

TEMPERATURE PROGRAMMED DESORPTION OF CO AND NO OVER GOLD/CERIA CATALYSTS FOR NO_x REDUCTION

Lyuba ILIEVA^{a*}, Giuseppe PANTALEO^b, Gabriel MUNTEANU^c, Anna Maria VENEZIA^d
and Donka ANDREEVA^a

^aInstitute of Catalysis - BAS, “Acad. G. Bonchev” str., bl.11, Sofia, Bulgaria

^bDipart. Chim. Inorg. e Analitica, Università di Palermo, Palermo, Italy

^cInstitute of Physical Chemistry “Ilie Murgulescu”, Splaiul Independenței 202, Bucharest-060021, Roumania

^dIstituto per lo Studio di Materiali Nanostrutturati, CNR, Palermo, Italy

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The present paper reports a study of gold catalysts supported on ceria and ceria-alumina (20 wt.% alumina) by means of temperature programmed desorption (TPD) technique.

It was observed that after the CO adsorption, at room temperature, on such samples, pre-treated either in helium or in hydrogen, CO₂ is desorbed. Only CO₂ was noted in desorption in the case of the pre-treatment in helium sample. In the case of the sample pre-treated in hydrogen a supplementary CO TPD peak was also detected. The formation of CO₂ – either during CO adsorption or its desorption – is in agreement with the high oxygen storage and oxidation capacity of this type of catalysts. The reverse water gas shift (RWGS) reaction between CO₂ and H₂ – incorporated in ceria structure during the pre-treatment – could explain the CO appearance.

After NO adsorption on both types of catalysts no trace of N₂ was detected in desorption. This means that on these catalysts only a reversible, *i.e.* a non-dissociative, NO adsorption takes place. This result shows that the adsorption properties of gold/ceria catalysts are completely different, compared to platinum group metals supported on ceria catalysts, fact which could determine a different NO+CO reaction mechanism.

INTRODUCTION

To decrease the emissions immediately following the start-up of the vehicle’s engine is still a hot topic problem. Promising results of a low temperature activity in NO_x reduction by H₂, CO or hydrocarbons over gold supported catalysts have been reported.¹⁻⁵

The present study is a part of the recently started investigation of gold supported catalysts on ceria and ceria alumina (10 or 20% Al₂O₃) for NO reduction by CO.^{6,7} The presence of alumina prevents-agglomeration even at extremely high for gold catalysts temperatures of operation. The highest conversion of both NO and CO obtained over gold supported on pure ceria has been explained by the low-average size of gold nano-particles. Comparing gold catalysts on ceria-alumina it was established that the activity is higher when the amount of alumina in the mixed support is higher. This fact has been attributed to

the lowest average size of ceria nano-particles and the highest amount of oxygen vacancies, generated in ceria structure in the case of 20% alumina content.⁶

It was established also that the type of pretreatment does not substantially influence the catalytic activity but both NO and CO conversion can be increased adding H₂ to the feed⁷. The 100% selectivity to N₂ obtained around 200°C over both ceria and ceria-alumina catalysts makes them promising for practical application during the “cold start” of combustion engines operating under stoichiometric air to fuel ratio.

In the present study a special attention is paid to CO and NO adsorption properties over gold catalysts supported on ceria and ceria-alumina. The aim of the present work is to investigate the adsorption and respectively desorption of CO and NO as a preliminary study of the NO reduction by CO, that will be the object of a following work. We performed this study by TPD measurements, this

* Corresponding author: luilieva@ic.bas.bg

method being a useful tool to obtain detailed information on adsorbate–surface interaction.

RESULTS

The chemical composition, BET surface area and the average size of gold and ceria particles are represented in Table 1. XRD data showed no

characteristic lines of ceria-alumina solid solution. In the case of AuCe sample the average particle size was 2.0 nm for gold as estimated by HRTEM,⁸ and 8.4 nm for ceria as estimated by XRD. Adding alumina, the average particle size of gold increases, while a decrease of the particle size of ceria was observed. The average particle size of alumina was 5 nm.

Table 1

Chemical composition, BET surface area and average size of gold and ceria nano-particles

Catalyst	Chem. composition (wt%)			S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Average size (nm)	
	Au	CeO ₂	Al ₂ O ₃		Au	CeO ₂
AuCe	3.0	97.0	-	108	2.0*	8.4
AuCeAl20	2.9	77.7	19.4	140	6.0	3.2

*estimated by HRTEM⁸.

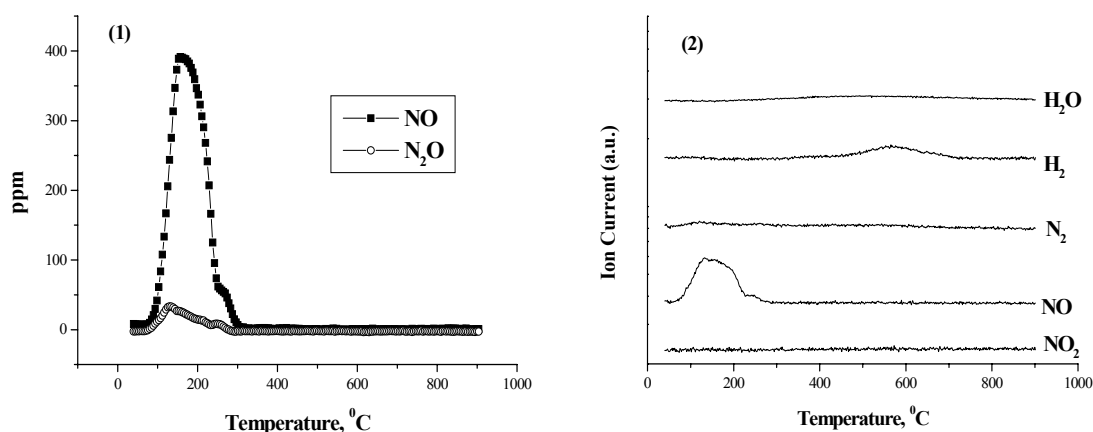


Fig. 1 – TPD after RT adsorption of NO over pre-reduced AuCe catalyst:

(1) – desorption products detected by UV and IR analyzers;

(2) – desorption products detected by MS.

In Fig. 1 the TPD profiles after room temperature (RT) NO adsorption on pre-reduced AuCe catalyst are presented. During the adsorption no products of NO transformation were observed. A predominantly reversible NO adsorption (TPD peak with T_{max} at 160-170°C) occurs, but for a small part of NO, below 9%, an irreversible adsorption takes part as well (a small TPD peak with $T_{\text{max}}=140^\circ\text{C}$ assigned to N_2O formation). This means that the NO adsorption is followed by a surface reaction:



A broad peak showing continuous water desorption in the interval 300-800°C and a TPD peak at $T_{\text{max}}=500^\circ\text{C}$ of hydrogen desorption are detected as well. No trace of N_2 formation was obtained.

This result motivated the experiment with AuCeAl20 catalyst to be also carried out. Fig. 2. represents the corresponding TPD profiles after the RT NO adsorption on the pre-reduced AuCeAl20 sample. During the RT NO adsorption no products of NO transformation were observed like in the case of AuCe sample.

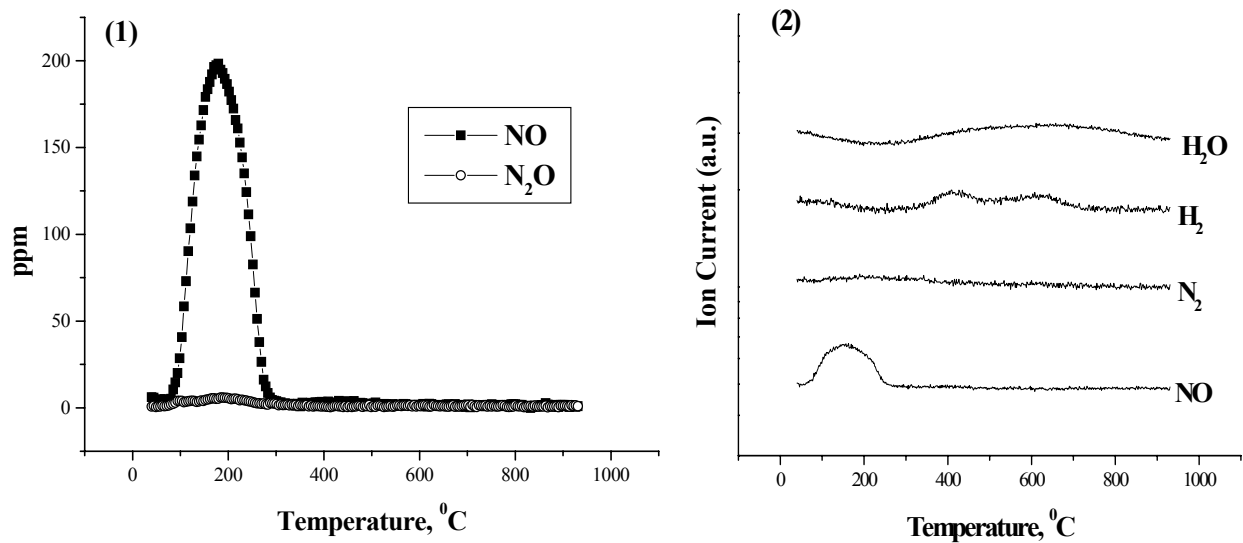


Fig. 2 – TPD after RT adsorption of NO over pre-reduced AuCeAl₂₀ catalyst:

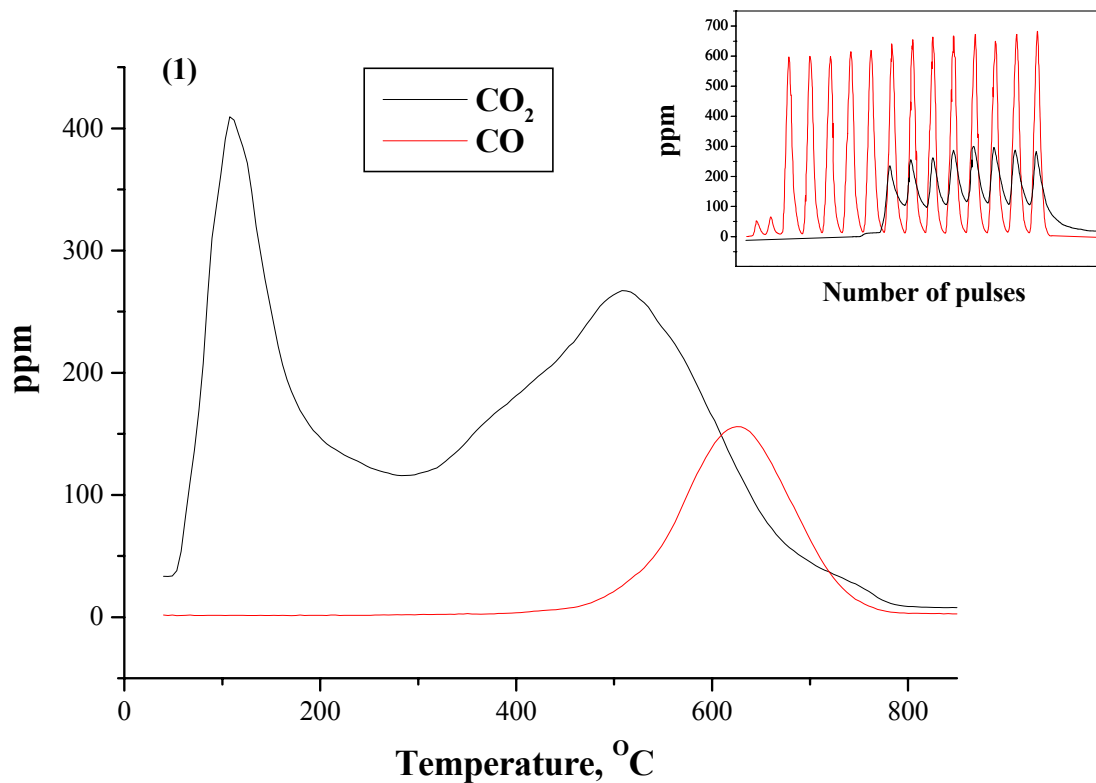
(1) – desorption products detected by UV and IR analyzers;

(2) – desorption products detected by MS.

Only reversible NO adsorption occurs evidenced by the presence of a single TPD peak of NO at 180°C. Water desorption between 300-800°C and hydrogen desorption at T_{\max} around 400 and 600°C are also recorded.

The TPD results clearly show no dissociative NO adsorption on AuCe and AuCeAl₂₀ catalysts as no trace of N₂ formation was detected with the both samples.

Fig. 3 represents the TPD data after RT CO adsorption on the pre-reduced AuCe catalyst: In the inset the RT adsorption by pulses of CO is given. After the 7th of the pulses the CO₂ formation was detected. Two TPD peaks of CO₂ are seen: a low temperature (LT) peak (T_{\max} =100°C) and a high temperature (HT) one (T_{\max} =500°C).



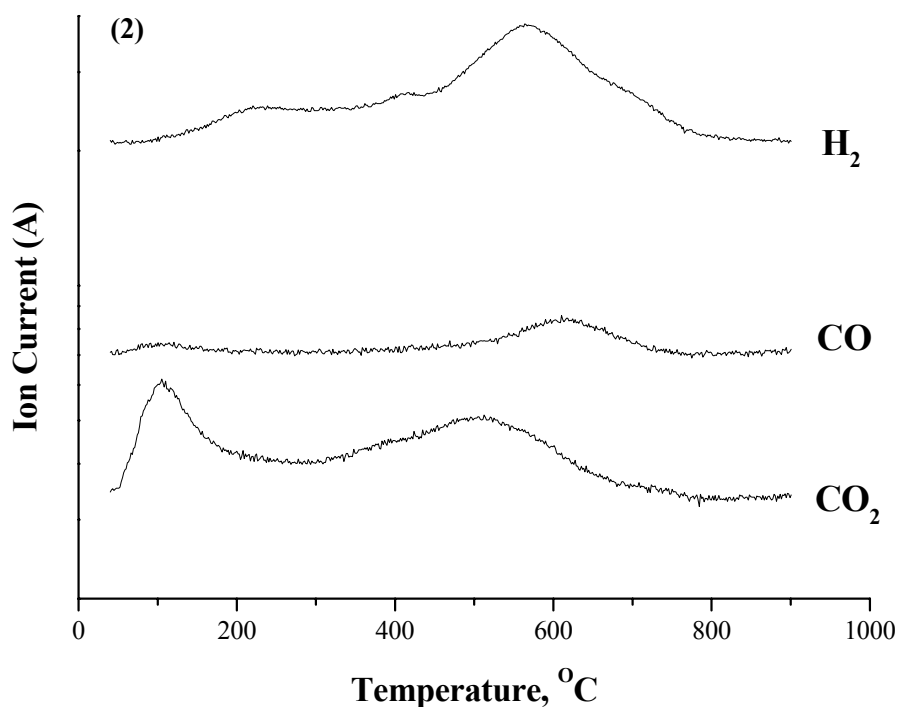
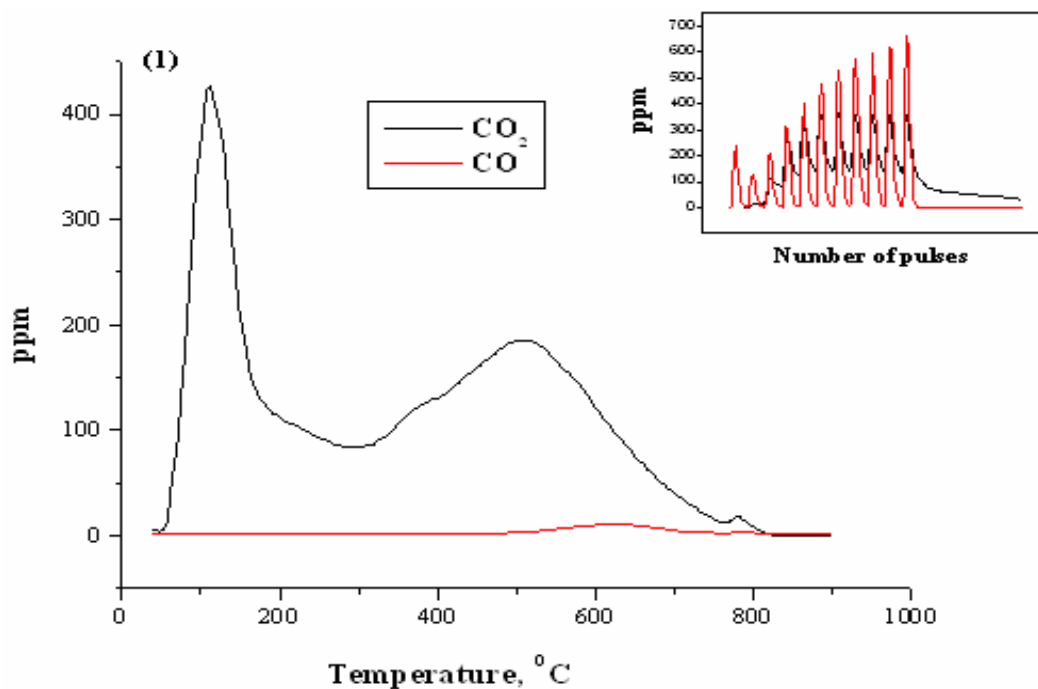


Fig. 3 – TPD after RT adsorption of CO over pre-reduced AuCe catalyst:
 (1) – desorption products detected by UV and IR analyzers; Inset – CO adsorption;
 (2) – desorption products detected by MS

In the front of the HT TPD peak there is a shoulder at about 350°C and also a small shoulder can be seen around 780°C. A single HT peak assigned to CO is registered at 630°C. The MS data show hydrogen desorption in the interval 500-600°C.

Fig. 4. represents the corresponding TPD data of AuCe sample pre-treated in pure He, in the inset

is given CO adsorption at RT. In this case CO₂ registration during the RT adsorption starts at the 3rd of the CO pulses. In the TPD spectra only irreversible adsorption of CO is observed evidenced by TPD peaks assigned to CO₂ desorption. No CO was detected.



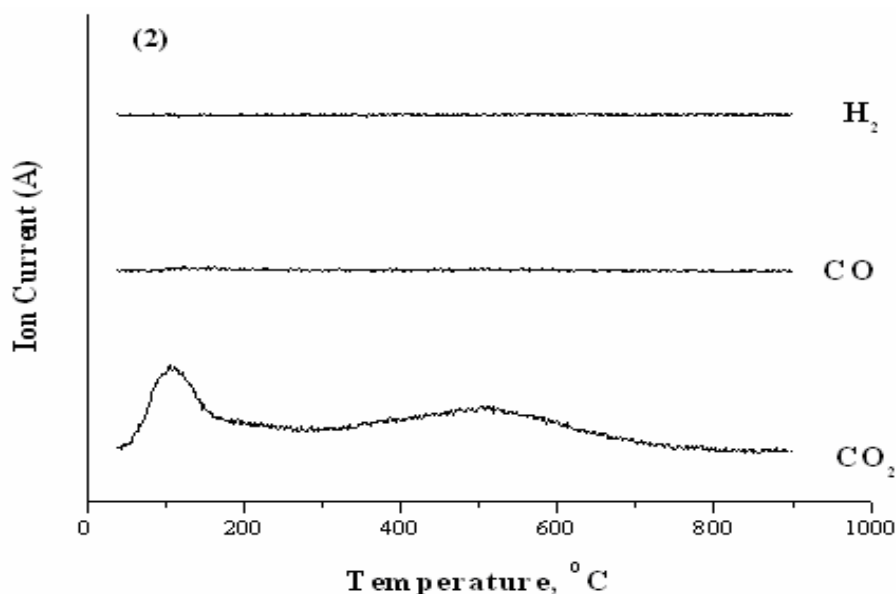


Fig. 4 – TPD after RT adsorption of CO over pre-treated in He AuCe catalyst:
 (1)– desorption products detected by UV and IR analyzers; Inset – CO adsorption;
 (2) – desorption products detected by MS.

DISCUSSION

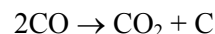
CO adsorption on gold catalyst has been widely investigated by different techniques since the pioneering work of Haruta⁹ showing that catalysts containing gold are extraordinarily active in CO oxidation at low temperatures. The RT CO oxidation on gold/ceria catalyst is expected and the data presented in the present study suggest that the CO₂ formation occurs at RT even over the pre-reduced AuCe catalyst. Interesting fact is that formation of CO₂ did not start immediately after the 1st of CO pulses. The amount of CO₂ started to be detected during the 3rd of the CO pulses for AuCe sample pre-treated in He and during the 8th one, when the sample was pre-reduced.

Recently, Wallace and Whetten¹⁰ studying CO oxidation on anionic gold dimmers have presumed the Au₆(CO)_M complexes formation. Socaciu et al.¹¹ have proposed CO oxidation through the interaction between CO and Au₂(CO)O₂⁻ intermediate. In our case the observed behaviour during CO adsorption could be also explained by the presumption of CO complexes formation with the eventual participation of mobile oxygen from the ceria structure.

The TPD profiles (Fig. 3 and 4) show that the catalyst surface is heterogeneous having mainly two types of active sites for irreversible CO adsorption. The first TPD peak is located in the temperature interval which is of interest for the LT NO + CO reaction. The CO₂ desorption can be due

to the CO oxidation by the mobile oxygen from ceria lattice. This is the most probable explanation taking into account the high activity in CO oxidation of this type of catalysts.

Another eventual explanation could be the CO disproportionation:



but this reaction is not typical for gold/ceria catalysts. A temperature programmed oxidation (TPO) experiment performed after long time operation of AuCe catalyst in the NO + CO reaction⁷ showed that CO disproportionation does not occur even at high temperatures. During TPO the desorption no uptake of O₂ was detected.

A HT peak of CO desorption is recorded only in the case of the pre-reduced AuCe catalyst. TPD peaks due to a reversible CO adsorption have been registered simultaneously with CO₂ desorption over platinum group metals (PGM) supported on ceria.^{12,13} However, a quite high T_{max} of the TPD peak of CO, recorded by us, makes the assignment to reversible adsorption improbable. The explanation could be searched taking into account that the peak of CO did not appear if the pre-treatment was in helium. During the pre-treatment in hydrogen some amount of H₂ could be retained in the ceria structure, which is in agreement with the detected by MC TPD peaks of hydrogen in all cases of the pre-reduced samples.

Hydrogen incorporation into the bulk of ceria has been also observed by Laachir et al.¹⁴ and the

reason could be the formation of H_yCeO_{2-x} bronze like species, established by other authors.¹⁵

The reverse WGS reaction between CO_2 and H_2 can be the reason for CO formation at the temperatures just around that corresponding to the liberation of H_2 from the bulk of ceria.

Concerning supported PGM it is generally accepted that NO reduction with CO proceeds by NO dissociation and CO oxidation by a Langmuir-Hinshelwood mechanism with adsorbed oxygen and CO. Oxygen vacancies associated with reduced ceria in the proximity of noble metal particles have been suggested by many researchers as active sites for NO and CO conversion.¹⁶

For gold catalysts, however, there is no experimental evidence that NO dissociation occurs. Galvagno and Parravano¹⁷ proposed that NO reduction by hydrogen proceeds via Eley-Rideal mechanism with molecularly adsorbed NO and gas phase H_2 . Nitrate species have been detected on a number of Au catalysts pointing out to the possible role of NO_2 as reaction intermediate³.

The TPD data in the present study clearly show reversible NO adsorption over pre-reduced AuCe sample. The registered very small TPD peak of N_2O means negligible ability for NO decomposition.

It was also interesting to see the adsorption properties of AuCeAl₂₀ catalyst, in which case more oxygen vacancies due to the presence of Al^{3+} are generated.⁶ The TPD experiment showed only a single TPD peak of reversible NO adsorption. Although, due to the ceria oxygen storage capacity the CO oxidation was observed even at RT, no NO_2 was detected among the desorption products during TPD on the both samples. This result means that unlike to the case of gold catalysts studied by Ueda and Haruta¹ the reaction step of NO oxidation to NO_2 is not probable over gold-ceria catalysts. It has to be stressed the fact that no trace of N_2 was detected during the TPD of AuCe as well as of AuCeAl₂₀ samples. These results are very different from those already reported for PGM/ CeO_2 catalysts. The TPD profile of adsorbed NO has shown only N_2 desorption over Pt/ CeO_2/Al_2O_3 and Rh/ CeO_2/Al_2O_3 samples.¹⁸ The authors have shown, by repeated TPD runs, that reoxidized ceria is much less effective in promoting NO dissociation due to the lack of available Ce^{3+} sites.

TPD experiments on CeO_2/Al_2O_3 , without precious metal have shown no appreciable desorption of N-containing species, suggesting that

the N_2 desorption peak is probably correlated to the interaction between the metal and the ceria surface.¹⁹ Gorte and coauthors have studied the desorption features of NO on model ceria-supported Pd and Rh catalysts. The TPD curves in the case of both large and small Rh particles on ceria have shown two TPD peaks of N_2 and a small one of NO.¹² The authors have observed that on Pd/ceria catalysts a significantly higher fraction of NO reacts to N_2 and pre-reduction of the catalyst increases the amount of NO that can be adsorbed.¹³ It has been accepted that re-oxidation of the reduced PGM/ CeO_2 catalysts with NO produces a small amount of N_2O and N_2 as a main product indicating that in the presence of ceria the activation energy for NO dissociation and/or the activation energy for N_2 desorption is lowered.¹⁶ Gold containing ceria catalysts investigated in the present study demonstrate completely different NO adsorption properties that could be connected with different mechanism of NO reduction by CO comparing to the PGM/ceria catalysts.

EXPERIMENTAL

Sample preparation

Gold supported on ceria and on ceria-alumina mixed support (20 wt.% alumina) were synthesized. The ceria-alumina mixed support was prepared by co-precipitation of the corresponding nitrates in desired ratio with a solution of K_2CO_3 . The gold was loaded by deposition-precipitation method using a "Contalab" laboratory reactor (Contraves, AG Switzerland) under full control of the parameters of preparation. After filtered and carefully washed, the samples were dried in vacuum at 80°C and calcined in air at 400°C for 2 h. The initial salts used $HAuCl_4 \cdot 3H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and K_2CO_3 were "analytical grade".

Sample characterization

The BET surface area of the samples was determined on a 'Flow Sorb II-2300' device. The amount of gold loaded was calculated using gravimetric analyses.

The XRD patterns were obtained on a DRON-3 automatic powder diffractometer, using $Cu K_{\alpha 1}$ radiation. The average size of the particles was calculated on the basis of the peak broadening using "Powder Cell" program. The instrumental broadening was taken into consideration. XRD profiles were approximated by Lorenz functions.

Sample pre-treatments

Before performing an adsorption that precedes any TPD experiment the samples were heated up to 120 °C for 30 minutes either in a mixture of helium + 5% H_2 or in pure helium. Like in a previous paper⁷ we named in this work "pre-reduced sample" any sample pre-treated in the mixture $He+5\%H_2$.

TPD measurements

The TPD measurements were carried out by means of Micromeritics Autochem 2910 using "ABB" UV and IR analyzers. Parallel mass spectrometry (MS) monitoring using on-line Pfeiffer mass quadrupole and Balzers Quadstar software was also performed.

The RT NO adsorption was carried out: under 0.5% NO in He flowing at 30 ml min⁻¹ for 30 min. TPD measurements with NO adsorptions were conducted only on pre-reduced AuCe and AuCeAl₂O₃ samples.

The analysis during the RT CO adsorption over pre-reduced AuCe catalyst (the same condition of preliminary reduction like for experiments with NO) using flow of 10% CO in He, have shown that even at room temperature the CO adsorption is accompanied with oxidation to CO₂. In order to have more detail information of this process the CO adsorption was performed using pulses of 10% CO in He (a volume of 1 ml) up to the sample saturation. The TPD results obtained with the pre-reduced catalyst motivated us to make also a TPD experiment after a pre-treatment in pure He during 30 min at 120°C.

After any adsorption, either of NO or CO, He was allowed to flow throughout the sample at RT during 30 min in order to remove physically adsorbed molecules. The weight of 0.05 g of the studied sample was loaded in a U shaped quartz reactor. The TPD experiments were performed by sample heating at 10°C min⁻¹ in He (99.9996) at a flow rate of 50 ml min⁻¹ up to 900°C.

CONCLUSIONS

The room temperature CO adsorption on the samples, pre-treated in helium as well as in hydrogen, leads to CO₂ formation, which is in agreement with the high oxygen storage capacity of gold/ceria catalysts. The catalyst surface is heterogeneous having mainly two types of active sites for irreversible CO adsorption. The high temperature TPD peak of CO in the case of the pre-reduced sample can not be related to the reversible CO adsorption. It could be explained by the reverse WGS reaction between CO₂ and H₂, retained in ceria structure during the pre-treatment.

A reversible adsorption of NO and the absence of any trace of N₂, *i.e.* a non-dissociative NO adsorption over gold catalysts, supported both on ceria and ceria-alumina, is confirmed. These

adsorption properties are completely different, compared to platinum group metals, supported on ceria, which is an indication of a different NO+CO reaction mechanism.

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