REPRODUCIBILITY AND ACCURACY PROBLEMS OF THE GAS-CHROMATOGRAPHIC RESPONSE FACTORS FOR THE REACTION PRODUCTS RESULTING FROM THE CATALYTIC BIO-ETHANOL CONVERSION

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Introduction

The heteropoly compounds-HPCs are strong acid and they are much more active as ordinary solid acids, for example, zeolites and silica-alumina. Among the HPCs, the $H_3PW_{12}O_{40}$-H_3PW shows the highest acidity. The conversion of alcohols to hydrocarbons on acidic solid catalysts was one of the most studied reactions, especially ethanol conversion on the H_3PW and their acidic salts as the production and use of bio ethanol increase.

In this work was studied the quantitative analysis of the reaction products from the catalytic conversion of ethanol on the H_3PW and its Cesium salts and the specific problems of the accuracy and the reproducibility of the results.

Experimental

The conversion of ethanol was studied on the H3PW and CsxH3-xPW, x=1; 2; 2.25, 2.5 and 3 catalysts by pulse reactant technique-PRT and continuous flow of reactant technique-CFRT. A micro reactor connected to GC-FID was operated by PRT (Fig.!) and CFRT (Fig. 2) at temperatures between 473 K and 623 K. The reaction products observed were ethylene, diethyl ether, C1-C6 hydrocarbons and unreacted ethanol.

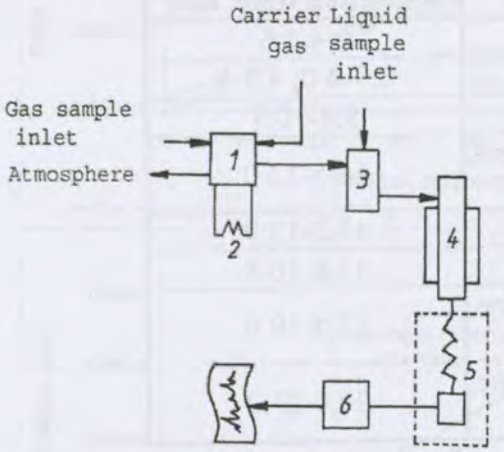


Fig.1. The installation scheme for catalytic the activity measurement by PRT: 1. Six port valve; 2. Gas sample loop; 3. Liquid sample evaporator; 4. Microreactor heated by electric furnace; 5. Gas-chromatograf; 6. Integrator.

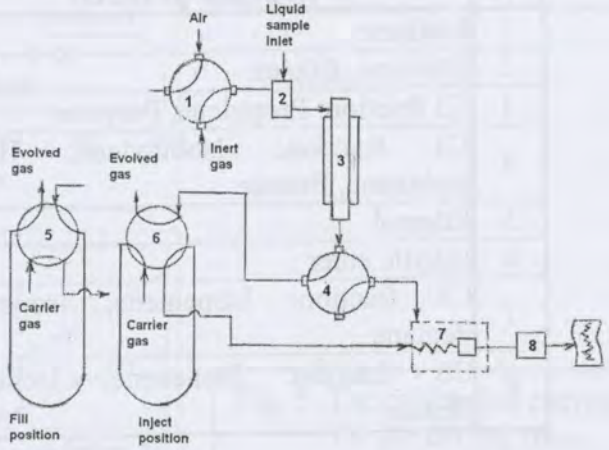


Fig.2. The installation scheme for catalytic the activity measurement by CFRT:
1. Four port valve; 3. Liquid sample evaporator; 3. Micro reactor heated by electric furnace; 4. Four port valve, 5-6 Six port valve with gas sample loop; 7. Gas-chromatograph; 8. – Integrator.

The GC-FID was equipped with a stainless steel column of 3 m length, 2 mm inner diameter packed with Porapak QS 80-100 mesh. The N_2 carrier gas with the flow of the 30 cm^3/min was used. The splitting was of 1:6 volume ratio.

For a better separation of reaction products, a temperature programme for the column was set up: 5 min at 323 K, then heating from 323 K to 473 K with the heating rate of 10 K/min and the last an isothermal heating at 473 K for 5 min. The total time for a complete analysis was 25 min.

The calibration curves and response factors for the reaction products were determined by using the liquid samples of the ethanol or ethanol-diethyl ether-water, respectively, gas samples of pure methane, propylene, isobutylene and n-hexane in liquid phase. The liquid samples were introduced in GC with a 10 microliters Hamilton syringe, type 801 RN and the gas samples were introduced by the six-port valve from the loops of 0.5-1.5 ml volume or with a gastight Hamilton syringes, type 1002 LTN of 2.5 ml and type 1001 of 1.0 ml.

Results and discussion

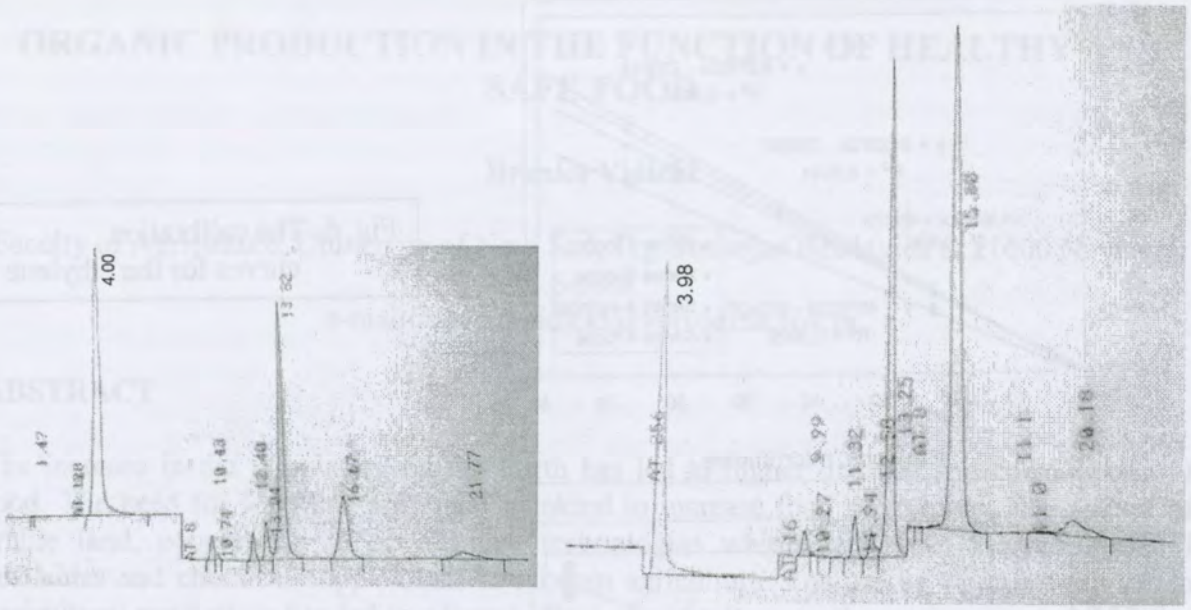
The ethanol conversion over H_3PW and its Cs salts as catalysts led to ethylene as main reaction products. The secondary reaction products are: methane, C2 hydrocarbon fraction (Ethylene, Ethane), C3 hydrocarbon fraction (propene, propane), C4 hydrocarbon fraction (Isobutylene, Butene, Isobutane, and Butane), C5 hydrocarbon fraction (Isopentene, Isopentane, Pentane), C6 hydrocarbon fraction (Isohexene, Isohexane, and Hexane) and Diethyl ether. The retention time for the reaction products are showed in Table 1 and two examples of typical chromatograms can be seen in Fig. 3a,b.

Table 1. The reaction products from the ethanol conversion on $Cs_xH_{3-x}PW$ catalysts and their retention time

No	Reaction products	Retention time, min
1	Methane	1.4-1.5
2	Ethylene, Ethane	3.7-4.0; 4.5-5
3	C3 fraction: Propylene, Propane	9.8-10.7
4	C4 fraction: Isobutylene, Butene, Isobutane, Butane	11.5-13.0
5	Ethanol	13.2-13.9
6	Ethylic ether	15.8-16.8
7	C5 fraction: Isopentene, Isopentane, Pentane	17.5-19.0
8	C6 fraction: Isohexene, Isohexane, Hexane	20.0-23.0

The normal symmetrical shape was observed for the main peaks (Ethylene, Propene, Isobuthylene, Ethanol and Ethylic ether), which is an important requirement for the accuracy and reproducibility of analyses results.

The calibration curves are showed in Fig. 4a,b,c.d. for the main reaction products. The concentration ranges of calibration curves for all reaction products were in concordance with the experimental values obtained of catalytic test of activity for ethanol conversion, what is a guarantee for the accuracy of the analyses results.



a) b)

Fig. 3a,b. The chromatograms of reaction products for ethanol conversion on $Cs_{2.5}H_{0.5}PW$ at the temperature of 523 K, continuous flow of reactant: a) 11mol% EtOH; b) 22 mol% EtOH

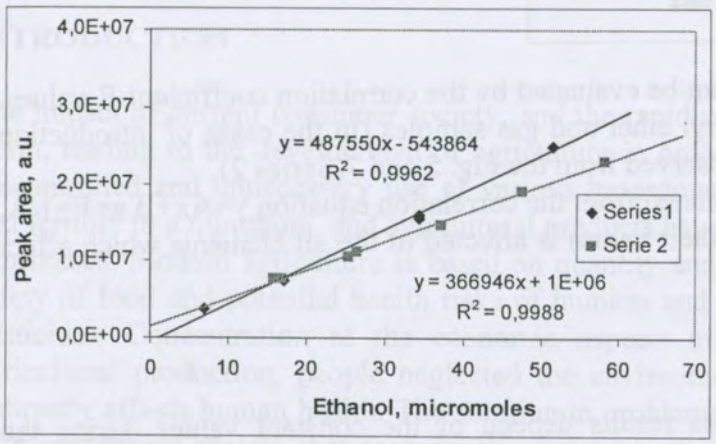


Fig. 4. The calibration curves for the ethanol

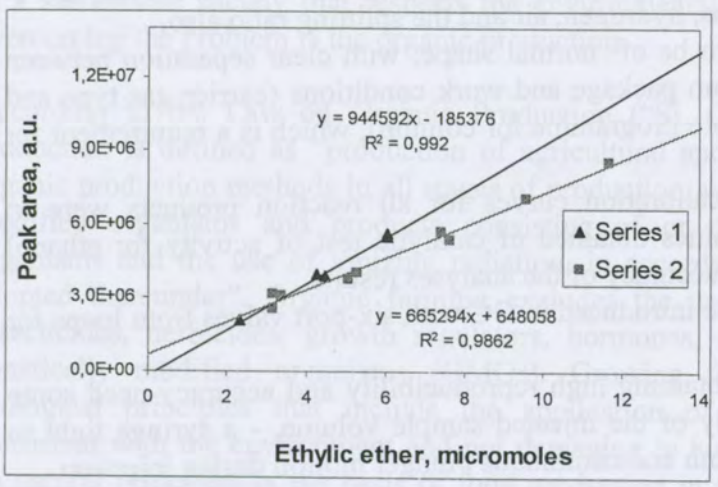


Fig. 5. The calibration curves for the ethylic ether

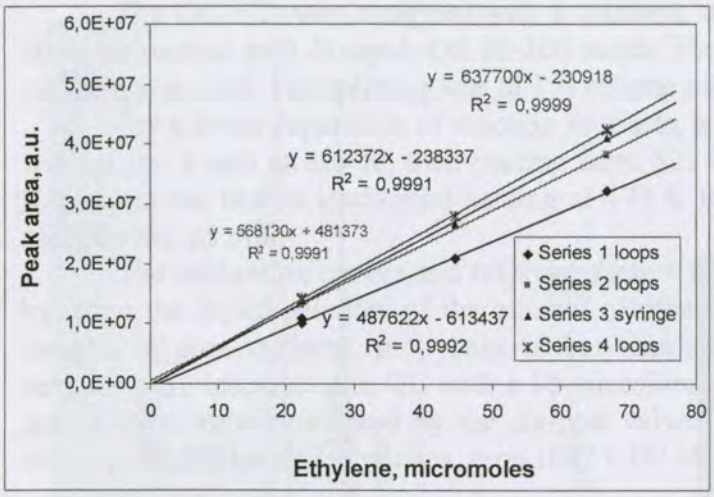


Fig. 6. The calibration curves for the ethylene

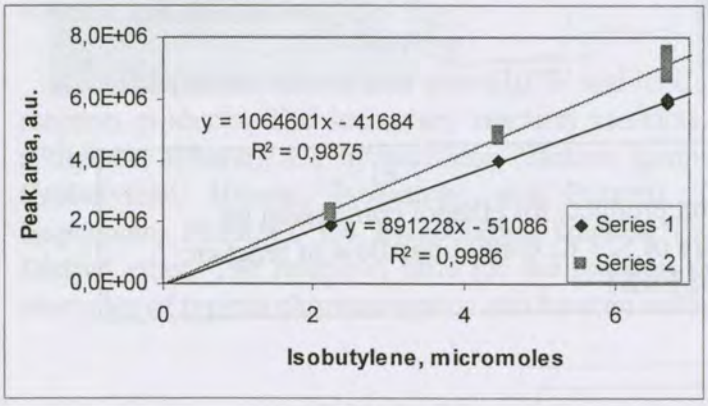


Fig. 7. The calibration curves for the isobutylene

The precision of the analyses can be evaluated by the correlation coefficient-R values. The precision for the analyses of diethyl ether and gas samples (in the cases of introduction with syringes) was poorly, as can be observed from the Fig. 5 and 7(Series 2).

The response factors were calculated from the correlation equation y=Ax+B as F=1/A, micromoles/a.u and the confidence in their values is affected of the all elements which affect the accuracy of the analyses results.

Conclusions

The reproducibility of the analyses results depend of the constant values during the measurements for the flow of carrier gas, hydrogen, air and the splitting ratio also.

The chromatographic peaks have to be of normal shape, with clear separation between them, it means good choices for column package and work conditions (carrier gas type and flow, hydrogen and air flow, temperature programme for column), which is a requirement for a good accuracy.

The concentration ranges of calibration curves for all reaction products were in concordance with the experimental values obtained of catalytic test of activity for ethanol conversion, what is a guarantee for the accuracy of the analyses results.

The gas samples are preferable to be introduced in GC with six-port valves from loops for higher reproducibility and accuracy.

The liquid samples injection for obtaining high reproducibility and accuracy need some precautions like: - the reading carefully of the injected sample volume, - a syringe tight to pressure of the column head and a smooth and continuous plunger motion during injection.