INFLUENCE OF Pt ON THE PROPERTIES AND ACTIVITY OF CuO-BASED CATALYSTS FOR LOW TEMPERATURE OXIDATION OF CARBON MONOXIDE

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Abstract

A series of mono-oxide and multi-oxide catalysts: 10 wt.%CuO/γ-Al$_2$O$_3$; 10 wt.%CuO +10 wt.%Cr$_2$O$_3$/γ-Al$_2$O$_3$; 10 wt.%CuO + 20 wt.%CeO$_2$/γ-Al$_2$O$_3$, and 10 wt.%CuO + 10 wt.%Cr$_2$O$_3$ +20 wt.%CeO$_2$/γ-Al$_2$O$_3$ have been prepared and modified by Pt with contents from 0.05 up to 0.3 wt.%. Physico-chemical properties of the catalysts were determined by the methods of BET N$_2$-Adsorption, Hydrogen Pulse Chemisorption (HPC), XRD, TPR, EDS and IR-CO adsorption. The oxidative activity of the catalysts was studied at the temperature range 75 – 300 ^{o}C and CO concentration of 0.5 mol.%. Addition of Pt led to weakening of the interaction between CuO and Al$_2$O$_3$, CuO and Cr$_2$O$_3$ that enhanced the reducibility of CuO, resulting in increase of activity of CuAl, CuCeAl and CuCrCeAl catalysts. Meanwhile, due to the reduction of CuCr$_2$O$_4$ formation, the activity of catalysts CuCrAl decreased. The catalyst sample CuCeAl, containing 0.1 wt.% Pt, has been shown to be the best one for the complete oxidation of CO. At the given conditions on this catalyst the complete oxidation of CO to CO$_2$ occurred at 125 ^{o}C and space velocity 75,000 h^{-1}.

Keywords: CO, CuO, Low temperature oxidation, Pt-modified catalysts

Introduction

Deep oxidation of CO and volatile organic compounds (VOCs) plays increasingly important role in controlling emissions. CO and VOC combustion requires high cost due to the reaction takes place at high temperature, and the fuel must be provided. In addition, large amounts of emissions could be released from vehicles and engines in the first minutes, after the "cold boot", before the temperature of catalyst reaches the required value for the conversion of toxic gases [1,2]. Hence preparation of highly effective catalyst for the conversion of toxic compounds at low temperatures becomes new targets for future system of exhaust gas treatment. Pt – based and the oxide catalysts are the traditional catalysts for such applications, received wide attention [1,3,4]. Supported noble metal catalysts are usually more active for CO and VOCs complete oxidation, but transition metal oxides are cheaper, more thermo-stable and greater resistance to poisoning of impurities. In the single transition metal oxide catalysts, Co- [5,6] and Cu- based [7-11] catalysts are considered to be highly active for deep oxidation.

Naturally, metal oxides should express lower catalytic activity compared to precious metals and they must operate at higher temperatures. Mixtures of noble metal and metal oxide are considered as attractive catalysts for total oxidation, since both components have

distinct characteristics. Namely, noble metals have moderate affinity to oxygen, so oxygen is liberated slowly. Therefore, the catalytic activity of precious metals can be increased when combining it with other substances, such as metal oxides, thanks to it the mobility of oxygen increased. The role of metal oxides is also to diminish the CO inhibition, which is typical characteristic of reaction at low temperatures on platinum catalysts [4]. On the other hand, Pt makes metal oxides to have a multivalent state that promoted the transfer of oxygen from the gas phase to the catalyst [12]. Adding Pt and Pd to metal oxides catalyst can also lead to increase the selectivity towards CO_2 [12].

In our previous studies [13-15] the following combinations in multi-oxide catalysts have been shown to be optimal catalysts for carbon monoxide oxidation: 10 wt.%CuO/γ-Al_2O_3 (CuAl); 10 wt.%CuO + 10 wt.%Cr_2O_3/γ-Al_2O_3 (CuCrAl); 10 wt.%CuO + 20 wt.%CeO_2/γ-Al_2O_3 (CuCeAl); 10 wt.%CuO + 10 wt.%Cr_2O_3 + 20 wt.%CeO_2/γ-Al_2O_3 (CuCrCeAl). The purpose of this study is to look for highly active oxide catalysts, modified by Pt for low temperature oxidation reaction.

Experimental

Catalysts on the basis of mixed metal oxides were prepared by impregnation as indicated in [13, 14]. The precursors for the catalysts were solutions of $Cu(NO_3)_2.3H_2O$, $Cr(NO_3)_3.6H_2O$, and $Ce(NO_3)_3.6H_2O$. The calcination process was carried out at 450 ^{o}C for 4 h. Pt-modified oxide catalysts were obtained by impregnation of oxide catalysts with a solution of H_2PtCl_6 in distilled deionized water. The impregnated samples were left overnight in the air, then dried and calcined for 2 h at 300 ^{o}C for avoiding the sintering of Pt particles. The content of Pt in catalyst samples varied in the interval 0.05 – 0.3 wt.%. The Pt-modified catalysts were symbolized by adding the figure, indicating the weight percentage of Pt in front of the symbols of mixed oxide samples. For example, symbol 0.2PtCuCeAl denotes the mixed oxide sample 10 wt.%CuO + 20 wt.%CeO_2/γ-Al_2O_3, impregnated with 0.2 wt.% of Pt.

Physico-chemical characteristics of the catalysts such as specific surface area, pore volume, and dispersion of metals as well as their reducing character were determined in the apparatus CHEMBET-3000. The X-ray diffraction (XRD) spectra were registered on the X-Ray Diffractometer XD-5A instrument (Shimadzu) with CuKα radiation. The characteristics of CO adsorption on catalysts were defined by the method of IR spectroscopy. The IR spectra were recorded on apparatus Nicolet – Spectrometer 460 in the range of 4000 – 400 cm^{-1} with a resolution of 4 cm^{-1}. The catalyst samples were pre-treated in a pure oxygen flow of velocity 5 L/h for 1 h at 600 ^{o}C for metal oxide catalysts and at 300 ^{o}C for Pt containing samples. After treatments, the samples were cooled to room temperature followed by adsorption of CO at room temperature with P_{CO} = 8 mmHg or 13 mmHg for 20 min and IR spectra of the CO adsorbed were recorded. At the final step, the cell was evacuated to a pressure of approximately 10^{-3} Torr at room temperature or 100 ^{o}C for 20 min for partial desorbing of CO, and then IR spectra of CO on catalysts were again recorded.

The procedure in activity characterization of the studied catalysts, as well as the method, used for analysis of reaction mixtures, has been shown in our previous study [14].

Results and Discussion

Physico-chemical Characteristics of Catalysts

XRD spectrum of sample CuAl [15] comprises peaks, characteristic of γ-Al_2O_3 (with 2θ = 37°, 45° and 68°), CuO (2θ = 35°, 38°, 49° and 62°) and a small amount of spinel $CuAl_2O_4$ with 2θ = 61°. The addition of 0.05 – 0.3 wt.%Pt did not change the character in XRD pattern of the sample CuAl. As seen on Figure 1a, the CuO phase is characterized by the most intensive

peaks ($2 = \theta35$,$°38$,$°49°$ and $62°$), the characteristic peaks of γ-Al_2O_3 ($2 = \theta37$,$°45°$ and $68°$) and of aluminate $CuAl_2O_4$ ($2 = \theta66°$) are very weak; at the same time one can observe the characteristic peaks of Pt ($2 = \theta39$,$°46°$ and $67.5°$) with low intensity. For the catalyst CuAl, with additions of Pt up to 0.2 wt.% the cluster size and dispersion of copper did not change, although one can see reductions in the values of specific surface area (Table 1). This can be explained that PtCuAl catalyst were synthesized by sequential impregnations, the second impregnation on CuAl catalyst with a solution of H_2PtCl_6 complex reduced the specific surface area of CuAl catalyst modified Pt.
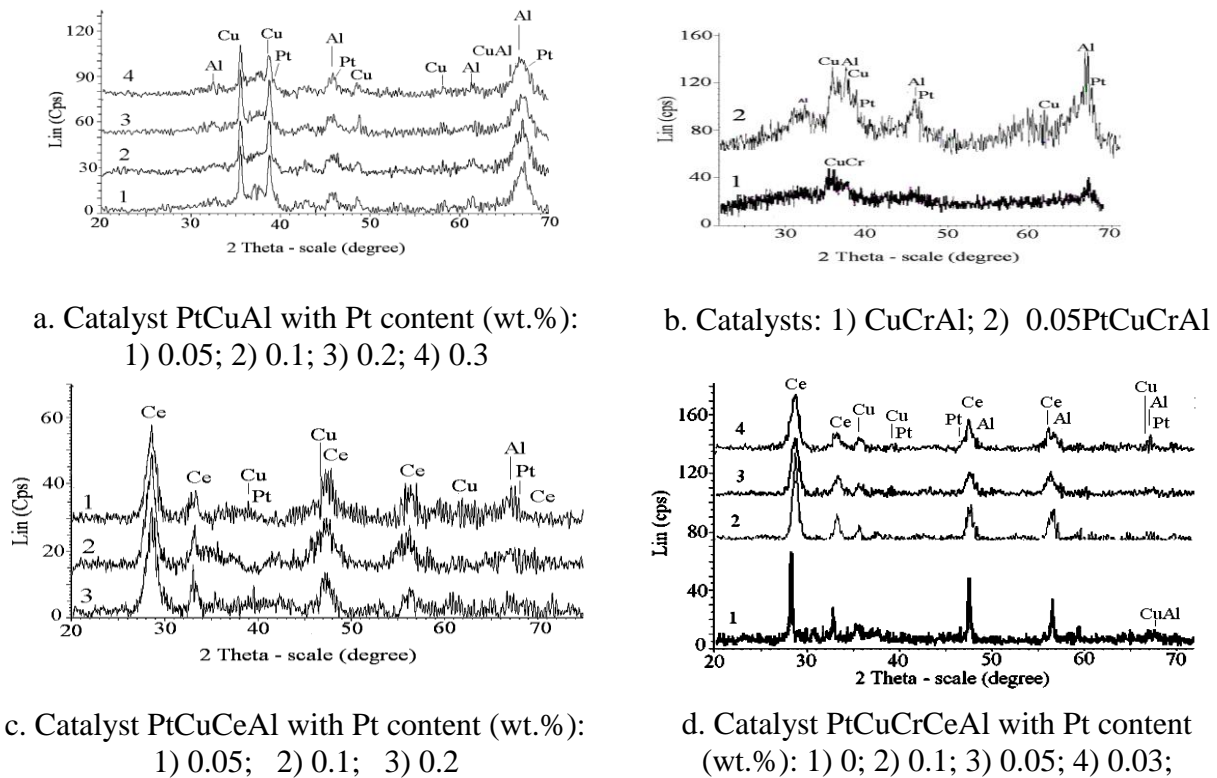

a. Catalyst PtCuAl with Pt content (wt.%):
1) 0.05; 2) 0.1; 3) 0.2; 4) 0.3

b. Catalysts: 1) CuCrAl; 2) 0.05PtCuCrAl

c. Catalyst PtCuCeAl with Pt content (wt.%):
1) 0.05; 2) 0.1; 3) 0.2

d. Catalyst PtCuCrCeAl with Pt content
(wt.%): 1) 0; 2) 0.1; 3) 0.05; 4) 0.03;

Figure 1. XRD patterns of Pt-modified oxide catalysts
(Cu - CuO; Pt - Pt; Al - Al_2O_3; CuCr - $CuCr_2O_4$; CuAl - $CuAl_2O_4$; Ce - CeO_2)

Table 1. Specific Surface Area (S_{BET}), Cluster Size of Cu (d_{Cu}) and Dispersion of Cu (γ_{Cu}) of the Studied Catalysts

Catalysts	S_{BET} (m^2/g)	d_{Cu} (nm)	γ_{Cu} (%)
Oxide Catalysts			
CuAl	177.0	11.9	13.1
CuCrAl	166.0	15.5	10.0
CuCeAl	67.0	-	-
CuCrCeAl	59.0	-	-
Pt-containing oxide catalysts			
0.1PtCuAl	95.9	11.6	13.4
0.2PtCuAl	95.1	-	-
0.05PtCuCrAl	89.2	18.8	8.3
0.1PtCuCeAl	80.1	35.2	4.4
0.2PtCuCeAl	86.0	-	-
0.05PtCuCrCeAl	48.0	37.6	4.2
0.1PtCuCrCeAl	48.7	-	-

(specific surface area of γ-Al_2O_3 is 252 m^2/g)

When chromium oxide was added to catalysts CuAl, due to the interaction between CuO and Cr_2O_3, leading to the formation of the spinel $CuCr_2O_4$ ($2\theta = 36^o$ and 37°), the interaction $CuO-Al_2O_3$ should be weakened, so the characteristic peak of $CuAl_2O_4$ disappeared [13]. The consequences of this phenomenon are: the CuO phase became more bulky, its cluster size increased from 11.9 up to 15.5 nm, the dispersion of Cu decreased from 13.1% down to 10% and the value of specific surface area reduced about 6% compared to that of the original sample CuAl (see Table 1). For the catalyst CuCrAl, addition of 0.05 wt.% Pt (Figure 1b) led to the appearance of characteristic peaks of Pt ($2 = \theta 40 ,^\circ 46.3 ,^\circ 67.7^\circ$). Characteristic peaks of the spinel $CuCr_2O_4$ appeared with low intensity and less sharp compared to those observed on the original sample of CuCrAl. This indicates that Pt weakened the interaction of Cu with Cr as well as with aluminium oxide, which in principle should weaken the formation of appropriate spinels. Probably this is the reason for increasing in the cluster size of Cu from 15.5 nm up to 18.8 nm, decreasing its dispersion from 10% down to 8.34% and reducing the value of specific surface area about 50 %, as shown Table 1.

In XRD patterns of catalysts, containing CeO_2 (Figure 1c and d), beside the characteristic peaks of $\gamma-Al_2O_3$, CuO, there are characteristic peaks of CeO_2 and copper aluminate $CuAl_2O_4$. However, as indicated in [14], in the CeO_2-modified catalysts the intensities characteristic peaks of CeO_2 increase with the CeO_2 content. Since in these catalysts CeO_2 exists in a non-associated state with high content, the value of specific surface area of CuCeAl sample decreased about 2.6 times compared to that of CuAl sample. The XRD peaks, characterizing CuO and CeO_2 in the multioxide catalyst CuCrCeAl (Figure 1d) are less intensive than in the sample CuCeAl (Figure 1c). This fact indicates that under the effect of chromium the given oxides scattered into smaller crystallites. On the other hand, in both catalysts the characteristic peak of copper aluminate still existed but with lower intensity than in the sample CuAl.

In the multioxide catalyst CuCrCeAl, copper existed only in the form of CuO; other forms of copper have not been observed. In the Pt-modified multi-oxide catalysts PtCuCeAl and PtCuCrCeAl, as in the case of unmodified samples, one can observe XRD peaks, characterizing the crystalline phase of $\gamma-Al_2O_3$, CuO, CeO_2; moreover, the characteristic peaks of Pt at $2 = \theta 40 ,^\circ 46.3^\circ$ and 67.7° also appeared (see Figure 1c and d). However, it should be noted that all the peaks are not sharp and the peak, characterizing the spinel $CuAl_2O_4$ is not clear enough. This fact once again leads us to the idea that the added Pt weakened the interaction Cu-carrier which should cause Cu to be crystallized in bigger particles ($d_{Cu} = 35-37$ nm) and metal dispersion to be poor (~ 4.5%).

Thus, the analysis of XRD data shows that although with very little content, the addition of Pt may clearly influence the phase state of catalysts. Pt weakens the interaction of active phase with the support material, which should lead to the reduction of $CuAl_2O_4$ and $CuCr_2O_4$ crystallites in the catalyst sample CuCrAl.

The EDS image (Figure 2a) show that Cu and Cr are fairly evenly distributed on the surface of aluminium oxide of the CuCrAl catalyst. Meanwhile the EDS image (Figure 2b) shows that the distribution of CuO particles of sample CuCeAl is uneven. On the surface of the Pt-modified catalyst 0.05PtCuCeAl (Figure 2c) one can observe different regions of metal particles distribution; Pt and Cu are concentrated more on CeO_2 than on Al_2O_3.

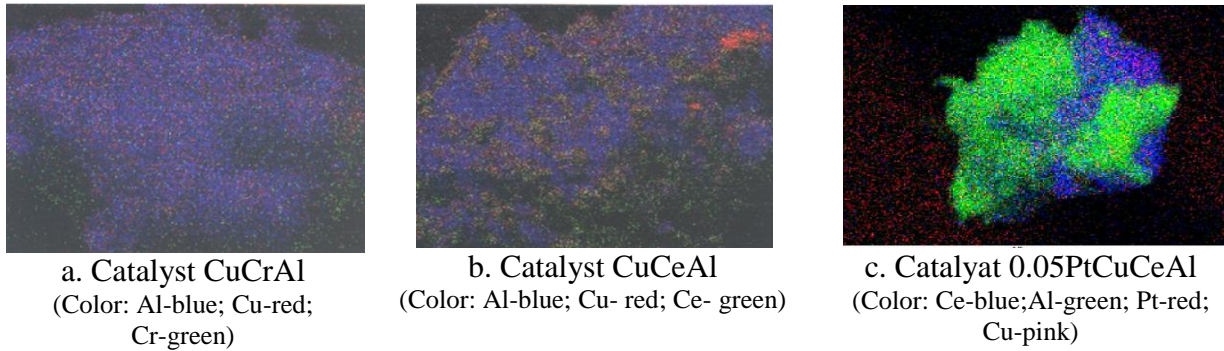|		
a. Catalyst CuCrAl (Color: Al-blue; Cu-red; Cr-green)	b. Catalyst CuCeAl (Color: Al-blue; Cu- red; Ce- green)	c. Catalyat 0.05PtCuCeAl (Color: Ce-blue;Al-green; Pt-red; Cu-pink)

Figure 2. EDS images of the studied catalysts

From Figure 3a it follows that the obtained IR spectrum is typical for CO adsorption on γ-Al_2O_3 (Al_2O_3–CO), including one main band of CO vibration at 2204 cm^{-1} and two weaker bands at 2155 and 2232 cm^{-1}. Acoording to Davydov [16], weak Lewis acid sites corresponding to coordinatively unsaturated Al^{3+} cations in tetrahedral coordination (band at ~2200 cm^{-1}) and octahedral coordination (band at ~2190 cm^{-1}, dominates at higher CO corverage) are revealed by FTIR of CO adsorbed at 77 K. It means, in this case the Al^{3+} tetrahedral coordination is dominant in the structure of γ-Al_2O_3.

a. γ-Al_2O_3

b. Catalyst CeAl

c. Catalyst CuAl

d. Catalyst CuCeAl
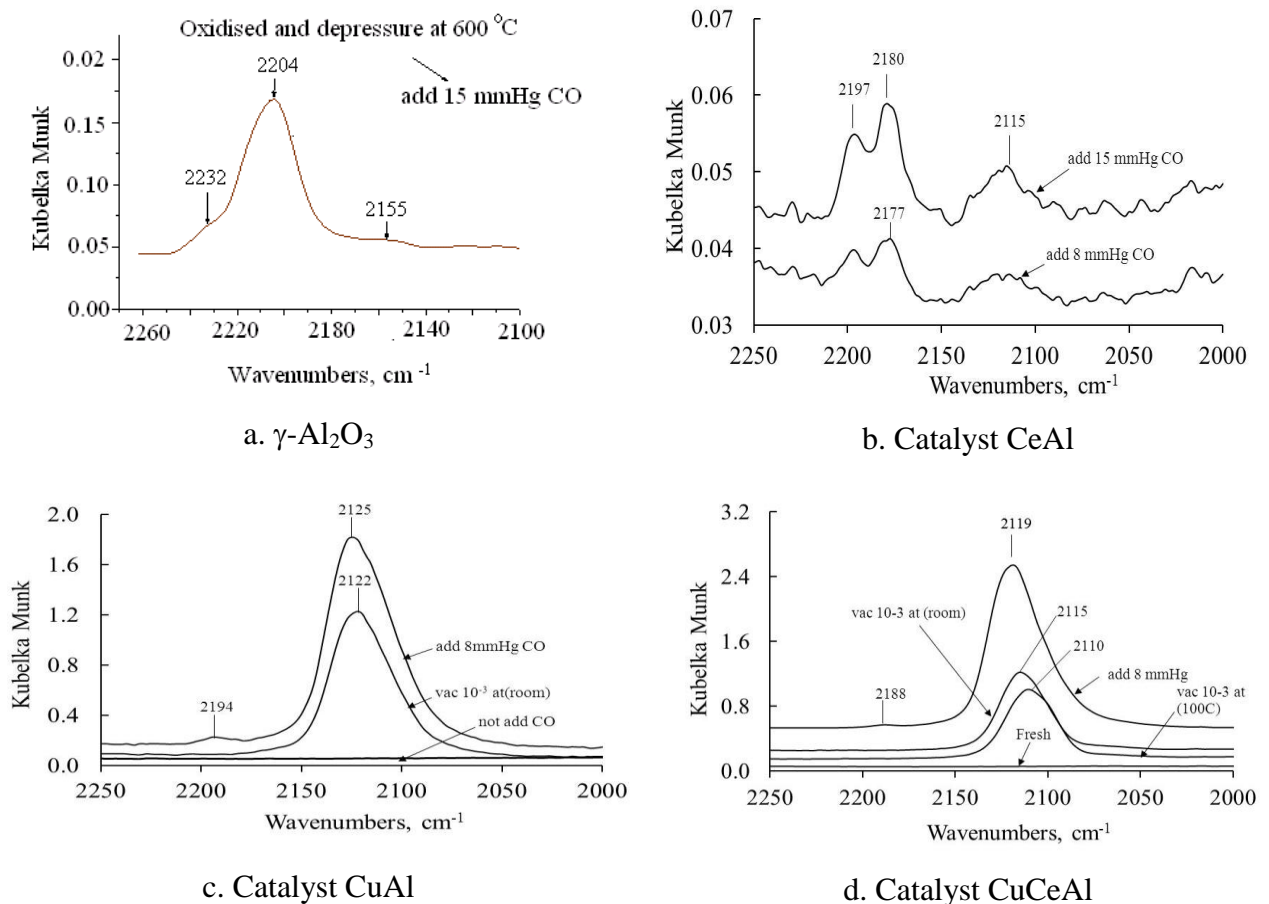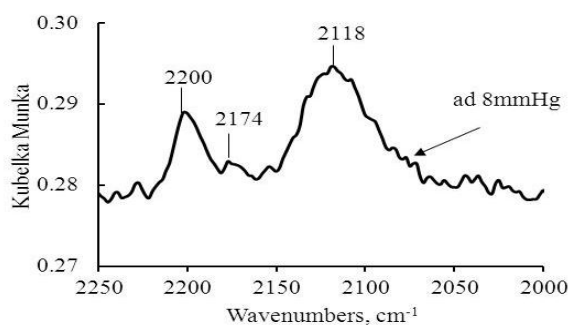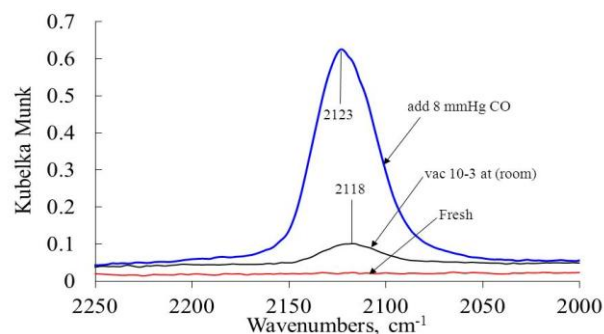
e. Catalyst 0.5PtAl

f. Catalyst 0.5PtCuAl

Figure 3. IR spectra of CO adsorbed on γ-Al$_2$O$_3$ and on different catalysts
pre-treated in a pure oxygen flow of velocity 5 L/h for 1 h

In the case of CO adsorbed on 20 wt.% CeO$_2$/Al$_2$O$_3$ (Figure 3b), the IR spectrum contains two absorption bands at 2115 cm^{-1} and 2177 – 2180 cm^{-1}, characterizing CeO$_2$–CO type and one band at 2197 cm^{-1}, characterizing the adsorption of CO on coordinatively unsaturated Al^{3+} cations in octahedral coordination. When increasing the partial pressure of the adsorbed CO from 8 mm Hg up to 15 mm Hg, the position of the characteristic band of CeO$_2$–CO type moved towards the region of longer wavenumbers (2180 cm^{-1} vs 2177 cm^{-1}). On the basis of these results it should be proposed that on the surface of the catalyst there are two types of CeO$_2$ sites (CeO$_2$–Al$_2$O$_3$ and free CeO$_2$); at low concentration, CO was preferably adsorbed on sites with a lower number of coordination and then, at higher concentration, the CO adsorption should proceed on sites with a higher number of coordination, this is due to the well-known effect of long-range dipole-dipole interaction between CO molecules [17]. This indicates that probably the interaction CeO$_2$–Al$_2$O$_3$ has been formed.

In IR spectrum of CO adsorbed on CuAl (Figure 3c), except for the characteristic band of Al$_2$O$_3$–CO at 2194 cm^{-1}, there is a vibration peak at 2125 cm^{-1}. According to Sadykov et al [18], the band appearing at frequency 2180 cm^{-1} exhibits the vibration of CO in complex Cu^{2+}–CO, and the band at frequency 2120 cm^{-1} characterized its vibration in complex Cu$^+$– CO. Besides, CO molecules adsorbed on the surface of metallic Cu are characterized by the peak of lower frequency 2100 cm^{-1}. For the clustered copper cations supported on bulk partially stabilized zirconia or alumina the band at frequency 2130 – 2115 cm^{-1} characterized complex Cu$^+$–CO and the band at frequency 2185 – 2175 cm^{-1} characterized complex Cu^{2+}– CO [19]. Thus it is possible to suppose that the band at frequency 2125 cm^{-1} characterizes the vibration in complex Cu$^+$–CO; copper ions in the state of Cu$^+$ are formed by the reduction of Cu^{2+} at conditions of CO adsorption. The appearance of the vibration band at 2125 cm^{-1} indicates that the reduction of ions Cu^{2+} in the given catalyst occurred easily even at low temperatures [20]. In this case, as in the case of CeAl, the adsorption of CO on weak Lewis acid sites of coordinatively unsaturated Al^{3+} cations in octahedral coordination appeared at the band at frequency 2194 cm^{-1}. As observed on Figure 3c, the intensity of the characteristic band of Cu$^+$–CO is much higher than that of the band, characterizing Al$_2$O$_3$–CO that means, on this catalyst CO mainly was adsorbed on copper ions. After achieving the value of vacuum 10^{-3} mmHg at room temperature during 20 min, the band at 2194 cm^{-1} of Al$_2$O$_3$–CO disappeared, at the same time the vibration band of Cu$^+$–CO moved to the region of shorter wavenumber (2122 cm^{-1}) and its intensity reduced to about one-third. These observations indicate that the adsorption of CO on copper centres is stronger than on the support material. From these results it follows that in this sample copper existed mainly in form of Cu$^+$ cations

and the surface of catalyst CuAl contains various copper centres, which should be characterized by different values of adsorption heat.

In IR spectrum of CO adsorbed on CuCeAl (Figure 3d) there is a characteristic band of Cu^+–CO at 2119 cm^{-1}. Compared to the CO spectrum on the sample CuAl, characteristic bands Cu^+–CO in the spectrum of CO on sample CuCeAl slightly moved to the region of shorter wavenumber, which should be an evidence of interaction between CuO, CeO_2 and Al_2O_3, leading to the formation of Al_2O_3–CeO_2–Cu. According to authors [20], shifts in CO band frequencies have often been related to changes in exposed Cu surface planes. After achieving vacuum at room temperature and at 100°C, this band moved to the region of shorter wavenumbers – 2115 and 2110 cm^{-1}, and the intensity reduced to about half. This indicates that the state of CO adsorbed on this catalyst is relatively stable, but copper centres are characterized by different numbers of coordination and probably different sizes too. At the pressure of CO at 8 mmHg, one can observe a weak vibration band at 2188 cm^{-1}, possibly characterizing adsorption of CO on weak Lewis acid sites of coordinatively unsaturated Al^{3+} cations. The disappearance of this band after achieving vacuum gives us the basis to confirm the weak state of CO adsorption on Al_2O_3.

IR spectrum of CO adsorbed on Pt/Al_2O_3, oxidized at 300 ^{o}C (Figure 3e) contains a band at 2200 cm^{-1}, characterizing Al_2O_3–CO complex and another band at 2118 cm^{-1}. According to authors [21], there are four distinguishable types of metallic Pt sites for the linear adsorption of CO on Pt/Al_2O_3. The lowest coordination Pt atoms appeared at $v_{CO} < 2030$ cm^{-1}, whereas the highest coordination sites in large ensembles of Pt atoms appeared at 2080 cm^{-1}, and sites of intermediate coordination – at 2030–2060 cm^{-1}. Sites in smaller two-dimensional ensembles of Pt atoms, similar to sites for the adsorption of CO in a bridging configuration, were characterized by a band at 2060–2065 cm^{-1}. Chafik et al [22] reported that on a three-way catalyst PtRhCeO$_2$/Al_2O_3, the main adsorbed species is linear CO configuration characterized by the band at 2063 cm^{-1}, probably formed on platinum atoms. According to authors [23], the adsorption of CO on $Pt^{\delta+}$ was characterized by a band at $v_{CO} < 2030$ cm^{-1}. Thus, it is possible that the band appeared at wavenumber 2118 cm^{-1} and the weak vibration peak at 2174 cm^{-1} characterize the association of $Pt^{\delta+}$–CO, but not the adsorption of CO on the metallic platinum.

In IR spectrum of CO adsorbed on PtCuO/Al_2O_3 pre-treated in oxygen at 300 ^{o}C (Figure 3f) one can observe only the band at 2123 cm^{-1}, characterizing complex Cu^+–CO; the characteristic bands of CO adsorbed on Al_2O_3 and Pt did not appeared. After achieving vacuum, the intensity of the band at 2123 cm^{-1}, characterizing Cu^+–CO decreased significantly with a simultaneous appearance of the band at 2118 cm^{-1}, characterizing the Pt^{2+}–CO complex. Probably on this catalyst CO was adsorbed both on Cu^+ and Pt^{2+} centers, but at CO pressure 8 mmHg, the intensity of the band, characterizing Cu^+–CO was much greater and covered the band, characterizing Pt^{2+}–CO complex; the vacuum mostly removed molecules of CO adsorbed on Cu^+ centres, but molecules of CO adsorbed on Pt^{2+} still remained. This means that the adsorption of CO on Pt^{2+} centres was stronger than on Cu^+ ions.
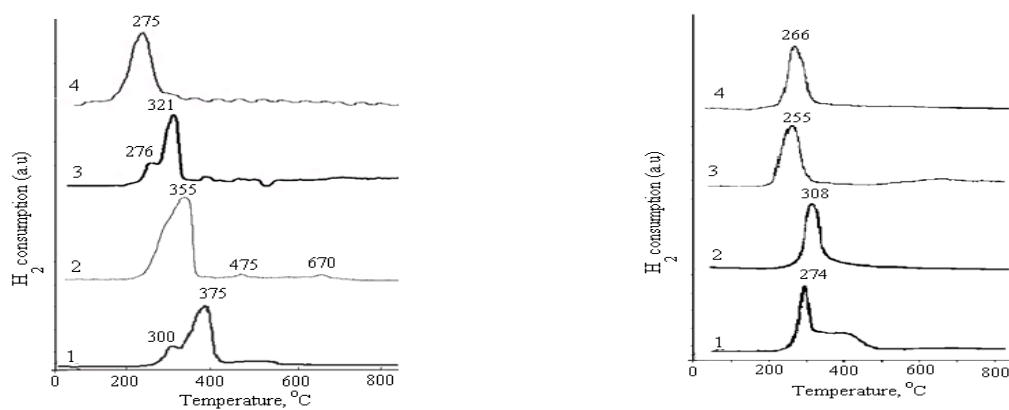
a. Catalysts: 1) CuAl; 2) CuCrAl;
3) CuCeAl; 4) CuCrCeAl

b. Catalysts: 1) 0.1PtCuAl; 2) 0.05PtCuCrAl;
3) 0.1PtCuCeAl; 4) 0.05PtCuCrCeAl

Figure 4. TPR profiles of Pt-containing catalysts

Table 2. Maximum Reduction Temperature (T_{max}) and Extent of Reduction (K_{Red}) of the Studied Catalysts

Catalysts	T_{max} (°C)	K_{Red} (%)
Oxide Catalysts		
CuAl	300; 375	13.0
CuCrAl	355; 470; 670	27.2
CuCeAl	276; 321	18.0
CuCrCeAl	275	13.2
Pt-containing oxide catalysts		
0.1PtCuAl	274	36.7
0.05PtCuCrAl	308	29.9
0.1PtCuCeAl	255	45.8
0.05PtCuCrCeAl	266	40.7

As follows from TPR diagram (Figure 4) CuO-based catalysts are characterized by 2 reduction peaks, one appearing at a temperature lower than 300 °C and the other at temperature higher than 300 °C. Combined with results of IR spectra it can be said that the first reduction peak is characteristic of the reduction of Cu^{2+} and the second one characteristic of the reduction of Cu^{1+}. Comparison of the area of two reduction peaks shows that in these samples Cu^{1+} centres are dominant. The addition of Cr and Ce additives leads to the decrease of maximum reduction temperature (T_{max}) and increase of the extent of reduction (K_{Red}). This proves that the Cr and Ce improve the reduction of CuO-based catalyst. On the catalyst CuCrAl, except for Cu^{1+} (reduced at T_{max} = 355 °C), there is a small quantity of spinel $CuCr_2O_4$, which is reduced in two stages $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{o}$ at T_{max} = 475 °C and 670 °C. For the catalyst CuCrAl, the presence of Pt was able to weaken the interaction Cu – Cr, so the amount of spinel $CuCr_2O_4$ decreased and on the surface remained mostly only CuO (Figure 4b) with a lower reduction extent (29.9%) compared to other Pt-modified catalysts. Moreover, in this catalyst the effect of Pt is expressed in the decrease of Cu dispersion and increase of Cu clusters size (Table 1). The low value of the temperature maximum and high value of reduction extent for the CuO catalyst, modified by CeO_2 (CuCeAl) should be explained by the association of CuO with the carrier through CeO_2 bridge that leads to the reduction of coordination of Cu^{+} ions, as indicated by IR spectral data. In the meantime, in

the TPR profile of catalyst CuCrCeAl (Figure 4b) there is only one characteristic peak of Cu^{2+} with $T_{max} = 275$ °C with the extent of reduction as low as that of non-modified CuAl catalyst.

From data in Table 2, as well as from Figure 4 it follows that, for CuO-based catalysts, addition of Pt enhanced the reducibility of catalysts, expressed in the decrease of reduction temperature and increase in the reduction extent K_{Red}. On all the CuO-based catalysts, modified by Pt, one can observe only the peak indicating the reduction of CuO with T_{max} not higher 300°C; the characteristic peak of Pt did not appear, probably due to its very low concentration.

Activity of the Catalysts

Table 3. Temperatures of 50 %-conversion (T_{50}) and 100 %-conversion (T_{100}) of Carbon Monoxide on Different Catalysts. Reaction Conditions: V = 75,000 h^{-1}; Initial Concentrations $C^o_{CO} = 0.5$ mol.%; $C^o_{O_2} = 10.5$ mol.%.

Catalyst	T_{50} (°C)	T_{100} (°C)	Catalyst	T_{50} (°C)	T_{100} (°C)
CuAl	225	300	CuCeAl	100	125
0.05PtCuAl	232	300	0.05PtCuCeAl	90	115
0.1PtCuAl	175	275	0.1PtCuCeAl	85	110
0.2PtCuAl	230	275	0.2PtCuCeAl	90	125
0.3PtCuAl	200	275	0.3PtCuCeAl	85	125
CuCrAl	210	250	CuCrCeAl	150	200
0.05PtCuCrAl	215	275	0.03PtCuCrCeAl	146	195
0.1PtCuCrAl	225	275	0.05PtCuCrCeAl	137	190

Thus, from the obtained results in Table 3 it is possible to order the oxide catalysts based their activities (temperatures of 50 %- and 100 %-conversion of carbon monoxide) as follows: CuCeAl > CuCrCeAl > CuCrAl > CuAl.

Bi-oxide catalysts expressed higher activity than monoxide one due to appearance of newly active sites. The addition of Ce and Cr led to changes in the physico-chemical properties of the CuAl catalysts that increased the activity of copper catalysts. The highest activity was observed on the catalyst containing 20 wt.%CeO_2. On this catalyst the temperature of 50 %- and 100 %-conversion of CO were 100 °C and 125 °C lower than that of the catalyst CuAl. The observed positive effect of CeO_2 can be explained by two observations: i) from analyzing the IR spectra of the adsorbed CO it follows that CeO_2 enhanced the adsorption of CO because cerium oxide also provides adsorption centres and ii) the presence of Cu^{2+} and a big amount of Cu^+ clusters in sample CuCeAl, as indicated in the data of IR and TPR studied above, that should lead to better reducibility of copper and enhancement of catalytic activity. As it was indicated in our previous paper [15] from analysis of the kinetic data, on these catalysts the reaction rate is directly proportional to partial pressure of CO. Authors [24] suggested that the formation of anionic vacancies was a result of the penetration of Cu^{2+} into the CeO_2 lattice that made the reduction of CuO occurs at lower temperatures. Lue et al [25] proposed that the enhancement of CO oxidation could be related to two facts; either the adsorption proceeded only on copper cites interacted with CeO_2 or the presence of a small amount of Cu^+ clusters in high dispersion and immobilized by CeO_2.

The interaction of copper oxide with chromium oxide led to the formation of spinel $CuCr_2O_4$ – a precursor of highly active sites, at the same time weakening the link CuO – γ-Al_2O_3, leading to the limiting of the formation of copper aluminate $CuAl_2O_4$ – a preceding phase of low or inactive sites. This leads to an increase of catalysts activity.

Data in Table 3 indicates that Pt expresses unequal influences on different groups of catalysts. For catalysts not containing chromium oxide (PtCuAl, PtCuCeAl), the added Pt increased their activities and the optimal content of Pt is 0.1 wt.%. In the case of 0.1 wt.% added Pt, on the catalyst CuAl, the temperature for 50%-conversion of CO reduced from 225

^{o}C down to 175 ^{o}C, and the temperature for 100%-conversion of CO reduced from 300 ^{o}C down to 275 ^{o}C. With the same amount of added Pt, the catalyst PtCuCeAl was capable of converting completely CO to CO_2 even at 125 ^{o}C at very high space velocity (75,000 h^{-1}). This was the most active catalyst among the studied ones. The reason of the positive effect of platinum is related to different kinds of interactions between active phases as well as between an active phase and the support material of the catalyst. As indicated above, the main active centres on the surface of the catalysts CuAl and CuCeAl are Cu^+. The added Pt, by weakening the interaction Cu-Al_2O_3, enables it to limit or annul the formation of inactive species in form of copper aluminate and naturally at the same time the reducibility of catalyst must be enhanced.

For CuCrAl catalyst, addition of Pt leads to a decrease of activity and the higher the content of Pt the lower the activity of catalysts. The reason for this dependence should be summarized in the following: by weakening the interaction Cu-Al_2O_3, the added Pt makes CuO easier reducible and its reducibility become higher, but at the same time the added Pt weakens the interaction of Cu-Cr. The result of the last effect of Pt is included in complete disappearance of the spinel $CuCr_2O_4$ that expressed in the decline of catalyst activity. In case of the multi-oxide catalyst CuCrCeAl containing both oxides Cr_2O_3 and CeO_2, the 0.05 wt.% the added Pt increased its reducibility about three times and lowered the temperatures of 50%-conversion and 100%-conversion of CO by 13 degrees and 10 degrees respectively.

Conclusions

In small amounts (~ 0.1 wt.%), the added Pt was capable of changing considerably the physico-chemical and activity of oxide/multi-oxide catalysts on the basis of CuO/γ-Al_2O_3 in the oxidation of carbon monoxide.

By weakening the interaction of copper with the support material, Pt prevented the formation of copper aluminate, enhanced the reducibility of ions Cu^{2+}, so the activity of catalysts CuAl and CuCeAl increased. Nevertheless, at the same time, in Cr_2O_3-containing catalysts, Pt reduced the activity of catalysts, because it also weakened the interaction Cu-Cr that prevented the formation of $CuCr_2O_4$ as a precursor of highly active centers.

The sample 0.1PtCuCeAl expressed the highest activity in CO oxidation; at the given conditions (0.5 mol.% CO, 10.5 mol.% O_2 in N_2 balance and space velocity 75,000 h^{-1}), it was capable of oxidizing 50% of CO at 89 °C and 100% of CO at 125 °C at space velocity of 75,000 h^{-1}. It is very promising that this catalyst could be used for low temperature oxidation of hazardous gases.

Acknowledgements

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