Solid-State Catalysts Based on Bentonites and Pd(II)-Cu(II) Complexes for Low-Temperature Carbon Monoxide Oxidation

T.L. Rakitskaya[1*], T.A. Kiose[1], A.M. Zryutina[1], R.E. Gladyshevskii[2], A.S. Truba[1], V.O. Vasylechko[2], P.Yu. Demchenko[2], G.V. Gryschouk[2] and V.Ya. Volkova[1]

Abstract. *The results of testing of Pd(II)-Cu(II)/Bent catalyst samples in the reaction of CO oxidation with air oxygen are presented. Bentonites from three Ukrainian deposits: Gorbskoye, Dashukovskoye, and Kirovogradskoye are used as supports. Natural bentonites, their modified forms, and the catalysts have been characterized by X-ray diffraction phase analysis, FT-IR spectroscopy, and chemical analysis. It has been found that the activity of Pd(II)-Cu(II)/Bent catalysts increases with increasing amorphous silica content and with decreasing pH of their water suspensions.*

Key words: catalysis, bentonites, Pd(II)-Cu(II) complexes, carbon monoxide, oxidation.

I. INTRODUCTION

Despite a great number of publications devoted to functionalizing the properties of bentonites and to their application in catalysis [1,2], there is an apparent absence of research on ways the structural and physicochemical properties of bentonites influence activity of ecologically purposed bentonite-based metal-complex catalysts for CO, O_3, and SO_2 mitigation at ambient temperature.

II. EXPERIMENTAL

In this work, the results of testing Pd(II)-Cu(II)/Bent catalyst samples in the reaction of CO oxidation with air are presented. Bentonites from three Ukrainian deposits, Gorbskoye – Bent(G), Dashukovskoye – Bent(D), and Kirovogadskoye – Bent(K) - were used as the supports. Natural bentonites and the catalysts were characterized by X-ray diffraction phase analysis using an automatic diffractometer (STOE STADIP, monochromatic CuKα radiation). Infrared analysis was carried out using a Fourier transform infrared spectrometer (Perkin Elmer FT-IR Spectrometer).

Samples of Pd(II)-Cu(II)/N-Bent catalysts were prepared by incipient wetness impregnation of each support and by their subsequent drying at 110 °C until constant weight. The samples used in this work contained, in mol/g: Pd(II) – $2.72 \cdot 10^{-5}$, Cu(II) – $2.9 \cdot 10^{-4}$, and Br^- – $1.02 \cdot 10^{-4}$.

The catalyst samples were tested using a gas flow setup with a fixed bed reactor at 20 °C, relative humidity of 65 %, and the gas-air mixture linear velocity of 4.2 cm/s. Catalyst grain size was 0.5-1.0 mm. CO oxidation was monitored by measuring the final carbon monoxide concentration (C_{CO}^{f}) at its initial concentration (C_{CO}^{in}) of 300 mg/m^3 using electrochemical gas analyzer 621EKh04, with minimal detectable CO concentration of 2 mg/m^3 and detection time of 45 s).

III. RESULTS AND DISCUSSION

Results of chemical analysis of the sample components that according to our previously published data [3,4] can considerably affect the activity of Pd(II)-Cu(II) catalysts in carbon monoxide oxidation, as well as pH values of bentonite water suspensions, are presented in Table 1.

Table 1. Comparative chemical composition (main components in wt. %) of some natural Ukrainian bentonites and pH of their suspensions

Sample	SiO_2	Al_2O_3	Fe_2O_3	SiO_2/Al_2O_3	pH_s
N-Bent(D)	49.6	13.5	7.2	3.67	8.75
N-Bent(K)	60.5	12.5	5.0	5.04	6.27
N-Bent(G)	50.0	18.5	7.6	2.70	3.96

Table 1 shows that N-Bent(G) has low values of both SiO_2/Al_2O_3 ratio and pH of its water suspension.

Diffractograms of the samples of natural bentonites are shown in Figure 1.

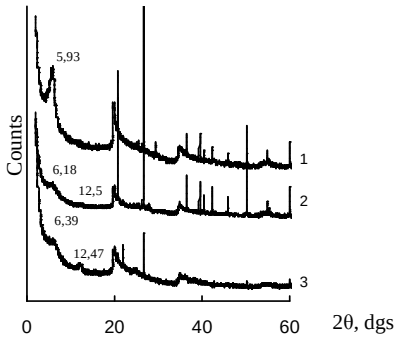

Fig. 1. Diffractograms of the samples of natural bentonites: 1 – N-Bent(D); 2 – N-Bent(K); 3 – N-Bent

It was found that all of these bentonites, in addition to their main montmorillonite (Mont) phase, contain an α-quartz phase (2θ = 26.630 °, d = 3.34 Å), which is most abundant in N-Bent(D) sample. Kaolinite phase impurity was distinctly detectable at 2θ = 12.470 ° (7.09 Å) and 25.080 ° (3.55 Å) for N-Bent(G) and at 2θ = 12.500 ° (7.08 Å) for N-Bent(K). Assignment of kaolinite phase for

[1] Faculty of Chemistry, Odessa I.I. Mechnikov National University, Odessa, Ukraine,
[2] Faculty of Chemistry, Ivan Franko National University of Lviv, Lviv, Ukraine
[*] TLR@onu.edu.ua

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N-Bent(D) was ambiguous. Main montmorillonite phase was identified in the three bentonite samples at the following values of angles of reflection, 2θ, and interplanar spacing (d, Å): 5.930 ° (14.90) – 19.820 ° (4.48) – 34.925 ° (2.56) – 54.905 ° (1.67) for N-Bent(D); 6.180 ° (14.29) – 19.925 ° (4.46) – 35.165 ° (2.55) – 54.890 ° (1.67) for N-Bent(K); and 6.395 ° (13.82) – 20.015 ° (4.44) – 35.075 ° (2,56) for N-Bent(G). Position and intensity of semi-amorphous halo change in a small angle range from $2\theta = 5.930$ ° for N-Bent(D) to $2\theta = 6.395$ ° for N-Bent(G). Absolute intensities of this and other reflections of Mont phase are half as large for N-Bent(G) as for N-Bent(D). Such a lowering is an evidence of amorphization of Mont phase. Judging by the intensity of the strongest reflex for α-quartz (2θ = 26.630 °), the content of this phase and the crystallinity of the samples lowers in the following sequence: N-Bent(D) > N-Bent(K) > N-Bent(G). Creation of Pd(II)-Cu(II)/N-Bent catalysts is not accompanied either by significant structural changes in Mont phase or by formation of new phases that would include catalyst components.

IR spectral data, along with X-ray phase analysis, confirm a polyphase composition of natural bentonites. A sharp, intensive, high-resolution band at 3697 cm^{-1} in the range of stretching vibrations of OH groups bound to octahedral cations, in addition to a band at 913-915 cm^{-1} corresponding to deformation vibrations for N-Bent(G) and N-Bent(K), denotes the presence of crystal kaolinite in the samples. The band at 3697 cm^{-1} appears only as a shoulder for N-Bent(D), which suggests the latter has a low kaolinite content. A characteristic doublet at 798 and 779 cm^{-1} suggests that N-Bent(D) and N-Bent(K) samples contain free α-SiO_2 (α-quartz) phase. For N-Bent(G), this doublet is overlapped by a wider band at 800 cm^{-1} corresponding to amorphous SiO_2 therefore the spectrum contains a wide band at 797 cm^{-1} with a shoulder at 778 cm^{-1}. The data of X-ray phase analysis suggest that N-Bent(G) sample is more amorphous than N-Bent(D) and N-Bent(K) samples (Fig. 1).

Dominant montmorillonite phases in the three bentonites have similar spectral characteristics corresponding to their structural groups in octahedral (Al-O) and tetrahedral (Si-O) lattices regardless of the bentonite origin. Thus, for all of the three samples, a band at 3622 cm^{-1} corresponding to Al-Al-OH is observed in the range of stretching vibrations corresponding to OH groups bound to octahedral cations, whereas a band at 915 cm^{-1} is most intensive for N-Bent(G) sample, which has the highest Al_2O_3 content out of the three bentonites (Table 1).

Stretching vibrations in the range characteristic of silicate structure are observed for all three bentonite samples. Besides a band at 1039 cm^{-1} characteristic of stretching vibrations of Si–O–Si (tetrahedral Si), there are also distinct vibrations at 1087-1095 cm^{-1}, which suggests the presence of free (amorphous) SiO_2 in all natural bentonite samples. The spectra of Pd(II)-Cu(II)/Bent catalysts demonstrate no significant differences from natural bentonite samples except for the reduced intensity of the band at 3623 cm^{-1}. Therefore, surface reactions during either Pd(II) and Cu(II) supporting or catalyst formation do not result in structural changes in the supports.

Samples of Pd(II)-Cu(II)/Bent catalysts have been tested in the reaction of low-temperature carbon monoxide oxidation with oxygen. Change in the final carbon monoxide concentration (C^{f}_{CO}) over time during CO oxidation in the presence of Pd(II)-Cu(II)/Bent catalysts is plotted on Fig. 2.

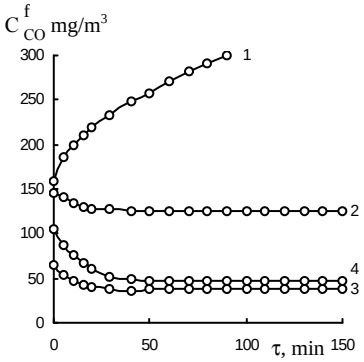

Fig. 2. Time dependence of C^{f}_{CO} in CO oxidation with oxygen in the presence of K_2PdCl_4-$Cu(NO_3)_2$-KBr-H_2O/Bent catalyst samples based on: 1 – N-Bent(D); 2 – N-Bent(K); 3 – N-Bent (G); 4 – H-Bent(D)-1 ($C_{Pd(II)} = 2.72 \cdot 10^{-5}$; $C_{Cu(II)} = 2.9 \cdot 10^{-5}$; $C_{KBr} = 1.02 \cdot 10^{-4}$ mol/g; $C^{in}_{CO} = 300$ mg/m^3)

It is apparent from Fig. 2 that shapes of C^{f}_{CO} vs. τ kinetic curves depend on the bentonite origin. The final CO concentration rapidly reaches the initial concentration (300 mg/m^3) for Pd(II)-Cu(II)/N-Bent(D) catalyst (curve 1), whereas CO oxidation proceeds in a steady state (C^{f}_{CO} = const) when the catalysts based on N-Bent(K) and N-Bent(G) are used (curves 2 and 3). CO oxidation efficiency is used as a measure of activity of the catalysts. It is obvious that the catalyst based on Bent(G) (curve 3) is the most active, with CO oxidation efficiency of 87 % under steady-state conditions. It was demonstrated that acid activation of a N-Bent(D) sample at mild conditions (1 M HNO_3, 100 °C, 1 h treatment) dramatically changes the behavior of Pd(II)-Cu(II)/H-Bent(D)-1 catalyst (Fig. 2, curve 4).

IV. CONCLUSIONS

To conclude, the activity of Pd(II)-Cu(II)/Bent catalysts in the reaction of CO oxidation goes up with increasing amorphous silica content and decreasing pH_s.

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