether and to propene. The highest conversion of ethanol had observed between 110 and 200 °C. Within the temperature window of 120–150 °C, PTA-CM and PTA-CM(OX) catalysts are capable of selective producing diethyl ether from ethanol. Besides, ethylene can form with 100% selectivity in the temperature range of 180–205 °C. Our results obtained at the catalytic and adsorption studies clearly display the importance of the oxygen-containing surface groups. They present on the carbon carriers, act as centers of PTA immobilization and also are ethanol adsorption centers, promoting its dehydration. We suggest that the use of such solid acid catalysts will help integrate bioethanol into chemical industry and could be a solution in the producing a renewable bioethylene.