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Adsorption and catalytic reactions of acetonitrile and acetonitrile–oxygen mixture on TiO_2-supported rhodium catalysts

J. Raskó [*], J. Kiss

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

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Abstract

The adsorption and surface reactions of acetonitrile and acetonitrile–oxygen gas mixture were studied on TiO_2-supported Rh 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 (2319 cm^{-1}), to very strong Lewis acid centres (2347 cm^{-1}) of titania; it can be coordinated linearly through the lone electron pair of the N atom on Rh sites (2193 cm^{-1}) and η^2 (C,N) CH_3CN species can be formed on Rh particles (1691–1708 cm^{-1}). CH_3CN dissociates on Rh sites, the resulting $CN_{(a)}$ can be oxidized into NCO surface species. $CN_{(a)}$ can be dissociated only on Rh particles into $N_{(a)}$ and $C_{(a)}$. The hydrogenation of $N_{(a)}$ resulted in the appearance of NH_3 among the gaseous products from Rh/TiO_2 catalysts. The formation of other products (CH_3NH_2, H_2, CO_2, CH_4, C_2H_4 and CO) was demonstrated and discussed.

Keywords: Acetonitrile adsorption; Effect of gaseous oxygen; Surface species; Gas phase products; FTIR; MS

1. Introduction

The geometrical structures and bonding configurations of acetonitrile (CH_3CN) on single crystal metal surfaces were the subjects of several papers [1–9]. It has been demonstrated that acetonitrile adsorbs mainly through both C and N atoms of CN groups on Pt(1 1 1) [4,5] and on Pd(1 1 1) [8] single crystal surfaces. The acid–base properties of supported catalysts were also demonstrated [10–13] by acetonitrile adsorption. No significant difference existed 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]. Beyond these valuable surface studies there are only few works [14,15] dealing with the heterogeneous catalytic reactions of acetonitrile. It was experienced that adsorbed acetonitrile can be – at least partly – hydrogenated on Pt/SiO_2 catalyst [14]. From the results obtained in UV irradiation (in O_2) of CH_3CN adsorbed on TiO_2 the formation of surface isocyanate (NCO) with the help of TiO_2-lattice oxygen was postulated [15].

The catalytic reactions of CN-containing (sometimes hazardous) compounds in general, however, would have a practical importance, which needs detailed information on reaction mechanisms of the above transformations.

As a continuation of our previous work using Al_2O_3 as support [16], in the present work attempts have been made on the characterization of adsorbed species and gas phase products formed during the interactions of acetonitrile and acetonitrile–oxygen gas mixture on titania-supported rhodium catalysts.

2. Experimental

TiO_2 was the product of Degussa (P25, 50 m^2/g). One and five percent Rh/TiO_2 catalyst was prepared by impregnating TiO_2 with an aqueous solution (Rh content was 4 g/100 ml) of $RhCl_3 \cdot 3H_2O$ salt (Johnson Matthey, 99.99% metal basis) to yield a nominal 1 and 5% metal content. The impregnated powders were dried in air at 383 K for 3 h. The dispersity of the reduced catalysts was determined by hydrogen adsorption in a conventional volumetric apparatus: it was 30% for 1% Rh/TiO_2 and 27% for 5% Rh/TiO_2. Acetonitrile (Reanal, 99.8% purity) was used after a freeze and pump purification process.

For IR studies the catalysts' powders were pressed onto a Ta-mesh (30 mm × 10 mm, 5 mg/cm^2). The mesh was fixed to the

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[*] Corresponding author. Fax: +36 62 420 678.
E-mail address: rasko@chem.u-szeged.hu (J. Raskó).

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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). Briefly, the samples were (a) heated (20 K/min) to 573 K in 1.33 hPa O_2, (b) oxidized with 1.33 hPa O_2 for 30 min at 673 K, (c) evacuated for 15 min and (d) reduced in 1.33 hPa of H_2 for 60 min at 573 K. 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 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 of the gas phase in the IR cell was performed with the help of a Balzers QMS 200 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 the possible products were followed by mass spectrometer.

3. Results and discussion

Spectra recorded at 300 K on TiO_2 in CH_3CN of different pressures are collected in Fig. 1. In the C–H stretching region (3100–2600 cm^{-1}) the 2929 cm^{-1} band (ν_s (CH)) became dominant in the pressure range (1.33–1.33 hPa) applied. Besides the band at 2295 cm^{-1} due to CH_3CN molecularly adsorbed on weak Lewis acid sites (Ti^{3+}) a band at 2272 cm^{-1} attributed to physisorbed acetonitrile was observed in the C–N stretching region; the increase in intensity of the 2272 cm^{-1} band with the increase of CH_3CN pressure was more pronounced than that of the 2295 cm^{-1} band. The bands due to δ_{as} (CH_3) (1456 cm^{-1}), δ_s (CH_3) (1379 cm^{-1}) and ρ (CH_3) (1058 cm^{-1}) of molecularly adsorbed CH_3CN can be clearly distinguished at lower wavenumbers [16].

The IR features observed at 2864 and 1121 cm^{-1} can be assigned to adsorbed CH_3NH_2 [17,18]. The formation of CH_3NH_2 might be connected with the participation of titania OH groups in the surface reactions.

The appearance of the bands at 1647 cm^{-1} (δ (H_2O)), at 1590 and 1544 cm^{-1} (possibly due to surface carbonates) is the result of the surface oxidation of acetonitrile by active oxygen of titania.

Some new spectral features were detected on the spectra of CH_3CN on Rh-containing TiO_2 (Fig. 2). Besides the band due to CH_3CN molecularly adsorbed on weak Lewis sites (here at 2286 cm^{-1}) the bands due to CH_3CN adsorbed on strong (2319 cm^{-1}) and on very strong (2347 cm^{-1}) Lewis acid sites appeared in the room temperature adsorption of 1.33 Pa to 1.33 hPa acetonitrile on 5% Rh/TiO_2. The formation of strong and very strong Lewis acid sites on Rh/TiO_2 catalysts may be due to the electron donation of Ti^{3+} to Rh particles, which would increase the electron withdrawing power of the Ti^{3+} cationic sites (i.e. the strength of Lewis acidity). The electron transfer from TiO_2 to Rh may be interpreted on the basis of work function ($\Delta\phi$) values: the work function of reduced TiO_2 is 4.8 eV [19], and $\Delta\phi$ value of polycrystalline Rh is 4.98 eV

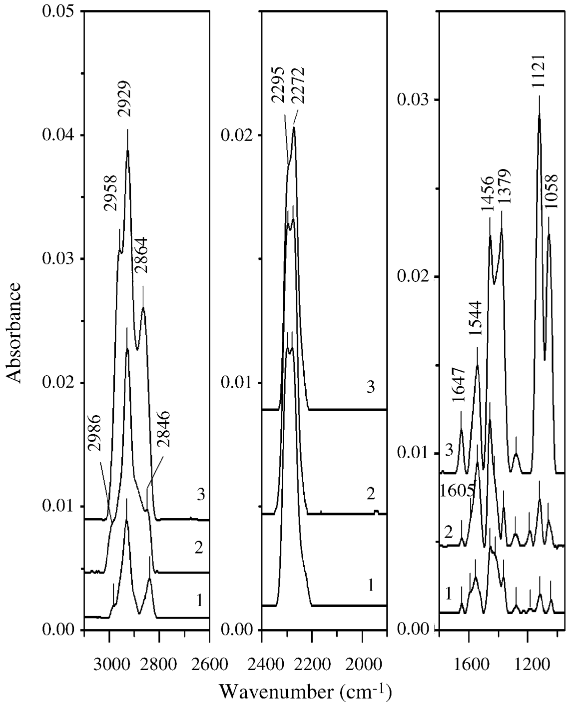

Fig. 1. Infrared spectra registered during the adsorption of acetonitrile with different pressures on TiO_2 at 300 K: (1) 1.33 Pa, (2) 13.3 Pa and (3) 1.33 hPa.

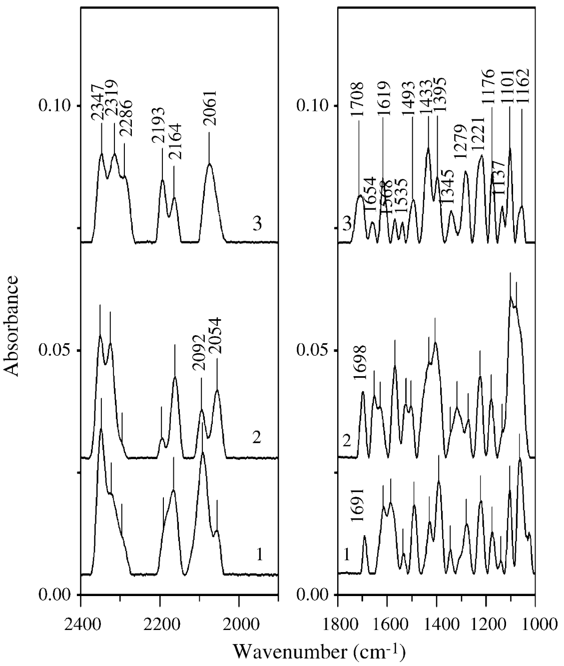

Fig. 2. Infrared spectra taken during the adsorption of acetonitrile with different pressures on 5% Rh/TiO_2 at 300 K: (1) 1.33 Pa, (2) 13.3 Pa and (3) 1.33 hPa.

[20]. This small difference in work function suggests that electron may flow from titania to Rh at the interface.

The 2193 cm^{-1} band appearing on the spectra of Rh/TiO_2 catalysts is attributed to the CN vibration of CH_3CN molecules coordinated linearly through the lone electron pair of the N atom on Rh sites. The appearance of the bands at 2164, 2092 and 2054 cm^{-1} can be due to $CN_{(a)}$ formed in the dissociation of acetonitrile on Rh particles in different surface environments [21].

Below 1800 cm^{-1} a new band at 1691 cm^{-1} was registered in 1.33 Pa CH_3CN, the position of which shifted to higher wavenumbers with the increase of the pressure; it was detected at 1708 cm^{-1} in 1.33 hPa CH_3CN (Fig. 2). The band observed at 1615 cm^{-1} on Pt(1 1 1) [22] and at 1755 cm^{-1} on Pd(1 1 1) [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(1 1 1) than on Pt(1 1 1). Based on the above results obtained on single crystal surfaces the band at 1691–1708 cm^{-1} detected in our studies is assigned to η^2 (C,N) CH_3CN species formed on Rh particles.

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 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

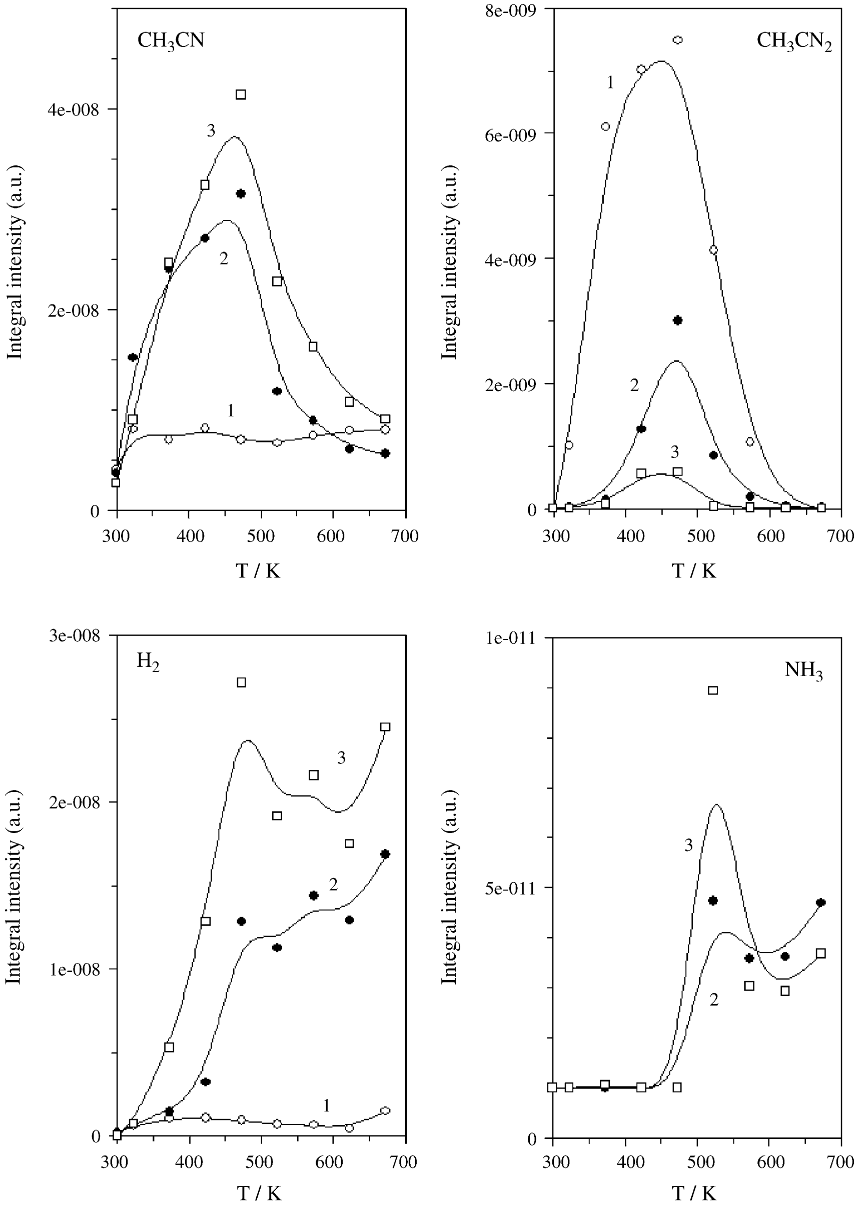

Fig. 3. (A and B) Formation of some gaseous products during the vacuum treatments of adsorbed CH_3CN layer at different temperatures (see text): (1) TiO_2, (2) 1% Rh/TiO_2 and (3) 5% Rh/TiO_2.

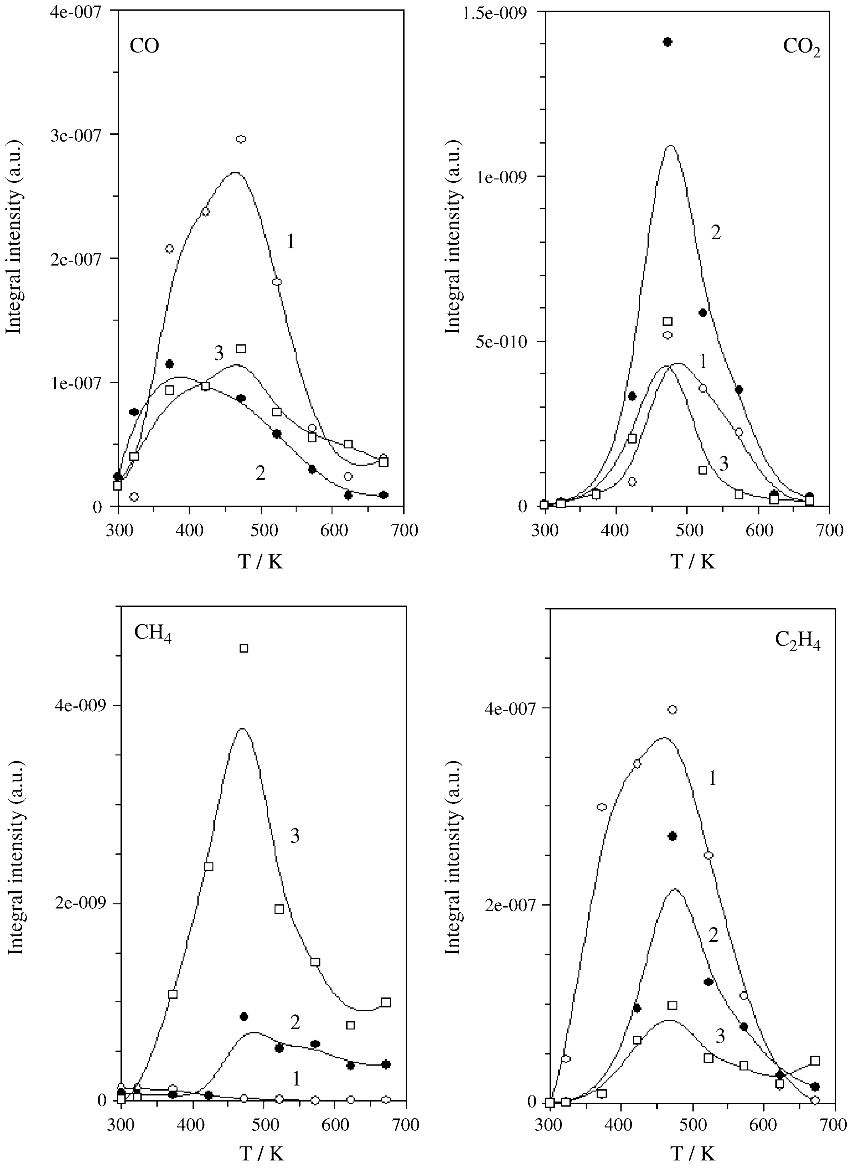

Fig. 3. (*Continued*).

applied here (673 K) the IR features 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 integrated MS intensities during the whole heating process due to different products as a function of the temperature were plotted in Fig. 3. No molecular desorption of CH_3CN was observed from TiO_2. In the cases of Rh-containing TiO_2 catalysts, however, a T_{max} at 473 K appeared on the molecular CH_3CN desorption curves; the amounts of the desorbed CH_3CN increased with the increase of the metal content. The highest amount of methylamine (CH_3NH_2) was measured from TiO_2 ($T_{max} = 473$ K), the amount of desorbed CH_3NH_2 decreased with increasing metal content of the catalysts. From these data we may conclude 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 diminish with the increase of metal concentration on the oxide surface. The desorption curves for C_2H_4 were very similar to those for CH_3NH_2: T_{max} of C_2H_4 desorption appeared at 473 K and the amount of C_2H_4 desorbed decreased with the increase of metal content of the catalysts. We have no plausible explanation yet for the obvious connection existing between CH_3NH_2 and C_2H_4 formations.

Hydrogen formed only on Rh/TiO_2 catalysts. The amount of H_2 depended on the Rh content: more H_2 evolved on 5% Rh/TiO_2 than on 1% Rh/TiO_2. The CH_4 desorption curves show similarities to those for H_2: there was no CH_4 formation on TiO_2 and the amount of CH_4 increased with increasing Rh content. The appearance of H_2 and CH_4 among the gas phase products is the consequence of CH_3CN dissociation (i.e. the formation of $CN_{(a)}$ and $CH_{3(a)}$) and the dehydrogenation and hydrogenation of CH_3 occurring exclusively on Rh particles of the catalysts.

Appreciable amounts of NH_3 were experienced ($T_{max} = 523$ K) on Rh/TiO_2 catalysts; no NH_3 was formed on pure TiO_2. The formation of ammonia can be regarded as a proof for the C–N bond breakage in $CN_{(a)}$ produced via the dissociation of CH_3CN on Rh particles. These findings point out that Rh/TiO_2 catalysts would be possible candidates for catalytic elimination of hazardous CN-containing molecules by dissociating of their C–N groups.

The detection of oxidation products (CO and a smaller amount of CO_2) revealed the occurrence of a reaction between adsorbed CH_3CN and mobile surface oxygen of titania.

The stability of adsorbed CH_3CN layer was also investigated in the presence of oxygen. In these experiments, the CH_3CN adsorbed layer (produced on the catalysts by the adsorption of 1.33 hPa CH_3CN, 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 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. 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 Rh/TiO_2 samples the bands in the CN region were registered even after the treatment at 673 K and a small band at around 2210 cm^{-1} (due to Ti–NCO [22–24]) appeared at and above 473 K. The intensity of this band was higher on 5% Rh/TiO_2 than on 1% Rh/TiO_2 catalyst at any temperature and showed a maximum at 573 K on both surfaces.

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 (473 K) both in the absence and in the presence of O_2, its amount, however, was highly suppressed by O_2. CH_3NH_2 desorption shows a maximum at 523 K on 1% Rh/TiO_2 and CH_3NH_2 formed only

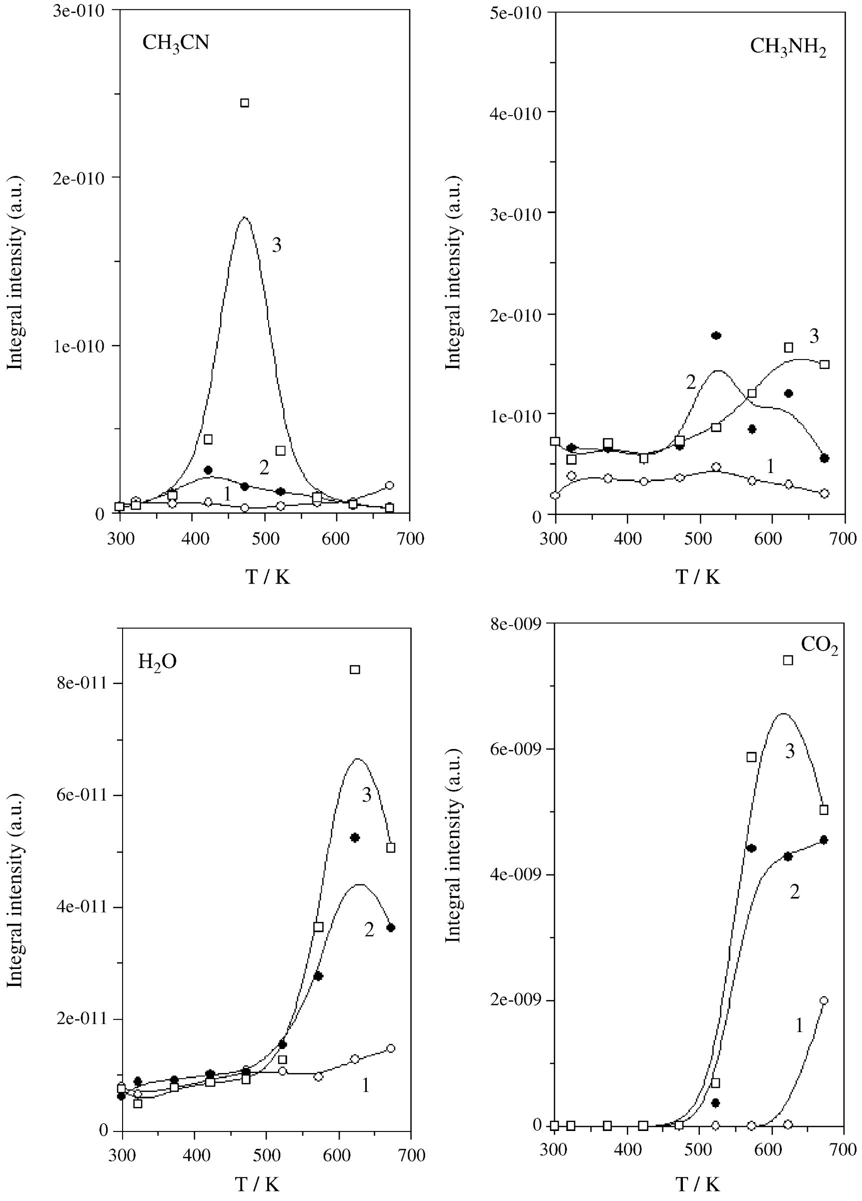

Fig. 4. Formation of some gaseous products during the oxygen treatments of adsorbed CH_3CN layer at different temperatures (see text): (1) TiO_2, (2) 1% Rh/TiO_2 and (3) 5% Rh/TiO_2.

above 523 K on 5% Rh/TiO_2 in the presence of O_2. A small decrease in the amount of oxygen above 473 K and the appearance and increase of H_2O and CO_2 above 473 K (Fig. 4) show that the oxidation reaction between gaseous oxygen and adsorbed CH_3CN starts at 473 K. H_2, NH_3, 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 from 1% Rh/TiO_2 with the same T_{max} value (523 K) and appeared above 523 K on 5% Rh/TiO_2, as did CH_3NH_2, which may show again a possible connection between the formation of a hydrogenated product (CH_3NH_2) and that 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_4 and CO on TiO_2, CH_3NH_2, H_2, NH_3, CH_4, C_2H_4 and CO on Rh/TiO_2 catalysts) 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 amount of gas phase CH_3CN decreased and in the cases of Rh/TiO_2 samples oxygen was completely missing in the gas phase. The amounts of gas phase products (CO_2 and CO on TiO_2, H_2, CO_2 and CO on Rh/TiO_2 catalysts) slightly increased at these temperatures. CH_4 and C_2H_4 were not present among the reaction products in $CH_3CN + O_2$ gas mixture. Very interestingly a small amount of HCN was detected in $CH_3CN + O_2$ gas mixture on 5% Rh/TiO_2 at 573 K.

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 [23–25] with appreciable intensity appeared already at 373 K on 1 and 5% Rh/TiO_2 catalysts. The intensity of this band was higher at any temperatures on 5% Rh/TiO_2, than on 1% Rh/TiO_2 and it increased with increasing reaction temperature upto 473 K; at 573 K this band was absent from the spectra. It can be concluded that the higher Rh content of the catalyst and the presence of gas phase O_2 favoured the formation of Ti–NCO surface species. We think that the dissociation of CH_3CN on Rh particles resulting in $CN_{(a)}$ species and the consecutive oxidation of $CN_{(a)}$ would lead to the formation of NCO. After its formation on the metal particles NCO migrates quickly to the support and localizes there [22–24]. We mention here that on single crystal Rh(1 1 1) surface the band due to $NCO_{(a)}$ appeared at 2160 cm^{-1} [26].

4. Conclusions

An electron donation from TiO_2 to Rh particles leads to the formation of strong Lewis acid sites on TiO_2 and electron-rich Rh particles on Rh/TiO_2 catalysts. CH_3CN dissociation on Rh particles occurs resulting in $CN_{(a)}$ on the metal. The reaction of $CN_{(a)}$ with the surface oxygen of titania and/or adsorbed oxygen on metal 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. $CN_{(a)}$ can dissociate on Rh, the hydrogenation of $N_{(a)}$ species resulted in the formation of NH_3.

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