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Adsorption and surface reactions of acetonitrile on Al₂O₃-supported noble metal catalysts

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Abstract

The adsorption and surface reactions of acetonitrile on Al₂O₃-supported noble metal (Pt, Rh, Au) catalysts at 300–673 K were studied by FT-IR and mass spectrometry. It was found that acetonitrile adsorbs molecularly in different forms on these surfaces: besides the H-bridge-bonded and physisorbed forms monodentate CH₃CN (on strong and weak Lewis acid sites) and $\eta^2(\text{C}, \text{N})\text{CH}_3\text{CN}$ -adsorbed species were formed at 300 K. CH₃CN, on the other hand, dissociates producing CN_(a) species even at this temperature. Among the gas phase products formed during the heat treatments of adsorbed CH₃CN layer methylamine (CH₃NH₂) was detected, the amount of which depended on the nature of the surfaces. The appearance of gas phase NH₃ can be connected with the rupture of C–N bond in CN_(a). In the presence of oxygen the formation of isocyanate (NCO) surface species was observed on Pt/Al₂O₃, Rh/Al₂O₃ and (in a very small extent) on Al₂O₃ at and above 473 K; no NCO formation was found on Au/Al₂O₃.

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1. Introduction

Acetonitrile (CH₃CN) and its isomer, methyl isocyanide (CH₃NC) have been relatively oft used for determining of geometrical structures and bonding configurations on single crystal metal surfaces [1–9]. Their application is based on the fact that these compounds are isoelectronic with CO (the most frequently applied probe molecule).

Probe molecule character of acetonitrile has also been explored in the study of acid–base properties of supported catalysts [10–13].

Heterogeneous catalytic transformations of acetonitrile have rarely been investigated. It was found that CH₃CN adsorbed on Pt/SiO₂ could be – at least partly – hydrogenated [14]. The UV irradiation of CH₃CN adsorbed on TiO₂ in the presence of oxygen [15] led to the formation of H₂O, CO₂, surface CO₃²⁻ and surface isocyanate (NCO). The formation of surface CH₃CONH₂, $\eta^2(\text{N}, \text{O})\text{-CH}_3\text{CONH}$, CH₃COO_(a), HCOO_(a), NCO_(a) and CN-containing species was observed, when the UV

irradiation of CH₃CN adsorbed on TiO₂ was performed in the absence of oxygen [16].

The aim of the present work is to determine the surface species formed and to detect the gas phase products during the interaction of acetonitrile and acetonitrile–oxygen gas mixture with Al₂O₃-supported noble metal catalysts. This study would be the first step to find an effective catalyst in breaking of C–N bond of cyanide compounds. The supported noble metal catalysts seemed to be promising candidates for this purpose.

2. Experimental

Al₂O₃ was the product of Degussa (P110 C1, 100 m²/g). Metal/Al₂O₃ catalysts (1%) were prepared by impregnating of Al₂O₃ with aqueous solutions of RhCl₃ × 3H₂O (Johnson-Matthey) and H₂PtCl₆ × 6H₂O (Reanal). The powders were dried at 383 K for 3 h in air. For the preparation of 1% Au/Al₂O₃ the pH of the HAuCl₄ aqueous solution (Fluka AG) was adjusted to pH 7.5 by adding 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 with continuous stirring. The suspension was aged for 24 h at room temperature and washed with distilled water repeatedly, dried at 353 K and

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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 Tamesh (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): they were heated in 1 Torr of H_2 (1.33 hPa) 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) FT-IR spectrometer with a wave number accuracy of $\pm 4 \text{ cm}^{-1}$. 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 FT-IR 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 head when reacting gases were present in the cell. The changes in the signal intensity of the main fragments of acetonitrile and that of the possible products were followed by mass spectrometer.

3. Results

3.1. Adsorption at 300 K

Infrared spectra registered during the adsorption of acetonitrile with increasing pressure (1.33–1.33 hPa) on Al_2O_3 at 300 K are shown on Fig. 1A. The negative features above 3600 cm^{-1} on the subtracted spectra are due to the consumption of surface OH groups in the course of acetonitrile adsorption. The broad band centered around 3546 cm^{-1} is characteristic for the building up of H-bridged bonds on the surface. In the C–H stretching region (3200 – 2600 cm^{-1}) the dominant band was the 2967 cm^{-1} absorption. Bands at 2357, 2329, 2250 and 2199 cm^{-1} appeared in the range of C–N stretchings, while bands at 1695 (sh), 1611, 1515, 1449, 1387, 1346 (sh), 1287, 1167, 1116, 1071 and 1040 cm^{-1} were detected below 2000 cm^{-1} . Except the bands at 3102 and 2250 cm^{-1} , the bands proved to be stable against evacuation (15 min) at 300 K.

Spectra of 1% Pt/ Al_2O_3 catalysts in acetonitrile of increasing pressure were basically different from those on pure Al_2O_3 (Fig. 1B). The main differences appeared in the C–H and C–N stretching regions: the dominant band in the C–H range was the 2929 cm^{-1} band and the 2300, 2155 and 2023 cm^{-1} bands did not appear on the spectra of pure Al_2O_3 . The intensities of the bands in the C–N range, on the other hand, were substantially higher on 1% Pt/ Al_2O_3 , than on Al_2O_3 .

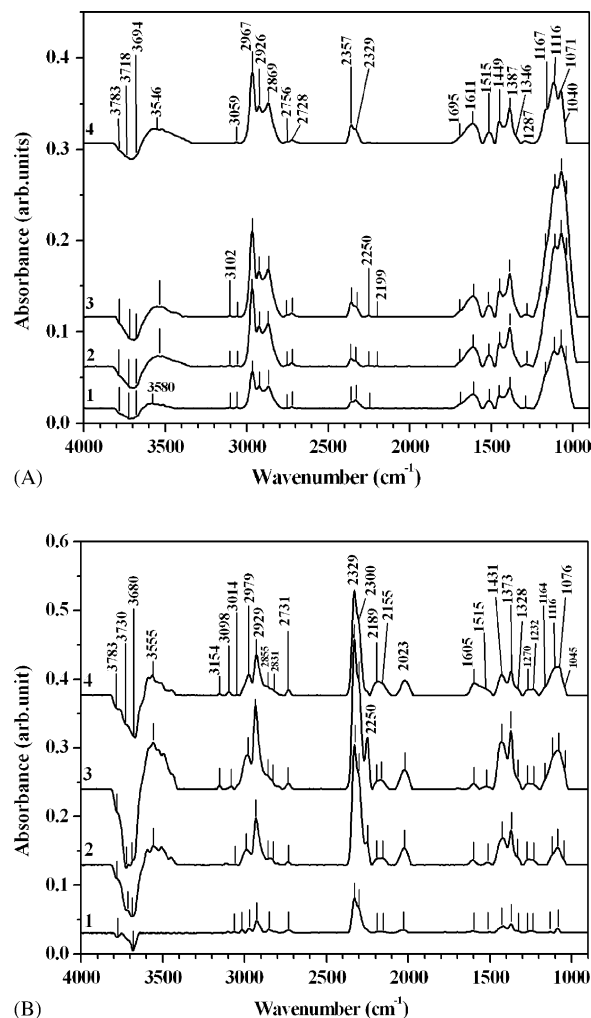


Fig. 1. The effects of acetonitrile pressure on the spectra registered at 300 K on Al_2O_3 (A) and on 1% Pt/ Al_2O_3 (B): (1) 1.33 Pa; (2) 13.3 Pa; (3) 1.33 hPa and (4) evacuation at 300 K for 15 min.

The spectra of 1% Rh/ Al_2O_3 and 1% Au/ Al_2O_3 were basically corresponded to those of 1% Pt/ Al_2O_3 . Besides the bands at 2329, 2300 and 2250 cm^{-1} , however, only one band at 2187 cm^{-1} appeared on the spectra of 1% Rh/ Al_2O_3 , and the bands at 2194, 2165 and 2057 cm^{-1} were detected at slightly different wave numbers, than the corresponding bands on the spectra of 1% Pt/ Al_2O_3 . In the lower wave number range a band at 1769 cm^{-1} (1% Rh/ Al_2O_3) and at 1756 cm^{-1} (1% Au/ Al_2O_3) was detected, which was not observed neither on 1% Pt/ Al_2O_3 , nor on Al_2O_3 .

3.2. Stability of adsorbed CH_3CN

In the following experiments the stability of the CH_3CN -adsorbed layer (produced on the catalysts by the adsorption of 1.33 hPa CH_3CN at 300 K for 15 min) was monitored. 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 for the better comparison. Changes caused by the above treatments in the C–N and the C–H stretching ranges can be seen in Fig. 2A and B, respectively.

The intensities of the 2357 and 2329 cm^{-1} bands observed on the spectrum of Al_2O_3 at 300 K were diminished by the increase of the temperature. Besides the very small bands at 2237 and 2199 cm^{-1} detected at 300 K, a new band of very small intensity at 2154 cm^{-1} appeared after the treatment at 373 K; all these bands were observable even after the treatment at 673 K. Changes in the C–N range in the spectra of 1% metal/ Al_2O_3 catalysts were different from those of Al_2O_3 and depended on the nature of the noble metal. The treatment at 373 K caused only the diminution of the bands at 2329 and 2302 cm^{-1} on all metal/ Al_2O_3 catalysts; all other spectral features corresponded well to those observed after the evacuation at 300 K. Concerning the C–N spectral region, the obvious differences among the alumina-supported noble metal catalysts appeared after the treatment at and above 373 K. The drastic decrease of the bands at 2329 and 2302 cm^{-1} bands caused by the treatment at 473 K was accompanied by the

appearance of a new band at 2128 cm^{-1} (1% Pt/ Al_2O_3), at 2070 cm^{-1} (1% Rh/ Al_2O_3) and at 2172 cm^{-1} (1% Au/ Al_2O_3). At this temperature the bands at 2360 and 2333 cm^{-1} appeared on the spectra of 1% Rh/ Al_2O_3 and 1% Au/ Al_2O_3 . After the treatment at 673 K all bands in the C–N range disappeared from the spectrum of 1% Au/ Al_2O_3 , while small bands at 2288, 2128 and 2050 cm^{-1} (1% Pt/ Al_2O_3), and at 2360, 2333 and 2047 cm^{-1} (1% Rh/ Al_2O_3) were observed.

The bands in the C–H stretching region on the spectra of Al_2O_3 decreased monotonously with the increase of the temperature, but they were detected with small intensities even after the treatment at 673 K (Fig. 2B). On alumina-supported noble metal catalysts the bands due to C–H stretchings disappeared at lower temperature, than on alumina: these bands were practically absent after the heat treatments above 473 K. Interestingly, among the three most intense bands of this range, the bands at 2967 and 2928 cm^{-1} were observed on 1% Pt/ Al_2O_3 and on 1% Rh/ Al_2O_3 , respectively, while the bands at 2977 and 2878 cm^{-1} were detected on the spectrum of 1% Au/ Al_2O_3 after the treatment at 473 K.

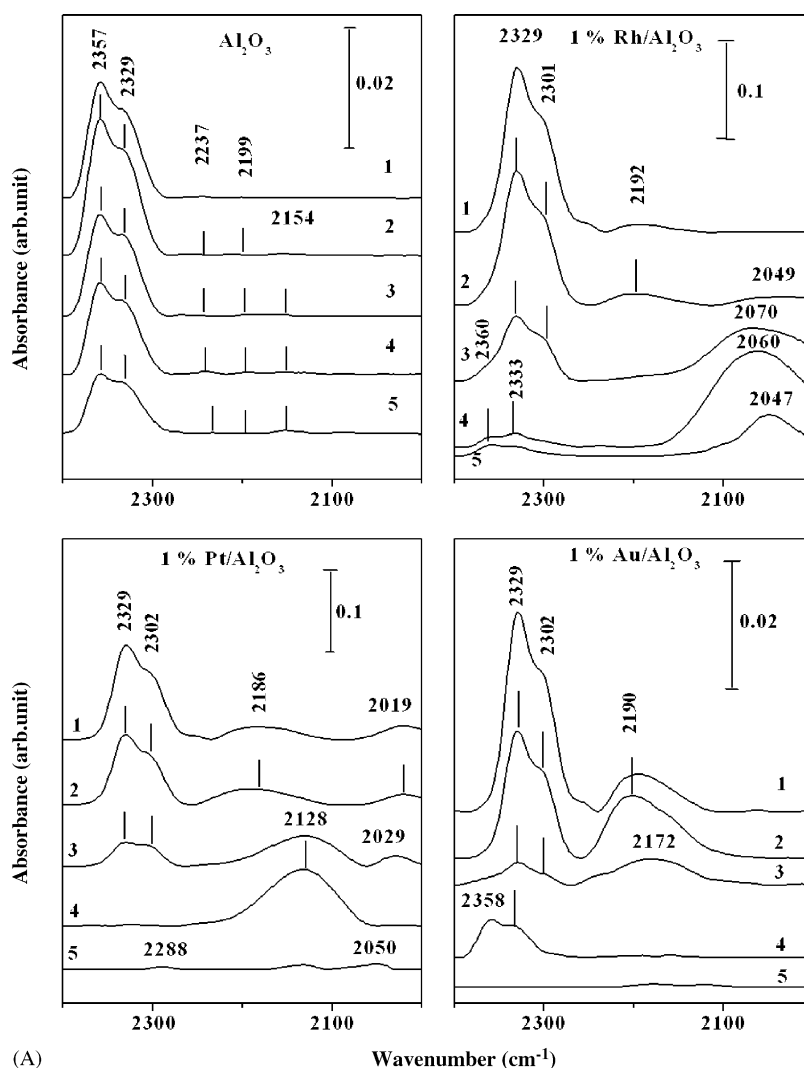


Fig. 2. Effects of vacuum heat treatments of adsorbed CH_3CN layer (see text) on different catalysts: (A) $\nu(\text{CN})$ range ($2400\text{--}2000\text{ cm}^{-1}$) and (B) $\nu(\text{CH})$ range ($3200\text{--}2600\text{ cm}^{-1}$); (1) 300 K; (2) 373 K; (3) 473 K; (4) 573 K and (5) 673 K. The spectra were taken at 300 K.

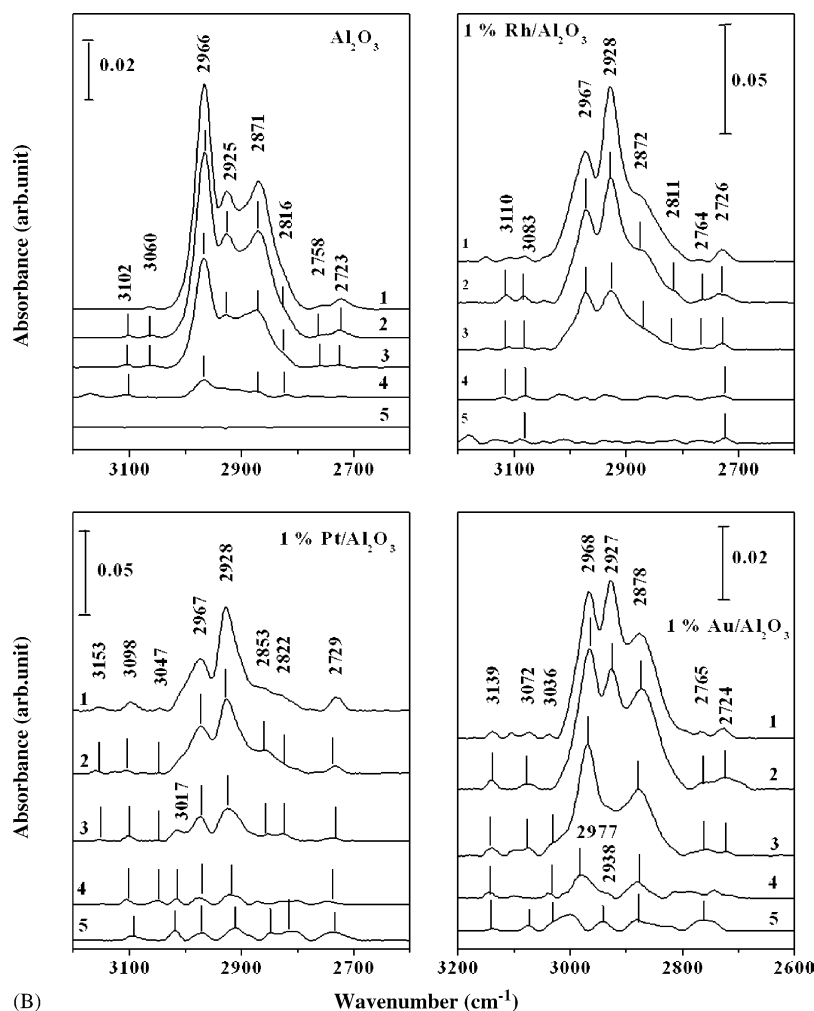


Fig. 2. (Continued).

The broad absorption centered around 3560 cm⁻¹ disappeared after the treatment at 473 K from the spectra of alumina-supported noble metal catalysts, while this feature was detected even after the treatment at 573 K on the spectra of Al₂O₃.

The bands due to surface OH groups were restored by the treatment at 673 K in the cases of 1% Pt/Al₂O₃ and 1% Au/Al₂O₃, while negative features due to OH-consumption still remained on the subtracted spectra of Al₂O₃ and 1% Rh/Al₂O₃.

The intensities of the bands below 2000 cm⁻¹ on the spectra of Al₂O₃ decreased monotonously with the increase of the temperature. After the treatment at 673 K only the small bands at 1449 and 1364 cm⁻¹ were observed. On the spectra of alumina-supported noble metal catalysts dramatic changes occurred due to the treatments at and above 373 K in the spectral range of 1800–1500 cm⁻¹: instead of the bands detected at 300–373 K, new bands with relatively high intensities appeared at 1587–1585 and 1512–1505 cm⁻¹, the intensities of which decreased with the further increase of the temperature. They were detected, however, even after the treatment at 673 K. The bands below 1500 cm⁻¹ diminished continuously with increasing temperature; they were absent after the treatment at 673 K.

While the samples were heated up to and kept at the desired temperatures, the appearance of the gas phase products was monitored by mass spectrometry. The changes of some MS intensities due to different products as a function of the temperature were plotted in Fig. 3A and B. Interestingly, there was no acetonitrile desorption from Al₂O₃. From Al₂O₃-supported noble metal catalysts, however, acetonitrile was detected among the gas phase products. It appeared in the highest amounts when these samples were heated to and kept for 1 min at 473 K. The amount of desorbed acetonitrile in the treatments at 473 K decreased in the order of 1% Pt/Al₂O₃ > 1% Rh/Al₂O₃ > 1% Au/Al₂O₃. Another interesting observation was the detection of methylamine during these treatments. The highest amounts of methylamine appeared in the gas phase, when the samples were heated up to and kept at 473 K: its amount measured in the treatment at 473 K decreased in the order of Al₂O₃ > 1% Au/Al₂O₃ > 1% Rh/Al₂O₃ > 1% Pt/Al₂O₃, which is the reverse found for acetonitrile desorption.

Above 423 K hydrogen evolved from acetonitrile adsorbed layer on 1% Rh/Al₂O₃ and 1% Pt/Al₂O₃. No H₂ formation was observed from Al₂O₃ and 1% Au/Al₂O₃.

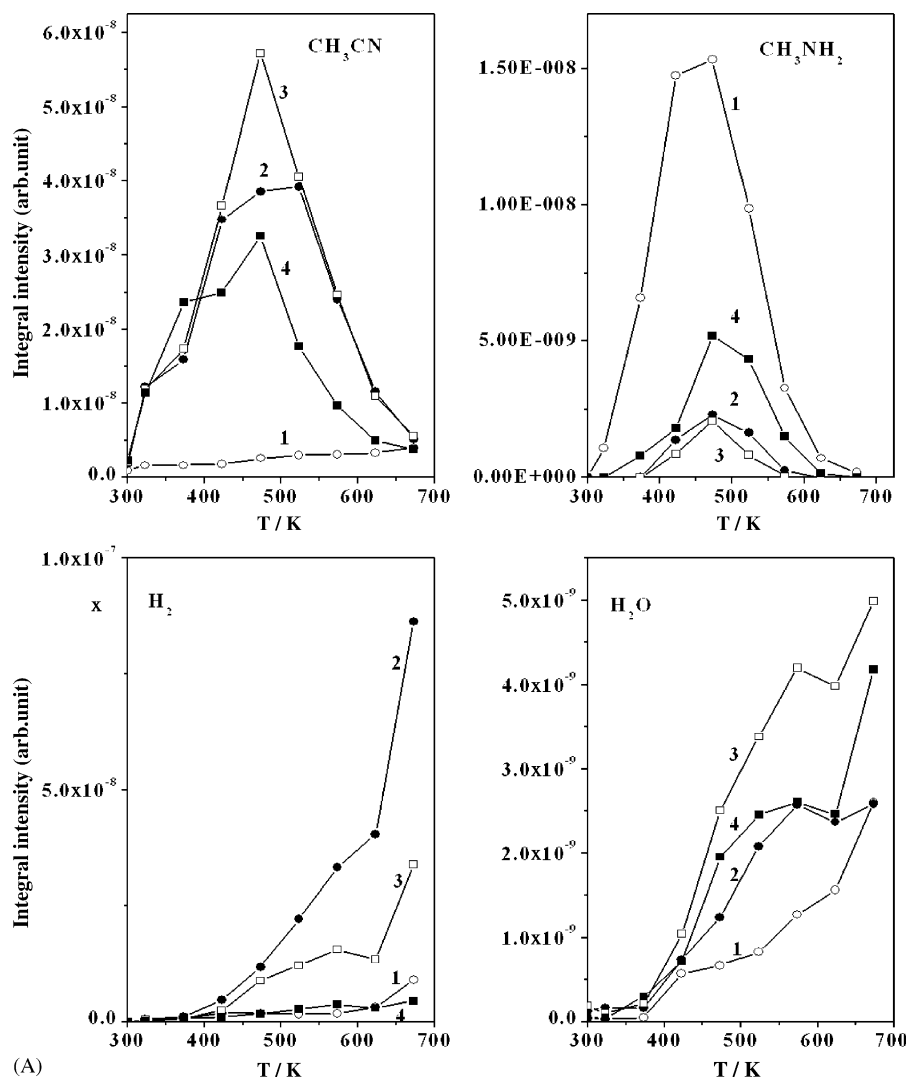


Fig. 3. Mass spectroscopic detection of gas phase products formed during the vacuum heat treatments of adsorbed CH₃CN layer: (1) Al₂O₃; (2) 1% Rh/Al₂O₃; (3) 1% Pt/Al₂O₃ and (4) 1% Au/Al₂O₃.

When the samples were heated up to the temperatures above 373 K, the formation of water was detected from all surfaces. The amount of H₂O increased with the increase of the temperature.

In the temperature range of 300–573 K the MS intensities due to the formation of gas phase CO₂ displayed small maxima between 423 and 473 K from all surfaces. The amount of CO₂ started to increase drastically above 600 K.

Above 423 K the formation of ammonia was observed from Al₂O₃-supported noble metal catalysts. NH₃ was formed in the highest amounts when the samples were heated up to 573 K. No ammonia formation was detected from Al₂O₃.

Hydrocarbons were also measured among the gas phase products formed in the above treatments. Methane was detected from 1% Rh/Al₂O₃ (its maximum amount was observed in heating up to 523 K) and from 1% Pt/Al₂O₃ (its highest amount appeared in the treatment at 473 K). No CH₄ formation was observed from 1% Au/Al₂O₃ and Al₂O₃. Ethylene development was detected from all surfaces: the highest amount of C₂H₄ was measured from Al₂O₃ when this sample was heated up to 423 K. Smaller amounts of ethylene appeared in the gas phase from

Al₂O₃-supported noble metal catalysts; its highest amounts in these cases were measured in the treatments at 473–573 K.

CO formed only from acetonitrile adsorbed on Al₂O₃-supported noble metal catalysts; no CO formation was observed from Al₂O₃. Its highest amounts were measured in the treatment at 373 K (1% Au/Al₂O₃), at 423 K (1% Rh/Al₂O₃) and at 473 K (1% Pt/Al₂O₃).

During the above treatments no N₂, HCN and C₂N₂ were detected by mass spectrometer.

The stability of adsorbed CH₃CN layer was also investigated in the presence of oxygen. In these experiments the CH₃CN-adsorbed layer (produced on the catalysts by the adsorption of 1.33 hPa CH₃CN, at 300 K for 15 min and evacuation at 300 K, 15 min) was heated up to and kept at the desired temperature for 1 min in 13.3 Pa O₂ and then the samples were quickly cooled down to 300 K in O₂ and after a short evacuation (300 K, 5 min) the IR spectra were registered at 300 K. In comparison with the results obtained during evacuation (Fig. 2A), the presence of oxygen modified the spectral features in the range of 2400–2000 cm⁻¹ (Fig. 4).

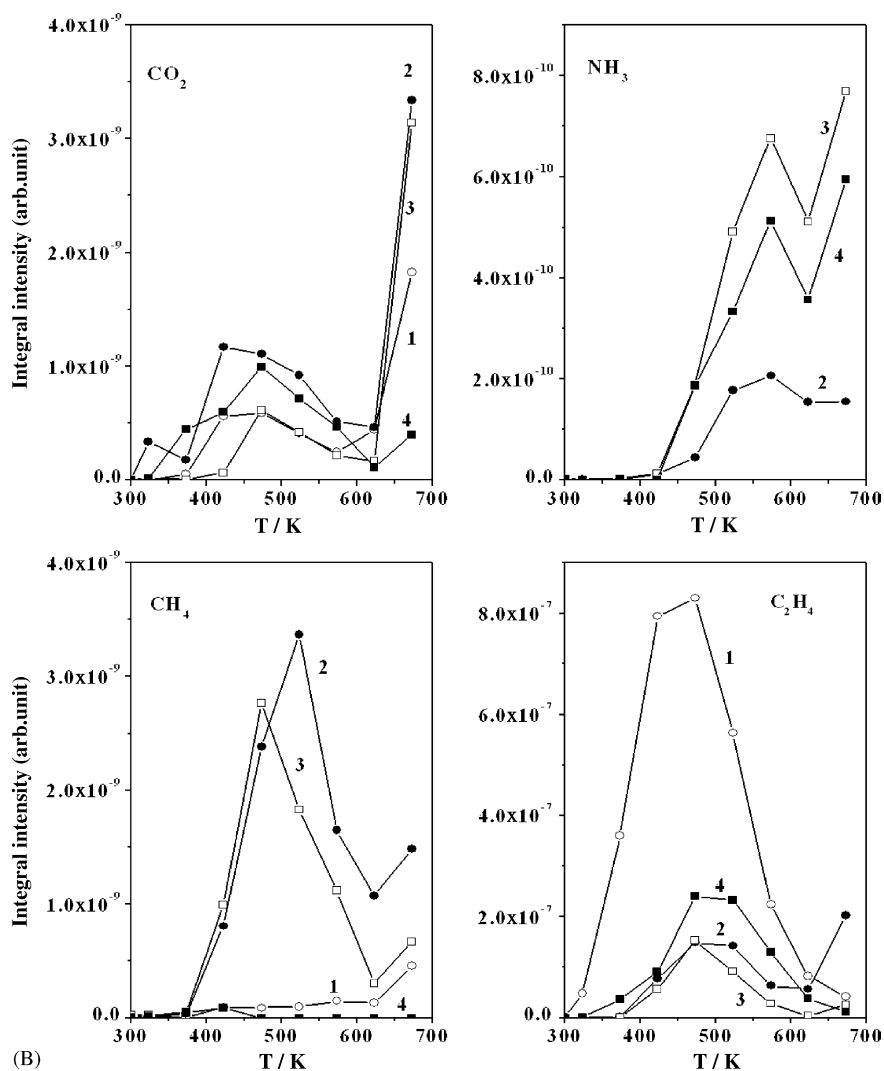


Fig. 3. (Continued).

The bands above 2300 cm⁻¹ on the spectra of Al₂O₃ disappeared at 300 K in the O₂ treatment of the adsorbed CH₃CN layer. Very small bands at 2255, 2224, 2163 and 2090 cm⁻¹, however, could be observed after the oxygen treatments at 300–673 K.

The presence of O₂ stabilized the surface species causing the bands at 2329 and 2300 cm⁻¹ on 1% Au/Al₂O₃ catalyst, as these bands could be registered even after O₂ treatment at 673 K. The stability of the bands at 2330 and 2302 cm⁻¹ observed on the spectra of 1% Rh/Al₂O₃ and 1% Pt/Al₂O₃, on the other hand, was not affected by the presence of O₂.

The most obvious effect of oxygen was the disappearance of the bands in the 2100–2000 cm⁻¹ range on the spectra of 1% Rh/Al₂O₃ and 1% Pt/Al₂O₃ (Fig. 2A), and the appearance of new bands between 2300 and 2100 cm⁻¹. On the spectra of 1% Rh/Al₂O₃ well observable new bands at 2220, 2185 and 2114 cm⁻¹ appeared already at 300 K due to O₂ treatment. At 473 K another band at 2252 cm⁻¹ was detected, which shifted to higher wave numbers with the further increase of the temperature; the 2114 and the 2220 cm⁻¹ bands could be observed up to 473 and 573 K, respectively. New band (not

observed in vacuum) at 2170 cm⁻¹ was detected on the spectra of 1% Pt/Al₂O₃ treated at 300–473 K with O₂. At 573 K – with a substantial decrease of the 2170 cm⁻¹ band – a new band at 2270 cm⁻¹ was developed. The intensity of the 2270 cm⁻¹ band decreased and bands at 2359, 2330 and 2191 cm⁻¹ appeared when the 1% Pt/Al₂O₃ sample was heated in O₂ at 673 K. On the spectra of 1% Au/Al₂O₃ the bands at 2213 and 2187 cm⁻¹ were detected after treating of the sample at 300–373 K in O₂. At and above 473 K only the 2187 cm⁻¹ band (with very low intensity) could be observed.

The presence of oxygen at 300–673 K did not affect appreciably the positions and the intensities of the bands below 2000 cm⁻¹ observed during the vacuum treatments in the same temperature range.

Mass spectroscopic analysis revealed that the formation of CH₂NH₂, H₂, H₂O, C₂H₄, CO and NH₃ was suppressed, when the samples with adsorbed CH₃CN layer were heated up in O₂. In the O₂ treatments the highest amount of CH₃CN desorbed from alumina-supported noble metal catalysts at 473 K. CO₂ formed only when the noble metal/Al₂O₃ catalysts were heated up above 500 K in O₂.

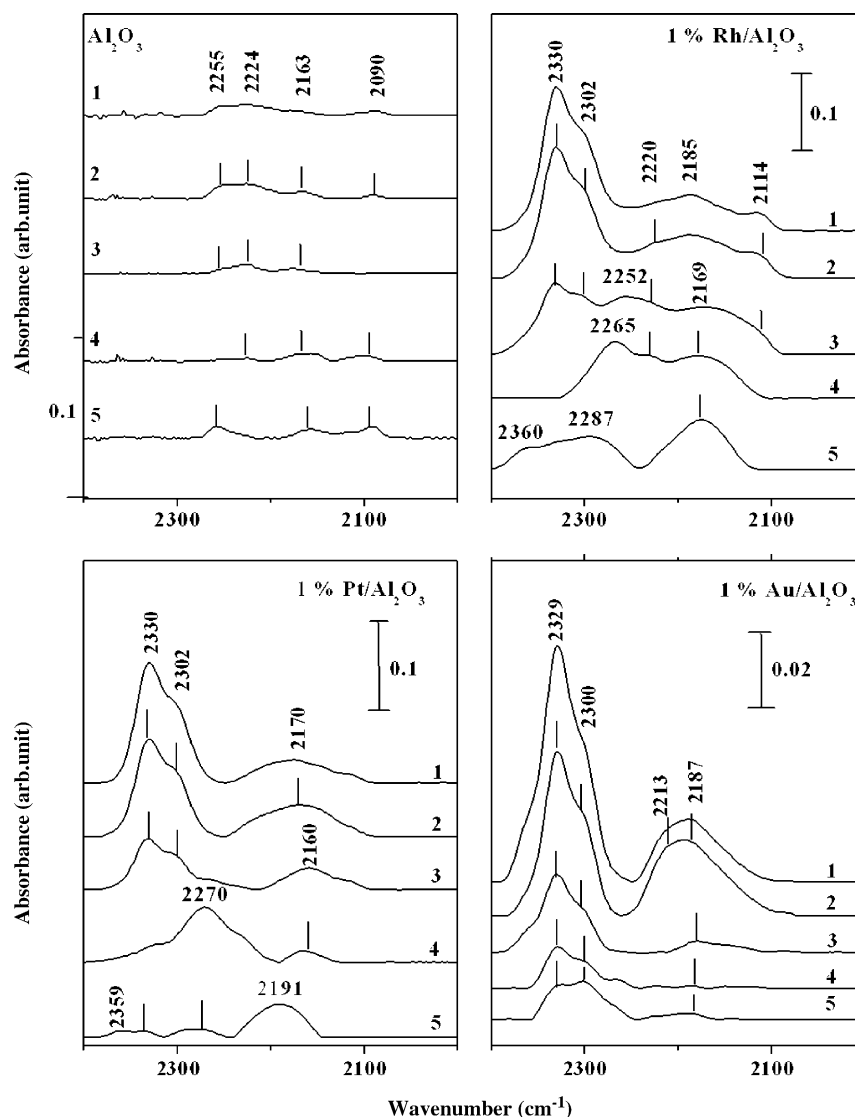


Fig. 4. Spectral changes in $\nu(\text{CN})$ range of the spectra of different catalysts after heating up of the adsorbed CH_3CN layer in O_2 (13.3 Pa): (1) 300 K; (2) 373 K; (3) 473 K; (4) 573 K and (5) 673 K. The spectra were registered at 300 K.

3.3. Isotherm studies at 300–573 K

Next the interactions of 1.33 hPa CH_3CN and that of 1.33 hPa CH_3CN + 13.3 Pa O_2 gas mixture were investigated isothermally 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 the gas phase were subtracted from the spectra registered in the reacting gas.

The spectra registered at 300 K on different catalysts in 1.33 hPa acetonitrile after 60 min of adsorption time were collected in Fig. 5A. Some spectral features different from those observed on Al_2O_3 appeared in these experiments due to the presence of metal components: (i) the dominant 2969 cm^{-1} band observed on Al_2O_3 shifted to 2988 cm^{-1} and appeared with smaller intensity on metal/ Al_2O_3 catalysts; (ii) on metal/ Al_2O_3 catalysts the 2931 cm^{-1} band was of the highest intensity in the C–H stretching range; (iii) the bands registered in the range of $2400\text{--}2000\text{ cm}^{-1}$ appeared with drastically higher

intensities on metal/ Al_2O_3 catalysts than on Al_2O_3 ; (iv) the bands at 2183, 2104 and 2050 cm^{-1} registered on metal/ Al_2O_3 catalysts were not observable on Al_2O_3 ; (v) below 2000 cm^{-1} the appearance of the bands at 1755, 1686–1666, 1603–1590, 1548–1539 and 1252 cm^{-1} should be connected with the presence of metals on Al_2O_3 . Among the bands depicted on Fig. 5A the band at 2250 cm^{-1} disappeared, while the others diminished on the effect of evacuation (15 min) at 300 K. The presence of O_2 at 300 K did not modify basically the spectral features observed in acetonitrile alone (Fig. 5B).

The intensities of the bands registered at 300 K both in CH_3CN and in $\text{CH}_3\text{CN} + \text{O}_2$ gas mixture decreased when the isotherm experiments were made at 373 K on all surfaces. The positions of the bands, however, did not change with the increase of the temperature from 300 to 373 K. New bands (not observed at 300–373 K) appeared first in isotherm experiments at 473 K.

Spectra taken at 473 K both in CH_3CN and in $\text{CH}_3\text{CN} + \text{O}_2$ gas mixture were collected on Fig. 6A for Al_2O_3 and on Fig. 6B

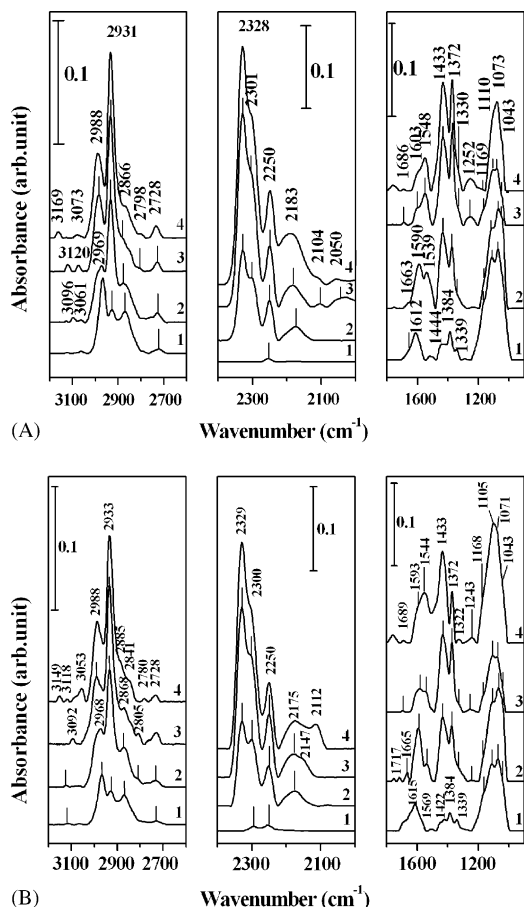


Fig. 5. Spectra taken at 300 K in (A) 1.33 hPa CH_3CN and in (B) 1.33 hPa CH_3CN + 13.3 Pa O_2 after 60 min on different catalysts: (1) Al_2O_3 ; (2) 1% $\text{Au}/\text{Al}_2\text{O}_3$; (3) 1% $\text{Pt}/\text{Al}_2\text{O}_3$ and (4) 1% $\text{Rh}/\text{Al}_2\text{O}_3$.

for 1% $\text{Rh}/\text{Al}_2\text{O}_3$. (We note here that the spectral features observed on 1% $\text{Pt}/\text{Al}_2\text{O}_3$ at 473 K were nearly the same as presented for 1% $\text{Rh}/\text{Al}_2\text{O}_3$.)

In the range of 2300–2200 cm^{-1} new band at 2253 cm^{-1} (Al_2O_3) and at 2257 cm^{-1} (1% $\text{Pt}/\text{Al}_2\text{O}_3$ and 1% $\text{Rh}/\text{Al}_2\text{O}_3$) appeared in the interaction of $\text{CH}_3\text{CN} + \text{O}_2$ gas mixture with these surfaces at 473 K. The integrated absorbances of the 2253–2257 cm^{-1} bands as a function of time at 473 K on different catalysts were plotted on Fig. 7. These bands were not detected on these surfaces at lower temperatures and in the absence of oxygen. In CH_3CN alone a band at 2211–2238 cm^{-1} was observed on all surfaces at 473 K and above. The development of the 2257 cm^{-1} band was not detected on 1% $\text{Au}/\text{Al}_2\text{O}_3$ neither in CH_3CN , nor in $\text{CH}_3\text{CN} + \text{O}_2$ gas mixture at 473 K and above. At 573 K all bands observed at 473 K appeared with smaller intensities. In the case of 1% $\text{Rh}/\text{Al}_2\text{O}_3$ bands with increasing intensities appeared at 2087 and 2039 cm^{-1} in the interaction of $\text{CH}_3\text{CN} + \text{O}_2$ gas mixture at 573 K; no bands were observed in this range on Al_2O_3 , 1% $\text{Pt}/\text{Al}_2\text{O}_3$ and 1% $\text{Au}/\text{Al}_2\text{O}_3$ catalysts.

The band at 2253–2257 cm^{-1} proved to be stable against evacuation at 473–573 K. The intensities of the other bands decreased or (above 2300 cm^{-1}) disappeared due to the evacuation following the isotherm experiments at 473–573 K.

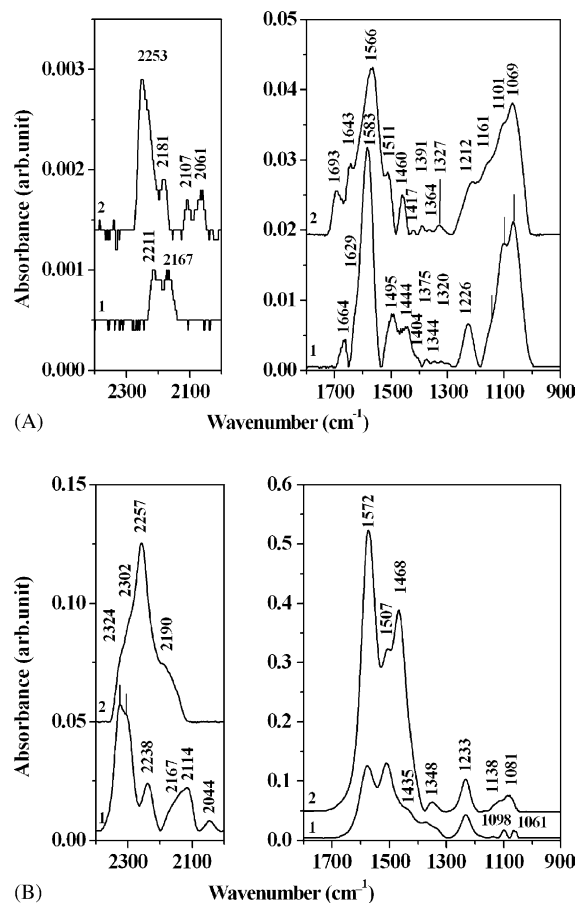


Fig. 6. Spectra registered at 473 K after 60 min on Al_2O_3 (A) and on 1% $\text{Rh}/\text{Al}_2\text{O}_3$ in: (1) 1.33 hPa CH_3CN and (2) 1.33 hPa CH_3CN + 13.3 Pa O_2 .

Mass spectrometric analysis of the gas phase during the interaction of acetonitrile with the catalysts revealed only the occurrence of dehydrogenation (evolution of H_2) on 1% $\text{Rh}/\text{Al}_2\text{O}_3$ and 1% $\text{Pt}/\text{Al}_2\text{O}_3$ at 473–573 K. The interaction of

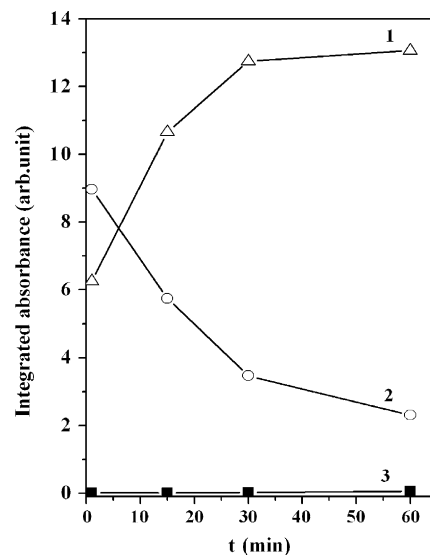


Fig. 7. Changes in integrated absorbances of the 2257 cm^{-1} band in 1.33 hPa CH_3CN + 13.3 Pa O_2 at 473 K: (1) 1% $\text{Pt}/\text{Al}_2\text{O}_3$; (2) 1% $\text{Rh}/\text{Al}_2\text{O}_3$ and (3) Al_2O_3 .

CH₃CN + O₂ gas mixture with the catalysts at 473–573 K resulted in the formation of H₂ on 1% Pt/Al₂O₃ and 1% Rh/Al₂O₃ and that of CO and CO₂ on all surfaces.

4. Discussion

4.1. Literature survey

Before interpreting our data it seems useful to summarize the main results published on CH₃CN adsorption in the last decades.

Acetonitrile (CH₃CN) and its isomer methyl isocyanide (CH₃NC) have been frequently used as probe molecules for determining of geometrical structures and bonding configurations on single crystal metal surfaces [1–9]. Acetonitrile and methyl isocyanide are isoelectronic with CO molecule. All three molecules (CO, CH₃CN and CH₃NC) contain a heteronuclear triple bond with occupied σ -non-bonding and doubly degenerated π -bonding orbitals and doubly degenerated π^* -antibonding orbitals. Comparison between CO and CH₃CN shows that although these orbitals have the same relative ordering, CH₃NC is the stronger σ -donor while CO is the stronger π^* -acceptor. For the isomeric CH₃CN and CH₃NC the higher electronegativity of nitrogen leads to a more strongly bond σ -non-bonding orbital in CH₃CN. In this way CH₃CN is expected to be the weaker donor ligand [5], than CH₃NC.

Concerning the coordination chemistry results it has been stated that acetonitrile has two possible types of coordination to a metal atom centre: (i) an end-on interaction via the nitrogen lone pair orbital or (ii) a side-on coordination via the π system of C \equiv N group [17]. Infrared spectroscopy had shown that the ν (CN) stretching frequency is sensitive to the mode of coordination. For end-on coordination via the N atom an $<100\text{ cm}^{-1}$ increase in ν (CN) is usually found from the gas phase value of 2268 cm^{-1} [17]. In the side-on bonded trifluoroacetonitrile complex, a considerable decrease in ν (CN) to 1734 cm^{-1} had been found [18]. It had been proposed that this complex is π -bonded, with the reduction in bond order caused by back donation of electrons from the metal to the ligand. A third coordination mode had also been postulated in the Fe₃(η^2 -NCCH₃)(CO)₉ complex, where both C and N atoms of the CN group are attached to the Fe₃ plane [19]. This complex exhibits a ν (CN) vibrational frequency of 1610 cm^{-1} .

The formation of η^2 (C, N) surface species was demonstrated in the adsorption of acetonitrile on Pt (1 1 1) by EELS [4,5] and IRRAS [6] methods. Acetonitrile was proposed to adsorbed in an η^2 (C, N) configuration on Pd (1 1 1), too [8].

Among the two isomers, acetonitrile is significantly more stable thermodynamically than methyl isocyanide, with an isomerization energy of $\sim 173\text{ kJ/mol}$ [20]. Consequently, the high activation barrier for the isomerization of CH₃CN to CH₃NC makes the formation of CH₃NC impossible in the course of CH₃CN adsorption [6]. In spite of the thermodynamical possibility, the surface isomerization of methyl isocyanide to acetonitrile up to 400 K has not been presented yet; it has been demonstrated [5,9] that adsorbed CH₃NC is not reversibly desorbed, instead, it decomposes at about 400 K. Its

isomerization to the more stable CH₃CN has been observed with very low extent only at high coverage and at 430 K on Pt (1 1 1) [5].

Hydrogenation of C–N bond on Pt (1 1 1) resulted in the formation of aminomethylidyne, CNH₂ (in the case of HCN), that of diaminoethylene, H₂NC=CNH₂ (when the adsorbing agent was C₂N₂) [7] and that of methylaminocarbyne, CNHCH₃ (in methyl isocyanide adsorption) [9]. No hydrogenation of C–N bond in acetonitrile adsorbed on Pt (1 1 1) was experienced [7,9].

The weaker donor character of CH₃CN has been explored with its use in determining of acid–base features of H-beta zeolites [11], the silica supported heteropoly acids [13] and Pd/Mg(Al)O catalysts [12]. On the basis of the bands observed in acetonitrile adsorption strong Al-Lewis sites ($2325\text{--}2330\text{ cm}^{-1}$), weak Al-Lewis sites ($2310\text{--}2315\text{ cm}^{-1}$), Brønsted sites ($2296\text{--}2299\text{ cm}^{-1}$), terminal hydroxyls (Si–OH, $2277\text{--}2284\text{ cm}^{-1}$) and sodium cations ($2283\text{--}2285\text{ cm}^{-1}$) have been assigned as adsorption sites on the surface of H-beta zeolites [11].

The bands at 2308 and 2278 cm^{-1} detected in the room temperature adsorption of acetonitrile on Mg(Al)O-mixed oxide [12] were assigned to the ν (CN) fundamental mode of acetonitrile N-bonded to Lewis acid sites (Al³⁺), split by coupling with the ν (CC) + δ_s (CH₃) combination. As known, the blue shift of these bands with respect to liquid acetonitrile (2292 and 2254 cm^{-1}) depends on the electron withdrawing power of the cationic site and can be taken as a measure of the Lewis acidity [21,22].

The presence of Lewis and Brønsted acid sites on Al₂O₃, on the other hand, were explicitly showed by the adsorption of acetonitrile [23]. The band at 2253 cm^{-1} was attributed to CH₃CN adsorbed on OH group (Brønsted site) and the 2328 cm^{-1} band was assigned to CH₃CN (linearly) adsorbed on Al³⁺ (Lewis site). No significant difference appeared between the spectra obtained on bare supports and those registered on the corresponding catalysts of low Pd content. From these data it was concluded that low Pd content did not modify the acid–base properties of the supports [12].

In the IR study of acetonitrile adsorption on Pt/SiO₂ [14] the bands at 2300 and 2270 cm^{-1} were assigned to physisorbed CH₃CN, and the 2195 and 2155 cm^{-1} bands were attributed to the C=N vibration of CH₃CN molecules coordinated linearly through lone electron pair of the N atom on Pt sites. It was experienced that adsorbed acetonitrile can be – at least partly – hydrogenated on the Pt surface, as two strong bands at 3350 and 3280 cm^{-1} appeared on the spectra due to N–H stretchings in H₂ addition to adsorbed acetonitrile.

The IR bands at 2318 , 2298 and 2274 cm^{-1} appearing in acetonitrile adsorption on TiO₂ [15] were assigned respectively to CH₃CN bonded on surface Lewis sites, to the Fermi resonance mode of ν (CN) and to CH₃CN bonded on surface OH groups. From the results obtained in UV irradiation (in O₂) of CH₃CN adsorbed on TiO₂ the formation of surface isocyanate (NCO) with the help of TiO₂-lattice oxygen was postulated besides the detection of H₂O, CO₂ and surface CO₃²⁻. It has been mentioned in this work that the intensity of the isolated OH bands (3228 , 3677 and 3608 cm^{-1}) decreased and that of associated OH bands

($\sim 3440\text{ cm}^{-1}$) increased with the increase of the temperature from 126 to 165 K during CH_3CN adsorption on TiO_2 . These spectral features are usually regarded as the IR evidences for the development of H-bridge bonding.

4.2. IR and MS studies of acetonitrile adsorption on Al_2O_3 -supported noble metal catalysts

The room temperature adsorption of acetonitrile resulted in a variety of surface bondings including CN group of acetonitrile. The diminution of the bands above 3600 cm^{-1} and the broad absorption centered at $\sim 3550\text{ cm}^{-1}$ (Fig. 1A and B) are due to the development of H-bridge bonding between the surface OH groups and acetonitrile via its N atom. These surface species in the adsorbed layer were stable up to 473 K (on noble metals/ Al_2O_3) and 573 K (Al_2O_3), respectively. Taking into account the disappearance of the IR bands due to H-bridge bonding of acetonitrile and the appearance of CH_3CN in the gas phase during the heat treatments in vacuum (Fig. 3A), it can be stated that the main part of H-bridge-bonded acetonitrile desorbs as intact molecule from noble metal/ Al_2O_3 catalysts.

The surface species causing the appearance of the band at 2250 cm^{-1} in acetonitrile at higher pressures (13.3 Pa–1.33 hPa) can be regarded as physisorbed acetonitrile, because due to a short evacuation at room temperature this band disappeared completely from the spectra.

The behavior of the H-bridge-bonded and physisorbed acetonitrile was not affected by the presence of oxygen.

Further spectral features in the $\nu(\text{CN})$ range ($2400\text{--}2000\text{ cm}^{-1}$) indicate the presence of different types of acetonitrile bondings to the surfaces.

The small bands appeared in acetonitrile at 2357 and 2329 cm^{-1} on the spectra of Al_2O_3 are very close to those characteristic of adsorbed carbon dioxide [24]. We did not find, however, CO_2 neither in the MS analysis of acetonitrile added to Al_2O_3 , nor during the heat treatments of adsorbed acetonitrile layer on Al_2O_3 . Thus, we are strongly convinced that the bands at 2357 and 2329 cm^{-1} are due to $\nu(\text{CN})$ in acetonitrile adsorbed on very strong Lewis acid (Al^{3+}) sites and on strong Lewis acid (Al^{3+}) sites, respectively. Formerly these bands were detected at lower frequencies (2332 and 2300 cm^{-1}) on Al_2O_3 [12]; it should be mentioned, however, that the band at 2345 cm^{-1} had been attributed to a $\text{CH}_3\text{CN}\text{--Al}$ surface species [25]. The stability of the 2357 and 2329 cm^{-1} bands experienced in this study may strengthen our assignment, as these bands were observed with very low intensity even after the heat treatment at 673 K (Fig. 2A).

On the spectra of noble metal/ Al_2O_3 catalysts bands appeared at 2329 and 2302 cm^{-1} , which are assigned to acetonitrile adsorbed on strong Al-Lewis sites (2329 cm^{-1}) and to acetonitrile adsorbed on weak Al-Lewis sites (2302 cm^{-1}) [11]. If we considered that the blue shifts of the corresponding bands (2292 and 2254 cm^{-1}) of liquid acetonitrile could be taken as a measure of the Lewis acidity [21,22], it would be plausible to suppose that the addition of noble metals onto the alumina surface reduces the electron withdrawing power of the Al^{3+} cationic sites (i.e. strength of Lewis acidity) possibly due to the electron donation of noble metal particles to uncoordinated Al^{3+} ions of Al_2O_3 surface.

Bands at 2196 and 2154 cm^{-1} of very low intensity appeared on the spectra of Al_2O_3 and a band with appreciable intensity at $2192\text{--}2186\text{ cm}^{-1}$ was observed on the spectra of noble metal/ Al_2O_3 catalysts at $300\text{--}373\text{ K}$ (Fig. 2A). We suppose that these bands are due to $\text{CN}_{(\text{a})}$ on Al-sites formed in the dissociation of acetonitrile. Accordingly, the extent of acetonitrile dissociation is very low on Al_2O_3 , in the cases of noble metal/ Al_2O_3 catalysts, however, the dissociation of acetonitrile on Al_2O_3 occurred with a measurable rate. We mention here that HCN dissociation on TiO_2 and Rh/TiO_2 catalysts resulted in the appearance of the 2195 cm^{-1} band, which was assigned to $\nu(\text{Ti}\text{--CN})$ species [26].

The heat treatments of adsorbed acetonitrile layer on $\text{Rh/Al}_2\text{O}_3$ and $\text{Pt/Al}_2\text{O}_3$ above 373 K caused the appearance of the bands at $2070\text{--}2047\text{ cm}^{-1}$ ($\text{Rh/Al}_2\text{O}_3$) and at 2128 and $2050\text{--}2019\text{ cm}^{-1}$ ($\text{Pt/Al}_2\text{O}_3$). These bands are assigned to $\text{CN}_{(\text{a})}$ on the metal sites formed in the dissociation of acetonitrile on Rh and on Pt, respectively. No band due to Au–CN species was observed in this study. We note that the dissociation of HCN on Rh/SiO_2 and on Rh/TiO_2 catalysts resulted in a band at 2062 and 2054 cm^{-1} , respectively, which was attributed to Rh–CN surface species [26]. The development of the band(s) due to metal–CN species was hindered by the presence of oxygen (Figs. 4 and 5B), possibly due to blocking of metal sites by oxygen.

The band observed at 1615 cm^{-1} on Pt (1 1 1) [4] and at 1755 cm^{-1} on Pd (1 1 1) [8] was attributed to $\eta^2(\text{C}, \text{N})\text{CH}_3\text{CN}$ -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 (1 1 1) than on Pt (1 1 1) [8]. Based on the above results obtained on single crystal surfaces the bands at 1605 cm^{-1} ($\text{Pt/Al}_2\text{O}_3$), at 1769 cm^{-1} ($\text{Rh/Al}_2\text{O}_3$) and at 1756 cm^{-1} ($\text{Au/Al}_2\text{O}_3$) appeared in our studies are assigned to $\eta^2(\text{C}, \text{N})\text{CH}_3\text{CN}$ species formed on the metal particles, and it can be concluded that the softening of CN stretching mode in $\eta^2(\text{C}, \text{N})\text{CH}_3\text{CN}$ on metal particles increases in the order of

Table 1
Characteristic CH bands (in cm^{-1}) observed in CH_3CN adsorption on different surfaces

Assignment	Gas [27]	Pt (1 1 1) monolayer [4]	Pd (1 1 1) [8]	$\text{Al}_2\text{O}_3^{\text{a}}$	$\text{Pt/Al}_2\text{O}_3^{\text{a}}$	$\text{Rh/Al}_2\text{O}_3^{\text{a}}$	$\text{Au/Al}_2\text{O}_3^{\text{a}}$
$\nu_{\text{as}}(\text{CH})$	3009	3005		2966	2967	2967	2968
$\nu_{\text{s}}(\text{CH})$	2954	2960		2925	2928	2928	2927
$\delta_{\text{as}}(\text{CH}_3)$	1448	1435	1447, 1410	1444	1433	1433	1433
$\delta_{\text{s}}(\text{CH}_3)$	1385	1375	1371	1384	1372	1372	1372
$\rho(\text{CH}_3)$	1041	1060	1040	1043	1043	1043	1043

^a This work.

Table 2
Characteristic CN bands (in cm^{-1}) observed in CH_3CN adsorption on different surfaces

Assignment	Gas [27]	H/beta zeolites [11]	Pt (1 1 1) [4]	Pd (1 1 1) [8]	Al_2O_3^a	Pt/ Al_2O_3^a	Rh/ Al_2O_3^a	Au/ Al_2O_3^a
$\nu(\text{CN})$ in CH_3CN on very strong Al-Lewis sites					2357			
$\nu(\text{CN})$ in CH_3CN on strong Al-Lewis sites		2325–2330			2329	2329	2329	2329
$\nu(\text{CN})$ in CH_3CN on weak Al-Lewis sites		2310–2315				2300	2303	2303
$\nu(\text{CN})$ in free molecular CH_3CN	2267							
$\nu(\text{Al-CN})$					2199	2189	2192	2190
$\nu(\text{M-CN})$						2128, 2050–2019	2070–2047	
$\eta^2(\text{C, N}) \text{CH}_3\text{CN}$			1615	1755	1611	1605	1769	1756

^a This work.

Rh < Au < Pt on Al_2O_3 -supported noble metals. The appearance of the 1611 cm^{-1} band on the spectra of Al_2O_3 (Fig. 1A) can be considered as a sign for the formation of $\eta^2(\text{C, N})\text{CH}_3\text{CN}$ species even on Al_2O_3 surface, too.

The positions of the bands due to stretching and deformation modes of CH_3 in acetonitrile (Table 1) were nearly the same on all surfaces investigated. This implies that C–H bonds were not affected strongly by the nature of the adsorption sites where acetonitrile molecules bond to the surface. The bands due to C–H vibrations could be hardly detected above 473 K (Fig. 2B), which corresponds well to the desorption curves of intact acetonitrile (Fig. 3A).

Formerly it has been established that acetonitrile adsorbs only molecularly on the surfaces studied so far [4,7,8,11–13]. Exceptional examples were W (1 0 0) and W (1 0 0)–(5 × 1)–C surfaces, where irreversible decomposition dominates [28]. As a consequence of the supposed intact molecular acetonitrile on Pt (1 1 1) there was no indication of the formation of hydrogenated species (CNH_2) from CH_3CN on Pt (1 1 1) [4,7]. It has been expressed, however, that neither through investigation on the thermal chemistry of acetonitrile nor attempt to verify the non-dissociative adsorption of acetonitrile had been performed on Pt (1 1 1) [7].

Our data clearly show that the dissociation of acetonitrile (formation of $\text{CN}_{(\text{a})}$ species) occurred on the surfaces investigated: we detected bands due to $\text{CN}_{(\text{a})}$ species (Table 2), and mass spectrometric analysis revealed the gas phase molecules (CH_4 and C_2H_4) (Fig. 3B), the formations of which should be connected with the rupture of C–C bond in CH_3CN (i.e. dissociation of CH_3CN). The detection of NH_3 in the gas phase (Fig. 3B), on the other hand, suggests the occurrence of the C–N bond rupture, too. The formation of NH_3 was detected on Al_2O_3 -supported noble metal catalysts, NH_3 did not form on pure Al_2O_3 . This means that the disruption of C–N bond occurs only on metal particles and $\text{N}_{(\text{a})}$ thus formed can be hydrogenated above 450 K on these catalysts.

Bands observed in this work at 2815–2847, 2756–2773, 1164–1167 and 1105–1119 cm^{-1} may be due to adsorbed CH_3NH_2 [31,32]. We have no plausible interpretation for the appearance of methylamine (in the adsorbed layer and in the gas phase) and for the inverse changes of the amounts of

molecular acetonitrile and CH_3NH_2 from different catalysts. A possible explanation would be the different bonding configurations formed on pure Al_2O_3 and on Al_2O_3 -supported noble metal catalysts. The different ratios of $\nu_{\text{as}}(\text{CH})$ ($2967\text{--}2979 \text{ cm}^{-1}$) and $\nu_{\text{s}}(\text{CH})$ ($2926\text{--}2932 \text{ cm}^{-1}$) may strengthen the assumption for the different bonding configurations on Al_2O_3 and Al_2O_3 -supported noble metal catalysts, respectively.

The band at $2253\text{--}2257 \text{ cm}^{-1}$ appeared in $\text{CH}_3\text{CN} + \text{O}_2$ gas mixture at and above 473 K (Fig. 7) on Pt/ Al_2O_3 , on Rh/ Al_2O_3 and with very small intensity on Al_2O_3 is due to NCO species localized on Al_2O_3 [29,30]. The prerequisite of NCO formation is also the dissociation (C–C bond rupture) of CH_3CN , and the oxidation of $\text{CN}_{(\text{a})}$ results in the development of $\text{NCO}_{(\text{a})}$. The dissociation step is facile on metallic sites, very possibly the oxidation step is also occurring on the metal. Isocyanate formed on the metallic sites, however, migrates very quickly from the metal to the support and localizes there [29,30].

5. Conclusions

1. Acetonitrile bonds molecularly to the studied surfaces through H-bridge bonding, through lone pair electrons of its nitrogen to strong and weak Lewis acid sites of the support and through both carbon and nitrogen atoms of its CN ($\eta^2(\text{C, N})$ species).
2. Acetonitrile dissociates producing $\text{CN}_{(\text{a})}$.
3. Adsorbed acetonitrile can be hydrogenated into methylamine.
4. $\text{CN}_{(\text{a})}$ species on noble metal sites dissociate at higher temperature, the hydrogenation of $\text{N}_{(\text{a})}$ thus produced led to the formation of gas phase ammonia.
5. Surface isocyanate (NCO) formation was detected in $\text{CH}_3\text{CN} + \text{O}_2$ mixture at and above 473 K.

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