

Structural-adsorption characteristics of natural and chemically modified clinoptilolite

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Natural clinoptilolite (N-CLI) is a polyphase mineral containing clinoptilolite, α -quartz, mordenite, and hematite at certain ratios. We use clinoptilolite in its acid-modified forms (H-CLIs) as a support for Pd(II)-Cu(II) complexes (Pd-Cu/H-CLIs) characterized by catalytic properties in the reaction of CO oxidation. N-CLI used in the study was provided from Sokirnitskoye deposit (Trans-Carpathian region). (0.25-3)H-CLI-0.5H-CLI samples were prepared by N-CLI boiling for 0.5 h in nitric acid solution at its concentrations ranged from 0.25 to 3 M. Since water molecules directly participate in the formation of Pd(II)-Cu(II) surface complexes, we investigated ad/desorption of water vapor into/from N-CLI, (0.25-3)H-CLI-0.5, and Pd-Cu/H-CLIs using well-known McBain gravimetric method. All water vapor ad/desorption isotherms obtained were of the similar form with an expressed loop of capillary-condensation hysteresis indicating the nonuniform porous structure with the prevalence of meso- and macroporosity and their adsorption branch followed the BET equation in its linear form up to $P/P_s \approx 0.3$ (correlation factor $R^2 = 0.98-0.99$). As can be seen from Table, as opposed to BET constant C (Q_1) decreased with C_{HNO_3} (likely, due to weakening the energy of interaction between water molecules and the adsorbent surface), a_m and a_∞ parameters, as well as the specific surface (S_{sp}) increase for H-CLIs and remain practically unchanged after anchoring Pd(II)-Cu(II) complexes.

Table. Structural-adsorption characteristics of natural and chemically modified clinoptilolite

Sample	BET equation constants		a_∞ , mmol/g	Q_1 , kJ/mol	S_{sp} , m ² /g
	a_m , mmol/g	C			
N-CLI	1.53	133.40	3.30	12.09	100
0.5H-CLI-0.5	1.72	26.3	4.25	8.10	110
1H-CLI-0.5	1.89	29.1	5.53	8.35	123
3H-CLI-0.5	2.04	10.5	5.67	5.86	133
Pd-Cu/0.5H-KЛ-0.5	1.70	31.7	5.40	8.56	110
Pd-Cu/1H-KЛ-0.5	1.78	25.4	5.18	8.00	115
Pd-Cu/3H-KЛ-0.5	2.06	10.4	6.80	5.84	134