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Sol-gel Ag + Pd/SiO_2 as a catalyst for reduction of NO with CO

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Mono – (Ag/SiO_2, Pd/SiO_2) and bimetallic (Ag + Pd/SiO_2) catalysts have been obtained via sol-gel method from tetra-ethoxy-silane (TEOS) and their activity in reduction of Nitric oxide (NO) with carbon monoxide (CO) has been investigated. The highest activity in the process of reduction of NO with CO possesses the sample Ag + Pd/SiO_2. It has been found that the sol-gel method for preparation of bimetallic catalysts allows the formation of various catalytic active centers (CAC) which leads to high activity in reaction of NO reduction. The presence of Ag_2O and PdO in these CAC allows the elimination of NO. The process of this elimination includes reduction of NO with CO at temperatures up to 200 °C as well as direct decomposition of NO at higher temperatures.

KEY WORDS: sol-gel method; catalysts; NO reduction with CO; catalytic active complex.

1. Introduction

One of the major environmental problems of our time is the presence of nitrogen oxides (NO_x) in the exhaust gases from motors [1–3]. A particularly convenient route for simultaneous elimination of Nitric oxide (NO) and carbon monoxide (CO) could be their red-ox reaction to N_2 and CO_2.

In series of papers [4–9] it has been shown that the selective catalytic reduction (SCR) of NO with hydrocarbons (HC) under oxidizing conditions has been made over Cu and Ag – ZSM-5 catalysts which are prepared by ion-exchange technique. Other authors [10] was studied the SCR-HC reaction over the Pt, Ir, Pd, Rh and Ru on Al_2O_3, obtaining the best results. G. Prevot *et al.* [11] has shown that the dissociation of NO is the key step for the reduction of NO by CO over Pd clusters supported on MgO(100) surfaces as a model catalyst. After the dissociation of NO authors denote that two type of adsorbed nitrogen atoms are obtained and the oxygen atoms resulting from NO desorption react with the adsorbed CO or diffuse in the lattice of palladium particles. The rate of the conversion depends on both the particle size ant the particle morphology.

Nitric oxide reduction with CO on the Pd(111) surface has been studied in [12]. Subsequent temperature programed desorption (TPD) measurements are performed in order to determine the nitrogen coverage under steady-state conditions. Finally, the results are discussed with respect to the rate-controlling character of the different elementary steps of the reaction system. An important point of catalysts obtaining for neutralizing of NO is the formation of the surface catalytic active complex (CAC) in which different ions take part as well as ions from the support [13–15]. Therefore, the choice of the synthesis method is of a great importance. Two methods could be used in order to achieve a preliminary formation of a sample of catalyst with an appropriate composition. The first way is by using the precipitation method which advantages during the synthesis of catalysts are shown in work [16]. The second way for preparing of catalysts is the sol-gel route. As is known this route provides an excellent way for obtaining mechanically stable catalysts with a high metal dispersion. The general advantages of the sol-gel method are: the possibility to obtain materials with high purity and predetermined structure and properties; the permission to control the microstructure and the homogenity of the reaction products and despersity of the oxide and the metal nanoparticles in the nonmetallic matrices that stabilizes the existing phase [17–19]. Bimetallic particles composed of two different metal elements are of greater interest than monometallic ones: they could work as catalysts [20, 21]. There are only few reports on the synthesis and characterization of Ag-Pd bimetallic particles and their catalytic applications [22–24].

The aim of the present paper is to study the catalytic behavior of sol-gel prepared Ag + Pd/SiO_2, Ag/SiO_2 and Pd/SiO_2 catalysts in reaction of NO reduction with CO.

2. Experimental

2.1. Preparation of catalysts by sol-gel method

The gels of all samples have been prepared via sol-gel method from TEOS: C_2H_5OH:H_2O in a volume ratio 1:1:1 as well as the following $AgNO_3$ and $PdCl_2$. A few

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drops of HCl acid have been added as acid catalyst for the hydrolysis of TEOS [25]. THF and DMSO are used to produce colloids "*in situ*". The samples are gelated at 25 °C and pH are used in the presence of NH_4F. The obtained gels are dried at 70 °C overnight. "As prepared" samples are thermally treated at 550 °C for 2 h.

2.2. Catalyst characterization

The phase formation and structural evolution during thermal treatment of gels have been investigated by FTIR, XRD analysis and SEM. X-ray diffraction analysis (XRD) is made using TUR-M62 apparatus equipped with a computer directed H2G-4 goniometer with Cu-K$_\alpha$ radiation in the range from 5 to 60 θ.

Infrared spectra are recorded with FTIR spectrophotometer by the KBr disc method in a range 4000–400 cm^{-1}.

The surface structure of the samples has been observed by SEM (JEOL-Superprobe 733).

The specific surface area of the sample is carried out by adsorption of nitrogen (77.4 K) using a conventional volumetric apparatus and is determined by BET method.

2.3. Catalytic activity measurements

The catalytic experiments are carried out in a flow apparatus described in [26]. NO reduction with CO is investigated in the temperature range 20–300 °C. The catalytical tests are performed with two gas mixture: (i) NO + CO + Ar, containing 1200 ppm NO and 1200 ppm CO; (ii) NO + Ar, containing 1200 ppm NO. Argon (purity 99.99 vol.%) is used as a carrier gas at a total gas-flow rate of 433 cm^3 min^{-1} (GHSV = 26,000 h^{-1}). A 1 cm^3 sample of a catalyst (the 0.3–0.6 mm fraction) is placed into the reactor with a quartz tube, d = 10 mm. After catalytic test at 25 °C and isothermal desorption state in Ar flow a TPD is carried out in the same catalytic apparatus at a heating rate 13 °C min^{-1} with an Ar flow at 25–300 °C. The concentrations of NO and CO are continuously measured by gas analyzers. The outlet concentrations of NO and CO are controlled by "UNOR 5 – Maihak" (Germany) and the CO_2 by "Infralyt 2106" (Germany). N_2O is measured spectrophotometrically by "Specord 75 IR" (Germany). N_2 and O_2 are measured on-line by gas chromatographic analysis using "Pye Unicam 104" apparatus (England) with a calibrated volume sampler and a column with a molecular sieve.

3. Results and discussion

The data on samples' chemical composition and specific surface area are shown in table 1.

The X-ray spectra of the samples are presented in figure 1.

Table 1
Chemical analysis and BET surface area

Samples	Chemical components (g)			S (m^2/g)
	Ag	Pd	SiO$_2$	
Ag/SiO$_2$	0.02	–	2.72	117
Pd/SiO$_2$	–	0.02	2.72	168
Ag + Pd/SiO$_2$	0.04	0.72	2.72	118

The synthesized gels are in amorphous state without any crystalline phases in the cases when only one metal (Ag or Pd) presents in the system. In the gels of Ag + Pd/SiO$_2$ system (curve e) two phases are formed – AgCl [27] and $PdCl_2$ [JCPDS 01-0228]. In all calcinated at 550 °C for 4 h gels Ag/SiO$_2$ (curve b), Pd/SiO$_2$ (curve d) and Ag + Pd/SiO$_2$ (curve f), Ag_2O and PdO are observed [28, 29].

The results of FTIR study are presented in figure 2. As could be seen, the characteristic bonds are similar in all samples. In the IR-spectra the typical bands of the silica glass and silica gels assigned to the anti-symmetric stretching vibrations of the Si–O–Si bond (~1090 cm^{-1}), the symmetric stretching vibration (~800 cm^{-1}) and bending vibrations of same chemical bond (~478 cm^{-1}) are observed. The absorption band at 707 cm^{-1} could be assigned to the vibration of S = O bond [30] and the band at ~1637 cm^{-1} could be assigned to H–O–H.

It has been already reported by [31] that the presence of a predominant peak at ~1090 cm^{-1} is characteristic for the formation of a siloxane network. The high intensity of this peak indicates the presence of a linear Si–O–Si chain in the inorganic polymer. The bands at 1386 cm^{-1} and 1405 cm^{-1} have been assigned to C–O–H vibrations. The absorption band at ~563 cm^{-1} for the all samples is assigned to the vibrations of metal-oxygen (Me–O) bond [19, 32]. It is very interesting that in FTIR spectra the absorption band at 560 cm^{-1} appears in all monometallic and bimetallic samples. The FTIR data denotes that the silica network is completely formed during the sol-gel synthesis at room temperature.

The SEM images of the undoped with Ag + Pd (a), doped with Ag + Pd (b) and thermal treated at 550 °C Ad + Pd/SiO$_2$ (c) samples prepared by sol-gel method are shown in figure 3. It could be seen from the micrographs that the as prepared gels undoped sample possesses a surface without any heterogeneous microstructure (figure 3a), whereas the Ag + Pd doped sample has some kind of skeletal features (AgCl + $PdCl_2$ and Ag_2O + PdO) in the "as prepared" (figure 3b) and thermal treated gels (figure 3c). The data from SEM analysis is in a very good agreement with the data from the X-ray diffraction analysis. The chemical content in the samples has been also determined by EDX analysis. The presence of Si, Ad, Pd and Cl (in "as prepared" samples) has been detected.

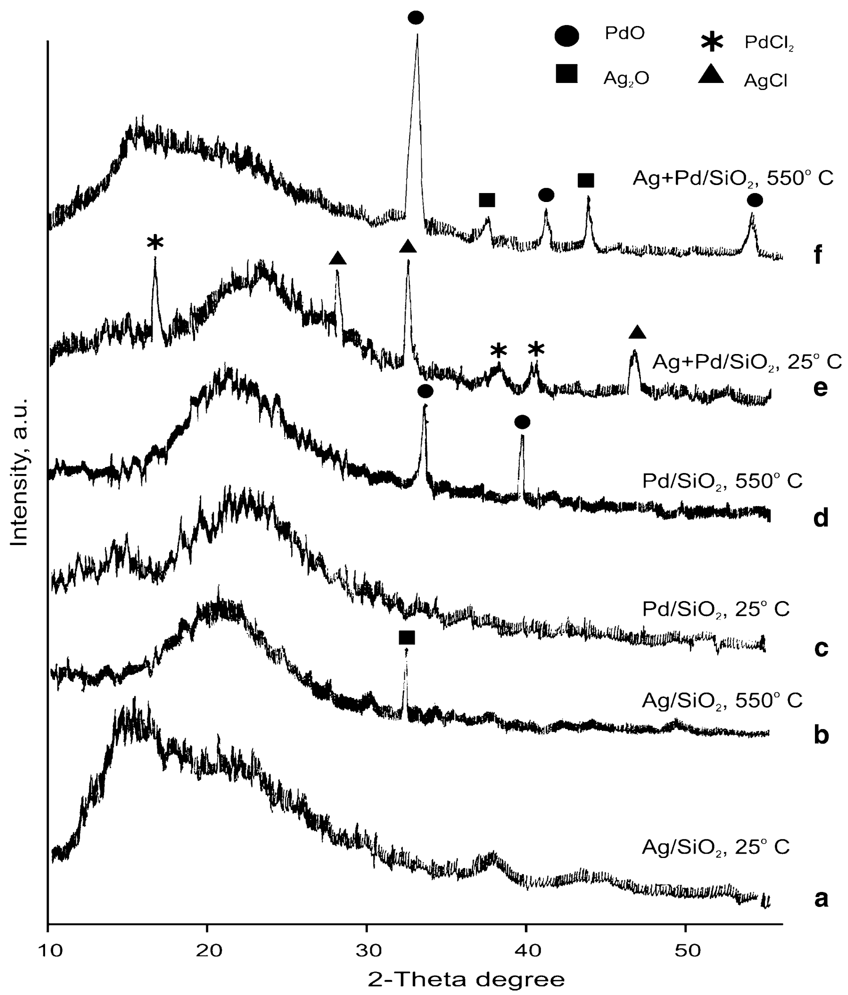

Figure 1. XRD patterns of "as prepared" gels and thermal treated at 550 °C for 4 h samples.

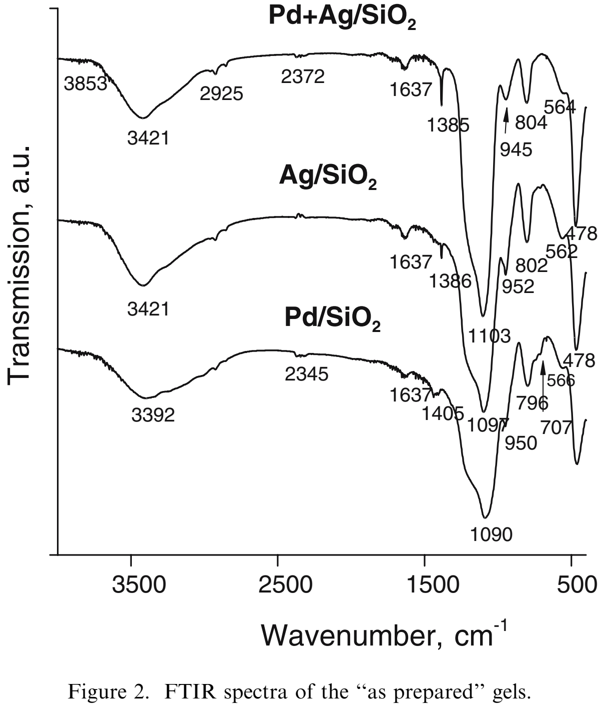

Figure 2. FTIR spectra of the "as prepared" gels.

The results from the investigations on the catalytic activity of the Ag/SiO_2, Pd/SiO_2 and Ag + Pd/SiO_2 samples with respect to the reduction of NO with CO are shown in figures 4, 5 and 6.

As could be seen from the figures, the three samples show efficiency in the reduction of NO with CO at temperatures over 200 °C. It should be mentioned that the formation of N_2O as an intermediate product is not registered for the three samples, which is observed for some oxides of transient metals. Therefore, the following reaction occurs mainly on the investigated catalysts:

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \qquad (1)$$

The catalyst containing Pd (figure 5) is more active than the catalyst containing only Ag (figure 4). However the most active is the sample containing both metals – Ag + Pd/SiO_2. It has been established that for Ag + Pd/SiO_2 there is presence of 50% transformation of NO at temperature 220 °C as at 300 °C the purification of NO is 90% (figure 6).

Figure 7 presents the transient response curves at room temperature of NO and CO obtained for the

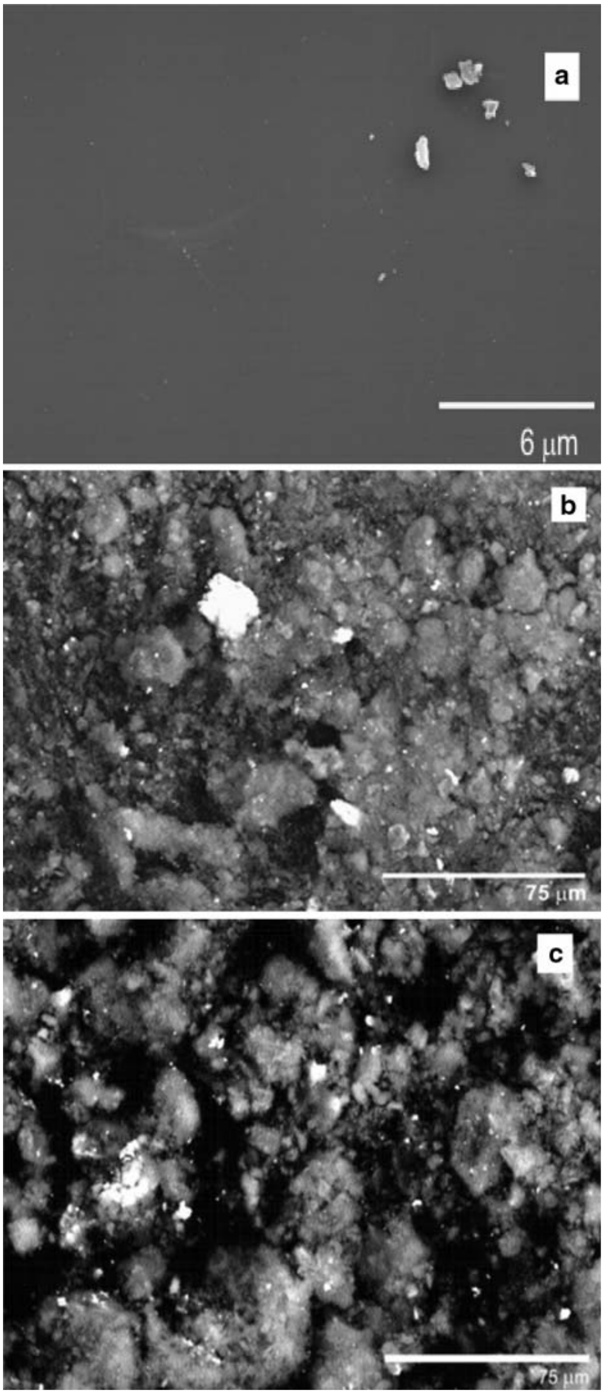

Figure 3. SEM micrographs of the undoped with Ag + Pd precursor (a), doped with Ag + Pd/SiO$_2$ precursor (b) and thermal treated at 550 °C Ad + Pd/SiO$_2$ catalyst (c).

investigated samples – Ag/SiO$_2$, Pd/SiO$_2$ and Ag + Pd/SiO$_2$ in the conditions of gas mixture NO + CO + Ar. It also presents the desorption spectra of NO from TPD investigations at temperatures 25–300 °C after the performed NO + CO reaction at 25 °C. It is obvious that the transient response curves of NO and CO are of instantaneous type according to Kobayashi's classification [33] and reveals the surface reaction to be the rate determining stage.

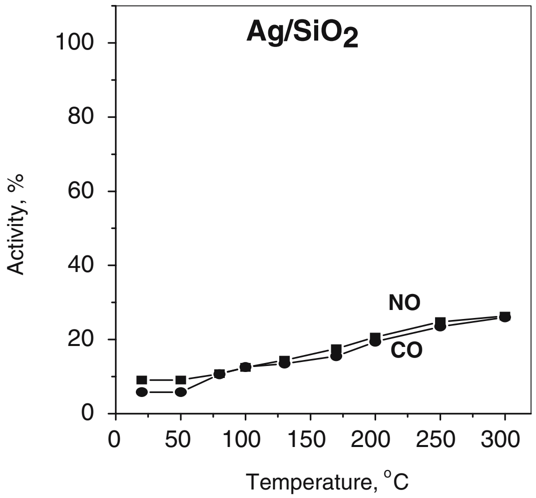

Figure 4. Dependence of the degrees of NO and CO conversions on temperature for catalyst Ag/SiO$_2$ in a NO + CO + Ar mixture.

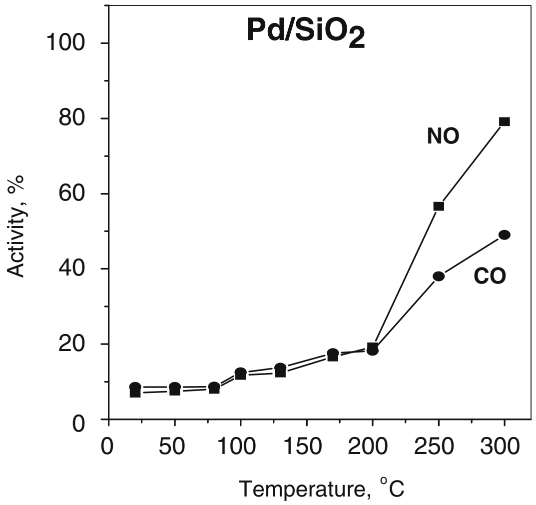

Figure 5. Dependence of the degrees of NO and CO conversions on temperature for catalyst Pd/SiO$_2$ in a NO + CO + Ar mixture.

The data from the TPD investigations show that the desorption peaks for NO are observed for the three samples and but not for CO and CO$_2$. The desorption peak for NO is one desorption peak with t_{max} at 80 °C for samples Ag/SiO$_2$ and Pd/SiO$_2$. Probably NO is adsorbed on the surface of these samples in a same form. Quite different is the TPD spectrum for Ag + Pd/SiO$_2$ where the desorption peaks of NO are two – at 80 °C and 130 °C. It is clear denoted that have two forms of adsorption of NO for this type of samples. The amount of the NO desorbed on the sample Ag + Pd/SiO$_2$ is higher compared to the other two samples. These results correspond well to the higher activity of the sample Ag + Pd/SiO$_2$ with respect to the reduction of NO by CO shown above. Probably the presence of two metal ions in the sample Ag + Pd/SiO$_2$ leads to the forming of

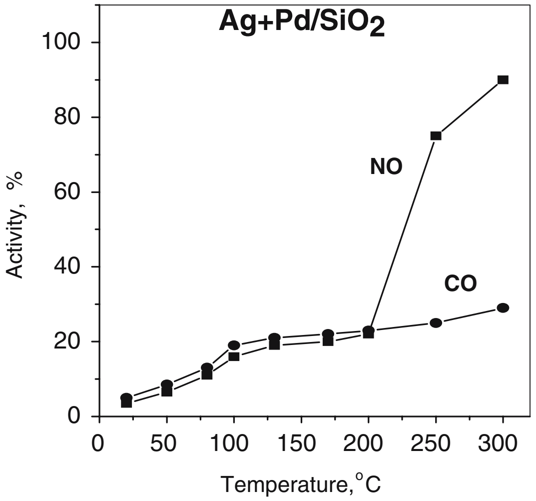

Figure 6. Dependence of the degrees of NO and CO conversions on temperature for catalyst Ag + Pd/SiO$_2$ a NO + CO + Ar mixture.

catalytic centers different from those of the other samples Ag/SiO$_2$ and Pd/SiO$_2$.

An interesting conclusion could be drawn from the results for the catalytic activity. It is obvious that the decrease of the NO content in catalytic reactions on the samples containing palladium is higher than that for CO. These amounts should be equal according to the equation of the reaction as it is for the sample containing only silver (figure 4). Therefore, two reactions occur on the Pd-containing sample.

Reaction (1) of NO with CO as a result of which is formed N_2 and CO_2 and direct decomposition of NO, which can be presented with the following equation:

$$2NO \rightarrow N_2 + O_2 \tag{2}$$

If this statement is true this reaction should occur even in the lack of CO. Because of this reason the catalysts are studied with respect to direct decomposition of NO

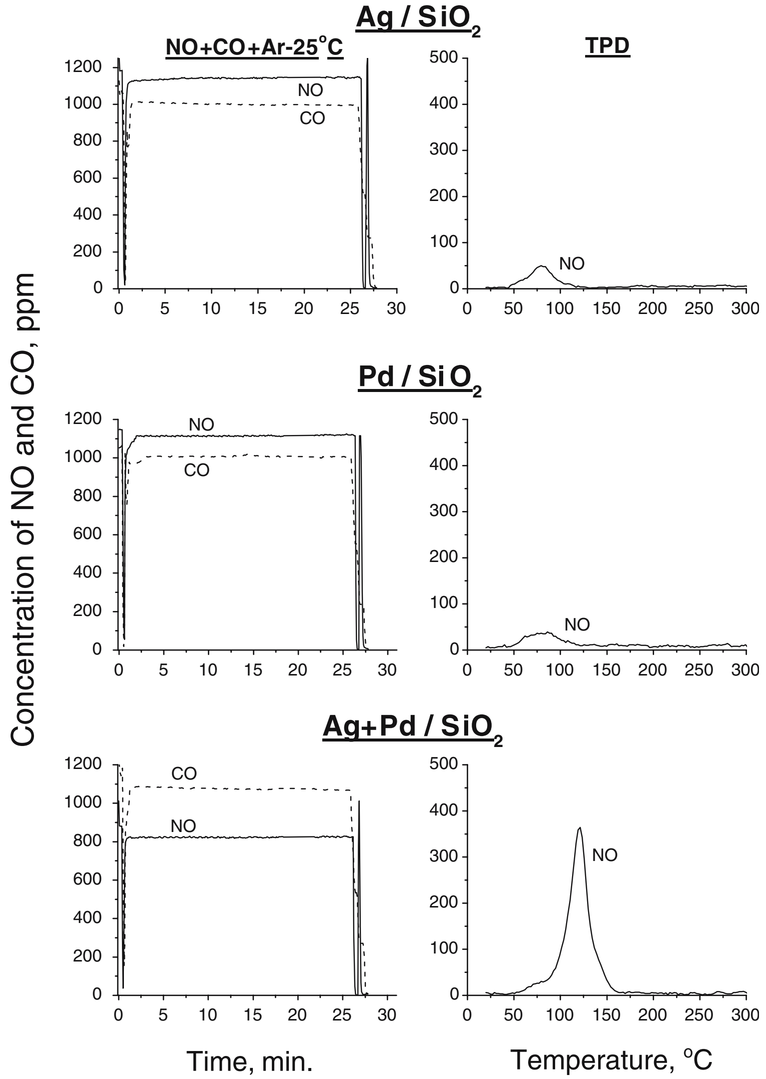

Figure 7. Transient response curves obtained during the reaction stages with a NO + CO + Ar flow and desorption stages with an Ar flow performed at 25 °C and temperature programed desorption (TPD) spectra of nitric oxide desorbed by Ar flow on catalyst – Ag/SiO$_2$, Pd/SiO$_2$, and Ag + Pd/SiO$_2$.

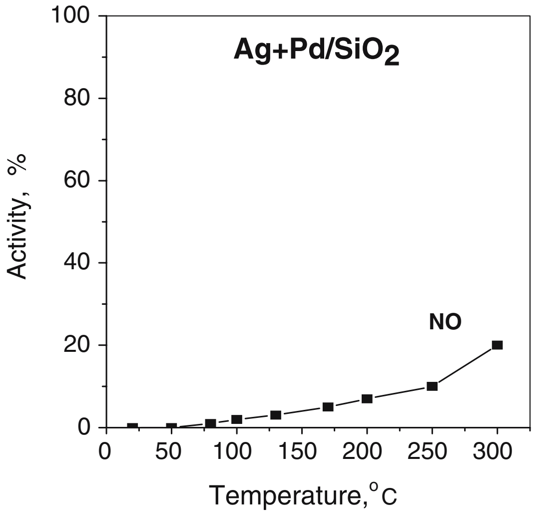

Figure 8. Dependence of the degrees of NO conversion on temperature for catalyst Ag + Pd/SiO2 in a NO + Ar mixture.

in conditions of the gas mixture NO + Ar. The results obtained are presented in figure 8.

As could seen the catalysts show activity towards NO in absence of a reductor. The gas-chromatographic analysis shows that N_2 and O_2 are formed as a result of direct decomposition of NO.

4. Conclusion

Mono – (Ag/SiO$_2$, Pd/SiO$_2$) and bimetallic (Ag + Pd/SiO$_2$) catalysts are obtained via sol-gel method at room temperature from tetra-ethoxy-silane (TEOS). The reduction of NO with CO has been investigated over Ag/SiO$_2$, Pd/SiO$_2$ and Ag + Pd/SiO$_2$ catalysts. The most significant results have been obtained on Ag + Pd/SiO$_2$ which exhibits the highest activity in the process of the reduction of NO with CO.

The use of sol-gel method for obtaining bimetallic catalysts allows the formation of different catalytic active centers (CAC) which leads to higher activity in reaction to the reduction of NO. The presence of Ag_2O and PdO (i.e. of Ag^+ and Pd^{2+}) in these catalytic active centers allows the elimination of NO. The process of elimination includes reduction of NO with CO at temperatures up to 200 °C as well direct decomposition of NO at higher temperatures.

Bimetallic catalysts obtained via sol-gel method are more active and perspective with respect to elimination of different waste gases at relatively low temperatures.

Acknowledgments

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