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HC-SCR of NO_x over Ag/alumina: a combination of heterogeneous and homogeneous radical reactions?

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Abstract

Matrix isolation combined with EPR and FT-IR technique at low temperature has been used to study the gas phase species involved in HC-SCR over a highly active Ag/alumina catalyst. A combination of heterogeneous and homogeneous (radical) reactions is proposed to take place over a Ag/alumina catalyst during HC-SCR. Radicals of low molecular weight were trapped in a growing argon matrix behind the Ag/alumina catalyst. In the same matrix, cyanogen isocyanate was detected and is suggested to be a key intermediate for the formation of amines and ammonia via the hydrolysis of isocyanate species.

Keywords: HC-SCR; Ag/alumina; MS; EPR; FT-IR; Matrix isolation

1. Introduction

Since the early work of Held et al. [1] and Iwamoto et al. [2] selective catalytic reduction of NO_x with hydrocarbons (HC-SCR) has received a lot of interest. A large number of solid catalyst systems applying various hydrocarbons have been reported in the open literature. Among these, silver supported on alumina has proven to be a highly active catalyst both in laboratory and engine bench tests [3]. However, the reaction mechanism has not been comprehensively explained for any of the model hydrocarbons reported due to the complicated reactions over the catalyst and therefore the optimisation of the low temperature region (150–300 °C) has remained as a challenge.

Strongly bound nitrates and nitrites as well as adsorbed oxygenates have commonly been suggested to be the main surface species. Isocyanate species (–NCO) are considered to be one of the key intermediates during the reduction path [4–8]. Such results are based on extensive in situ surface FT-IR measurements, which reveal fundamental information about the reaction mechanism. However, Eränen et al. [9] and Klingstedt et al. [10] have shown that HC-SCR over Ag/alumina is not purely a heterogeneous reaction, but a combination of heterogeneous and homogeneous reactions. The specificity of such phenomenon is that the catalyst surface can generate radicals or other type of activated species, which effectively desorb from the catalyst surface and react in the gas phase. Radical generation over heterogeneous surfaces has been reported by Cavani and Trifiro [11]. Thus, although the surface sensitive methods (e.g. surface FT-IR) are of crucial importance to elucidate reactions occurring on the surface, they cannot alone provide all the essential data needed to explain the whole reaction mechanism. Nanba et al. [12] have found NO, NO_2, NH_3, C_2H_4, HCHO, HCN, HNCO and nitroethylene in the gas phase formed in HC-SCR over H–ferrierite. In [13], we propose that one of the key roles of the Ag/alumina catalyst is to activate NO (possibly transform it into radicals or ions),

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which then react in the gas phase with N-containing functional groups. However, the detection of activated species, such as radicals, is difficult due to their limited lifetime, which can be calculated in fractions of second.

Experimental detection of free radicals can be done with matrix isolation of radicals, combined with IR and EPR spectroscopy, photoelectron spectroscopy, multiphoton and resonance ionisation methods [14,15]. In this work the effluent from a Ag/alumina catalyst was isolated in argon matrix and studied by means of EPR and FT-IR technique to identify different gas phase species formed over the catalyst.

2. Experimental

2.1. Catalyst preparation and activity tests

The 2 wt.% Ag/alumina catalyst was prepared by impregnation of commercial alumina support (A 201, LaRoche Chemicals Inc.), which is a mixture of χ, ρ, η and pseudo-γ phases, with a silver nitrate solution according to the procedure described in Ref. [3]. The catalyst was dried at room temperature and at 100 °C before calcination at 550 °C for 3 h in air. Before testing in a fixed bed quartz reactor, the catalyst was crushed and sieved to fractions between 250 and 500 μm. A temperature range of 150–600 °C with sampling at steady-state conditions with GHSV = 60 000 h^{-1} and total flow rate of 550 ml/min was used for the catalytic activity runs. The fed gas mixture used in the activity tests consisted of 500 ppm NO, 375 ppm octane, 6 vol.% O_2, 10 vol.% CO_2, 350 ppm CO, 12 vol.% H_2O and He as a balance. All the gases were of high purity (AGA) and were introduced into the reactor by means of mass flow controllers (Brooks 5850). The addition of octane took place via a syringe pump (CMA 102/ Microdialysis). The effluent gas was analysed by a Chemiluminescence NO_x-analyzer (API model 200AH) and a GC (HP 6890 series). In separate experiments a commercial Pt supported oxidation catalyst (Johnson Matthey) was placed directly after the Ag/alumina catalyst to prove the gas phase reactions (Table 1).

Table 1
NO to N_2 conversion over single bed Ag/alumina vs. Ag/alumina together with commercial oxidation catalyst (JM)

NO to N_2 conversion (%)		
Temperature (°C)	Ag/alumina	Ag/alumina + oxidation catalyst (0 mm between beds)
300	0	0
350	35.7	7.2
400	80.1	27.4
450	91	53.9
500	89.8	60.9
550	77.1	61.2
600	56.4	47.1

2.2. Transient experiments using mass spectrometry

A quadrupole mass spectrometer (Balzers Omnistar) was used to analyse the gas phase components during transient experiments. In transient experiments, 0.4 g of the Ag/ alumina was packed in a quartz reactor and the effect of changing compositions and introduction sequences of O_2, NO and octane at 250 and 450 °C on the mass spectra were recorded. In parallel the amounts of CO, CO_2 and N_2 were determined using the GC technique as described earlier. Prior to the experiments the catalyst was oxidised in a gas mixture containing 6 vol.% O_2 and 10 vol.% water at 400 °C for 30 min. During the experiments the concentrations of O_2, NO and octane were 6 vol.%, 500 ppm and 375 ppm, respectively.

2.3. EPR and FT-IR combined with matrix isolation technique

Matrix isolation in combination with EPR and FT-IR were used for qualitative study of the species evolving from the catalyst surface into the gas phase. Two gas mixtures: (a) 1000 ppm NO, 750 ppm *n*-octane and Ar as balance, total pressure in the bulb 1000 mbar and (b) 60 000 ppm O_2 and Ar as balance, total pressure in the bulb 1000 mbar were prepared in 1 dm^3 glass bulbs for EPR measurements. The mixtures were led in separate lines to the reactor inlet, where they were mixed before reaching the catalyst. The rate of pressure drop in the bulb measured by pressure controllers (MKS Baratron Capacitance Manometers, type 622) was 2.6 mbar/min. Deposition time was 15 min resulting in total deposition of 40 mbar. Behind the catalyst bed the effluent gas was trapped immediately in the growing argon matrix at 18 K and the spectrum was scanned using EPR spectrometer (Bruker ESP-380). After this, the spectrum was annealed to 34 K and re-scanned. A reference run without the catalyst was measured using the same temperature and gas mixtures. Catalyst temperature was kept at 350 °C by using a block heater during the deposition.

For FT-IR experiments following gas mixtures: (a) 1500 ppm C_8H_{18}, 12 vol.% O_2 and (b) 2000 ppm NO, were prepared. Argon was used as balance gas in both bulbs and the total pressure was fixed to 1000 mbar. The two gas mixtures were led in separate lines to the reactor inlet, where they were mixed before reaching the catalyst. Flow rate of 1.3 mbar/min was used according to the method described for EPR and the total amount of deposition was 65 mbar in each run. The effluent was trapped immediately behind the catalyst bed in the growing argon matrix at 10 K in the cryostat (Displex DE-202S (10 K)). After the deposition the spectra were recorded using FT-IR spectrometer (Nicolet Magna-IR 760 ESP). Two catalyst temperatures, 250 and 400 °C, were used for all experiments. In both EPR and FT-IR experiment the pressure in the cold cell was approximately 7×10^{-7} bar.

3. Results and discussion

3.1. Catalyst activity

The results of the activity tests carried out over Ag/alumina alone and Ag/alumina in combination with an oxidation catalyst are shown in Table 1. As can be seen the single bed Ag/alumina catalyst reaches maximum NO to N_2 conversion of approximately 90% at 450 °C. Characteristic for the catalyst is the coinciding production of CO from the incomplete combustion of the hydrocarbon. Therefore, an oxidation catalyst was placed behind the Ag/alumina to remove the formed CO. As a consequence the NO to N_2 conversion drops significantly, which is a clear indication that gas phase reactions take place immediately after the Ag/alumina bed. The formed N-containing species are likely to get oxidised over the Pt containing catalyst prior to reaction to N_2.

3.2. Transient experiments using mass spectrometry

In the first experiment, at 250 °C, octane and oxygen was fed through the catalyst bed resulting in a characteristic mass spectrum of octane (not shown). From GC analyses it was calculated that 35.2% octane was converted into CO (∼1.5%) and CO_2 (∼33.7%) using only oxygen and octane as reactants. When NO was added to the gas mixture the corresponding conversion of octane rose slightly to 45.7% (CO_2 ∼ 42.2% and CO ∼ 3.5%) but the peak pattern remained almost unchanged (not shown). The experiment was repeated at 450 °C. When only octane and oxygen was fed through the catalyst a characteristic mass spectrum for octane was recorded again (Fig. 1). In the GC analyses the conversion of octane to CO (∼10%) and CO_2 (∼58.7%) increased to 68.7% compared with experiment at 250 °C. After NO addition, a drastic change of the mass spectrum took place (Fig. 1). Most of the characteristic octane peaks were consumed to a great extent. Interestingly, only the strongest peaks in the pattern disappeared or decreased considerably in sizes, whereas the peaks with lower intensities changed less. The peak pattern became tilted to the opposite and strong peaks started to dominate at the mass numbers where earlier in the presence of only octane and oxygen were weaker peaks. This means probably that most of the octane is oxidised to CO and CO_2 and the rest is transformed into other species, giving rise to a fully new mass spectrum pattern. It has been shown [9] that nitriles are formed over Ag/alumina at 400 °C using octane + NO in excess of oxygen. As can be expected peaks at mass numbers 30 (NO), 28 (CO or N_2) and 44 (CO_2 or N_2O) appeared or grew immediately when NO was introduced the feed. GC analyses showed a 94.1% conversion of octane into CO (∼12.9%) + CO_2 (∼81.2%) in the presence of NO, which means that NO significantly contributes, at this temperature, to the oxidation activity of octane over Ag/alumina. It is to be noted that at 450 °C most of the introduced NO is converted to N_2.

In order to investigate how fast the reaction between NO and octane takes place, the catalyst was scanned during 30 cycles. The five first cycles were carried out using octane and oxygen, whereas the rest of the cycles contained NO in addition. Every cycle was completed in 24 s, which means that the response was rather fast as can be seen in Fig. 2. Already in the first cycle containing NO (sixth), the intensities differed considerably from the previous scan containing only oxygen and octane. In the eighth cycle, at steady state, the mass spectrum has drastically changed, especially regarding the characteristic peaks of octane.

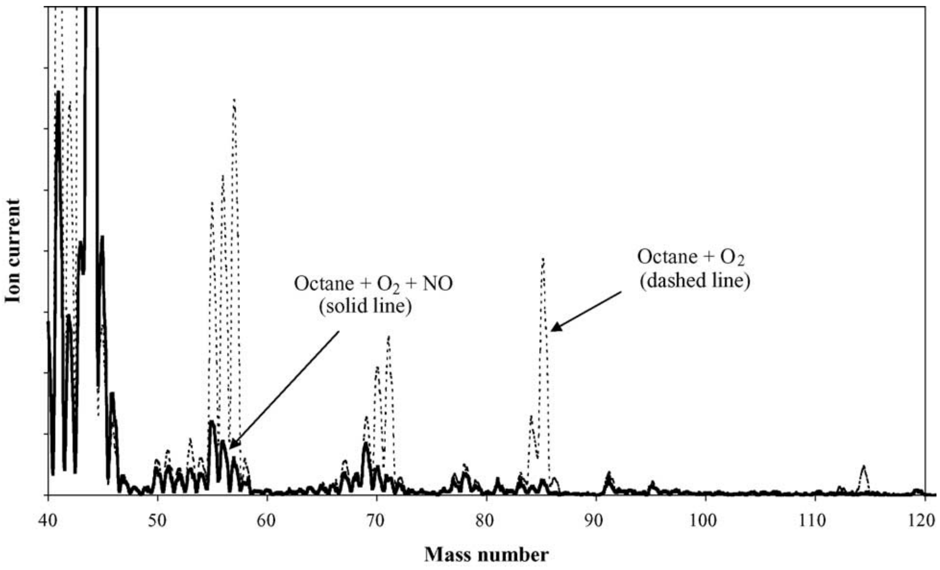

Fig. 1. Mass spectrum of leaving gases from Ag/alumina at 450 °C, using gas mixtures containing 375 ppm C_8H_{18} and 6 vol.% O_2 (dashed line) and 375 ppm C_8H_{18}, 500 ppm NO and 6 vol.% O_2 (solid line).

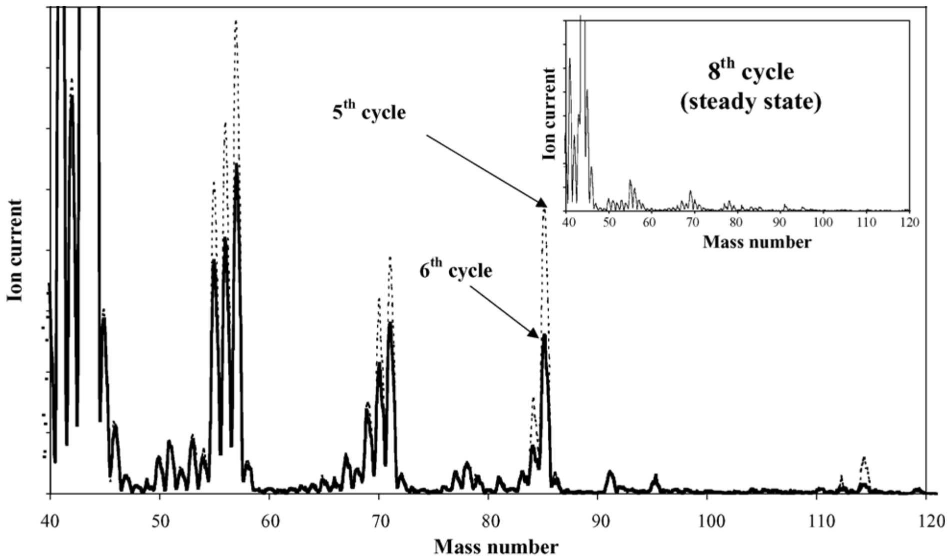

Fig. 2. Mass spectrum of fifth (375 ppm C_8H_{18} + 6 vol.% O_2; dashed line), sixth (375 ppm C_8H_{18} + 500 ppm NO + 6 vol.% O_2; solid line) and eighth (375 ppm C_8H_{18} + 500 ppm NO + 6 vol.% O_2; upper right corner) cycles over Ag/alumina at 450 °C. Note that eighth cycle represents steady state.

This indicates that NO reacts instantaneously with octane to form different types of N-containing hydrocarbons such as R–CN, R–NCO, R–NO_2, R–NO, etc. These species are shown in our ongoing work to transform over Ag/alumina into ammonia and/or amines, which in the gas phase react with activated NO_x species into N_2.

3.3. EPR and FT-IR combined with matrix isolation

The first intensity spectrum of EPR was obtained from the matrix formed when NO, octane and oxygen where fed through the Ag/alumina catalyst at 350 °C and trapped immediately in the argon matrix at 18 K (Fig. 3a). Characteristic for the spectra were triplets, which most probably mean that they belong to species, containing N nucleus. The main feature trapped in the matrix at 18 K was identified as NO_2. The identification of NO_2 is based on a reference run without the catalyst. NO_2 trapped in argon matrix at 18 K has pronounced broadening and anisotropy. Line-shape simulation of the experimental spectrum has confirmed its assignment as randomly oriented NO_2. The best fit was obtained by choosing the principal values of g- and A-tensors (1.991, 2.0025, 2.0052) and (4.55 mT, 6.3 mT, 5.07 mT), respectively.

When the matrix was annealed to 34 K and scanned again, a new spectrum appeared (Fig. 3b). It comprises a triplet, centred at $g = 2.0079$ with hyperfine splitting constant $A_{iso} = 0.83$ mT. Its appearance clearly manifests the presence of active intermediates, which are first generated on the catalyst surface, subsequently desorbed into the gas phase and finally trapped in Ar matrix. As a matter of fact, in argon matrix, the thermal activated diffusion starts above 30 K promoting low temperature chemical reactions and leading to formation of new radical species.

The triplet could be tentatively ascribed to formation of NO_3 radical, via reaction of $NO_2 + O$. Such assignment would indicate that there is O atom isolated in the matrix. NO_3 could also be formed as a loosely bounded complex

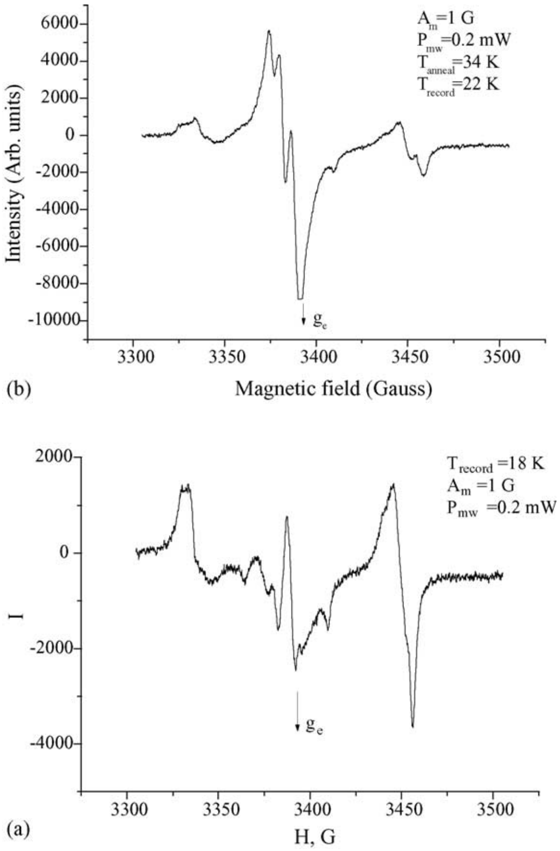

Fig. 3. EPR spectrum of 1000 ppm NO, 750 ppm octane and 6 vol.% O_2 deposition in the argon matrix scanned at 18 K (a) and 34 K (b). Catalyst temperature 350 °C.

between NO and O_2 molecules: ON···OO [16]. Another possible explanation would be a reaction between NO and some small hydrocarbon clusters with formation of nitroxyl-like radical O–N–(R, R′) with unpaired electron density centred on oxygen atom. The details of low temperature reactions responsible for changes in ESR spectra upon annealing the Ar matrix is the scope of further work

FT-IR measurements from the gas phase show that Ag/alumina does not significantly promote the production of NO_2 when a gas mixture containing NO + O_2 + HC is used. It should also be noted that EPR is extremely sensitive towards NO_2, which means that already trace amounts in the matrix are detected. Because of the changes in the spectra when annealed, radical reactions are certainly taking place. Whether these reactions are due to $O^\bullet$ or O–N–R, R′) is the scope of a separate study. However, it can be concluded with certainty that radicals of low molecular weight desorb from the Ag/alumina to the gas phase for further reactions leading to the final formation of N_2.

The FT-IR spectra recorded from the argon matrix are presented in Figs. 4–6. When octane and oxygen were fed at 250 °C through the catalyst intensive bands at approximately 662, 2279, 2345, 2860, 2933 and 2967 cm^{-1} were recorded. The strong band at 662 cm^{-1} and the very strong band at 2345 cm^{-1} are characteristic for CO_2 [17]. The CO_2 originates mainly from the combustion of octane but small

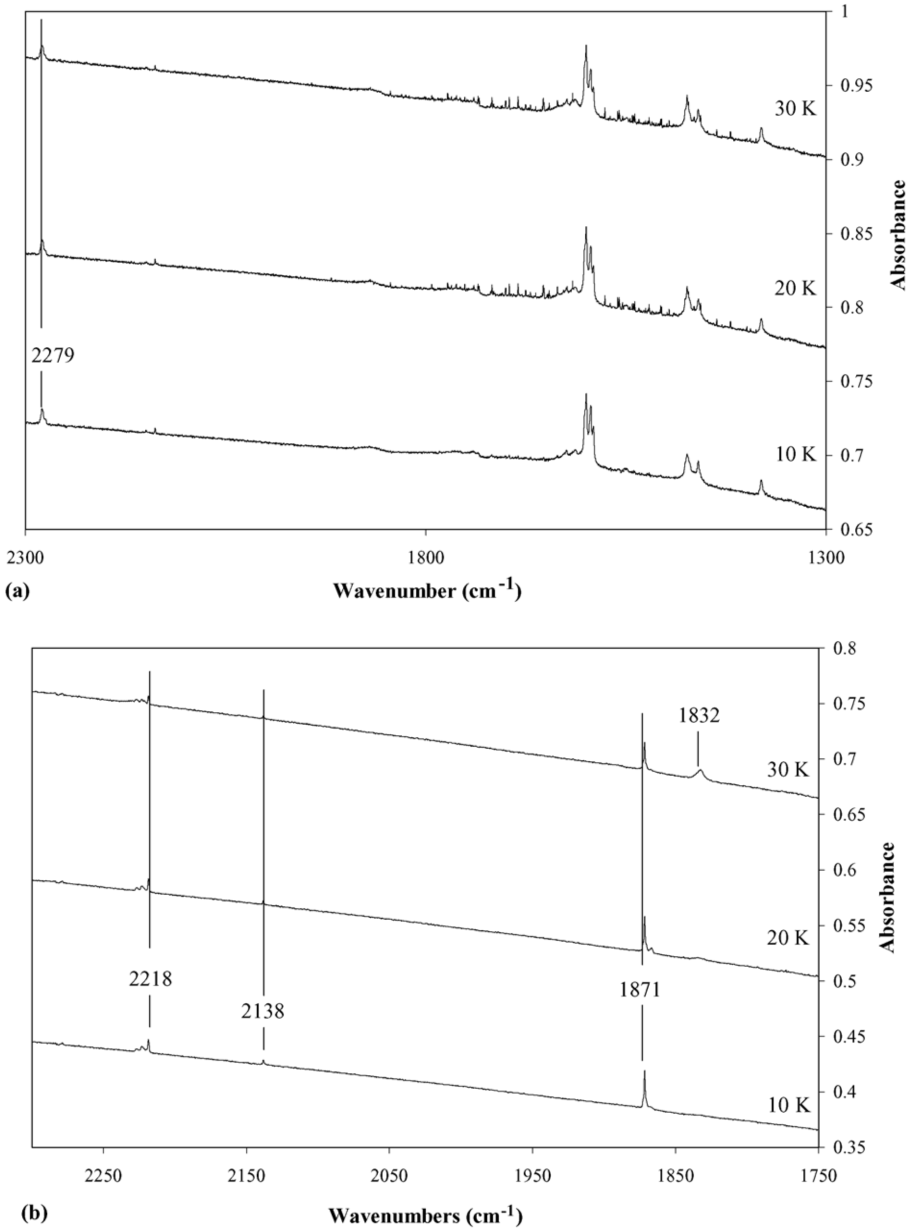

Fig. 4. FT-IR spectra of C_8H_{18} and O_2 deposition in the argon matrix (a) and C_8H_{18}, O_2 and NO in the argon matrix (b) scanned at 10, 20 and 30 K. Catalyst temperature 250 °C.

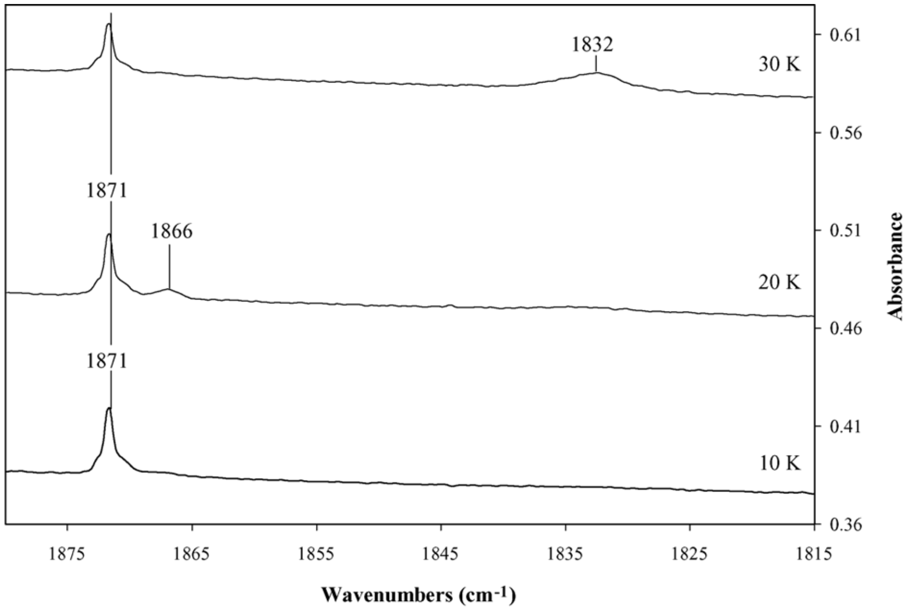

Fig. 5. Formation of new peaks upon annealing the matrix to 20 and 30 K. Deposition: C_8H_{18}, O_2 and NO in argon. Catalyst temperature 250 °C.

amount of carbon dioxide is always present in the matrix due to atmosphere (approximately 7×10^{-7} bar). The triplet region detected at 2860–2967 cm^{-1} originates from the impurities on cold window and is specific only for the used cold window (CsI). In addition, a broad peak formation was recorded at around 1595 and 3500–3750 cm^{-1} (Fig. 4a). These bands can be attributed to H_2O. Similar to CO_2, water is formed due to oxidation of octane and some traces are due to atmosphere. Also traces of CO at 2138 cm^{-1} [18] and an unidentified small peak were detected at 2279 cm^{-1} (Fig. 4a). According to activity tests using only octane and oxygen, the formation of CO at 250 °C is only minor, which explains the very low peak intensity for the characteristic CO peak. When the spectrum was annealed to 20 and 30 K, respectively, no changes in the peak pattern were detected.

When NO was added to the gas mixture (250 °C), a new spectrum was scanned (Fig. 4b). As expected, characteristic peaks of CO_2, H_2O and the persisted specific triplet due to impurities on cold window were detected again. The following new peaks were observed: CN stretch at 2218 cm^{-1} and NO (N_2O_2) stretch at 1871 cm^{-1}. The appearance of a CN group is in good agreement with observation made by Eränen et al. [9], where they isolated nitrile species evolving from the Ag/alumina catalyst

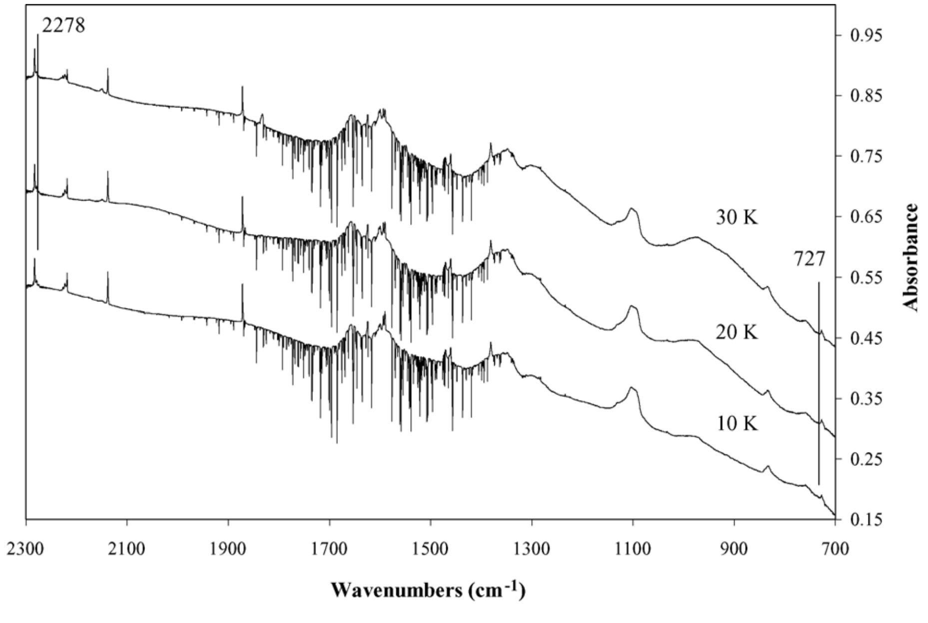

Fig. 6. FT-IR spectra scanned at 10, 20 and 30 K. Deposition: C_8H_{18}, O_2 and NO in argon. Catalyst temperature 400 °C.

surface during HC-SCR at 400 °C. Interestingly, the peak at 2279 cm^{-1} (Fig. 4a) disappeared in parallel to the formation of the CN group (Fig. 4b). It indicates that this unidentified specie is involved in the formation of cyanogen group or that the specie is consumed in the oxidation of octane, which is accelerated in the presence of NO as shown in the MS studies (above). Upon annealing of the matrix to 20 K a satellite peak was formed in the root of the NO peak at 1871 cm^{-1} (Fig. 5). This peak can be attributed to $(NO)_2$ complex [18] due to dimerisation of NO upon annealing. An important observation was made when the matrix was annealed further to 30 K. In this scanned spectrum the $(NO)_2$ peak vanished totally and a new clear peak at 1832 cm^{-1} was formed (Fig. 5). This peak is attributed to asymmetric N_2O_3 [19]. It is worth mentioning that this peak is not visible at 10 K. N_2O_3 is in equilibrium with NO and NO_2 and the equilibrium favours N_2O_3 formation at low temperatures [20]. However, reaction between NO and NO_2 to form N_2O_3 should be very slow at the temperature of the matrix. The detection of N_2O_3 would indicate that both NO and NO_2 are trapped in the matrix. However, as no NO_2 was detected in the matrix at 10 K and N_2O_3 appears when annealed it is reasonable to suggest, that there are O atoms trapped in the matrix, which react with NO to form NO_2. Formation of isolated O atoms was also proposed based on our EPR studies. For more certain identification of N_2O_3 it should be isomerised upon irradiation at 720 nm to symmetrical form and back upon irradiation at 380 nm, which is a scope of future work. However, NO can not be detected by EPR technique and no NO_2 was detected by FT-IR, which means that the main oxide of nitrogen evolving from the Ag/alumina surface is NO or activated NO. Explanation for detected NO_2 in EPR spectrum is that NO_2 is always present to some extent in the effluent formed over Ag/alumina. These traces are then captured in the matrix and found by EPR. In the same manner as proposed for FT-IR where NO was suggested to react with isolated O atoms to form NO_2 (radical), NO_2 reacts with O atoms to form NO_3 (radical) as shown earlier.

Alternatively, N_2O_3 could be formed as a loosely bounded complex $ON\cdots NO_2$ upon annealing the matrix [19].

When octane and oxygen were fed at 400 °C through the catalyst, a similar spectrum as at catalyst temperature 250 °C was recorded (not shown). CO_2 is again detected at 662 and 2345 cm^{-1}. Also H_2O and the cold window specific triplet were detected at the same bandwidths as at catalyst temperature 250 °C. The CO band at 2138 cm^{-1} has clearly increased after the temperature rise, which is well in accordance with the results from the activity tests over Ag/alumina. The unidentified small peak at 2279 cm^{-1} was detected again, although it was increased. When the spectrum was annealed to 20 and 30 K, respectively, no changes in the peak pattern were detected.

After NO was added to the gas mixture (400 °C), a new spectrum was scanned (Fig. 6). As expected, characteristic peaks for CO_2 and H_2O and for the cold window were again detected. The following new peaks were observed compared to the spectrum scanned at catalyst temperature 250 °C: 2282, 2278, 1100, 833, 727 and 611 cm^{-1}. Two of the peaks, 2278 and 727 cm^{-1}, belong to cyanogen isocyanate, NC–NCO [17]. The rest of the peaks (2282, 1100, 833, 611 cm^{-1}) are present also in the background spectrum as rather sharp features and therefore cannot be used for reliable identification. It is known that isocyanate, considered to be one of the key intermediates during the reduction path [4–8], is formed from cyanogens. In [13], it is shown that amine and ammonia are easily formed from R–NCO over Ag/alumina in excess of oxygen. Amine and ammonia then react in the gas phase with activated forms of NO_x after the catalyst bed.

Obuchi et al. [21] have proposed the following reactions in HC-SCR:

$$-CH_2-NO_2 \rightarrow CH{=}NO(OH) \rightarrow -C{=}N{=}O \tag{1a}$$

$$-C{=}N{=}O \rightarrow -N{=}C{=}O \rightarrow -NH_2 \rightarrow NH_3 \tag{1b}$$

$$-CH_2-NO \rightarrow -CH{=}N(OH) \rightarrow -C{\equiv}N \rightarrow -C{=}N{=}O \tag{1c}$$

The detection of isocyanate group in the matrix is important because according to (1a)–(1c) reaction scheme R–CNO type species form readily amines and ammonia, which in [13] have been shown to react with activated forms of NO_x in the gas phase to produce N_2. In addition, we have proved that R–NO_2 fed together with oxygen over Ag/alumina catalyst (250 and 400 °C) easily produces ammonia.

4. Conclusions

Application of the matrix isolated EPR and FT-IR technique to study the gas phase species involved in HC-SCR over a highly active Ag/alumina catalyst revealed, that a combination of heterogeneous and homogeneous (radical) reactions is taking place during HC-SCR. Radicals of low molecular weight, generated on catalyst surface and escaped to the gas phase, were trapped in a growing argon matrix behind the Ag/alumina catalyst. In the same matrix, cyanogen isocyanate was detected and is suggested to be a key intermediate for the formation of amines and ammonia via the hydrolysis of isocyanate species.

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References

[1] W. Held, A. König, T. Richter, L. Puppe, SAE Tech. Pap. Ser. No. 900496, 1990.
[2] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u, N. Mizuno, Appl. Catal. 70 (1991) 15.
[3] K. Eränen, L.-E. Lindfors, A. Niemi, P. Elfving, L. Cider, SAE Paper 2000-01-2813, 2000.
[4] Y. Ukisu, T. Miyadera, Catal. Lett. 39 (1996) 265.
[5] T. Chafik, S. Kameoka, Y. Ukisu, T. Miyadera, J. Mol. Catal. A: Chem. 136 (1998) 203.
[6] R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal. B 39 (2002) 283.
[7] N. Bion, J. Saussey, M. Haneda, M. Daturi, J. Catal. 217 (2003) 47.
[8] A. Satsuma, K.-i. Shimizu, Prog. Energy Combust. Sci. 29 (2003) 71.
[9] K. Eränen, L.-E. Lindfors, F. Klingstedt, D.Yu. Murzin, J. Catal. 219 (2003) 25.
[10] F. Klingstedt, K. Eränen, L.-E. Lindfors, S. Andersson, L.Cider, E. Jobson, C. Landberg, L.Eriksson, T. Ilkenhans, D. Webster, Top. Catal. 30/31 (2004) 27.
[11] F. Cavani, F. Trifiro, Catal. Today 51 (1999) 561.
[12] T. Nanba, A. Obuchi, Y. Sugiura, C. Kouno, J. Uchisawa, S. Kushiyama, J. Catal. 211 (2002) 53.
[13] K. Eränen, F. Klingstedt, K. Arve, L.-E. Lindfors, D. Yu. Murzin, J. Catal. 227 (2004) 328.
[14] L. Andrews, M. Moskovits, Chemistry and Physics of Matrix Isolated Spcies, Elsevier, Amsterdam, 1989.
[15] J. Eloranta, K. Vaskonen, H. Hakkinen, T. Kiljunen, H. Kunttu, J. Chem. Phys. 109 (1998) 7784.
[16] S. Bannov, V.A. Nevostruev, Radiat. Phys. Chem. 68 (2003) 917.
[17] NIST Chemistry Webbook. http://webbook.nist.gov/chemistry.
[18] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1990.
[19] X. Wang, Q-Z. Quin, J. Photochem. Photobiol. A 122 (1999) 1.
[20] G. Hägg, Allmän och oorganisk kemi, Almqvist & Wiksell, Stockholm, 1963.
[21] A. Obuchi, C. Wögerbauer, R. Köppel, A. Baiker, Appl. Catal. B 19 (1998) 9.