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INVESTIGATION OF METAL STATE IN METAL-CONTAINING ZEOLITE CATALYSTS BY DTA AND ESR METHODS

V. K. Yatsimirsky, L. P. Oleksenko, V. Ya. Zub and I. V. Kuzmich*

Kyiv Shevchenko University, Vladimirskaya Str. 64, Kyiv, Ukraine

Abstract

Thermal stability and its influence on the catalytic activity in CO oxidation of Cu, Pd and Pd–Cu zeolite systems were investigated. The increasing of catalytic activity in the first cycle of reaction is connected with the thermal decomposition of complex ions and consequently with the changing of metal state in catalyst in the case of Cu/ZSM-5 catalyst. This activity does not relate to initial zeolite with complex ions, but to the metal ions with the decreasing ligands number in the coordination sphere of metal ion. According to the EPR spectrum the copper ions form clusters in zeolite channels due to the spin changed interaction. It was established ESR method that 1.8% Cu/ZSM-5 catalyst in a reduced form has copper (I and II) ions by. The Pd/ZSM-5 catalysts with different metal content have high catalytic activity below the temperature decomposition in contrary to Cu-containing zeolites. On the one hand, it may be connected with the partial reduction of Pd ions during CO oxidation and, on the other hand, with the ability of Pd ions to form the respective label complexes with reagents as additional ligands. The same character of relation between thermal stability and catalytic activity for Pd-Cu/ZSM-5 catalyst was observed.

Keywords: catalysis, CO oxidation, metal-containing zeolites, thermal stability

Introduction

With the linking of the carbon monoxide to urban smog formation, which has harmful health effects, the removal of CO from the exhaust stream of various combustion sources has become increasingly important. The carbon monoxide conversion to CO_2 by molecular oxygen should be possible with effective catalysts. It is known that zeolites containing altervalent base-exchange metal cations show appreciable activity due to such zeolite properties as the high active site density, shape selectivity etc. and the peculiarities of metal state in zeolite [1]. As a consequence, the purpose of the present investigation is to define the metal state influence on the catalytic activity of metal-containing zeolite catalysts.

* Author for correspondence: E-mail: pavlisvv@phyche.freenet.kiev.ua

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Experimental

The used catalysts were 1.8% Cu/ZSM-5, 0.5% Pd/ZSM-5 and 2.7% Pd/ZSM-5 and 0.5% Pd–2.8% Cu/ZSM-5. These samples were obtained by ion exchange of H^+ form ZSM-5 using aqueous solutions of $[Cu(NH_3)_4]Cl_2$ and $[Pd(NH_3)_4]Cl_2$ at 25°C for 60 and 20 h respectively [2, 3]. A bimetallic catalyst was prepared from the same solutions using successive introduction of Cu and Pd ions. In order to obtain this catalyst the $[Cu(NH_3)_4]Cl_2$ solution was used and then the $[Pd(NH_3)_4]Cl_2$ one. After the ion exchange the samples were washed in water and dried at 60–80°C. The pretreatment of these catalysts in a reduced form for activity measurements was the reduction in H_2 at 450°C for 3.5 h.

The metal content of the catalysts was checked by an AAS-30 atomic-absorption spectrometer.

The studies of differential thermal and thermogravimetric analysis were made by using simultaneous Paulik–Paulik–Erdey derivatograph within the temperature range 25–500°C. The heating rate was 2.5°C min^{-1}. The mass of the investigated sample was 0.5 g.

The ESR spectra were obtained with the use of ADANI PC 100X ESR spectrometer at 293 K.

The catalytic activity measurements of zeolite catalysts in CO oxidation were made in a reactor of steady-state flow mode. The temperature was monitored by a chromel-alumel thermocouple that was in contact with the catalyst layer. The sample mass was equal to 0.25 g with the size of particles 0.5–1 mm. The reactant gas mixture of 2% CO and 20% O_2 in He was used. Product analysis was obtained using a gas chromatograph with a thermal conductivity detector. The separation column was packed with SKT carbon supported by $NiSO_4$ and gas separation was carried out in chromatographic column at 70°C. The flow rate of the carrier gas was 100 cm^3 min^{-1}.

Results and discussion

In order to determine the connection between the catalytic activity of metal-containing zeolites and their thermal stability the differential thermal and thermogravimetric analysis was made. The DTA and TG curves for the 1.8% Cu/ZSM-5 catalyst are represented in Fig. 1a. In the used temperature range one endothermic peak with a maximum value centred at 100°C and two exothermic peaks with a maximum at 250 and 350°C are observed. The endothermic peak corresponds to losing of catalyst molecular water, adsorbed as a multilayer on the surface. The latter peaks associated with the detachment of ammonia molecules from complex Cu ions in zeolite catalyst. The TG curve shows a continuous mass loss for the temperature interval studied.

The catalytic activity in CO oxidation as a function of degree conversion from temperature using 1.8% Cu/ZSM-5 catalysts is shown in Fig.1b. On the first stage the insignificant catalytic activity till 30°C was observed. The jump-likely character of dependence of conversion degree from temperature was fixed at temperature above

300°C for Cu/ZSM-5 catalyst in the non-reduced form. The conversion 50% degree is obtained at 330°C and the complete conversion – at 355°C.

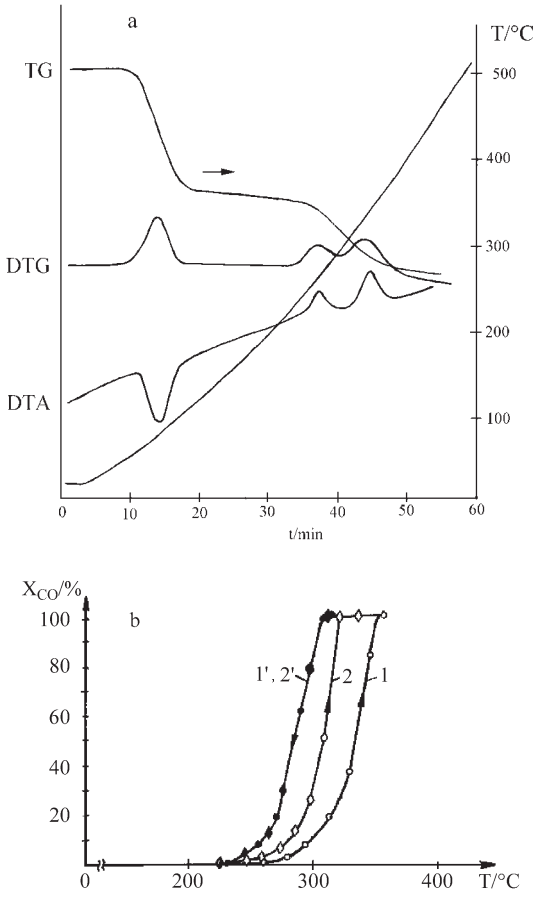

Fig. 1 The 1.8% Cu/ZSM-5 catalyst in non-reduced form: a – DTA analysis; b – catalytic activity in CO oxidation: 1,1' – the first cycle of catalysis; 2,2' – the second cycle of catalysis

This activity was constant till 300°C when the temperature decrease was carried out. Thus, the 'clock-counter' hysteresis of the reaction rate is observed on this catalyst. The Cu/ZSM-5 catalyst in the partly reduced form shows higher activity – the complete conversation is observed at 300°C. Besides, it is necessary to note the presence of wider hysteresis of the reaction rate for the reduced example that leads probably to the further increase of the catalytic activity (on 20°C) in the next cycle of heating.

The data of differential thermal analysis were used to explain the jump-like character of the catalytic activity increasing for Cu/ZSM-5 above 300°C. This catalytic effect is observed at those temperatures when Cu-aminocomplex ions decompo-

sition occur. As a result of this process, the metal state in catalyst has been changed – from initial complex Cu ions to the ions with decreasing ligands number in their coordination sphere.

The ESR spectra of 1.8% Cu/ZSM-5 in non-reduced and reduced forms were obtained. These spectra have an anisotropic form which is characteristic of axial symmetric substances of copper(II). The measured $g_{\|}$, $g_{\perp}$ values and $G(g_{\|}-2)/(g_{\perp}-2)$ are 2.279, 2.09 and 2.97 respectively. The hyperfine structure from copper nucleus is not resoluted. Thus, axes of molecules that occur in an elementary cells are disordered. It is known that metal impregnation of HZSM-5 zeolite can lead to the formation of both isolated copper ions [4, 5] and their clusters [6]. In our case, the ESR spectra showed the spin-changed interaction of copper ions due to forming of copper ion clusters in the channels of zeolite matrix. This phenomena can be observed when the quantity of Cu ions is higher than the adsorption capacity of the zeolites.

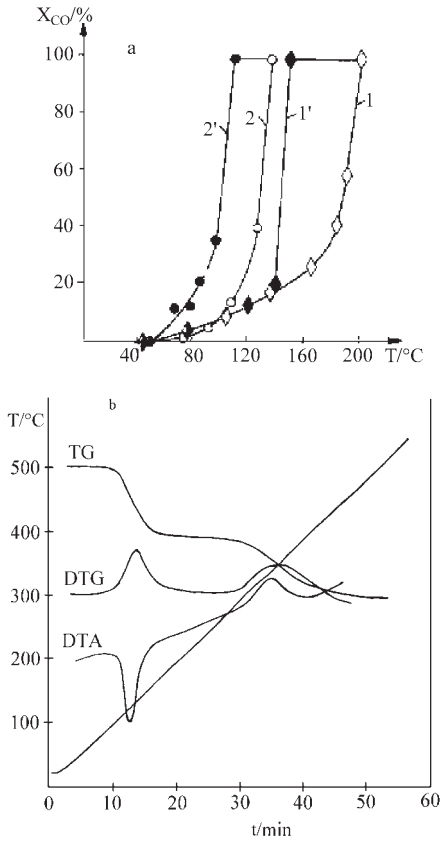

Fig. 2 The 2.7% Pd/ZSM-5 catalyst: a – catalytic activity in CO oxidation in non-reduced (1,1') and reduced (2,2') forms in the first cycle of catalysis; b – DTA analysis

The copper (I and II) ions were registered for partly reduced in hydrogen flow the Cu-containing zeolites by ESR method. For this purpose the catalyst sample was dissolved in toluene and then the solution of thiuramdisulfide was added. As a result the characteristic ESR spectrum for copper(II) diethyldithiocarbamate was obtained. In this way, the existence copper(I) ions in 1.8% Cu/ZSM-5 catalyst in partly reduced form together with copper(II) ions was detected.

The analogous investigation for Pd-containing catalysts was carried out. It was established that the catalysts 0.5% Pd/ZSM-5 and 2.7% Pd/ZSM-5 have higher activity in comparison with Cu-containing zeolites. It is important to note that the catalyst with a small content of metal (0.5% Pd) has a stable activity as compared with the catalyst 2.7% Pd/ZSM-5. The temperature dependences of the conversion degree for Pd-containing zeolites was characterized by hysteresis for the reaction rate and critical phenomena – the presence of two stationary states – low and high active in the different temperature range (Fig. 2).

The DTA analysis which was applied to Pd-containing catalyst (2.7% Pd) showed that in this case the exothermic effect with a maximum at 335°C and the corresponding mass loss (1.8%) was registered. At the same time, the temperature of complete CO conversion $T_{100\%}$=205°C for Pd/ZSM-5 catalyst is lower than the temperature of Pd-aminocomplexes decomposition.

Thus, the peculiarity of the high catalytic activity of Pd/ZSM-5 catalysts with different metal content is the fact that the temperature of their complete conversion is much lower than the temperature decomposition in contrary to Cu-containing zeolites. On the one hand, it may be connected with partly reduction of Pd ions during CO oxidation and, on the other hand, with the ability of Pd ions to form the respective label complexes with reagents as additional ligands.

The same character of the relation between the thermal stability and the catalytic activity for Pd–Cu/ZSM-5 catalyst was observed. It was established that this bimetal Pd–Cu zeolite system has a higher catalytic activity than zeolites containing only copper or palladium ions (Table 1).

Table 1 Catalytic activity of metal-containing zeolite catalysts in CO oxidation

Catalyst	Form of catalyst	$T_{50\%}$/°C	$T_{100\%}$/°C
1.8% Cu/ZSM-5	non-reduced	330	355
1.8% Cu/ZSM-5	reduced	275	300
0.5% Pd/ZSM-5	non-reduced	190	200
0.5% Pd/ZSM-5	reduced	183	190
0.5%Pd–2.8% Cu/ZSM-5	reduced	165	175

Conclusions

The various connection of thermal stability with catalytic activity in CO oxidation for 1.8% Cu/ZSM-5, 2.7% Pd/ZSM-5, 0.5% Pd/ZSM-5 and Pd–Cu/ZSM-5 zeolite cata-

lysts was found. In the case of Cu-containing zeolite the catalytic activity corresponds to the detachment of metal-aminocomplex ion. The presence of copper(I) and copper(II) ions in partly reduced form of this catalysts by ESR method was established. According to ESR spectra copper ions form clusters in the channels of zeolite matrix and it is favourable for CO oxidation. Such a bright correlation of the thermal stability with the catalytic activity as for Cu-containing zeolites is not observed in the case of Pd and Pd–Cu-containing zeolites.

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