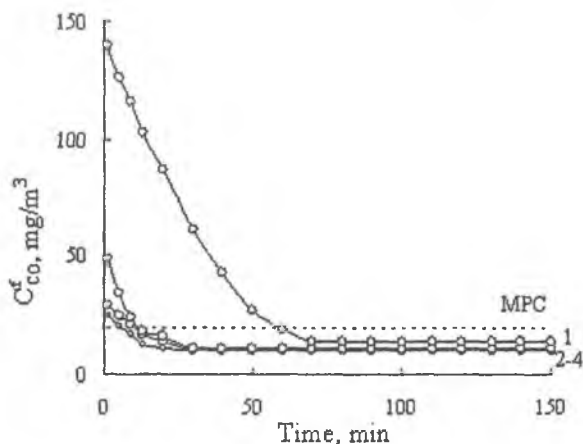


# The influence of concentration of nitric acid used in clinoptilolite modification on the activity of clinoptilolite based palladium-copper catalysts in the reaction of carbon monoxide oxidation

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The activity of supported palladium-copper catalysts in the reaction of low-temperature carbon monoxide oxidation can be controlled by varying Pd(II) and Cu(II) precursors, ligands ( $L = Cl^-$ ,  $Br^-$ ), Pd(II):Cu(II):L ratios, and structure-adsorption and physicochemical properties of supports. The latter can be changed by acid-thermal modification of natural sorbents often used as the supports. In the work, we modified natural clinoptilolite (N-CLI) by its boiling for 0.5 h in nitric acid at its concentrations ranged from 0.25 to 3 M and by impregnation of natural clinoptilolite or its acid-modified forms ((0.25–3)H-CLI-0.5) with aqueous  $K_2PdCl_4$ - $Cu(NO_3)_2$ -KBr solution with obtaining Pd(II)-Cu(II)/N-CLI or Pd(II)-Cu(II)/((0.25–3)H-CLI-0.5) samples, respectively. N-CLI and all chemically modified samples were studied by analysis of their XRD patterns and IR spectra. XRD data show that the acid-thermal modification of clinoptilolite results in some structural changes without destruction of its zeolite framework whereas Pd(II) and Cu(II) anchoring does not accompanied by formation of new phases such as their salts, oxides and metallic forms. A broad, high intensity IR band of complicated form at  $1063\text{ cm}^{-1}$  characteristic of N-CLI shifts to higher frequencies after its acid-thermal modification and the shift increases with acid concentration due to gradual dealumination of clinoptilolite. The presence of Pd(II) and Cu(II) does not affect the band positions that can be explained by their anchoring to the vacancies formed as a result of aluminum removal. The study of kinetics of CO oxidation with air oxygen has shown (Figure) that catalytic activity is



Time dependence of  $C_{CO}^f$  for CO oxidation over Pd(II)-Cu(II)/H-CLI-0.5 obtained at different concentrations (M) of  $HNO_3$  used for N-CLI modification: 0.25 (1), 0.5 (2), 1 (3), 3 (4).

observed only for the acid-modified clinoptilolite anchored Pd(II)-Cu(II) complexes. The nitric acid concentration affects the reaction rate only at the beginning of this reaction: the initial reaction rate increases (the final CO concentrations  $C_{CO}^f$  decrease). As a result, there is a decrease in the time required for attainment of reaction proceeding in the steady-state mode with air purification to maximum permissible CO concentration (MPC) equal to  $20\text{ mg/m}^3$ .

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