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In situ FT-IR spectroscopic investigation of gold supported on tungstated zirconia as catalyst for CO-SCR of NO_x

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ABSTRACT

The possibility for application of gold supported on tungstated zirconia as catalyst in the selective catalytic reduction of NO_x with CO (CO-SCR) has been investigated by means of in situ FT-IR spectroscopy. Tungstated zirconia containing 18 wt% of WO₃ was prepared by co-precipitation. Gold was deposited on zirconia and tungstated zirconia by cationic adsorption using [Au(en)₂]Cl₃ as a precursor (en = ethylenediamine). The FT-IR spectra obtained during the interaction of CO with NO_x species adsorbed on the Au/ZrO₂-WO_x and Au/ZrO₂ samples revealed the formation of surface isocyanates attached to the gold particles. The generation of Au-NCO species occurred at low temperature (25–50 °C). The W-containing sample was characterized by higher activity in the ad-NO_x + CO reaction than the W-free one. It is shown that the nitrate species or adsorbed NO₂ are essential for the generation of surface isocyanates and the oxidation of NO by oxygen is an important step. The obtained results suggest that Au catalysts supported on tungstated zirconia might be of interest for the selective reduction of NO_x with CO at low temperatures.

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1. Introduction

The selective reduction of NO_x in the presence of oxygen is a very promising technology to control the emissions from diesel and lean-burn engines. Reduction of NO_x using either the residual hydrocarbons or on-board fuel would be the most ideal technology. However, the traditional materials developed for the selective reduction of NO_x with hydrocarbons (HC-SCR) do not show sufficient activities under the conditions of lean exhaust especially at low temperatures (<150–250 °C) [1–4]. One of the typical reductant present in the car exhaust is CO. Recently Ir/SiO₂, Ir/WO₃ and Ir/WO₃/SiO₂ catalysts have been reported to be highly active in the selective reduction of NO with CO (CO-SCR) [5–11]. However, these catalysts show activity in the 260–400 °C temperature window. Supported gold catalysts are known to be highly active in variety of reactions at low temperatures [12,13]. In the present study, we report the results of FT-IR spectroscopic characterization of gold catalyst supported on tungstated zirconia. In order to evaluate the potential of a new material as a catalyst in a desired process, it is important to investigate the interaction of the reactants with the surface. For this purpose we studied the adsorption of CO and its co-adsorption with oxygen and NO over Au-promoted and Au-free tungstated zirconia.

2. Experimental

2.1. Sample preparation

The sample preparation is described in detail elsewhere [14]. In brief, tungstated zirconia was synthesized by co-precipitation [15] with nominal content of 18 wt% of WO₃. Gold was deposited on tungstated zirconia by cation adsorption for 2 h from aqueous solution of [Au(en)₂]³⁺ complex at pH=9.6 and room temperature. After drying of the washed solid at 80 °C for 48 h, the sample was calcined for 1 h at 400 °C. The cationic gold precursor was prepared following the procedure of Block and Bailar [16]. The sample was labeled as Au/18WZ-CP.

In order to study the effect of tungsten, gold was deposited on tetragonal zirconia also by cation adsorption of [Au(en)₂]³⁺ complex using the same conditions applied to the W-containing sample.

2.2. Sample characterization

The samples were characterized by XRD, DR-UV-vis spectroscopy, BET measurements and chemical analysis, and the results were reported earlier [14].

The FT-IR spectra were recorded using a Bomem Hartman & Braun MB-102 model FT-IR spectrometer with a liquid-nitrogen cooled MCT detector at a resolution of 4 cm⁻¹ (100 scans). The self-supporting discs (~0.01 g/cm²) were activated in the IR cell by heating for 1 h in a vacuum at 400 °C, and in oxygen (100 Torr,

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Table 1
Physico-chemical characterization of the investigated samples.

Sample	S _{BET} (m ² /g)	WO ₃ (wt%)	Au loading (wt%)	Average Au particle size (nm)
ZrO ₂	152	–	–	–
Au/ZrO ₂	143	–	1.43 ± 0.03	8
18WZ-CP	116	18.0	–	–
Au/18WZ-CP	118	17.6	2.27 ± 0.01	10

passed through a trap cooled in liquid nitrogen) at the same temperature, followed by evacuation for 1 h at 400 °C. The spectra of adsorbed gases were obtained by subtracting the spectra of the activated sample from the spectra recorded. The sample spectra were also gas-phase corrected.

3. Results and discussion

3.1. Structural characterization

Table 1 summarizes the chemical composition and BET surface areas of the samples. The results of the chemical analysis [14] show that the gold uptake on tungstated zirconia is higher than that on zirconia. It is well known that tungstated zirconia contains acidic protons [15,17–21] which in basic medium can undergo deprotonation. This can lead to the formation of greater number of M–O[–] anchoring sites (M = W and Zr) for the [Au(en)₂]³⁺ complex resulting in higher gold uptake.

According to the XRD data [14] the materials have the structure of tetragonal zirconia. The average size of gold particles (Table 1) is calculated by using Scherrer equation and the main gold diffraction line of $2\theta = 38.2^\circ$. The DR-UV-vis spectra of gold containing samples [14] exhibit broad absorption with maximum at 550–590 nm characteristic of the plasmonic oscillation mode of nanosized gold particles [22–24].

3.2. Adsorption of CO at room temperature

The analysis of the FT-IR spectra of CO adsorbed at room temperature on the samples can be very useful to obtain qualitative information on the nature of supported gold species. Fig. 1 displays the FT-IR spectra in the carbonyl region of CO (10 Torr) adsorbed on the activated Au-containing samples. The absorption at 2194–2198 cm^{–1} is assigned to CO adsorbed on Zr⁴⁺ surface sites [18,21,23,25–27]. The high-frequency shift exhibited in the WO_x-containing material is associated with the increased acidity of the coordinative unsaturated Zr⁴⁺ sites caused by the electron-withdrawing WO_x groups [18,21]. The band corresponding to the Zr⁴⁺–CO species and the composed band with maximum at 2113–2116 cm^{–1} are removed upon dynamic evacuation at room temperature. According to data from the literature [23,25–39], the absorption with maximum at 2113–2116 cm^{–1} is assigned to CO adsorbed on small three-dimensional gold clusters, whereas the shoulder at 2125–2130 cm^{–1} could be attributed to Au^{δ+}–CO species. Formation of positively polarized gold is assumed to be caused by the presence of adsorbed oxygen on the gold particles or their interaction with the support [23,24,26,28,31,32,35–37]. Hadjiivanov and coworkers [36,37] proposed that the absorption in the 2155–2130 cm^{–1} region could be attributed also to Au⁺–CO species in which the Au⁺ cation resides on the metallic gold particles. It should be noted that the last activation step of the samples consisted of evacuation at 400 °C and adsorbed oxygen cannot be expected under these conditions. Moreover, after the reduction of the samples at 400 °C with CO, the absorption at 2125–2130 cm^{–1} is still present in the spectra of CO adsorbed at room temperature. Therefore, it could be proposed that the feature at 2125–2130 cm^{–1}

could be associated with the presence of more defective gold sites located most likely at the interface. It cannot be excluded that the absorption at 2125–2130 cm^{–1} is associated with the presence of larger Au particles. This proposition could be supported by the fact that CO adsorbed on small gold particles is characterized by $\nu(\text{CO})$ mode at lower wavenumbers and the $\nu(\text{CO})$ stretching vibration is blue-shifted as the particle size increases [40]. Recently, absorption band at 2130–2140 cm^{–1} observed upon CO adsorption on Au/Nb₂O₅ has been attributed to CO coordinated to larger gold nanoparticles [41].

3.3. In situ FT-IR spectroscopic investigation of the NO + O₂ + CO reaction

3.3.1. NO + O₂ surface reaction

In general, the mechanism of SCR of NO_x on various oxide catalysts involves the interaction of strongly adsorbed NO_x[–] species (x is 2 or 3) with the reducer [2,42–46]. Therefore we studied the thermal stability of NO_x species adsorbed on the surface of the 18WZ-CP and Au/18WZ-CP samples.

NO_x species on the surface of the Au/18WZ-CP sample were created by adsorption of a (10 Torr NO + 25 Torr O₂) mixture at room temperature followed by evacuation for 20 min at the same temperature (Fig. 2A, spectrum (a)). The absorption bands in the 1700–1000 cm^{–1} range are typical of surface nitrates observed on tungstated zirconia [45–47] and are identified as monodentate (1582 and 1275 cm^{–1}) and bidentate (1629 and 1219 cm^{–1}) NO₃[–] species. The broad absorption centered at 2140 cm^{–1} is

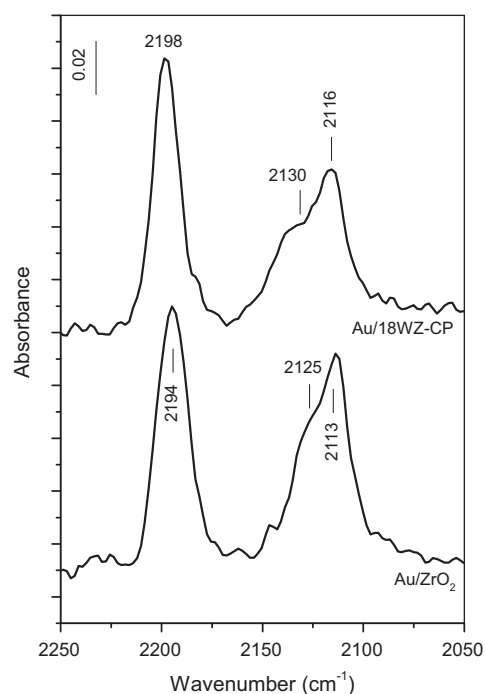


Fig. 1. FT-IR spectra of CO (10 Torr) adsorbed at room temperature on the samples studied.

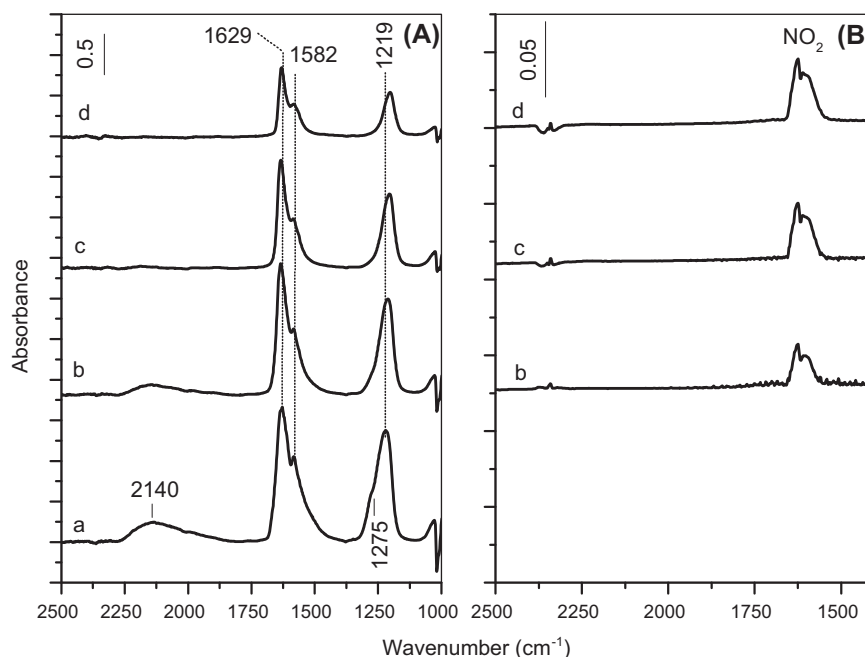


Fig. 2. Panel A: FT-IR spectra of the Au/18WZ-CP sample taken after the addition of a (10 Torr NO + 25 Torr O₂) mixture to the IR cell for 10 min at room temperature followed by evacuation for 20 min (a), and after heating the isolated IR cell for 10 min at 100 °C (b), 200 °C (c) and 300 °C (d). Panel B: Gas phase spectra collected at 100 °C (b), 200 °C (c) and 300 °C (d).

characteristic of NO⁺ species [45–47]. Heating the isolated IR cell in the temperature range 100–300 °C, leads to gradual decrease in the intensities of the nitrate bands. The spectra of the gas phase (Fig. 2B) show that the major product of decomposition of the surface nitrates is NO₂. The Au-free 18WZ-CP sample contains analogous type of adsorbed NO_x species which were generated by the same way as described above (the spectra are not shown). However, the surface nitrates on the Au-containing sample display higher thermal stability.

There are reports in the literature [35,37], showing that a mixture of NO + O₂ can cause oxidation of supported metallic gold particles to cationic gold species and this process can occur at room temperature. In order to find the effect of co-adsorption of NO + O₂ mixture on the oxidation state of gold in the Au/18WZ-CP sample, we investigated the adsorption of CO on the catalyst containing pre-adsorbed NO_x species. It is well known that the spectral features of adsorbed CO can provide information about the oxidation state of the adsorption site [34]. Surface nitrate species (absorption bands between 1700 and 1000 cm⁻¹) were generated by bringing in contact the Au/18WZ-CP sample with a mixture of 10 Torr of NO and 25 Torr of O₂ for 10 min at room temperature followed by evacuation at the same temperature for 20 min (Fig. 3, spectrum (a)). To the sample treated in this way, 10 Torr of CO were added. The spectrum detected at room temperature after 5 min contains a strong band with maximum at 2185 cm⁻¹ (Fig. 3, spectrum (b)). The intensity of this signal increases significantly after 10 min of contact with the CO (Fig. 3, spectrum (c)). Weak absorption at 2130 cm⁻¹ is observed as well whose intensity increases in parallel with the main band at 2185 cm⁻¹. The latter signal falls in the range of reported ν(CO) stretching vibrations of Au⁺–CO species (2197–2160 cm⁻¹ [31–37]). However, the increase in the intensity of the band at 2185 cm⁻¹ during the contact with CO contradicts the observed instability of the Au⁺–CO species in CO atmosphere [31–33,35] due to reduction of Au⁺ adsorption sites by CO.

In order to ensure more efficient oxidation of gold, the catalyst pellet was treated with a (10 Torr NO + 25 Torr O₂) mixture at 300 °C for 30 min. Then the temperature was lowered to 200 °C and the gas mixture was removed from the IR cell upon dynamic

evacuation while cooling to room temperature. Subsequent adsorption of CO (10 Torr) at room temperature results in the formation of weak absorption bands at 2190 and 2165 cm⁻¹ (Fig. 4, spectrum (a)). The spectrum in the nitrate region (not shown) displays the same set of nitrate bands as shown in Fig. 2A, although with weaker intensity. The band at 2190 cm⁻¹ resists the evacuation at room temperature (Fig. 4, spectrum (b)) and disappears upon outgassing at 100 °C (Fig. 4, spectrum (d)). The observed behavior of the absorption at 2190 cm⁻¹ is typical of Au⁺–CO species [34]. The CO adsorbed on Au⁺ sites is stabilized by the synergism between the σ-dative and π back-bonding components of the Au⁺–CO bond [34–37] and the carbonyl complex can be destroyed at temperature higher than 25 °C. The absorption at 2165 cm⁻¹ disappears upon evacuation at room temperature (Fig. 4, spectrum (b)) and could be attributed to Au^{δ+}–CO species or CO adsorbed on large

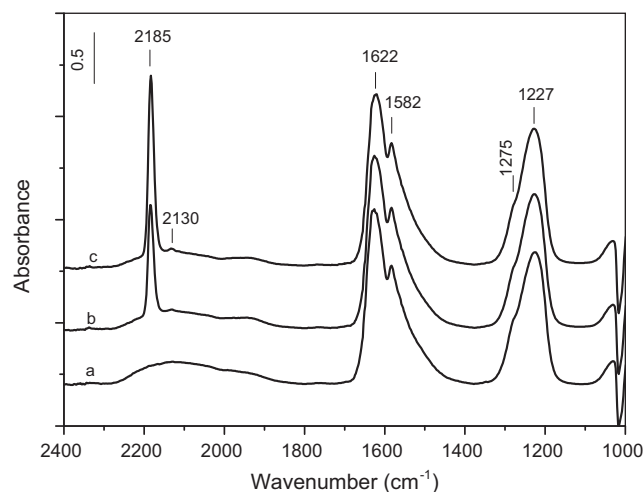


Fig. 3. FT-IR spectra of the Au/18WZ-CP catalyst collected after the adsorption of a (10 Torr NO + 25 Torr O₂) mixture for 10 min at room temperature followed by evacuation for 20 min at room temperature (a) and adsorption of 10 Torr CO at room temperature for 5 min (b) and 10 min (c).

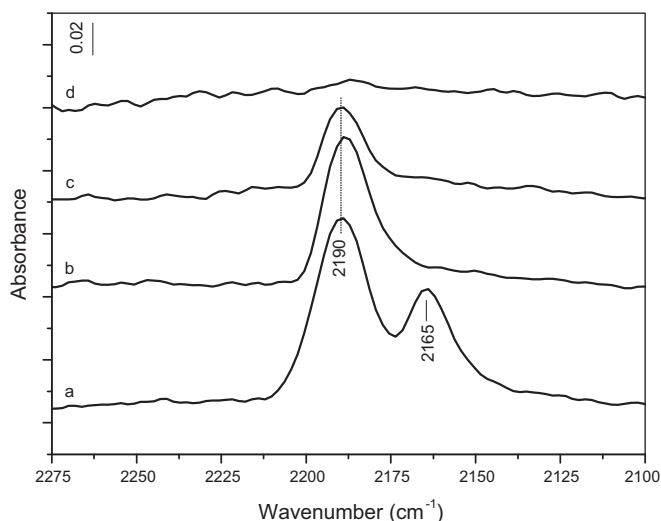


Fig. 4. FT-IR spectra of the Au/18WZ-CP sample collected after the adsorption of a (10 Torr NO + 25 Torr O₂) mixture for 30 min at 300 °C followed by dynamic evacuation from 200 °C to room temperature and subsequent adsorption of 10 Torr of CO for 10 min (a), evacuation for 15 min at room temperature (b), 50 °C (c) and 100 °C (d).

gold particles. This band is found at higher frequency than the corresponding band observed on the activated Au/18WZ-CP sample (see Fig. 1) indicating that either the Au^{δ+} sites bear a greater positive charge or there is agglomeration of the gold particles after the high-temperature treatment with NO + O₂ mixture. It is likely that the species giving rise to the band at 2165 cm⁻¹ could be Au⁺ adsorption sites dispersed on the surface of metallic gold particles as proposed in [36,37].

Spectrum (a) in Fig. 4 differs from the spectrum of adsorbed CO on the sample treated with NO + O₂ mixture at room temperature (Fig. 3, spectrum (c)). It seems that the oxidation of gold particles by the NO + O₂ mixture takes place at higher temperature (300 °C) and the absorption band at 2185 cm⁻¹ detected during the CO adsorption on the sample treated with NO + O₂ mixture at room temperature (Fig. 3, spectra (b) and (c)) cannot be ascribed to Au⁺-CO species. This conclusion is supported also by the fact that the color of the Au/18WZ-CP sample after the pre-treatment with NO + O₂ mixture at room temperature remained the same as that of the activated sample, i.e. gray-black. However, the treatment with NO + O₂ mixture at 300 °C causes changes in the color of the sample from gray-black to pale-violet.

Taking into account that the compounds adsorbed at room temperature on the Au/18WZ-CP sample are CO and NO_x species, it could be proposed that the strong band at 2185 cm⁻¹ in Fig. 3 could be attributed to NCO species formed on metallic gold sites. According to the literature [38,48,49] the Au-NCO species give rise to absorption band at 2180–2190 cm⁻¹. In order to verify this assumption we performed ¹³C adsorption on the sample treated with NO + O₂ mixture at room temperature (Fig. 5). The band at 2185 cm⁻¹ is shifted down by 57 cm⁻¹ and is positioned at 2128 cm⁻¹ on ¹³C substitution. The observed $\Delta\nu$ value is consistent with that reported by Celio et al. [50] for the isotopic shift detected on substituting ¹³C for ¹²C in NCO species adsorbed on Cu(100). From these results it can be concluded that the weak absorption at about 2130 cm⁻¹ in Fig. 3, spectrum (c) belongs to the ¹³CO satellite of the band at 2185 cm⁻¹.

The behavior of the absorption at 2185 cm⁻¹ in the presence of water vapor can be used as additional evidence supporting the assignment of this feature to Au-NCO species. It is well known that the NCO species can react with water producing ammonia and CO₂ through the formation of HNCO [11,51]. The species characterized

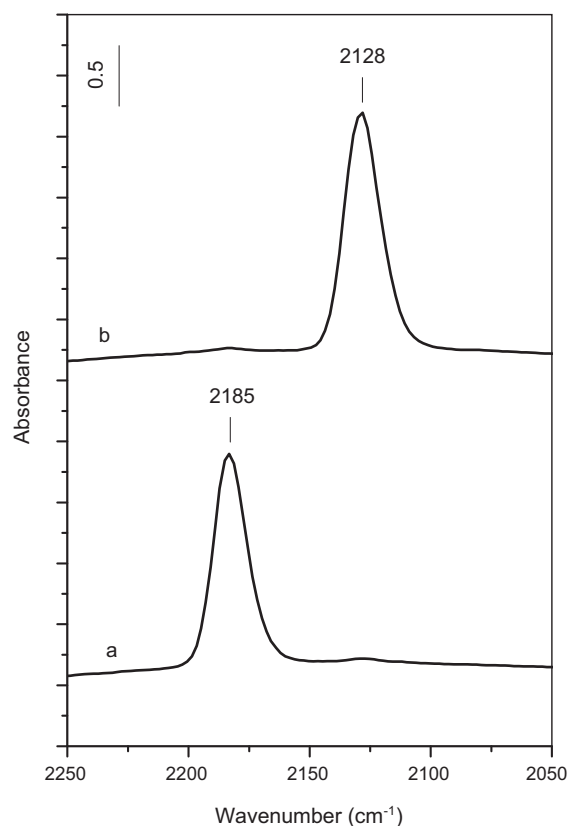


Fig. 5. FT-IR spectra of 10 Torr of CO (a) and 10 Torr of ¹³CO (b) adsorbed at room temperature on the Au/18WZ-CP sample.

by the absorption band at 2185 cm⁻¹ are generated by adsorption of CO (10 Torr, for 10 min) on the sample treated with NO + O₂ mixture at room temperature as described above and then the gaseous CO was evacuated for 15 min (Fig. 6A, spectrum (a)). The addition of 0.1 Torr of water vapor at room temperature causes significant decrease in the intensity of the band at 2185 cm⁻¹ (Fig. 6A, spectrum (b)) and appearance of CO₂ and HNCO ($\nu_{as}(\text{NCO})$ at 2266 cm⁻¹ [51]) in the gas phase (Fig. 6B, spectrum (b)). The formation of the latter compounds confirms unambiguously the assignment of the band at 2185 cm⁻¹ to Au-NCO species. Increasing the temperature to 100 °C results in further decrease in the amount of isocyanates (Fig. 6A, spectrum (c)) and they disappear completely at 200 °C (the spectrum is not shown). No ammonia was detected in the gas phase most likely because of its low concentration and/or adsorption on the catalyst surface. The sample spectra in the NH stretching region are noisy and are not representative. The bending modes of coordinated ammonia and NH₄⁺ ion fall in the region of stretching vibrations of the nitrates and if formed, they cannot be resolved. It should be noted that the adsorption of CO on the NO_x-precovered 18WZ-CP sample does not lead to the formation of NCO species which on oxides surfaces produce absorptions in the 2280–2200 cm⁻¹ region [38,46,48,49,52]. The absence of NCO species coordinated to the support in the case of Au/18WZ-CP sample can be explained by unavailability of adsorption sites which are blocked by the nitrate species.

The Au-NCO species observed on the Au/18WZ-CP sample are characterized by high thermal stability and they are removed by dynamic evacuation at 350 °C (Fig. 7).

3.3.2. NO_x + CO surface reaction

The aim of this experiment is to investigate the possibility of CO to act as reducing agent toward the NO_x species adsorbed on the

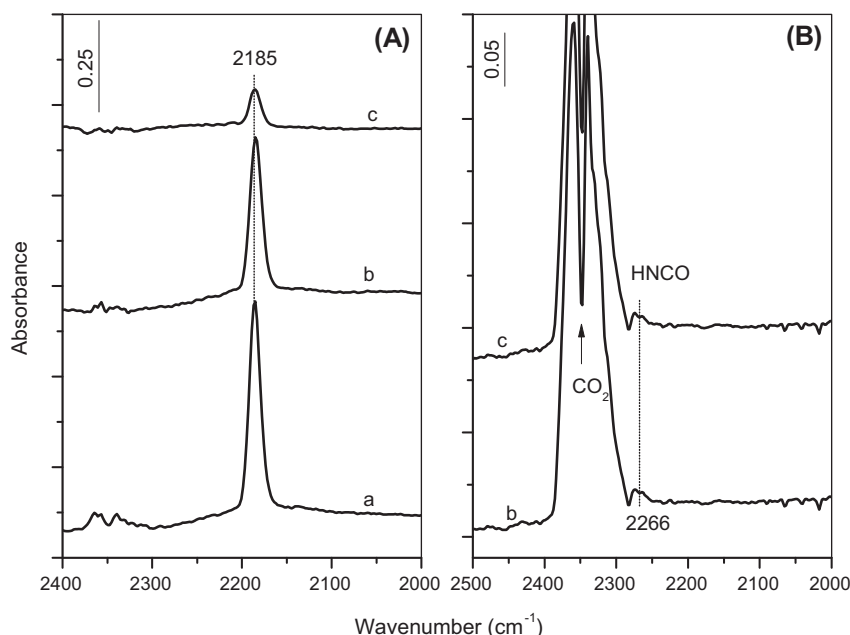


Fig. 6. Panel A: FT-IR spectra of the Au/18WZ-CP catalyst collected after the adsorption of a (10 Torr NO + 25 Torr O₂) mixture for 10 min at room temperature followed by evacuation for 20 min at room temperature, adsorption of 10 Torr CO at room temperature for 10 min and evacuation of the gaseous CO for 15 min (a), and subsequent addition of 0.1 Torr of water vapor for 10 min at room temperature (b) and 100 °C (c). Panel B: Gas phase spectra corresponding to the sample spectra (b) and (c).

surface of the Au/18WZ-CP catalyst. Adsorbed nitrate species were created by adsorption of mixture of 10 Torr NO and 25 Torr O₂ at RT for 10 min followed by evacuation for 20 min at RT (Fig. 8A, spectrum (a)). Then CO (10 Torr) was added (Fig. 8A, spectrum (b)) and

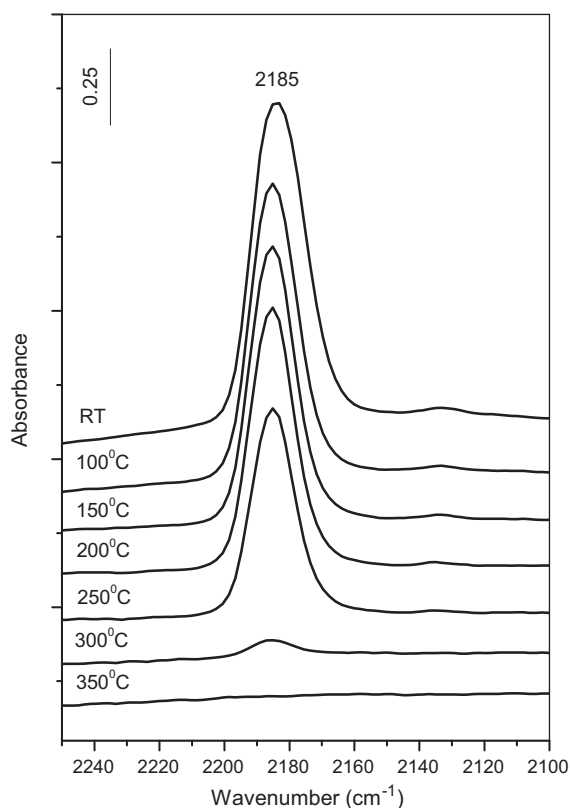


Fig. 7. FT-IR spectra of the Au/18WZ-CP catalyst collected after the adsorption of a (10 Torr NO + 25 Torr O₂) mixture for 10 min at room temperature followed by evacuation for 20 min at room temperature, adsorption of 10 Torr CO at room temperature for 10 min and evacuation of the gaseous CO for 15 min at various temperatures (RT = room temperature).

the isolated IR cell was heated for 10 min at various temperatures. The sharp band at 2185 cm⁻¹ assigned to Au–NCO species increases in intensity at 50 °C (Fig. 8A, spectrum (c)) and disappears at 200 °C (Fig. 8A, spectrum (f)) simultaneously with the NO₂ observed in the gas phase (Fig. 8B, spectrum (f)). It can be concluded that the NCO species react with the NO₂ leading to the formation of CO₂ and N₂. Some amounts of N₂O and NO are detected as well. The fact that in the absence of CO, the NO₂ is present in the gas phase (Fig. 2) supports the assumption that the NO₂ is reduced by CO through the intermediacy of Au–NCO species.

The spectra shown in Fig. 9 illustrate the reactivity of the Au–NCO species generated on the Au/18WZ-CP sample toward NO₂. The absence of CO in the gas phase prevents the formation of additional Au–NCO species at 50 °C (see Fig. 8A, spectrum (c)) and allows monitoring the onset temperature of the NCO + NO₂ reaction. The NCO species have been obtained by adsorption of 10 Torr of CO on the NO_x-precovered Au/18WZ-CP sample followed by evacuation for 20 min at room temperature (Fig. 9, spectrum (a)). After the admission of 0.4 Torr of NO₂ at room temperature (Fig. 9, spectrum (b)), the isolated IR cell was heated between 25 and 250 °C for 10 min at each temperature. The exposure of the sample to NO₂ at room temperature (Fig. 9, spectrum (b)) causes strong decrease in the intensity of the band at 2185 cm⁻¹ indicating that the NCO + NO₂ reaction takes place already at 25 °C. The surface concentration of the NCO species decreases rapidly with the temperature and they disappear at 250 °C (Fig. 9, spectrum (g)). The gas phase spectra (not shown) contain CO₂ and NO₂ that has been taken in excess. As shown above, the Au–NCO species have high thermal stability and leave the surface upon dynamic evacuation at 350 °C (Fig. 7). These results confirm the high reactivity of the isocyanates formed on the gold particles and suggest that the Au/18WZ-CP catalyst may have the potential for low-temperature reduction of NO_x with CO in the presence of oxygen.

In order to obtain information about the role of WO_x species in the NO_x + CO surface reaction, we studied the interaction of CO with nitrate species pre-adsorbed on the Au/ZrO₂ catalyst. Also in this case, nitrate species (bands between 1700 and 1000 cm⁻¹) were created by adsorption of mixture of 10 Torr NO and 25 Torr O₂ at RT for 10 min followed by evacuation for 20 min at RT

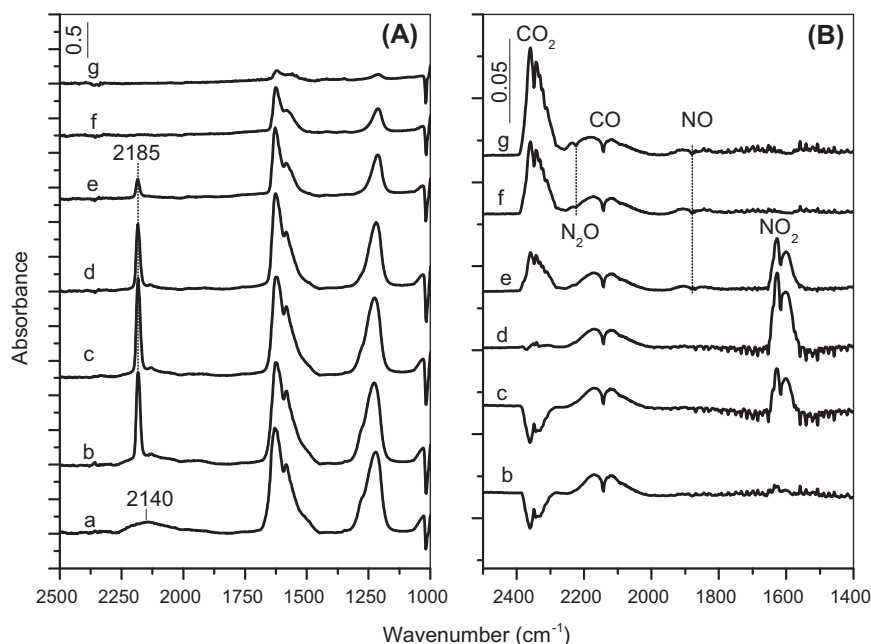


Fig. 8. Panel A: FT-IR spectra of the Au/18WZ-CP catalyst collected after the adsorption of a (10 Torr NO + 25 Torr O₂) mixture for 10 min at room temperature followed by evacuation for 20 min at room temperature (a), subsequent adsorption of 10 Torr CO at room temperature for 10 min (b) and heating the isolated IR cell for 10 min at 50 °C (c), 100 °C (d), 150 °C (e), 200 °C (f) and 250 °C (g). Panel B: Gas phase spectra collected at 25 °C (b), 50 °C (c), 100 °C (d), 150 °C (e), 200 °C (f) and 250 °C (g).

(Fig. 10A, spectrum (a)). After the addition of 10 Torr of CO at room temperature, the isolated IR cell was heated for 10 min at various temperatures. As with the Au/18WZ-CP sample, the sharp band at 2184 cm⁻¹ is characteristic of NCO species adsorbed on Au. The

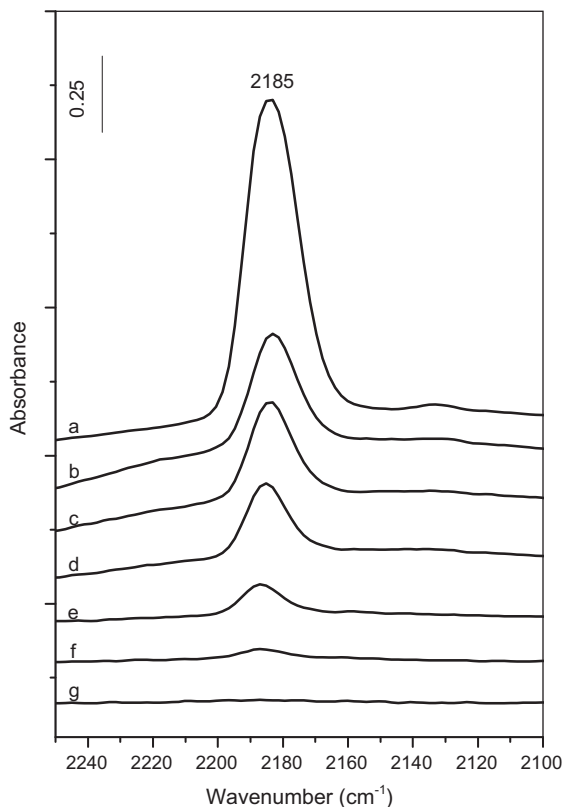


Fig. 9. FT-IR spectra of the Au/18WZ-CP catalyst collected after the generation of the Au–NCO species (a) (for the conditions see Fig. 7, spectrum (RT)) and subsequent addition of 0.4 Torr of NO₂ for 10 min at 25 °C (b), 50 °C (c), 100 °C (d), 150 °C (e), 200 °C (f) and 250 °C (g).

comparison of the spectra shown in Figs. 8 and 10 leads to the conclusion that the WO_x-containing catalyst should have higher activity because the adsorbed NCO species and NO₂ disappear at 200 °C whereas in the case of Au/ZrO₂ sample they are present at this temperature. Despite of the higher concentration of surface nitrates on the Au/ZrO₂ sample, the amount of evolved NO₂ is lower. This suggests that the surface tungstates lower the stability of the nitrate ions. In addition, the weak absorptions at 1450 and 1420 cm⁻¹ observed in the spectrum of Au/ZrO₂ detected at 250 °C indicate the formation of stable polydentate carbonates [53,54] which may have negative effect on the catalytic activity. No such species are found in the case of the Au/18WZ-CP sample.

Finally, it should be noted that the Au-free 18WZ-CP sample does not catalyze the interaction between adsorbed NO_x species and CO: the evolved NO₂ is present in the gas phase between 25 and 350 °C (the data are not shown).

3.3.3. Interaction of a (10 Torr NO + 14 Torr CO) mixture with Au/18WZ-CP

The aim of this experiment is to show the role of NO + O₂, respectively NO₂, for the formation of Au–NCO species. The spectra (Fig. 11) are collected in the presence of NO + CO reaction mixture at various temperatures. The band at 2230 cm⁻¹ observed in the spectrum taken at room temperature (Fig. 11A, spectrum (a)) is typical of adsorbed N₂O which is present as impurity in the gaseous NO (Fig. 11B). The absorption at 2198 cm⁻¹ corresponds to Zr⁴⁺–CO whereas the signal at 2118 cm⁻¹ is assigned to Au⁰–CO species (Fig. 11A). The spectrum recorded at RT contains absorption bands which are attributed to bidentate HCO₃⁻ (1606 and 1222 cm⁻¹), bidentate (1555 and 1305 cm⁻¹) and polydentate carbonates (1456 and 1420 cm⁻¹) [53,54]. The assignment of the absorptions in the 1700–1000 cm⁻¹ region to carbonate species is confirmed by the FT-IR spectra of adsorbed CO taken in the 25–250 °C temperature range. The data are not shown for the sake of brevity. The intensities of the bands at 2230, 2198 and 2118 cm⁻¹ decrease with the temperature and these absorptions are no longer present in the spectrum taken at 150 °C (Fig. 11A, spectrum (d)). Only Zr⁴⁺–NO nitrosyl (1937 cm⁻¹ [55]) and NO⁻ (1178 cm⁻¹ [47,55]) ion are

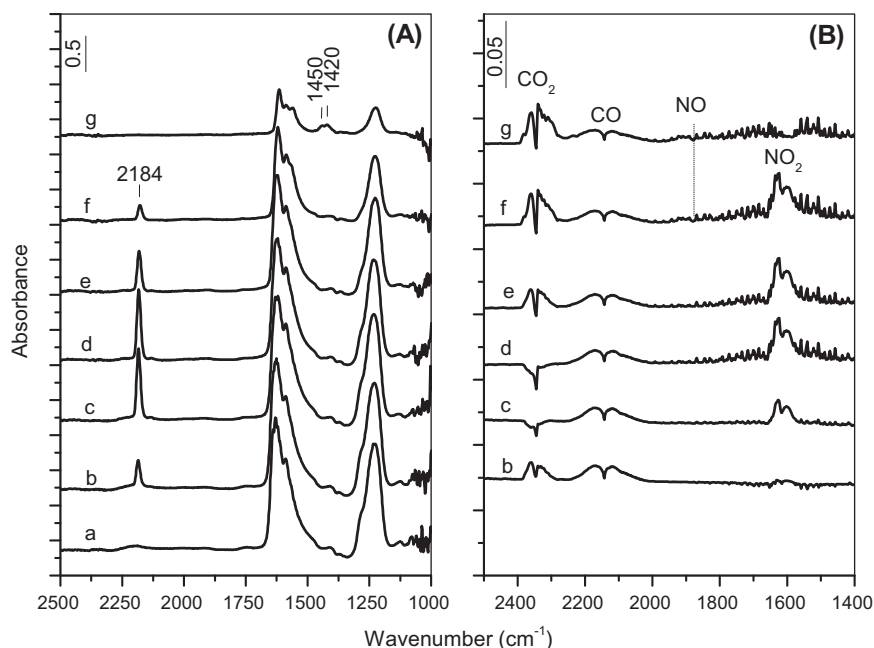


Fig. 10. Panel A: FT-IR spectra of the Au/ZrO₂ catalyst collected after the adsorption of a (10 Torr NO + 25 Torr O₂) mixture for 10 min at room temperature followed by evacuation for 20 min at room temperature (a), subsequent adsorption of 10 Torr CO at room temperature for 10 min (b) and heating the isolated IR cell for 10 min at 50 °C (c), 100 °C (d), 150 °C (e), 200 °C (f) and 250 °C (g). Panel B: Gas phase spectra collected at 25 °C (b), 50 °C (c), 100 °C (d), 150 °C (e), 200 °C (f) and 250 °C (g).

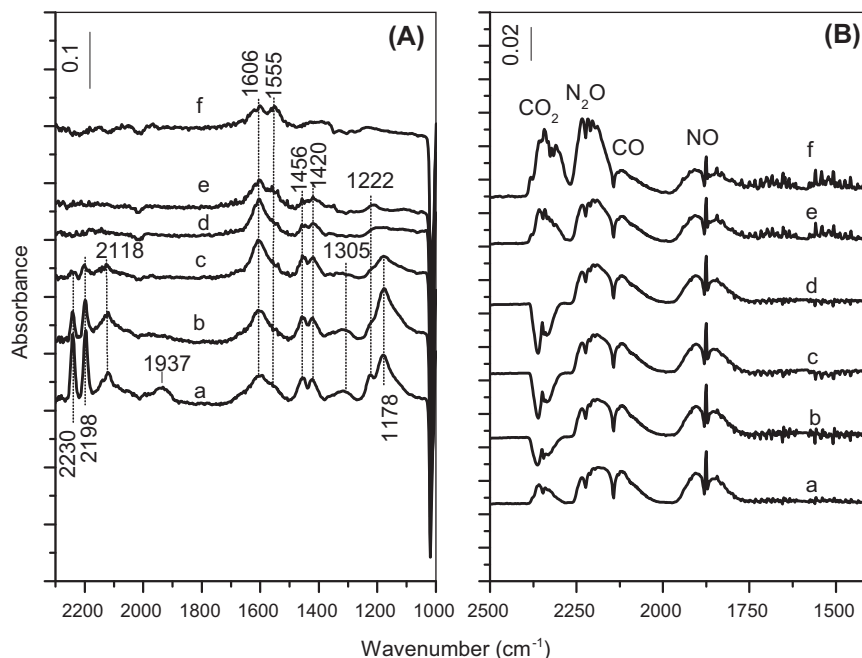


Fig. 11. Panel A: FT-IR spectra of the Au/18WZ-CP catalyst collected after the adsorption of a (10 Torr NO + 14 Torr CO) mixture for 10 min at room temperature (a) and subsequent heating the isolated IR cell for 10 min at 50 °C (b), 100 °C (c), 150 °C (d), 200 °C (e) and 250 °C (f). Panel B: Gas phase spectra collected at 25 °C (a), 50 °C (b), 100 °C (c), 150 °C (d), 200 °C (e) and 250 °C (f).

identified as NO_x species adsorbed at room temperature. No surface nitrates and Au–NCO species are formed even at higher temperatures. This fact indicates that the nitrate species or activated NO₂ are essential for the formation of Au–NCO species and that the oxidation of NO by oxygen is an important step. The gas phase spectra (Fig. 11B) show that the amount of N₂O increases with the temperature being the highest at 250 °C (spectrum (f)) when the NO[–] species are removed completely from the surface. The CO₂ detected in the gas phase at 200 °C (Fig. 11B, spectrum (e)) most likely appears as a result of decomposition of the surface carbonates.

4. Conclusions

Gold catalysts prepared by cationic adsorption of aqueous solution of [Au(en)₂]Cl₃ complex on zirconia and tungstated zirconia have been investigated by in situ FT-IR spectroscopy. The adsorption of CO shows the presence of positively charged (or large gold clusters) and neutral gold particles on both supports. Detailed FT-IR investigation of the interaction between CO and NO_x species pre-adsorbed on Au/ZrO₂ and Au/ZrO₂–WO_x samples reveal the formation of surface isocyanates attached to the gold particles.

The generation of Au–NCO species occurs at low temperature (25–50 °C). The gold isocyanates display high thermal stability. However, they react readily with NO₂ at room temperature. During the ad-NO_x + CO reaction over the Au/ZrO₂–WO_x sample, the gold isocyanates disappear at 200 °C simultaneously with the NO₂ that is generated in the gas phase by decomposition of the surface nitrates. This process on the Au/ZrO₂ catalyst takes place at higher temperature (250 °C). It is concluded that the incorporation of W to zirconia decreases the stability of the adsorbed nitrates. The Au-free tungstated zirconia does not catalyze the interaction between adsorbed nitrates and CO: the evolved NO₂ is present in the gas phase between 25 and 350 °C.

No formation of surface nitrates and Au–NCO species is detected during the NO + CO adsorption on Au/ZrO₂–WO_x catalyst in the 25–250 °C temperature range. This result implies that the nitrate species or adsorbed NO₂ are essential for the generation of gold isocyanates and the oxidation of NO by oxygen is an important step. In the absence of CO, gaseous NO₂ over both Au-containing catalysts is observed in the 25–350 °C temperature range. This fact supports the conclusion that NO₂ is reduced by CO with the intermediacy of Au–NCO species leading to the formation of N₂ and CO₂. The results of in situ FT-IR spectroscopic investigation presume that Au supported on tungstated zirconia might be potential candidate for the development of low-temperature catalyst for the selective reduction of NO_x with CO.

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References

- [1] M. Iwamoto, in: A. Corma, F.V. Melo, S. Mendioroz, J.L.G. Fierro (Eds.), *Stud. Surf. Sci. Catal.*, vol. 130, 2000, pp. 23–47.
- [2] R. Burch, J.P. Breen, F.C. Meunier, *Applied Catalysis B* 39 (2002) 283–303.
- [3] R. Burch, *Catalysis Reviews: Science and Engineering* 46 (2004) 271–334.
- [4] M.C. Kung, H.H. Kung, *Topics in Catalysis* 28 (2004) 105–110.
- [5] M. Haneda, T. Yoshinari, K. Sato, Y. Kintaichi, H. Hamada, *Chemical Communications* (2003) 2814–2815.
- [6] M. Shimokawabe, N. Umeda, *Chemistry Letters* 33 (2004) 534–535.
- [7] A. Takahashi, I. Nakamura, M. Haneda, T. Fujitani, H. Hamada, *Catalysis Letters* 112 (2006) 133–138.
- [8] H. Inomata, M. Shimokawabe, M. Arai, *Applied Catalysis A* 332 (2007) 146–152.
- [9] M. Haneda, H. Hamada, *Chemistry Letters* 37 (2008) 830–831.
- [10] T. Nanba, S. Shinohara, J. Uchisawa, S. Masukawa, A. Ohi, A. Obuchi, *Chemistry Letters* 35 (2006) 450–451.
- [11] T. Nanba, K.-I. Wada, S. Masukawa, J. Uchisawa, A. Obuchi, *Applied Catalysis A* 380 (2010) 66–71.
- [12] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, *Journal of Catalysis* 115 (1989) 301–309.
- [13] M. Haruta, M. Date, *Applied Catalysis A* 222 (2001) 427–437.
- [14] M. Kantcheva, M. Milanova, I. Avramova, S. Mametsheripov, *Catalysis Today* (2012), <http://dx.doi.org/10.1016/j.cattod.2012.02.027>, in press.
- [15] J.G. Santiesteban, J.V. Vartuli, S. Han, R.D. Bastian, C.D. Chang, *Journal of Catalysis* 168 (1997) 431–441.
- [16] B.P. Block, J.C. Bailar Jr., *Journal of the American Chemical Society* 73 (1951) 4722–4725.
- [17] R.A. Boyse, E. Ko, *Journal of Catalysis* 171 (1997) 191–207.
- [18] M. Scheithauer, R.K. Grasselli, H. Knozinger, *Langmuir* 14 (1998) 3019–3029.
- [19] D.G. Barton, M. Shtein, R.D. Wilson, S.T. Soled, E. Iglesia, *Journal of Physical Chemistry B* 103 (1999) 630–640.
- [20] E.I. Ross-Medgaarden, W.V. Knowles, T. Kim, M.S. Wong, W. Zhou, C.J. Kiely, I.E. Wachs, *Journal of Catalysis* 256 (2008) 108–125.
- [21] M. Kantcheva, C. Koz, *Journal of Materials Science* 42 (2007) 6074–6086.
- [22] R. Zanella, A. Sandoval, P. Santiago, V.A. Basink, J.M. Saniger, *Journal of Physical Chemistry B* 110 (2006) 8559–8565.
- [23] F. Boccuzzi, G. Cerrato, F. Pinna, G. Strukul, *Journal of Physical Chemistry B* 102 (1998) 5733–5736.
- [24] R. Kydd, J. Scott, W.Y. Teoh, K. Chiang, R. Amal, *Langmuir* 26 (2010) 2099–2106.
- [25] J.-D. Grunwald, M. Maciejewski, O.S. Becker, P.F. Fabrizioli, A. Baiker, *Journal of Catalysis* 186 (1999) 458–469.
- [26] M. Maciejewski, P. Fabrizioli, J.-D. Grunwald, O.S. Becker, A. Baiker, *Physical Chemistry Chemical Physics* 3 (2001) 3846–3855.
- [27] M. Manzoli, A. Chiorino, F. Boccuzzi, *Surface Science* 532–535 (2003) 377–382.
- [28] F. Boccuzzi, A. Chiorino, *Journal of Physical Chemistry B* 104 (2000) 5414–5416.
- [29] F. Vindigni, M. Manzoli, A. Chiorino, F. Boccuzzi, *Gold Bulletin* 42 (2009) 106–112.
- [30] D. Guillemot, V.Y. Borovkov, V.B. Kazansky, M. Polisset-Thfoin, J. Fraissard, *Journal of the Chemical Society, Faraday Transactions* 93 (1997) 3587–3591.
- [31] S. Minico, S. Scire, C. Crisafulli, A.M. Visco, S. Galvagno, *Catalysis Letters* 47 (1997) 273–276.
- [32] M. Li, Z. Wu, Z. Ma, V. Schwartz, D.R. Mullins, S. Dai, S.H. Overbury, *Journal of Catalysis* 266 (2009) 98–105.
- [33] M.A. Dekkers, M.J. Lippits, B.N. Nieuwenhuys, *Catalysis Letters* 56 (1998) 195–197.
- [34] K.I. Hadjiivanov, G.N. Vayssilov, *Advances in Catalysis* 47 (2002) 307–511.
- [35] T. Venkov, K. Fajerweg, L. Delannoy, H. Klimev, K. Hadjiivanov, C. Louis, *Applied Catalysis A* 301 (2006) 106–114.
- [36] M.A. Centeno, K. Hadjiivanov, T. Venkov, H. Klimev, J.A. Odriozola, *Journal of Molecular Catalysis A: Chemical* 252 (2006) 142–149.
- [37] M. Mihaylov, B.C. Gates, J.F. Fierro-Gonzales, K. Hadjiivanov, H. Knozinger, *Journal of Physical Chemistry C* 111 (2007) 2548–2556.
- [38] M. Kantcheva, O. Samarskaya, L. Ilieva, G. Pantaleo, A.M. Venezia, D. Andreeva, *Applied Catalysis B* 88 (2009) 113–126.
- [39] D. Andreeva, M. Kantcheva, I. Ivanov, L. Ilieva, J.W. Sobczak, W. Lisowski, *Catalysis Today* 158 (2010) 69–77.
- [40] R. Meyer, C. Lemire, S.K. Shaikhutdinov, H.-F. Freund, *Gold Bulletin* 37 (2004) 72–124.
- [41] K. Musialska, E. Finocchio, I. Sobczak, G. Busca, R. Wojcieszak, E. Gaigneaux, M. Ziolk, *Applied Catalysis A* 384 (2010) 70–77.
- [42] V.A. Sadykov, V.V. Lunin, V.A. Matyshak, E.A. Paukshtis, A.Y. Rozovskii, N.N. Bulgakov, J.R.H. Ross, *Kinetics and Catalysis (Eng.)* 44 (2003) 379–400.
- [43] M. Kantcheva, A.S. Vakkasoglu, *Journal of Catalysis* 223 (2004) 364–371.
- [44] M. Kantcheva, I. Cayirtepe, *Catalysis Letters* 115 (2007) 148–162.
- [45] B. Tsyntsarski, V. Avreyska, H. Kolev, T. Marinova, D. Klissurski, K. Hadjiivanov, *Journal of Molecular Catalysis A: Chemical* 193 (2003) 139–149.
- [46] T. Weingand, S. Kuba, K. Hadjiivanov, H. Knozinger, *Journal of Catalysis* 209 (2002) 539–546.
- [47] M. Kantcheva, I. Cayirtepe, *Journal of Molecular Catalysis A: Chemical* 247 (2006) 86–98.
- [48] F. Solymosi, T. Bansagi, T. Suli Zakar, *Physical Chemistry Chemical Physics* 5 (2003) 4724–4730.
- [49] F. Solymosi, T. Bansagi, T. Suli Zakar, *Catalysis Letters* 87 (2003) 7–10.
- [50] H. Celio, K. Mudalige, P. Mills, M. Trenary, *Surface Science* 394 (1997) L168–L173.
- [51] G. Piazzesi, O. Kröcher, M. Elsener, A. Wokaun, *Applied Catalysis B* 65 (2006) 55–61.
- [52] F. Solymosi, T. Bănsági, *Journal of Physical Chemistry* 83 (1979) 552–553.
- [53] B. Bachiller-Baeza, I. Rodríguez-Ramos, A. Guerrero-Ruiz, *Langmuir* 14 (1998) 3556–3564.
- [54] K. Pokrovski, K.T. Jung, A.T. Bell, *Langmuir* 17 (2001) 4297–4303.
- [55] M. Kantcheva, E.Z. Ciftikli, *Journal of Physical Chemistry B* 106 (2002) 3941–3949.