Catalysis Letters Vol. 109, Nos. 1–2, June 2006 (© 2006)
DOI: 10.1007/s10562-006-0059-1

Interaction of acetonitrile with oxygen on TiO_2-supported Au catalysts: FTIR–MS study

János Raskó* and János Kiss

Reaction Kinetics Research Group of the Hungarian Academy of Sciences at the University of Szeged, P.O. Box 168 Szeged H-6701, Hungary

Received 10 January 2006; accepted 2 February 2006

The adsorption and surface reactions of acetonitrile and acetonitrile-oxygen gas mixture were studied on TiO_2-supported Au catalysts at 300–673 K. FTIR spectra show different kinds of molecularly adsorbed CH_3CN:acetonitrile can be bonded to weak Lewis acid sites (2295 cm^{-1}), to strong Lewis acid sites (2337 cm^{-1}) of titania; it can be coordinated linearly through the lone electron pair of the N atom on Au sites and η^2 (C,N) CH_3CN species can be formed on Au particles. CH_3CN dissociates on Au sites, the resulting $CN_{(a)}$ can be oxidized in small extent by lattice oxygen and in a greater extent by gaseous oxygen into NCO surface species. The formation of other products (CH_3NH_2, H_2, CO_2, CH_4, C_2H_4 and CO) was demonstrated and discussed.

1. Introduction

The geometrical structures and bonding configurations of acetonitrile (CH_3CN) on the single crystal metal surfaces have been relatively oft investigated [1–7]. Probe molecule character of acetonitrile has also been applied in the study of acid-base properties of supported catalysts [8–10]. Relatively little attention has been paid to the heterogeneous transformations of acetonitrile, although the possible catalytic elimination of CN-containing molecules would have practical importance. It was demonstrated [11] that CH_3CN adsorbed on Pt/SiO_2 could be – at least partly – hydrogenated. The formation of gaseous products and surface species in the UV irradiation of CH_3CN adsorbed on TiO_2 has been studied in the presence [12] and in the absence [13] of oxygen.

The main goal of the present work is to determine (with FTIR experiments) the surface species and to detect (with MS measurements) the gas phase products formed during the interaction of acetonitrile and acetonitrile-oxygen gas mixture with TiO_2-supported gold catalysts. This information would lead to the better understanding of the mechanism of this reaction and to a promising heterogen catalytic process for elimination of the dangerous CN-containing compounds.

2. Experimental section

TiO_2 was the product of Degussa (P25, 50 m^2/g). For the preparation of 1 and 5 Au/TiO_2 catalysts the pH of the $HAuCl_4$ aqueous solution (Fluka AG) was adjusted to pH = 7.5 by adding of droplets of 1 M NaOH solution, and the fine powder of the oxide support was suspended in this solution and the suspension was kept at 343 K for 1 h during continuous stirring. The suspension was aged for 24 h at room temperature and washed with distilled water repeatedly, dried at 353 K and then calcined in air at 573 K for 4 h. Acetonitrile was the product of Reanal (99.8%).

For IR studies the catalysts powders were pressed onto a Ta-mesh (30×10 mm, 5 mg/cm^2). The mesh was fixed to the bottom of a conventional UHV sample manipulator. It was resistively heated and the temperature of the sample was measured by NiCr–Ni thermocouple spot-welded directly to the mesh. The pretreatments of the samples were performed in a stainless steel UV– IR cell (base pressure 1.33×10^{-5} Pa): the sample was heated in 1.33 hPa H_2 up to 573 K and it was kept at this temperature for 1 h, this was followed by degassing at the same temperature for 30 min and by cooling the sample to the temperature of the experiment.

Infrared spectra were recorded with a Genesis (Mattson) FTIR spectrometer with a wavenumber accuracy of ± 4 cm^{-1}. Typically 136 scans were collected. The whole optical path was purged with CO_2- and H_2O-free air generated by a Balston 75-62 FTIR purge gas generator. The spectrum of the pretreated sample (background spectrum) and the actual vapour spectrum were subtracted from the spectrum registered in the presence of vapour. All subtractions were taken without use of a scaling factor ($f = 1.000$). Mass spectrometric analysis was performed with the help of a QMS 200 (Balzers) quadrupole mass-spectrometer. The volume around the head of QMS 200 was continuously evacuated and it was connected with the UV–IR cell via a leak valve producing 2.66×10^{-3} Pa around the MS

---

*To whom correspondence should be addressed.
E-mail: rasko@chem.u-szeged.hu

1011-372X/06/0600–0071/0 © 2006 Springer Science+Business Media, Inc.

head when reacting gases were present in the cell. The changes in the signal intensity of the main fragments of acetonitrile and those of the possible products were simultaneously followed.

3. Results and discussion

The adsorption of 1.33 hPa CH_3CN on TiO_2 at 300 K caused the appearance of the bands at 2961, 2629, 2860, 2295 and 2269 cm^{-1} in the C–H stretching (3100–2600 cm^{-1}) and in the C–N stretching ranges of the spectrum. When gold (1 and 5) was present on TiO_2 surface all bands due to the adsorbed CH_3CN species were intensified, and new bands appeared at 2807, 2761, 2337, 2183, 2121, 2101, 2055–2033 and 1980 cm^{-1} (figure 1). It is noteworthy that the increase in intensity of the 2929 cm^{-1} band (ν_s (CH)) greatly exceeded that of the 2969–2987 cm^{-1} band (ν_{as} (CH)) on the spectra of Au/TiO_2 catalysts. This finding strengthens the assumption for different bonding configurations of CH_3CN on TiO_2 and on Au/TiO_2 catalysts.

Besides the band due to physisorbed CH_3CN (2269 cm^{-1}) a band at 2295 cm^{-1} on the spectrum of TiO_2 and two bands at 2337 and 2295 cm^{-1} on the spectra of Au/TiO_2 catalysts appeared. The 2295 cm^{-1} band can be assigned to CH_3CN bonded on weak Lewis sites and the band of smaller intensity at 2337 cm^{-1} can be due to CH_3CN coordinated on strong Lewis acid centres. The formation of strong Lewis acid sites on Au/TiO_2 catalysts may be due to the electron donation of Ti-cation on the surface to Au particles, which would increase the electron withdrawing power of the cationic sites (i.e. the strength of Lewis acidity). The electron transfer from TiO_2 to Au may be interpreted on the basis of work function ($\Delta\phi$) values: the work function of reduced TiO_2 is 4.8 eV [14], and $\Delta\phi$ value of polycrystalline Au is 5.38 eV [15]. These values suggest that electron may flow from titania to Au at the interface.

The 2183 cm^{-1} band appeared on the spectra of Au/TiO_2 catalysts is attributed to the CN vibration of CH_3CN molecules coordinated linearly through lone electron pair of the N atom on Au sites. The appearance of the bands at 2121, 2101 and 2055 cm^{-1} can be due to $CN_{(a)}$ formed in the dissociation of acetonitrile on Au particles. We note here that no such bands were observed on Al_2O_3-supported Au catalysts [16] (i.e. no acetonitrile dissociation occurred on Au/Al_2O_3 sample); this is probably a consequence of the electron donation from the support to Au resulting in a higher electron concentration on Au particles, if the support was TiO_2.

The band observed at 1615 cm^{-1} on Pt (111) [4] and at 1755 cm^{-1} on Pd (111) [8] was attributed to η^2 (C,N) CH_3CN adsorbed species, and it was concluded that the above difference in the positions of the bands is the consequence of the different softening of CN stretching mode: it was softened slightly less on Pd(111) than on Pt(111) [8]. Based on the above results obtained on single crystal surfaces the bands at 1759 and 1704 cm^{-1} (1% Au/TiO_2) and at 1709 cm^{-1} (5% Au/TiO_2) appeared in our studies are assigned to η^2 (C,N) CH_3CN species formed on Au particles.

Bands observed in this work at 2850, 2761 and 1134 cm^{-1} can be assigned to adsorbed CH_3NH_2 (methylamine) [18,19]. The formation of adsorbed CH_3NH_2 will be discussed later.

In the following experiments the stability of the CH_3CN adsorbed layer (produced on the catalysts by the

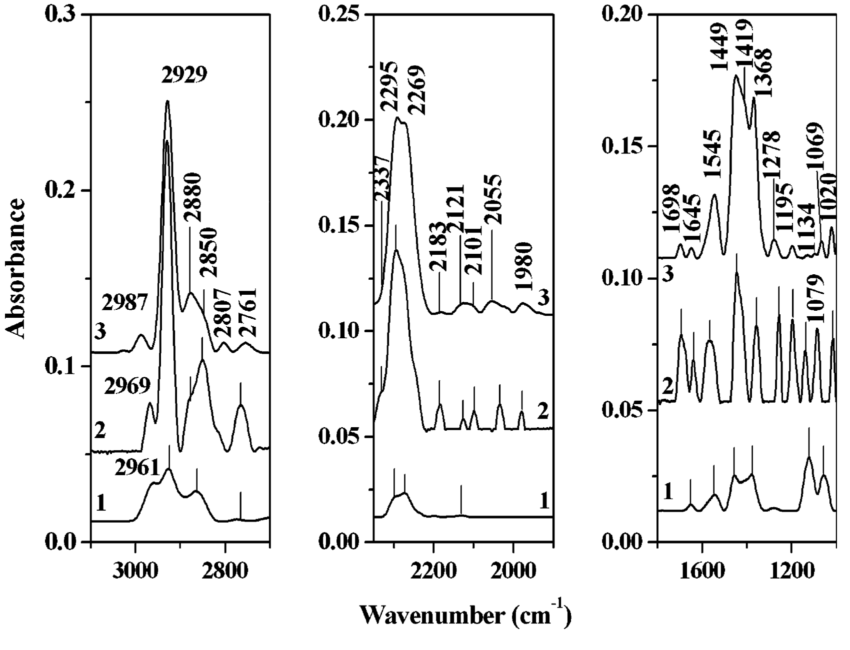

Figure 1. Infrared spectra registered after 15 min adsorption of 1.33 hPa CH_3CN at 300 K on reduced catalysts: 1 – TiO_2; 2 – 1 Au/TiO_2 and 3 – 5 Au/TiO_2.

adsorption of 1.33 hPa CH_3CN at 300 K for 15 min) was studied. For this purpose the samples with the adsorbed CH_3CN layer on their surfaces were heated up under evacuation to different temperatures (in 50 K steps) and were kept at the given temperature for 1 min; after this treatment the samples were cooled down to room temperature and the IR spectra were always taken at 300 K.

The intensities of the above bands decreased monotonously with the increase of the temperature, at the highest temperatures applied here (573–673 K) the bands were practically missing from the spectra.

While the samples were heated up to and kept at the desired temperatures the formation of the gas phase products was monitored by mass spectrometer. The changes of some MS intensities due to different products as a function of the temperature were plotted in figure 2. Practically no acetonitrile desorption was observed from TiO_2, in the cases of 1 and 5 Au/TiO_2 catalysts, however, the acetonitrile desorption showed a maximum at 423 K. The highest amount of desorbed methylamine (CH_3NH_2) during these treatments was detected from TiO_2 ($T_{max} = 423$ K); the amount of methylamine was decreased and T_{max} characteristic for its desorption shifted to higher temperatures with increasing Au content of the catalysts ($T_{max} = 473$ K for 1% Au/TiO_2 and $T_{max} = 523$ K for 5% Au/TiO_2). From these data we concluded that in the hydrogenation of adsorbed acetonitrile to methylamine the surface OH groups of titania play a decisive role, as the surface concentration of OH species possibly diminishes with the increase of the metal concentration on the oxide surface.

Interestingly, oxygen was detected among the products: its highest amount was experienced on TiO_2 and decreased with the increase of the metal content. T_{max} of O_2 desorption shifted from 323 K (TiO_2) to 473 K (1 Au/TiO_2) and to 573 K (5 Au/TiO_2). These data

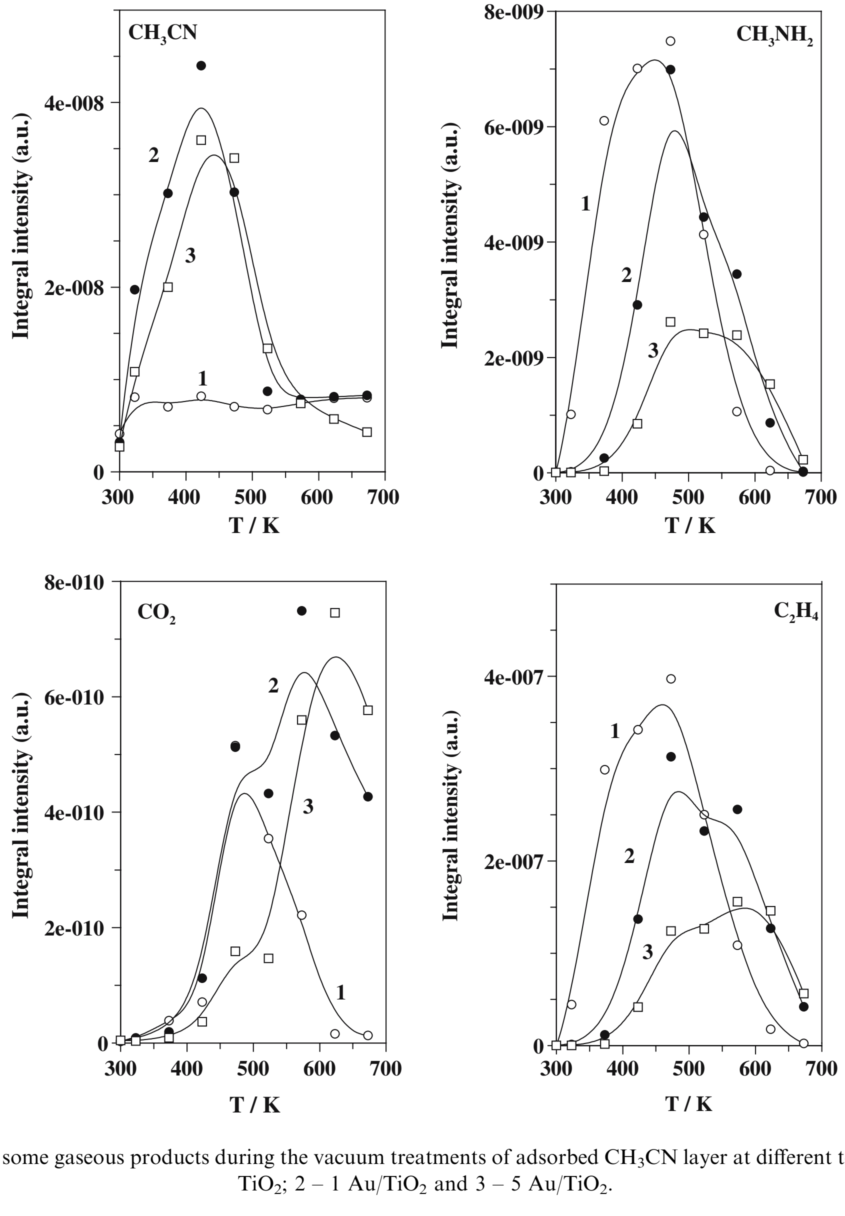

Figure 2. Formation of some gaseous products during the vacuum treatments of adsorbed CH_3CN layer at different temperatures (see text): 1 – TiO_2; 2 – 1 Au/TiO_2 and 3 – 5 Au/TiO_2.

clearly show the changes in the mobility of the lattice oxygen of titania:the binding energy of lattice oxygen proved to be the smallest on pure TiO_2, introduction of gold onto titania surface increased the binding energy of oxygen and decreased the amount of mobile surface oxygen.

Very probably the oxidation with mobile oxygen of titania led to the appearance of CO_2 in the gas phase (figure 2): besides $T_{max} = 473$ K observed in CO_2 production from TiO_2 another high temperature peak with T_{max} at 573–623 K was detected from Au/TiO_2 catalysts. The formation of ethylene (figure 2) during the above treatments is possibly due to the break of C–C bond in CH_3CN, and to the consecutive coupling and dehydrogenation of CH_3 groups. H_2 and CO were detected from all surfaces, the formation of H_2O and CH_4, however, was experienced only on Au-containing catalysts. No NH_3, C_2N_2 and N_2 were observed upto 673 K on any catalysts, which shows that the break of C–N bond in CH_3CN does not occur on TiO_2 and on Au/TiO_2 catalysts. We note that NH_3 formation was detected on Au/Al_2O_3 catalyst.[16]

The stability of adsorbed CH_3CN layer was also investigated in the presence of oxygen. In these experiments the adsorbed CH_3CN layer (produced on the catalysts by the adsorption of 1.33 hPa CH_3CN at 300 K for 15 minutes and evacuation at 300 K, 15 min) was heated up to and kept at the desired temperature for 1 min in 13.3 Pa O_2 and then the samples were quickly cooled down to 300 K in O_2 and after a short evacuation (300 K, 5 min) the IR spectra were registered at 300 K. The CN stretching regions of the spectra registered in this process were plotted in figure 3. In the presence of oxygen no bands in the 2400–1900 cm^{-1} range appeared on the spectra of TiO_2 above 473 K. On the spectra of Au/TiO_2 samples the bands in the CN region were stabilized by O_2, as bands were registered even after the treatment at 673 K. The bands at 2350–2358 and 2204–2212 cm^{-1} (not observed in vacuum treatments) appeared already at 300 K in O_2 on the spectra of Au/TiO_2 catalysts. The 2350–2358 cm^{-1} band is due to CO_2 and that at 2204–2212 cm^{-1} is characteristic of Ti–NCO species [20,21,22]. The intensities of these bands increased slightly with the increase of the temperature and whith of Au content. Interestingly, the position of the band due to CH_3CN bonded on weak Lewis sites (2303 cm^{-1}) of Au/TiO_2 samples shifted to higher wavenumbers with rising temperature in O_2. At higher temperatures (573–673 K) they appeared at 2313–2320 cm^{-1}, very close to the position of the band due to CH_3CN adsorbed on strong Lewis sites.

The distribution of the gas phase products and T_{max} values for different compounds formed from adsorbed CH_3CN layer were basically affected by the presence of oxygen. Although T_{max} of CH_3CN desorption was the same (423 K) both in the absence and in the presence of O_2, its amount, however, was highly suppressed by O_2. CH_3NH_2 desorbed in two maxima ($T_{max} = 373$ and 473 K) in the presence of O_2 and its amount exceeded that of acetonitrile desorbed from all surfaces. A small decrease in the amount of oxygen above 423 K and the appearance and increase of CO_2 above 473 K show that the oxidation reaction between gaseous oxygen and adsorbed CH_3CN starts at 423–473 K. H_2, H_2O, CO and CH_4 (all detected in vacuum treatments of adsorbed CH_3CN layer) were not experienced in the presence of O_2. In these experiments ethylene desorbed with the same T_{max} values (373 and 473 K), as did CH_3NH_2, which shows a possible connection between the forma-

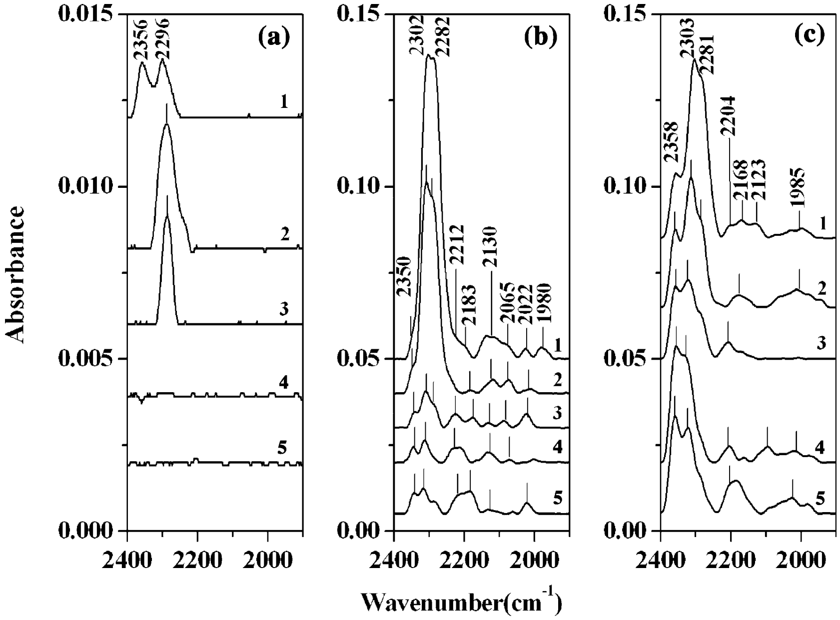

Figure 3. Infrared spectra taken at 300 K after oxygen treatments of adsorbed CH_3CN layer at different temperatures (see text): 1 – 300 K; 2 – 373 K; 3 – 473 K; 4 – 473 K; 5 – 573 K and 6 – 673 K. A – TiO_2; B – 1 Au/TiO_2 and C – 5 Au/TiO_2.

tion of a hydrogenated product (CH_3NH_2) and of a dehydrogenated product (C_2H_4), when the adsorbed CH_3CN layer was treated with O_2.

Next the interactions of CH_3CN (1.33 hPa) and $CH_3CN + O_2$ gas mixture (1.33 hPa + 1.33 Pa) were isothermally studied at 300, 373, 473 and 573 K for 60 min. In these experiments the IR spectra were taken at the reaction temperature, and the spectrum of the reduced catalyst and that of gas phase were subtracted from the spectra registered in the reacting gas. Changes in the gas phase composition were simultaneously followed by mass spectrometer.

Changes both in the IR spectra and in the gas phase composition occurred only at 473–573 K in CH_3CN. At these temperatures the intensities of the IR bands decreased, and parallel with the small decrease in the amount of CH_3CN the concentrations of the reaction products (CH_3NH_2, H_2, CO_2, CH_4, C_2H_4 and CO) slightly increased.

In $CH_3CN + O_2$ gas mixture signs for the occurrence of any reaction were observed at 473–573 K. At these temperatures the amounts of gas phase CH_3CN and O_2 decreased, while the amounts of gas phase products (CH_3NH_2, CO_2, C_2H_4 and CO) slightly increased. H_2 and CH_4 were not present among the reaction products in $CH_3CN + O_2$ gas mixture.

Infrared features basically different from those observed in CH_3CN alone were observed in the 2400–1900 cm^{-1} range, when the samples were kept isothermally in $CH_3CN + O_2$ mixture. A band at around 2200–2210 cm^{-1} due to Ti–NCO surface species [20,21,22] with appreciable intensity appeared already at 300 K on 1 and 5 Au/TiO_2 catalysts. The intensity of this band was higher at any temperatures on 5 Au/TiO_2 than on 1 Au/TiO_2 and it increased with increasing reaction temperature upto 473 K; at 573 K its intensity decreased. Spectra obtained at 473 K after 60 min of adsorption of CH_3CN and $CH_3CN + O_2$ mixture, respectively, on the catalysts can be seen in figure 4. An accurate analysis of the spectra revealed that this band also appeared with very low intensity in CH_3CN on Au/TiO_2 catalysts and on TiO_2 at and above 373 K. The integrated absorbances of the Ti–NCO band on different catalysts at 473 K were plotted in figure 5. It can be concluded that the higher Au content of the catalyst and the presence of gas phase O_2 favoured

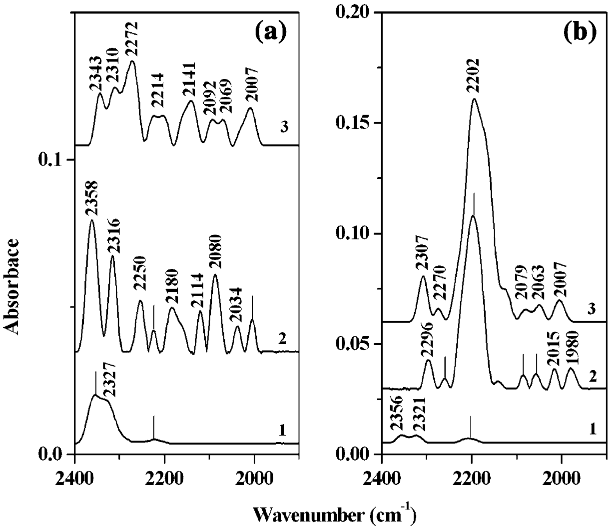

Figure 4. Infrared spectra detected at 473 K after 60 min adsorption of CH_3CN (a) and that of $CH_3CN + O_2$ (b) gas mixture: 1 – TiO_2; 2 – 1 Au/TiO_2 and 3 – 5 Au/TiO_2.

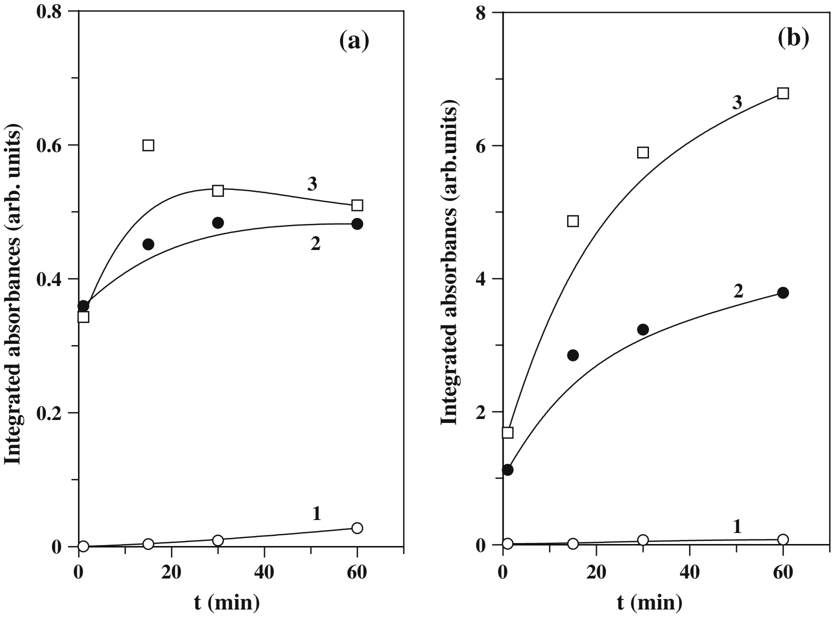

Figure 5. Integrated absorbances of the Ti–NCO band (2200–2212 cm^{-1}) determined at 473 K in CH_3CN (a) and in $CH_3CN + O_2$ (b): 1 – TiO_2; 2 – 1 Au/TiO_2 and 3 – 5 Au/TiO_2.

the formation of Ti–NCO surface species. We think that the dissociation of CH_3CN on Au particles resulting in $CN_{(a)}$ species and the consecutive reaction between $CN_{(a)}$ and (mainly) gaseous oxygen would lead to the formation of NCO. After its formation on the metal particles NCO migrates quickly to the support and localizes there [20, 21, 22].

4. Conclusions

An electron donation from TiO_2 to Au particles leads to the formation of strong Lewis acid sites on TiO_2 and electron-rich Au particles on Au/TiO_2 catalysts. CH_3CN dissociation on Au particles occurs resulting in $CN_{(a)}$ on the metal. The reaction of $CN_{(a)}$ with gaseous O_2 produces NCO surface species on the metal, after its formation, however, NCO migrates quickly from the metal to TiO_2 resulting in the formation of Ti–NCO species.

Acknowledgments

This work was financially supported by grants OTKA T 46351 and NKFP 3A058-04 of the Ministry of Education.

References

[1] R.R. Cavanagh and J.T. Yates Jr., Surf. Sci. 97 (1980) L335.
[2] K. Kishi and S. Ikeda, Surf. Sci. 107 (1981) 405.
[3] C.M. Friend, E.L. Mutterties and J.L. Gland, J. Phys. Chem. 85 (1981) 3256.
[4] N.R. Avery, T.W. Matheson and B.A. Sexton, Appl. Surf. Sci. 22(23) (1985) 384.
[5] E.C. Ou, P.A. Young and P.R. Norton, Surf. Sci. 277 (1992) 123.
[6] K. Murphy, S. Azad, D.W. Bennett and W.T. Tysoe, Surf. Sci. 467 (2000) 1.
[7] D.-H. Kang and M.J. Trenary, Phys. Chem. B 106 (2002) 5710.
[8] O. Bortnovsky, Z. Sobalik, B. Wichterlová and Z. Bastl, J. Catal. 210 (2002) 171.
[9] E. Prinetto, M. Manzoli, G. Ghiotti, M.J.M. Ortiz, D. Tichit and B. Coq, J. Catal. 222 (2004) 238.
[10] B. Pawalec, S. Damyanova, R. Mariscal, J.L.G. Fierro, I. Sobrados, J. Sanz and L. Petrov, J. Catal. 223 (2004) 86.
[11] T. Szilágyi, Appl. Surf. Sci. 35 (1988–1989) 19.
[12] J. Zhuand, C.N. Rusu and J.T. Yates Jr., J. Phys. Chem. B 103 (1999) 6957.
[13] C.-C. Chuang, W.-C. Wu, M.-X. Lee and J.-L. Lin, Phys. Chem. Chem. Phys. 2 (2000) 3877.
[14] Y.W. Chung, W. Lo and G.A. Somorjai, Surf. Sci. 64 (1977) 588.
[15] M. Uda, A. Nakamura, T. Yamamoto and Y. Fujimoto, J. Electron. Spectrosc. 88–91 (1998) 643.
[16] J. Raskó and J. Kiss, Appl. Catal. A-General 298 (2006) 115.
[17] B.A. Sexton and N.R. Avery, Surf. Sci. 129 (1983) 21.
[18] J. Gray and R.C.J. Lord, Chem. Phys. 26 (1957) 690.
[19] T.S. Nunney, J.J. Birtill and R. Raval, Surf. Sci. 427–428 (1999) 282.
[20] F. Solymosi, L. Völgyesi and J. Sárkány, J. Catal. 54 (1978) 336.
[21] F. Solymosi, L. Völgyesi and J. Raskó: Z. Phys. Chem. N.F. 120 (1980) 70 and refereces therein.
[22] F. Solymosi, T. Bánsági and T. Süli-Zakar, Phys. Chem. Chem. Phys. 5 (2003) 4724.