

Glucose transformation into 5-hydroxymethylfurfural over polycationic nanostructured faujasite zeolite catalysts

Patrylak L.*, Konovalov S., Yakovenko A., Pertko O., Povazhnyi V.

Department of Catalytic Synthesis, V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry of NAS of Ukraine, * E-mail: lkpg@ukr.net

Introduction

Exhaustion of fossil resources and deterioration of the ecosystems around the world contribute to intensive development of environmentally friendly processes of "green" chemistry and active use of renewable bioresources. Currently, the investigations in the field of biomass processing into valuable substances is extremely popular in whole world. Among simple sugars the catalytic dehydration of fructose is the most researched process, whereas glucose transformation is more difficult. Dehydration of glucose into 5-HMF usually is considered via intermediate stage of its isomerization into fructose over Lewis acid sites following by dehydration over Brønsted sites. Therefore, the catalysts must possess both Brønsted and Lewis acidity. Polycationic forms of faujasites are known as effective catalysts for isobutane with butenes alkylation and other petrochemical processes, which needs combination of both Brønsted and Lewis acid sites. Thus, it was interesting to give insight into their performing in glucose dehydration, which also needs simultaneously Brønsted and Lewis acidity.

Experimental

Catalysts were obtained from sodium forms of industrial powdered faujasite-type X and Y zeolites (JS "Sorbent", Nizhniy Novgorod, Russia). The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were 2.3 and 4.7, respectively. To obtain the polycationic forms, the NaX and NaY zeolite samples were modified by ion exchange. According to previous investigations, firstly calcium salts were used, secondly – lanthanum and ammonium ones. As a result, the polycation samples PCX and PCY were obtained. The PCY sample was subjected to steaming at 200 °C for 2 h in superheated water vapor stream in the special set-up and PCY-St sample was obtained. One part of the PCX sample was also calcined at 350 °C for 2 h for partial decomposition of ammonium ions and the PCX-T sample was obtained. The PCUSY sample based on NaY zeolite was prepared by using similar ion exchange procedures with intermediate calcinations after each exchange in the muffle furnace at 550 °C for 2 h in air presence.

Results

Stainless steel autoclaves (25 cm³) were applied for carrying out the transformation of glucose solutions in DMSO. Weighted samples of zeolite catalysts (0.75 g) were poured by 5 g of 10 wt % glucose solution. The reaction was performed at 160 °C for 4 hours. Reaction products were analyzed by using the gas chromatography method (Agilent GC 7890A chromatograph equipped with FID flame-ionization detector, split/splitless inlet, the capillary column J&W HP-5 (5%-phenyl)-methylsiloxane, 30 m, inner diameter 0.32 mm, film thickness 0.25 μm).

Table 1. Number of acid sites calculated from ammonia TPD profiles

Sample	Number of acid sites, mmol/g (%)			
	200–350 °C	350–450 °C	450–550 °C	Total content
PCY	0.58	0.52	0.54	1.63
PCY-St	0.68	0.39	0.58	1.65
PCUSY	0.27	0.23	0.15	0.65
PCX	0.45	0.50	0.56	1.51
PCX-T	0.33	0.29	0.15	0.77

Table 2. Adsorption characteristics of the samples

Catalysts	S_{BET} , m ² /g	S_{micro}^t , m ² /g	V_{Σ} , cm ³ /g	V_{micro}^t , cm ³ /g	$V_{\text{micro}}/V_{\Sigma}$, %	R_{DFT} , nm	R, nm	R_{BJH} , nm
NaY	576	572	0.256	0.241	94.1	1.09	0.89	1.66
PCY	528	515	0.262	0.233	88.9	1.53	0.99	1.65
PCY-St	413	380	0.223	0.156	70.0	2.64	1.08	2.42
PCUSY	446	423	0.225	0.181	80.4	2.64	1.01	1.99
NaX	615	608	0.277	0.267	96.4	1.01	0.90	1.51
PCX	572	565	0.257	0.240	93.4	2.64	0.90	1.98
PCX-T	515	510	0.245	0.216	88.1	2.64	0.96	1.97

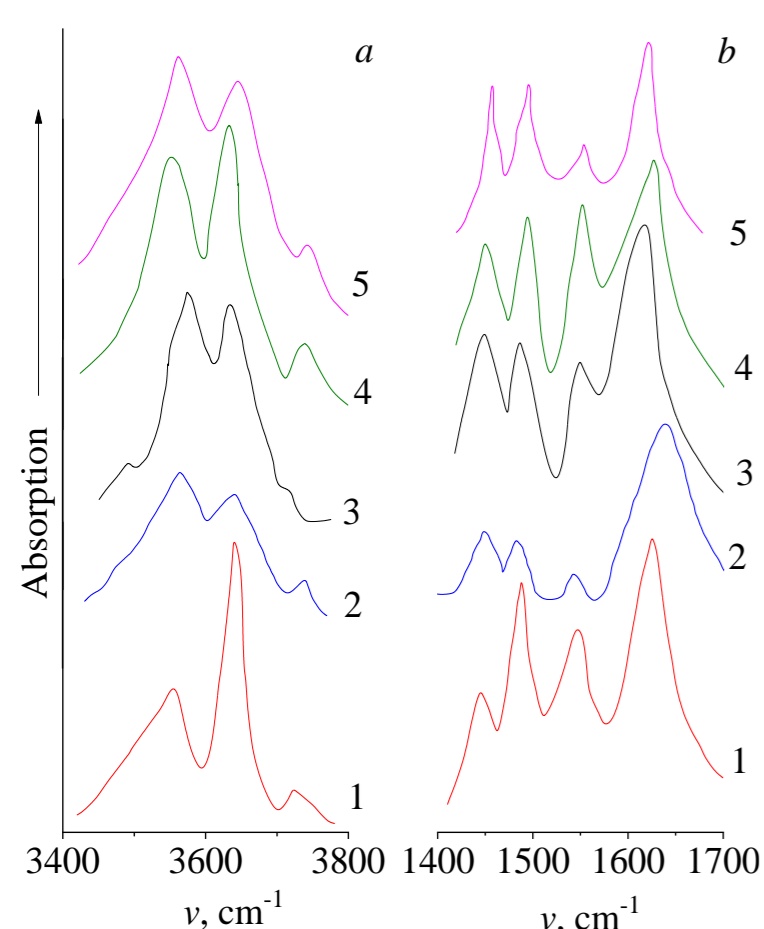


Fig. 1 IR spectra in the regions of valence vibrations of OH-groups (a) and chemisorbed pyridine vibrations (b): 1 – PCY, 2 – PCUSY, 3 – PCX, 4 – PCY-St, 5 – PCX-T

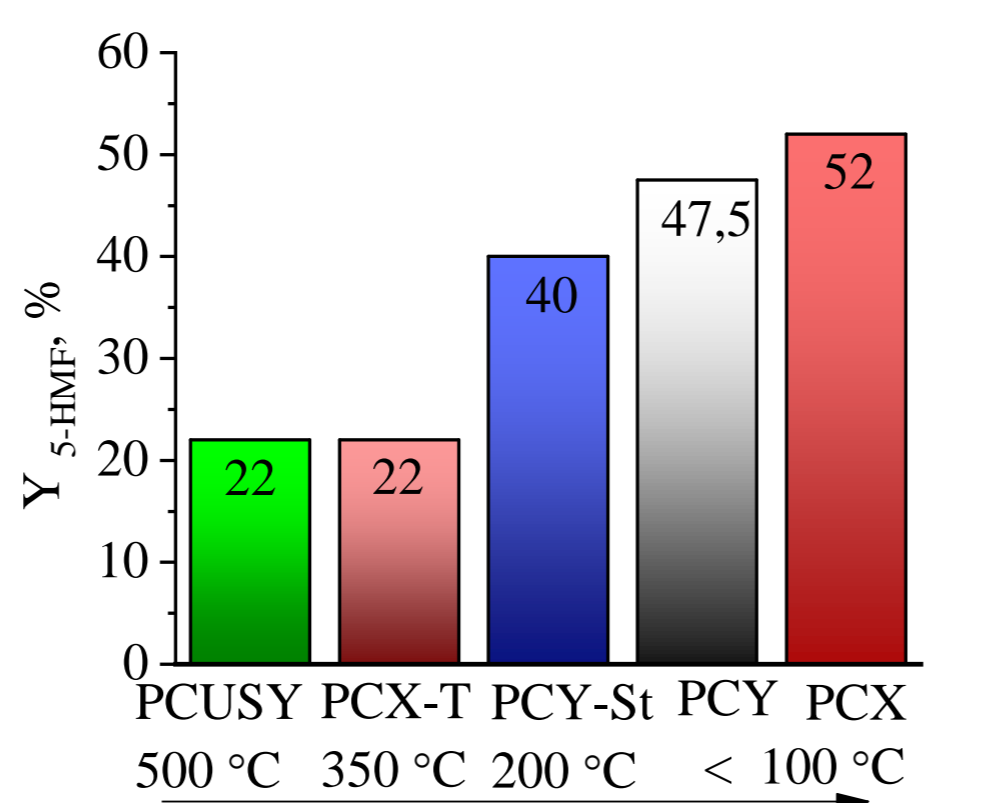


Fig. 2 5-HMF yields over polycationic catalysts

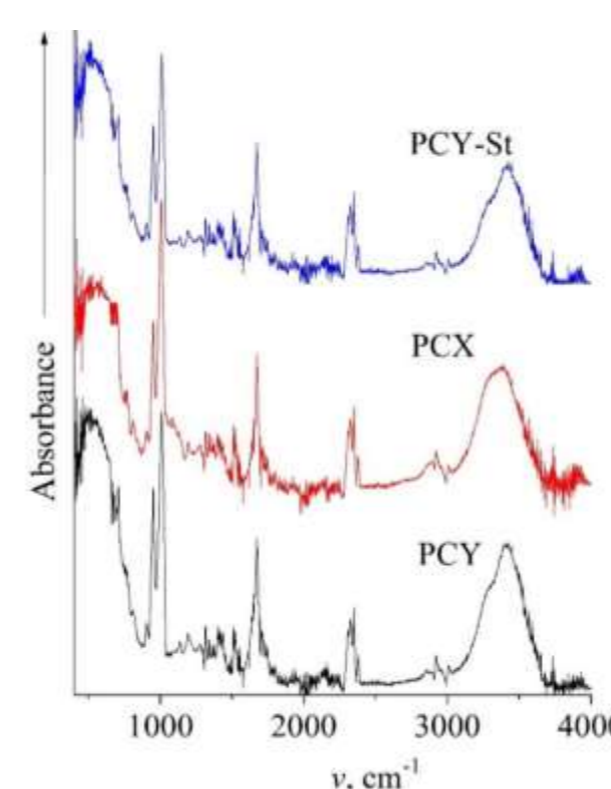


Fig. 3 FTIR spectra of liquid products

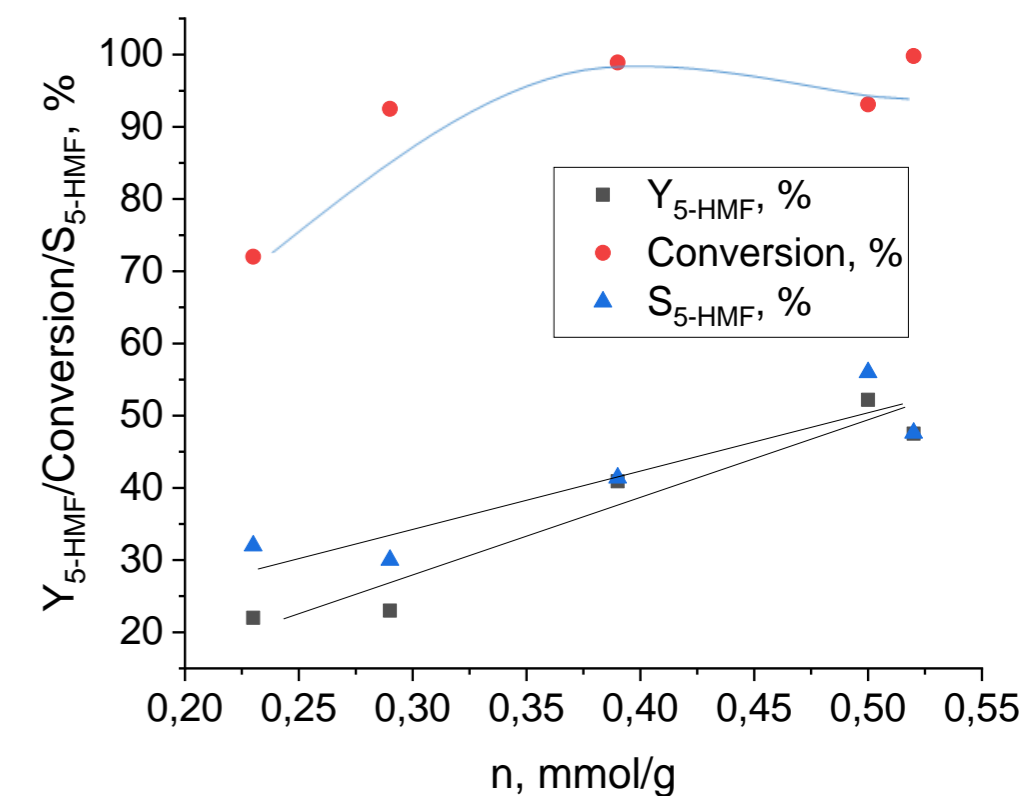


Fig. 4 Glucose conversion, 5-HMF yield and selectivity for 5-HMF as a function of number of medium strength acid sites

Glucose conversion, 5-HMF yields, and selectivity is suggested to depend on number of acid sites of medium strength (Figure 4). It is possible that weak acid sites cannot provide proceeding of any glucose transformation, whereas strong acids sites lead to oligomerization reaction realization with formation of humins. And only acid sites with medium strength responsible for the 5-HMF formation. Concerning the nature of acid sites namely Lewis and Brønsted acidity one can see that predominance of Lewis acidity badly influence on target process proceeding (samples PCUSY and PCX-T). In contrary, the Brønsted acidity predominance and especially close to one ratio between Brønsted to Lewis sites has positive effect on 5-HMF formation (samples PCY, PCY-St, and PCX). Such peculiarities can be connected with extraframework alumina appearance after thermal treatment which leads to Lewis acidity rising [38, 39], but the first stage of glucose transformation is the reversible process of its isomerization to fructose over Lewis acid sites. The next step of reaction road realization needs Brønsted acidity and in the case of low Brønsted acidity it could not be realized.

Conclusions

Therefore, all the evidence suggests possible future use of polycationic faujasite zeolites as effective catalysts for glucose conversion into 5-hydroxymethylfurfural.

- Using different conditions of zeolite modification, a range of polycationic samples of similar chemical composition was synthesized. The samples having subjected to modification at mild temperatures show the best catalytic performance.
- Ammonia TPD profiles of zeolite catalysts demonstrate the highest acidity for zeolite Y samples obtained at mild hydrothermal conditions. Whereas high temperature using leads to substantial decrease of total acidity.
- It is found out that at the similar chemical composition of the synthesized samples the Brønsted to Lewis acidity ratio is different. The last is caused by additional appearance of extraframework alumina at high temperatures and steaming. Lewis acidity caused by presence of polyvalent cations is seemed to be preferable one in comparison with tricoordinated alumina. The best results have been obtained over sample with Brønsted to Lewis acidity ratio close to 1:1 or with Brønsted acidity predominance.
- Steaming of Y zeolite samples at 200 °C and ultrastabilization at 550 °C lead to increase of mesoporosity of catalysts. Ultrastabilization gives rise to simultaneous total acidity decrease.
- The main product of glucose conversion was 5-HMF. The yields of 5-HMF are found out to increase with increasing of fraction of strong acidity in the total acidity of samples. Yields in DMSO are three times higher than were found earlier in aqua medium.
- DTA/TG investigations of catalysts confirm proceeding of a number of processes including DMSO desorption, DMSO burning, deamination of zeolites, dehydroxylation of zeolites, and phase transition near 950 °C. It is observed that the more weight loss in TG analysis for catalysts the more 5-HMF yields. Weight losses is seemed to correlate with strong acidity of the catalysts.
- In DMSO medium humin byproducts are not deposited on catalyst surface. They remain dissolved in DMSO and precipitated only after water addition.

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