Catalysis Letters Vol. 94, Nos. 3–4, May 2004 (© 2004)

Reduction of NO by H_2 on carbon film supported Ni catalysts – *in situ* FTIR study

Marek Wiśniewski* and Jerzy Zawadzki

Faculty of Chemistry, N. Copernicus University, Gagarin St. 7, 87–100 Toruñ, Poland

Received 25 March 2003; accepted 19 February 2004

The NO/H_2 reaction has been studied over a Ni loaded carbon film catalysts using *in situ* FTIR spectroscopy at the temperature range 25–350 °C. On these catalysts, the differences in activity and selectivity were found depending on the nature of the surface functional groups. These differences were correlated with transient infrared spectral features which appeared during the reaction. It has been proved experimentally that the chemical character of the support is of vital importance during the process. The rise in NO conversion and N_2 selectivity was observed when the surface of the catalysts was changed by the NH_3 chemisorption. Amide and/or imide species formed due to the reduction of ammonium salts of carboxylic acids can play a significant role as active centers during the NO reduction.

KEYWORDS: carbon films; FTIR; NO reduction; $DeNO_x$ catalysis.

1. Introduction

The catalytic conversion of nitric oxide, one of the noxious components of exhaust gases, has provided one of the most important scientific challenges of the past decades. NO_x removal with the use of various reductants (CO, NH_3, hydrocarbons etc.) has been attracting the attention for the years [1,2].

Here we report the results of NO reduction by H_2 on carbon-supported Ni catalysts to explain the high activity and N_2 selectivity of this carbonaceous material. Although several investigations of NO reduction by H_2 have been reported in the literature, a comprehensive *in situ* IR study of this reaction on carbon-supported Ni catalysts has not been provided yet.

The reduction of NO with H_2 may result in the reactions 1–3:

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O \qquad (1)$$

$$2NO + H_2 \longrightarrow N_2O + H_2O \qquad (2)$$

$$2NO + 5H_2 \longrightarrow NH_3 + 2H_2O \qquad (3)$$

The latter two reactions give rise to the undesirable reaction products N_2O and NH_3.

Many authors suggested the mechanisms of this process. Kokes [3] proposed that the NO/H_2 reaction proceeds via the formation of (HNO_x), a solid species that decomposed readily to yield N_2O, NH_3, and H_2O. The same intermediates or their oligomers were also postulated by several other authors [4,5].

Hecker and Bell [6] postulated that over a Rh/SiO_2 catalyst the NO dissociation proceeds with the assistance of an adsorbed H atom.

There are other suggestions [e.g. 7,8] preferring the dissociative chemisorption of NO, whereas the surface nitrogen atoms can either pair up with other nitrogen containing species on the surface to form N_2O or N_2, or undergo the hydrogenation to the end product of NH_3 through a series of NH_x intermediates. It has also been reported that there is a direct correlation between the concentration of NH_4^+ and NO_x conversion over vanadia–titania catalysts [9], and NH_4^+ are active species for the NO/NH_3 reaction in order to produce N_2. The authors suggested that the dissociation of adsorbed NH_4^+ species via the series of NH_x intermediates is the major reaction path for producing N_2O according to the following equation:

$$NH_x + NO \rightarrow N_2O + {}^{x}/_{2}\, H_2O \qquad (4)$$

Generally, the reaction between NO and H_2 over catalytic surfaces is very complex so numerous reaction intermediates and mechanisms have been suggested. The mechanism is usually system–specific and the generalization for all catalysts is very difficult.

On the other hand, the IR spectroscopy provides the information on the nature of the bonds formed between adsorbates and the surface of catalysts; it provides a unique means to obtain information on the intermediates and products on the surface of the catalysts. IR spectroscopy of carbon-supported metal catalysts has not received much attention due to the difficulty in obtaining IR spectra on these highly opaque materials. Due to the application of the carbon film technique [10], the problems of experimental spectroscopic investigations of surface phenomena on carbons have been solved to great extent. The method of producing carbon films and recording IR spectra by using the vacuum cell [10,11] has enabled the quick analysis of the reaction

---

* To whom correspondence should be addressed.
E-mail: marekw@chem.uni.torun.pl

1011-372X/04/0500–0135/0 © 2004 Plenum Publishing Corporation

products with the absolute minimum of the disturbance of the samples so as to avoid intervening secondary reactions.

The present work follows the previous study [12] and uses *in situ* FTIR, a proven technique for probing a catalyst surface, so as to investigate the mechanistic details of the NO/H_2 reaction over carbon and carbon-supported Ni catalysts. The additional information could then be combined with the kinetic data to provide better explanation of the experimental results.

Therefore, and in view of the current catalysts, an *in situ* FTIR spectroscopic investigation of NO/H_2 reaction is required. In this paper we want to prove that the role of surface functionalities, in the reduction of NO by H_2 in the absence of oxygen, is meaningful.

2. Experimental

Carbon films used in this study were prepared from cellulose. The raw material used for carbonization was cellophane purified in 20% HCl and washed repeatedly in distilled water. The charring experiments were setup as follows: cellulose films carbonized at 300 °C in air for 1 h were evacuated at 600 °C for 1 h under dynamic vacuum (0.13 Pa). Then the samples were exposed to O_2 (101.3 Pa) at 300 °C for 1 h and evacuated (0.13 Pa) at 200 °C. Metal-loaded carbon samples denoted $C_{ox}Ni$, were prepared by the impregnation procedure using 0.5 M nitrate aqueous solutions as a precursor. For all samples the metal loading level was set at 1 wt%. For catalytic tests, the powdered carbon samples obtained from cellulose were prepared in a similar way. The samples after ammonia chemisorption at 25 °C for 1 h, were heated in pure Ar at 350 °C for 1 h are denoted $C_{ox}(NH)$ and $C_{ox}Ni(NH)$.

The activity measurements were made at the atmospheric pressure. The catalytic tests were carried out in a 4 mm ID, quartz tube, down-flow reactor. 50 mg of the catalyst was placed between two layers of glass wool, and pretreated for 1 h at 350 °C in Ar, at the flow rate of 50 ML/min and cooled to 25 °C in this gas. Then the catalysts were heated to the reaction temperature in the mixture of reagent gases. The gases: NO (1800 ppm in Ar) and H_2 (10% in Ar) were mixed to obtain the desired gas composition–1440 ppm of NO and 2.5% of H_2 in Ar. The total feed gas hourly space velocity GHSV was 60,000 $cm^3\ g^{-1}\ h^{-1}$ and H_2/NO ratio 17. Before the data were obtained, the reactions were maintained for a period of about 60 min, continuously observed, at each temperature to ensure steady-state conditions.

The analysis of products was performed on-line by FTIR. The gas stream flowed through a multiple pass IR cell (Sirocco Series Gas Cell, 2 m Total pathlength, and the volume 190 cm^3) in the beam of a Mattson Genesis II spectrometer. The spectra were acquired at 4 cm^{-1} resolution through the coaddition of 64 scans.

The integrating values of absorbances of individual lines NO (1970–1780 cm^{-1}), N_2O (2280–2150 cm^{-1}) and NH_3 (1221–745 cm^{-1}) were calibrated against diluted standard mixtures. The integration, and hence concentrations, were reproducible to less than 1%.

The N_2 concentration was obtained from the reaction relationship assuming that NO reacts to form either N_2 or other compounds as N_2O and NH_3. The selectivity was obtained from the relationship $[X]/([N_2]+[N_2O]+[NH_3])$ where $X = N_2, N_2O, NH_3$.

Infrared spectroscopic studies were carried out in a vacuum cell described previously [11]. The cell's construction enabled the thermal treatment of the carbon film up to 1000 °C in any controlled atmosphere or in the vacuum. IR spectra were recorded for the samples after they had been cooled down to the room temperature. Spectral changes accompanying the adsorption of reactants (presented in figure 4) were corrected for background by subtracting the original spectrum of the $C_{ox}Ni$ sample.

The surface characteristic was determined using a Micromeritics ASAP 2010 apparatus.

3. Results and discussion

Taking into consideration the results of low-temperature nitrogen adsorption isotherms the structure of carbons was characterized using the following methods:

- BET equation [13] (in the range of relative pressure 0.05 up to 0.3) to calculate the apparent surface areas S_{BET}.
- The DFT method [14] was applied to calculate pore volume V_{DFT} of the investigated samples. The micropore volumes V_{DFT}^{micro} were calculated for all the pores with diameters smaller and/or equal to 2 nm.

The parameters obtained using the methods mentioned above are shown in table 1.

Table 1
Structural data of carbon film samples

Adsorbent	Surface areas [m^2/g]	Pore volumes (cm^3/g)				Micropore diameters (nm)		
	S_{BET}	$V_{DFT,I}^{micro}$	V_{DFT}^{micro}	V_{DFT}^{meso}	V_{DFT}	$X_{av,DFT,I}$	$X_{av,DFT,II}$	$X_{av,DFT,tot}$
C_{ox}	520.1	0.178	0.202	0.008	0.210	0.536	1.432	0.626
$C_{ox}Ni$	496.8	0.174	0.196	0.014	0.210	0.537	1.348	0.577

It can be noticed that the investigated samples possess lower (by about 50%) apparent BET surface areas than typical commercial carbons [15]. It can be seen that the total volumes of mesopores as well as their surface areas are very small. Thus, the studied carbons, as it was previously reported [16] can be regarded as microporous solids.

The results obtained on the basis of DFT analysis indicate in the case of the studied samples, that the pores are grouped around two main diameters (table1). The first one approaches 0.5–0.6 nm while the other one oscillates in the range of 1.3–1.5 nm. It is seen that the volume of the primary micropores ($V_{\mathrm{DFT,I}}^{\mathrm{micro}}$) contributes about 90% to the total volume of micropores (determined from DFT – cumulative pore size distribution). The loaded metal (1% wt.) changes the above parameters slightly.

Thus, the studied materials, according to DFT method, possess nearly homogeneous microporosity and one should concentrate more on the surface chemistry instead of the pore structure.

The nitric oxide reduction by H_2, over carbon-supported Ni catalysts, was studied in the temperature range from 25 to 350 °C.

The different activities of the catalysts during the NO reduction by H_2, depending on the chemical character of the support, are shown in figure 1. It was found that, under the conditions of 50 mL/min of the total gas stream (the gas composition: 1440 ppm NO/Ar and the ratio $H_2/NO = 17$), the Ni-loaded oxidized carbon film ($C_{ox}Ni$) – line 1, was practically inactive when the temperature increased from the room temperature to 200 °C. Above the temperature 225 °C the percent of decomposition increased rapidly and reached 52% at 250 °C. The further increase in the reaction temperature caused a 100% conversion of NO at 300 °C. In the case of the sample after the chemisorption of NH_3 at the room temperature and heating in the Ar at 350 °C – $C_{ox}Ni(NH)$ (line 2) the percent of decomposition increased continuously from about 5% at 125 °C to 68% at 225 °C. The 100% conversion was reached at about 275 °C.

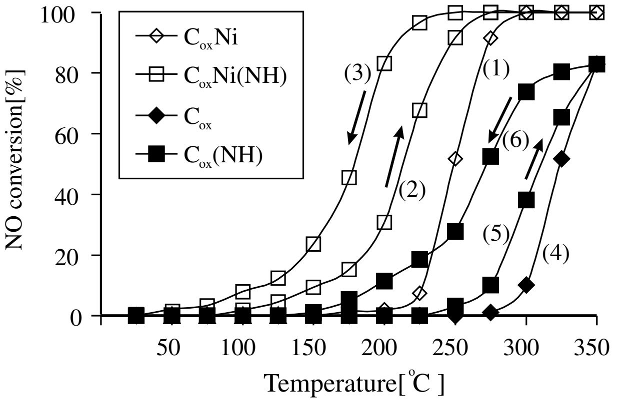

Figure 1. Catalytic activity for reduction of NO by H_2 on carbon and carbon-supported Ni catalysts. Reaction conditions: $[NO]_o = 1440$ ppm, $[H_2]_o = 2.5\%$, $m_{cat} = 50$ mg, total gas flow 50 mL/min.

The lines 2 and 3 in figure 1 show a heat and cool cycle under steady state conditions. Therefore, it is clear that a large hysteresis in the consumption of NO exists. The catalyst is more active on the cooling branch than on the heating branch.

After the heating the consumption of NO starts at 125 °C. It leads to the formation of N_2, NH_3, and H_2O. At about 275 °C the concentration of NO decreases to zero. On the cooling branch (line 3) the 100% NO conversion is maintained without changes until the temperature of 225 °C is reached. Although the NO conversion starts to drop after the further decrease in the reaction temperature it is still higher at adequate temperatures.

In the case of the sample without the metal loading the catalyst (C_{ox}) is inactive when the reaction temperature does not pass 275 °C. The further increase in the reaction temperature causes the increase in NO conversion to 83% at 350 °C. The sample after NH_3 chemisorption – $C_{ox}(NH)$ causes the rise in the activity – 3% at 250 °C, 38 % at 300 °C and 84% at 350 °C. The hysteresis (lines 5,6) on this sample is also observed and the catalyst is more active on the cooling branch.

The above results suggest that some surface species, formed during the reaction, could catalyze the process.

The NH_3 and N_2O have been previously suggested as unwanted reaction products during nitrogen formation in the process of NO reduction [17–19].

As shown in figure 2, the N_2 selectivity in NO/H_2 reaction over a $C_{ox}Ni$ catalyst increases continuously from 40% to 75% when the reaction temperature increases from 225 to 350 °C. The $C_{ox}Ni(NH)$ sample is characterized by higher selectivity at the same temperatures. It increases with the increase in the temperature from 31% to 80% at 100 °C and 350 °C respectively. On the cooling branch the N_2 selectivity is higher at the same temperatures and decreases slightly to 69% at 175 °C. After the further decrease in the reaction temperature the decrease in the N_2 selectivity to 35% at 50 °C is observed.

The N_2O selectivity on the $C_{ox}Ni$ sample decreases drastically from 40% at 200 °C to 3% at 250 °C. In the case of the $C_{ox}Ni(NH)$ sample the N_2O selectivity on the heating branch decreases with the rise in the reaction temperature from 69% at 100 °C and drops to zero at 225 °C. While cooling N_2O is not present in the gas stream unless the temperature drops below 200 °C. The further decrease in the temperature causes the continuous increase in the N_2O selectivity to 65% at 50 °C.

The NH_3 selectivity on $C_{ox}Ni$ sample increases drastically from 24% at 200 °C to 50% at 250 °C. The further rise in the temperature cases the decrease in NH_3 selectivity to 25% at 350 °C. In the case of the $C_{ox}Ni(NH)$ sample the NH_3 selectivity on the heating

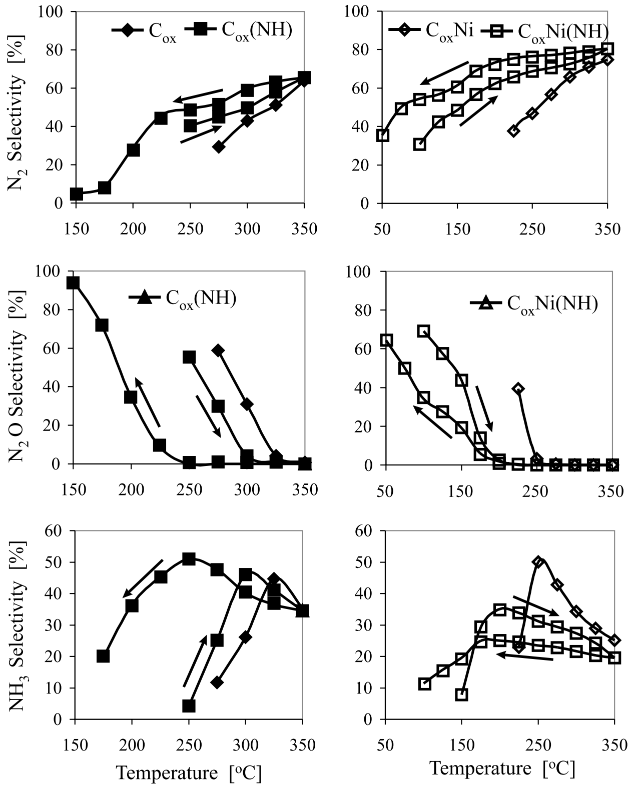

Figure 2. Selectivity of NO/H_2 reaction. Reaction conditions: $[NO]_o$ = 1440 ppm, $[H_2]_o$ = 2.5%, m_{cat} = 50 mg, total gas flow 50 mL/min.

branch reaches the maximum at 200 C (35%) and on the cooling branch at 175 °C (26%).

The changes in the selectivity of the reaction were also observed on the sample without metal loading and observed changes are analogous to those presented above. The rise in the reaction temperature caused the increase in the N_2 selectivity, the decrease in the N_2O selectivity and the initial increase and then the decrease in the NH_3 selectivity.

The observed phenomena can be explained by the fact, that not only NH_4^+ ions catalyze the reaction, as it was previously suggested [9]. The products of the reduction of ammonium salts of carboxylic acids, risen during the reaction of NH_3 with the carbon surface [11,20,21], also play a role as the active centers in the reaction.

The above results show clearly that in the case of carbon and carbon-supported Ni catalysts, the activity and selectivity are influenced by the supported surface functional groups.

It is not easy to explain the role of Ni in the process because XRD measurements of C_{ox}Ni, C_{ox}Ni(NH) catalysts, show no diffraction signal of Ni compounds. It suggests that the Ni species on the surface are of small size and are highly dispersed on the carbon film surface.

To get a better insight into the processes that are responsible for the observed phenomena, the knowledge of the species which are present on the surface during the reaction is needed.

Figures 3 and 4 show spectral changes of an oxidized Ni promoted carbon film after the exposure to NO in H_2 atmosphere.

The IR spectrum of the initial sample (spectrum 1 in figure. 3) reveals the presence of absorption bands at 1850, 1780 and 1753 cm^{-1}, which indicates that some of acidic surface groups of carbon are cyclic anhydrides and probably lactone structures. The results of surface acidity studies of a carbon film have been reported previously [11]. The band at 1600 cm^{-1} is probably due to a C\dbondC stretching mode that is weakly active in the IR because of the breakdown of selection rules. An oxidized layer gives enough asymmetry to a polyaromatic network, i.e. a dipole moment changes with vibrations to form what is basically a C\dbond C mode IR active at 1600 cm^{-1}.

After the exposure of the oxidized carbon containing Ni to the mixture of NO and H_2 at room temperature (spectrum 2) the characteristic bands of physically adsorbed NO molecules are not observed. The intensities of all the IR features change very little during the reaction at temperatures below 200 °C, suggesting that C_{ox}Ni did not exhibit any activities in the NO conversion at these temperatures.

The rise in the reaction temperature to 200 °C (spectrum 3) caused the rise in the intensity of broad absorption bands within the range of 3700–3200 cm^{-1} corresponding to OH stretching vibrations, which indicates the formation of hydrogen bonds. The presence of the ν_{OH} bands as well as the band at 1725 cm^{-1} indicates the formation of the carboxylic groups arisen as a result of the reaction of cyclic anhydrides with H_2O.

Such changes probably mean the dissociative adsorption of NO on the surface of the catalyst according to the scheme:

$$NO_{(g)} + s \longleftrightarrow NO_{(ad)} \tag{5}$$

$$NO_{(ad)} + s \longrightarrow N_{(ad)} + O_{(ad)} \tag{6}$$

$$N_{(ad)} + NO \longrightarrow N_2O_{(g)} \tag{7}$$

$$O_{(ad)} + H_2 \longrightarrow H_2O_{(ad)} \tag{8}$$

This sequence stays in good agreement with the findings of the catalytic test and other investigators suggestions [e.g. 23], according to whom the idea of the dissociation of NO is the first step in the NO reduction.

The further rise in the reaction temperatures above 200 °C caused the changes typical of the reaction of ammonia with a carbon surface (figure 3 spectra 4–6, figure. 4 spectra 1–3).

The disappearance of acidic structures (figure 4) as the negative peaks at 1850 and 1780 cm^{-1} was observed. The positive signals at 1575, 1380 and 1455 cm^{-1}, attributed to the ν_s (COO^-), ν_{as} (COO^-) and ν_{as} (NH_4^+) respectively, appear due to the process of the creation of

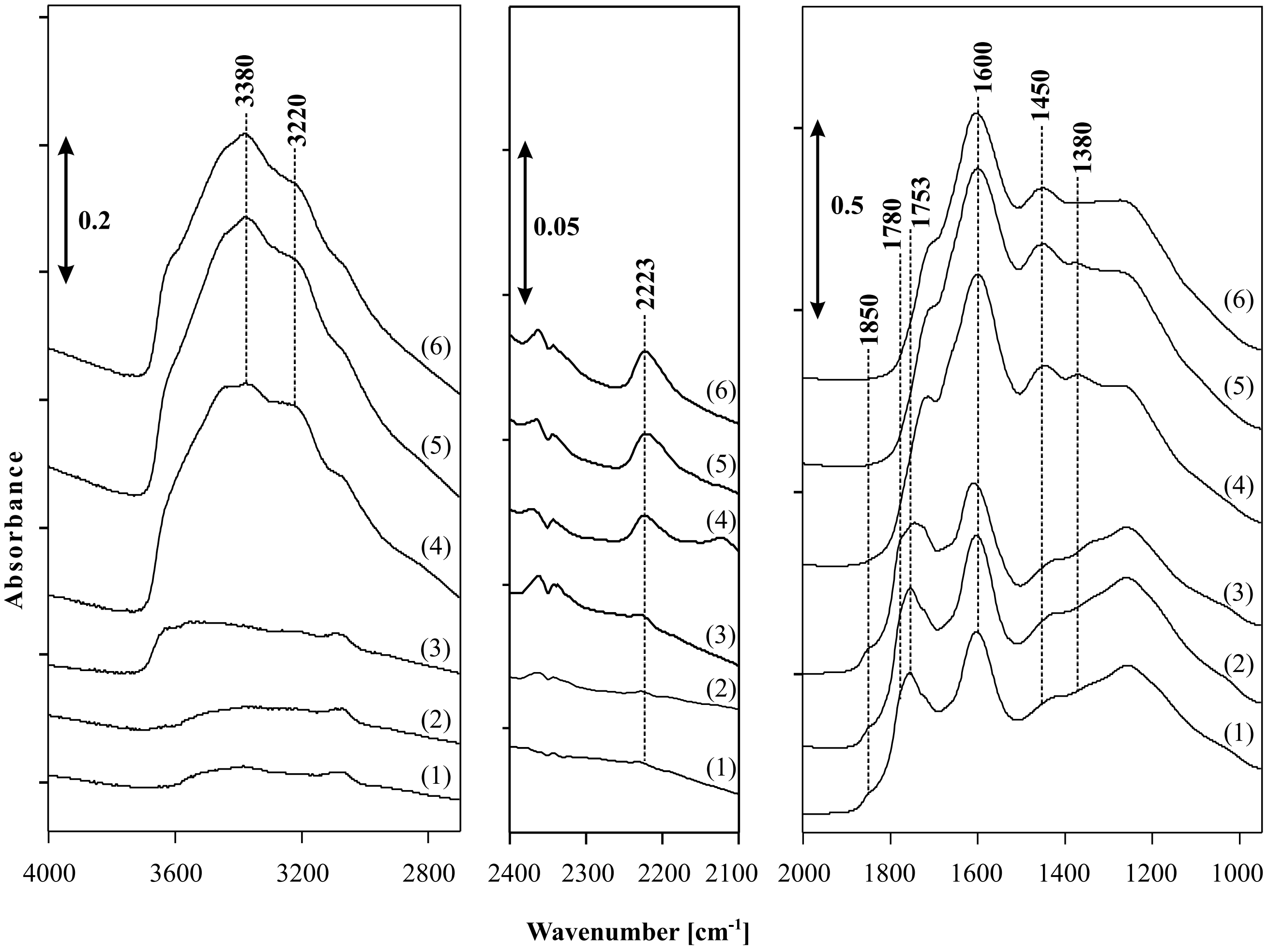

Figure 3. FTIR Spectra of $C_{ox}Ni$ sample (1) recorded after reaction of 2.29 kPa NO and 39,5 kPa H_2 at (2) 25 °C, (3) 200 °C, (4) 250 °C, (5) 300 °C, (6) 350 °C.

ammonium salts of carboxylic acids. The decomposition and rearrangement of surface ammonium structures starts at the temperatures of about 300 °C (figure 3 spectra 5, 6; figure 4 spectra 2, 3) where surface amide and imide structures are formed [11,22].

The above results prove that products of NH_3 chemisorption are of decisive importance in the process of NO reduction by H_2 on Ni loaded oxidized carbon surfaces.

IR spectra collected from $C_{ox}Ni$ after the NO/H_2 mixture reaction and then the following subsequent evacuation at 25 and 200 °C are shown in spectra 4, 5 in figure 4. After outgassing at 25 °C (spectrum 4) the decrease in the intensities of the following bands may be observed: 3220 cm^{-1} (ν_{as} NH_4^+), 1455 cm^{-1} (δ_s NH_4^+), as well as the bands at 1575 cm^{-1} (ν_s COO^-) and 1380 cm^{-1} (ν_{as} COO^-). Moreover, the desorption process at 25 and 200 °C reveals the presence of the overlapped bands in the region of NH/OH stretching vibrations with one clear band at 3380 cm^{-1}. In the region of 1700–1200 cm^{-1} after evacuation at room temperature the spectral features are diminished by strong and broad absorptions centered at 1585 and 1320 cm^{-1}. The bands appearing in the 1690–1650 cm^{-1} region, due to the C\doublebond O stretching vibrations are often referred to as the amide I band [24]. The amide II band – weakly marked as a left shoulder of the band at 1585 cm^{-1} – is the band at 1620 cm^{-1}.

The absorption bands near 1580 and 1320 cm^{-1} are observed frequently when NH_3 is present in the gas phase, either as a substrate or product of the process, and usually atributed to the surface $-NH_x$ ($x = 1, 2$) species [e.g. 11,23,25].

The presence of these compounds suggests the mechanism in which NO react with $-NH_x$ compounds producing the N_2 and H_2O over these catalytic systems.

The results presented above stay in good agreement with other authors who postulated that the NH_x surface species could be the intermediates of SCR pathway [11,23].

Presented data justify the hypothesis that over these Ni catalysts a path might be similar to that proven by isotopic labeling for different catalysts [26,27].

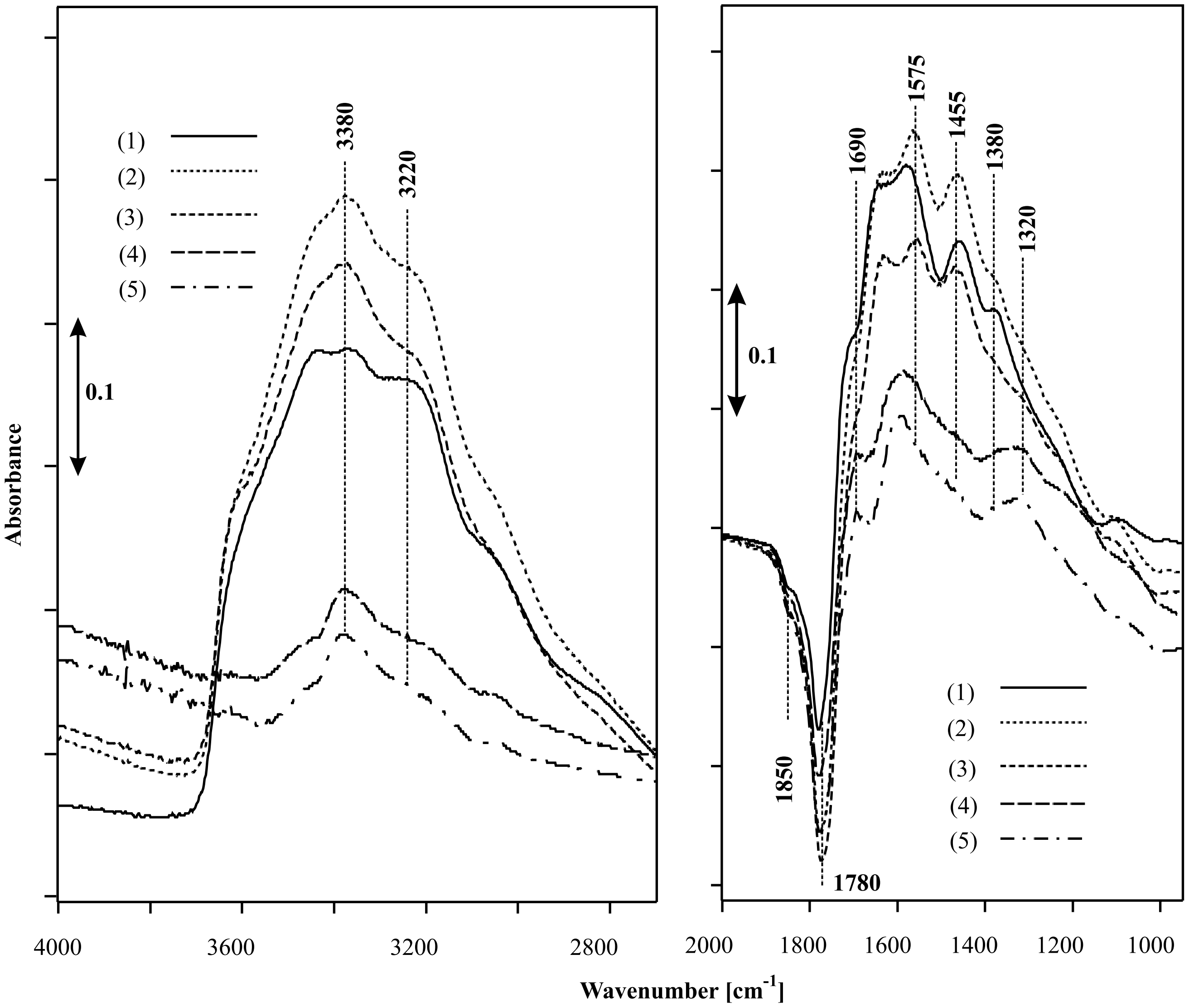

Figure 4. FTIR spectra recorded after exposure of $C_{ox}Ni$ to a gas mixture of 2.29 kPa NO and 39,5 kPa H_2 at (1) 250 °C, (2) 300 °C, (3) 350 °C and desorption processes of $C_{ox}Ni$ sample after NO/H_2 reaction at 350 °C at (4) 25 °C, (5) 200 °C. Spectra were corrected for the background by subtracting the original $C_{ox}Ni$ spectrum.

In which the N–N bond is formed between an N atom in a reduced state and another N atom in an oxidized state.

It is interesting to note that the exposure of NO/H_2 to the carbon–Ni catalyst at temperatures above 250 °C (figure 3) gave rise to the band at 2223 cm^{-1}. According to our previous reports [12,22,28] this corresponds to surface isocyanate (–NCO) species. According to the literature [29,30,31] the NCO species are formed due to the reaction between NO and CO.

Taking into consideration the fact that during catalytic tests CO was not present in the gas stream, we propose another possibility of forming the –NCO species on the carbon surface. NCO is probably formed due to the internal rearrangement and/or the decomposition of ammonium salts of carboxylic acids.

4. Conclusion

In this work the reduction of NO by H_2 was studied by *in situ* infrared spectroscopy combined with a continuous flow microreactor on a Ni loaded oxidized carbon film. The results of this study can be summarized as follows:

- the method of producing carbon films was an effective technique for FTIR investigations of carbon and carbon-supported catalysts;
- the NO/H_2 reaction in the strongly reducing atmosphere took place on a carbon-supported Ni catalyst at the temperatures relatively as low as 50–350 °C.
- the IR spectra show that the physical adsorption of NO on a carbon and carbon-supported Ni catalyst is very low;

- the conversion of NO and the N_2 selectivity depend on the chemical character of the support; NH_3 produced in this reaction reacted subsequently with the carbon surface to produce surface structures in the form of ammonium salts of carboxylic acids; due to their reduction amide species are formed; although all of these compounds can play a significant role as active centers in NO reduction, the surface nitrogen containing surface species in a form of $-NH_x$ probably promote the formation of N_2;
- it needs further investigations to explain the role of the –NCO surface structures in the process; it is still not clear whether those species are the intermediates in the main path or if they are the byproducts hampering the efficiency of the process.

References

[1] G. Busca, L. Lietti, G. Ramis and F. Berti, Appl. Catal. B 18 (1998) 1.
[2] F.G. Dwyer, Catal. Rev. 6 (1972) 261.
[3] R.J. Kokes, J. Phys. Chem. 70 (1996) 296.
[4] N.E. Tretyakov and V.N. Filimonov, Kinet. Katel. 11 (1969) 989.
[5] R.D. Gonzalez and D.E. Audette, J.Catal. 17 (1970) 116.
[6] W.C. Hecker and A.T. Bell, J. catal. 92 (1985) 247.
[7] K. Otto and H.C. Yao, J. Catal. 66 (1980) 229.
[8] A.A. Davydow and A.T. Bell, J. Catal. 49 (1977) 345.
[9] N.-Y. Topsoe, Science 265 (1994) 1217.
[10] J. Zawadzki, Polish J.Chem 54 (1980) 1257.
[11] J. Zawadzki, in: *Chemistry and physics of carbon*, Vol. 21, P.A. ed. Thrower, (Dekker, New York, 1989) pp. 147–380.
[12] J. Zawadzki and M. Wiœniewski, Carbon 40 (2002) 119.
[13] S. Brunauer, P.H. Emmett and E. Teller, J. Am. Chem. Soc. 60 (1938) 309.
[14] N.A. Seaton, J.P.R.B. Walton and N.A. Quirke, Carbon 27 (1989) 853.
[15] G. Rychlicki, A.P. Terzyk and W. Majchrzycki, J. Chem. Technol Biotechnol. 74 (1999) 329.
[16] A.P. Terzyk, P.A. Gauden, J. Zawadzki, G. Rychlicki, M. Wiœniewski and P. Kowalczyk, J. Coll. Inter. Sci. 243 (2001) 183.
[17] S.Galvagno and G. Parravano, J. Catal. 55 (1978) 178.
[18] J.Y. Lee and J. Schwank, J. Catal. 102 (1986) 207.
[19] T.M. Salama, R. Ohnishi, T. Shido and M. Ichikawa, J. Catal. 162 (1996) 169.
[20] J. Zawadzki, Carbon 19 (1981) 19.
[21] J. Zawadzki, Pol. J. Chem. 55 (1981) 1875.
[22] J. Zawadzki and M. Wiśniewski, Fuel Proc. Techn. 77–78 (2002) 389.
[23] G. Ramis, G. Busca, F. Bregani and P. Forzatti, Appl. Catal. 64 (1990) 259.
[24] J. Jakes and S. Krimm, Spectrochim Acta 27A (1971) 35.
[25] A.G. Moritz, Spectrochim. Acta 16 (1996) 1176.
[26] H-Y. Chen, T. Voskoboinikov and W.M.H. Sachter, J. Catal. 186 (1999) 91.
[27] Q. Sun, Z-X. Gao, H-Y. Chen and W.M.H. Sachter, J. Catal.201 (2001) 89.
[28] J.Zawadzki, M. Wiœniewski and Skowrońska, Appl. Catal. B 35 (2002) 255.
[29] S.S.C. Chuang and C. Tan, Catal. Today 35 (1997) 369.
[30] H. Oka, T. Okada and K. Hori, J. Mol. Catal. A 109 (1996) 51.
[31] A.Satsuma, A.D. Cowan, N.W. Cant and D.L. Trimm, J. Catal. 181 (1999) 165.