

Glucose conversion over nickel-containing zeolites in aqueous medium



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

Department of Catalytic Synthesis, V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry of NAS of Ukraine

* Corresponding author: lkpg@ukr.net

Introduction

The negative impact of significant human activity on the environment around the world contributes to the considerable development of «green» chemistry and the active use of renewable materials for the production of a new generation of polymers, fuels, pharmaceuticals, pesticides, nutrient additives and a range of important chemicals. The sugars can be converted into platform substances such as furan derivatives, furfural, 5-hydroxymethylfurfural (5-HMF), lactic or levulinic acids, etc. Several hundred syntheses can be done and a number of useful chemicals can be obtained from the platform substances [1, 2]. A large set of diverse heterogeneous catalysts can be synthesized and applied in a wide range of reaction conditions. Many solid catalysts were used for glucose or fructose conversion in aqueous or alcohol media, but zeolites have not been found yet sufficient application in this area [1, 2].

Ni-containing bifunctional zeolite catalysts showed high activity in the aromatization and in the isomerization of linear alkanes [3]. Therefore, the purpose of this work was to investigate glucose transformation in water solution over the middle- and the large-pore nickel-containing zeolites of different types.

Experimental

Hydrogen forms of zeolite Y (faujasite), M (mordenite), and ZSM-5 with SiO₂/Al₂O₃ ratio 4.7, 9, 41 respectively have been synthesized from sodium forms of zeolites produced by JS «Sorbert» (Nizhny Novgorod, Russia). To start with, sodium cations have been exchanged at 80 °C for 3 h by ammonium ones using 3 mol l⁻¹ ammonium nitrate solution. Thus, the obtained ammonium forms of zeolite have been separated by filtration and washed by distilled water. The exchange procedure has been repeated three times for Y and ZSM-5 and four times for M zeolite. NH₄-forms of zeolites have been calcined in a muffle furnace at 550 °C in the presence of air for 2 h after each exchange. In such a procedure the hydrogen forms of zeolites HY, HM, and HZSM-5 have been obtained. The last ones have been impregnated by the aqueous solution of nickel nitrate hexahydrate. Catalysts with 5 wt % of nickel have been heated at 50 °C for 5 h and then calcined at 400 °C for 2 h before investigations. In the result, three samples 5NiHY, 5NiHZSM-5, and 5NiHM have been obtained.

Nickel modified zeolites Y, M and ZSM-5 have been synthesized and characterized by FTIR spectroscopy, pyridine adsorption with IR-spectroscopic control, ammonia TPD, low-temperature nitrogen adsorption/desorption. Glucose transformation at 160 °C in an aqueous medium over synthesized catalysts has been done.

Results

Table 1 Number of acid sites for zeolite samples according to ammonia desorption data

Sample	Number of acid sites per 1 g, mmol			
	Low strength (T _{max1} =250-300 °C)	Medium strength (T _{max2} =350-400 °C)	Strong (T _{max3} =600-650 °C)	Total
HM	0.13	0.39	0.16	0.68
HY	0.21	0.74	0.16	1.11
HZSM-5	0.09	0.32	0.02	0.44
5NiHM	0.15	0.36	0.19	0.63
5NiHY	0.14	0.50	0.10	0.74
5NiHZSM-5	0.08	0.20	0.02	0.30

According to acid sites distribution by straight depending on ammonia desorption temperature nickel-containing catalysts can be ranged like 5NiHY < 5NiHZSM-5 < 5NiHM, whereas according to the total number of acid sites in another way 5NiHZSM-5 < 5NiHM < 5NiHY.

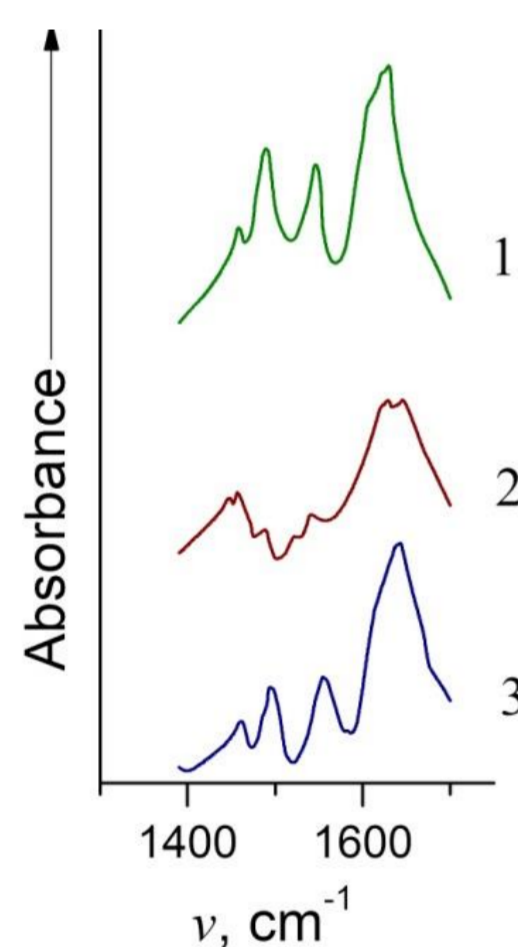


Figure 3 IR spectra of adsorbed pyridine over HY (1), HM (2) and HZSM-5 (3) samples

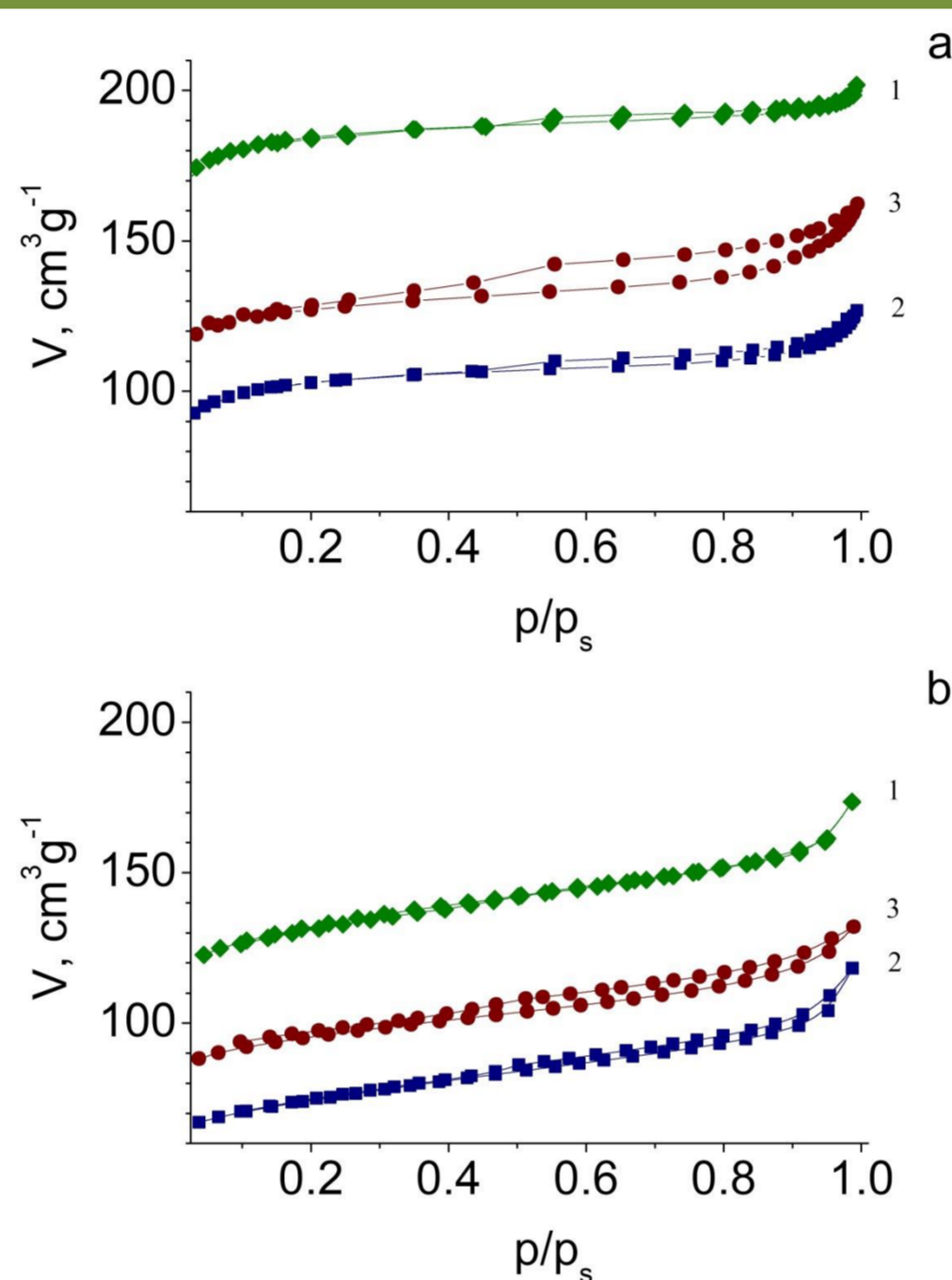


Figure 5 Low-temperature adsorption/desorption isotherms for H-forms (a) and Ni-containing catalysts (b): 1 - Y, 2 - ZSM-5, 3 - M

Table 2 Adsorption properties of the catalysts

Characteristic	Sample					
	HY	HZSM-5	HM	5NiHY	5NiHZSM-5	5NiHM
BET surface area, m ² g ⁻¹	645	361	445	486	272	353
BJH cumulative adsorption surface area of mesopores, m ² g ⁻¹	49.0	47.3	53.6	59.3	55.4	48.2
Micropore area, m ² g ⁻¹	558	275	366	458	242	321
Micropore volume, cm ³ g ⁻¹	0.248	0.122	0.16	0.205	0.114	0.141
Average mesopore diameter (4V/S), nm	3.8	4.9	5.9	5.8	6.5	6.3

Table 3 Yield of 5-HMF and its concentration in liquid reaction products

Sample	HPLC analysis		GC analysis	
	Concentration, mg ml ⁻¹	Yield, %	Concentration, mg ml ⁻¹	Yield, %
5NiHY	6.2	8.5	5.5±0.8	7.8±1.1
5NiHM	11.8	16.0	11.2±1.8	15.9±2.1
5NiHZSM-5	10.2	14.0	10.9±1.4	15.5±2.0
HY	-	-	8.0±0.7	11.3±1.0
HM	-	-	8.8±0.8	12.5±1.1
HZSM-5	-	-	2.4±1.0	3.4±1.4

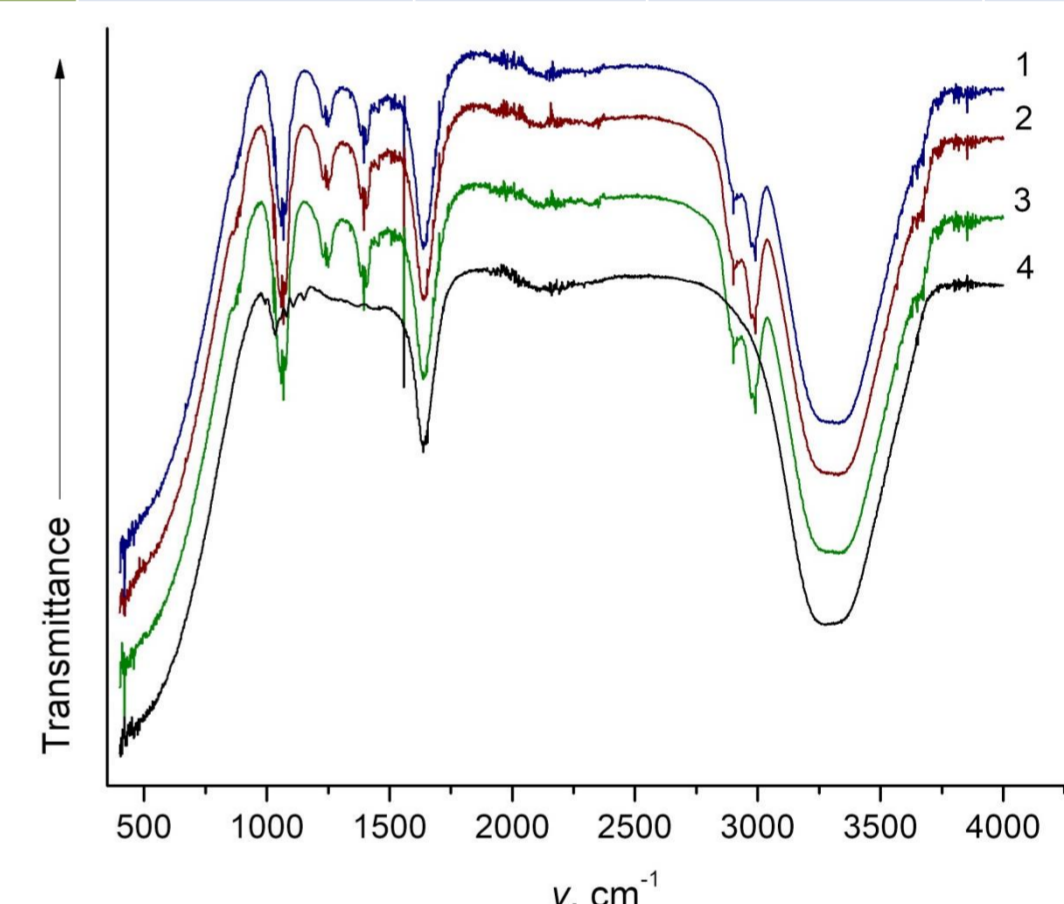


Figure 7 FTIR spectra of liquid products of glucose conversion over zeolites: 1 - 5NiHZSM-5, 2 - 5NiHM, 3 - 5NiHY, 4 - initial glucose

Table 4 Mass loss (mg) for deactivated samples

Sample	Temperature, °C			Total, mg
	Dehydration 20-200	Burning 200-450	Burning 450-600	
5NiHY	3.1	4.0	0.5	7.6
5NiHM	1.9	2.4	0.5	4.8
5NiHZSM-5	1.4	2.5	0.3	4.2

5NiHY catalyst is characterized by the biggest total mass loss (31 wt %). The losses for 5NiHM and 5NiHZSM-5 are 19 and 16 wt %. On 5NiHY sample the twice higher weight of coke deposits (18 wt %) has been found.

Conclusions

1. Nickel-containing zeolites catalyse glucose transformation into 5-HMF and humins. The 5-HMF yield up to 10-16 mol % has been obtained over middle-pore 5NiHZSM-5 and large-pore 5NiHM, 5NiHY zeolites during the transformation of 10 wt % aqueous solution of glucose. Glucose conversion was practically total.
2. Some mesoporosity of the zeolite samples indicated by low-temperature nitrogen adsorption/desorption appears during their synthesis. It is established that the average diameter of mesopores of mordenite and ZSM-5 samples is larger than of faujasite. The latter had a positive effect on the proceeding of the target reaction.
3. The yield of HMF correlates with the Lewis acid content. Bifunctional Lewis/ Brønsted acid catalysts with Lewis acidity predominance demonstrate better performance. Glucose conversion over the 5NiHY sample with the highest total number of acid sites proceeds with significant formation and accumulation in the faujasite supercages of reaction by-products humins.
4. The balance between catalyst acidity and textural properties plays a key role in the transformation of glucose into 5-HMF.
5. TG and DTA investigations gave quantitative information on the dehydration and decomposition of guest molecules of coke precursors that interact with the zeolite surface. Weight losses and heat effects due to the oxidative decomposition of coke compounds have been related to the analysis of peculiarities of their formation in zeolites and burning. 5NiHM and 5NiHZSM-5 deactivated samples showed a twice-lower weight of deposits (10 wt %) than on 5NiHY with the biggest total acidity. Low starting temperatures of deposits burning evidence about light or soft coke precursors formation over catalysts. FTIR investigations of the coked samples evidence that the degree of deactivation is not total.
6. Among tested samples, the mordenite and ZSM-5 modified by nickel look promising as catalysts for glucose conversion into HMF. Lewis acidity of the mordenite can be increased by acid dealumination or steaming. Increasing the mesoporosity of the samples also seems to be useful for a better process proceeding.

Acknowledgments

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