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DRIFTS study of the nature and reactivity of the surface compounds formed by co-adsorption of NO, O_2 and propene on sulfated titania-supported rhodium catalysts

Jorge Luis Flores-Moreno [a], Gérard Delahay [b], François Figueras [a,*], Bernard Coq [b]

[a] *Institut de Recherches sur la Catalyse (CNRS UPR5401), 2 avenue A. Einstein, 69626 Villeurbanne, France*
[b] *Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique UMR 5618 ENSCM-CNRS 8, Rue de l'Ecole Normale, 34296 Montpellier, France*

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Abstract

The selective reduction of NO with propene was investigated on sulfated TiO_2, either pure or containing 1 wt% Rh, using in situ diffuse reflectance Fourier infrared transform spectroscopy (DRIFTS). During the NO–C_3H_6–O_2 reaction, the main surface species detected were adsorbed nitrate, a carbonylic compound, acetate, cyanide (–CN), and isocyanate (–NCO). The formation of nitrates at the TiO_2 surface occurs by a fast disproportionation of NO, and by its oxidation on Rh. Rh promotes the formation of –CN and –NCO species. Different steps of the process were investigated using cycles of adsorption. The interaction of a nitrated surface with propene leads to the formation of a carbonylic compound tentatively identified as acetaldehyde. This carbonylic compound reacts very fast with a mixture NO + O_2, leading to the rapid formation of –CN and –NCO species. The appearance of ν(NH) bands ascribed to the formation of ammonia surface complexes was observed simultaneously with a decrease of the –NCO band, suggesting that the –NCO species is hydrolyzed to the –NH complexes by the reaction with some traces of water. A reaction mechanism can be proposed in which nitrate species react with acetaldehyde in an acid-catalysed process, yielding cyanates, which are further hydrolysed to ammonia and CO_2. N_2 is then be formed by the reaction of NH_3 with NO.

Keywords: Nitric oxide reduction; In situ DRIFTS; Propene; Rh oxide; Sulfated titania; Coadsorptions

1. Introduction

The selective catalytic reduction of NO_x by hydrocarbons (HC-SCR) under "lean" conditions (i.e., excess oxygen) has been studied extensively over the last 15 years for applications in emission control from diesel and lean-burning gasoline engines. The operation of such engines under excess oxygen provides energy savings from better fuel efficiency. However, under these conditions, the conventional three-way catalysts promote the reaction between the limited amounts of hydrocarbons with the excess amount of oxygen present in the exhaust, thus failing to reduce NO_x. The field of HC-SCR has been reviewed a number of times [1–4], and several mechanisms have been proposed. A simple mechanism that involves the dissociation of NO on a reduced metal surface to give N(ads) and O(ads), with subsequent desorption of N_2 and N_2O and removal of O(ads) by the reductant, can explain many of the results with the platinum group metal catalysts when using a support of low acidity. An additional contribution from organo–nitro-type species may contribute to the overall NO_x reduction activity when acidic supports are involved [5–7]. Indeed, using a purely acid catalyst, the reduction of NO by aldehydes is fast and selective at low temperature [8,9], clearly demonstrating a possible pathway to N through acid catalysis.

The results recently reported on the kinetics of SCR on Rh/sulfated titania agree with the importance of acidity in the reaction [10]. A bifunctional mechanism has been proposed, in which the rate is controlled by the oxidizing function at low Rh content and by acidity at high Rh loading. Investigation of the reaction by in situ infrared spectroscopy can provide useful information on the intermediates. For the SCR of NO_x with C_3H_6

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[*] Corresponding author. Fax: +33472445399.
E-mail address: figueras@catalyse.cnrs.fr (F. Figueras).

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on Ag/γ-Al_2O_3, Meunier et al. [11] proposed organo-nitrite species characterized by a band at 1645 cm^{-1} as intermediate. For Rh/MCM-41, Long and Yang [12] proposed a mechanism in which Rh–NO^+ reacts with adsorbed propene, leading to cyanates, the formation of acrolein being the path to the side reaction of combustion. In contrast, acrylic compounds formed by allylic oxidation were considered key intermediates on Ga_2O_3–Al_2O_3 [13]. We report here the results of a study in which we attempted to identify surface-adsorbed intermediates on Rh oxide/sulfated TiO_2. Data on the adsorption of simple gases (e.g., NO_x, CO, acrolein, propene) on Rh or titania are abundant, but those concerning mixtures are less common; thus that we tried to simulate different steps of the reaction on Rh/sulfated titania, performing co-adsorptions and successive adsorptions of the reactants.

2. Experimental

The titania support, denoted by G5 and commercialised by Millennium Chemicals, was prepared by hydrolysis of sulfates and contains sulfur. It was used after a standard calcination at 773 K in air for 2 h, which results in an S content of 0.32 wt% and a BET surface of 64 m^2/g. The number of acid sites retaining ammonia at 383 K was 0.36 mmol/g, as measured by thermogravimetry. By impregnation of 2.2% S, the number of acid sites increased only to 0.4 mEq/g, demonstrating that the original S content was sufficient to create most of the acidity [10]. As reported in Table 1, these acidities agree with those determined either by adsorption of ammonia, using volumetry, or the adsorption of pyridine, measured by Fourier transform infrared (FTIR) spectroscopy, using the integration of bands and the extinction coefficients reported by Rosenberg and Anderson for sulfates [14].

An Rh/TiO_2 catalyst containing 1 wt% Rh was prepared from this support by incipient wetness impregnation, using $RhCl_3 \cdot xH_2O$ as precursor. The catalyst was dried at oven temperature, then calcined in flowing air at 773 K for 10 h, reached at a ramp rate of 5 K/min.

These solids have been characterised previously [10]. The chemical analyses were performed by ICP on the solutions obtained by acid attack of the solid, the surface areas were determined from the isotherms of N_2 adsorption at 77 K, and acid properties were determined by adsorption of ammonia at 383 K, measured by gravimetry using a SETARAM microbalance. The solid was treated for 1 h in air at 773 K, in helium for 1 h at the same temperature, cooled in helium to 383 K, and contacted with NH_3 (1% in He) up to equilibrium. When this equilibrium was reached, pure He was passed over the solid to eliminate the small amount of physically adsorbed NH_3 retained by the solid. The number of acid sites measured by pyridine adsorption of Rh/G5 (0.19 mEq/g) was very close to that of G5 (0.21 mEq/g), suggesting that the metal content was insufficient to modify the characteristics of the support.

Table 1
Acidities of G5 either pure or treated by 1 N sulfuric acid, measured by different techniques

Sample	Ammonia adsorption ($mmol/g_{cat}$)		Pyridine adsorption ($mmol/g_{cat}$)
	ATG	Volumetry	
G5	0.36	0.31	0.21
G5-S-1N	0.40	0.41	0.59

In situ infrared spectra were recorded using a diffuse reflectance Fourier infrared transform spectroscopy (DRIFTS) cell mounted on a Bruker Equinox 55 spectrophotometer. The samples (≈60 mg) were placed in a Specac cell, which permits operation in controlled atmosphere at high temperatures. A total of 100 scans were accumulated at a resolution of 4 cm^{-1} in the temperature range 293–773 K. All spectra were ratioed against the background spectra collected on the adsorbate-free support at the corresponding temperatures. The adsorptions were performed on samples first treated at 723 K in air. This treatment was done to remove eventual contamination of the surface by organic compounds, and the calcination temperature (lower than that used for standardisation of the solid) ensured that the solid was not modified.

Pure gases (Air Liquide, 99.99% purity) were used as reagents. The standard reaction mixture comprised 1000 ppm NO, 1000 ppm C_3H_6, and 9% O_2 in He. The total flow rate was 60 cm^3/min, corresponding to a space velocity of about 35,000 h^{-1}. A helium stream containing 1000 ppm NO, 1000 ppm NO + 9% O_2, or 1000 ppm NO_2 was used for the study of adsorption or co-adsorption of reactants.

3. Results

Because both the support and Rh oxide can adsorb NO_x and propene, reactant adsorption was performed on both the support and the Rh catalyst. In a continuous-flow reactor, it appeared that, due to the low concentration of reactants, the SCR reaction was limited by diffusion above 573 K [10]. Work in the diffusion regime leads to lower selectivities for intermediates; thus the present experiments were performed at 523 K, to avoid diffusional limitations.

3.1. Adsorptions and co-adsorptions on the support

The G5 support treated at 723 K in air exhibited a band at 1361 cm^{-1} attributed to sulfates and another band at 3657 cm^{-1} of acid OH. This finding is similar to what is well known for sulfated zirconia [15]. Fig. 1 reports the DRIFTS spectra of G5 maintained in a flow of 1000 ppm NO in He at different temperatures. The adsorption of NO was weak, because desorption occurs below 523 K; therefore, adsorbed NO cannot participate directly in the reaction, which starts at about 550 K. At room temperature, NO adsorption induces the disappearance of the band of sulfate, which becomes negative, and the appearance of bands at 1613, 1584, 1513, 1490, 1294, and 1247 cm^{-1} assigned to different forms of nitrates [16]. Data obtained from the literature on the interaction of titania with NO, O_2, and NO–O_2 mixtures are listed in Table 2. Another feature is a broad band at about 3300 cm^{-1}, characteristic of H bonding. This H bonding is due to the formation of water, here resulting from the displacement of OH by nitrates. It was recently

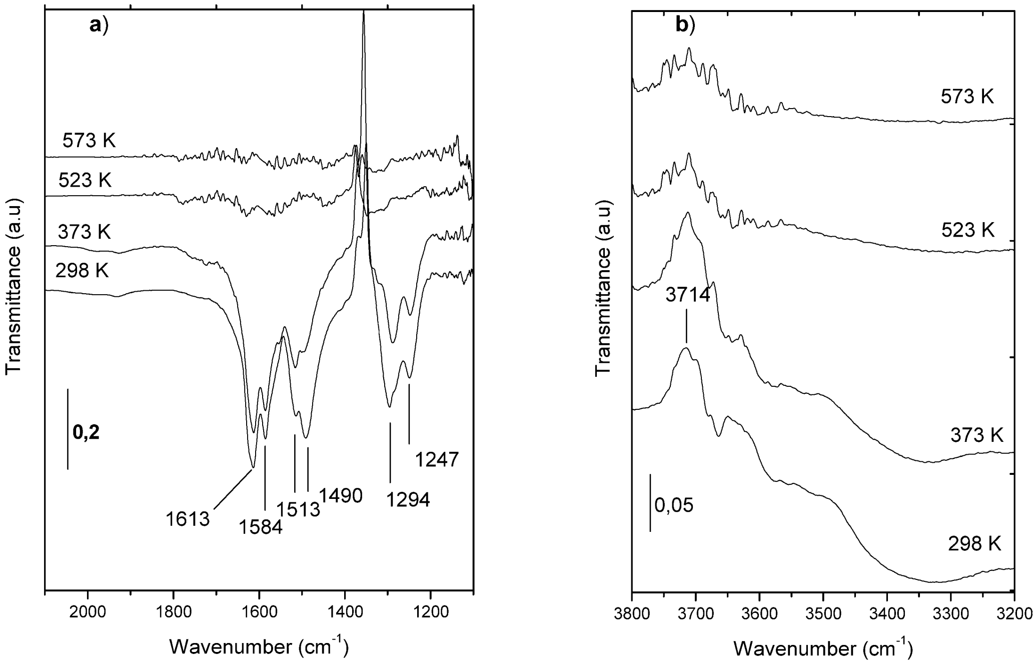
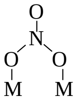
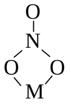
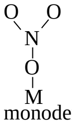
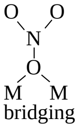


Fig. 1. DRIFTS spectra in the zones of nitrates (a) and OH (b), recorded on G5 maintained under a flow containing 1000 ppm NO in He at different temperatures.

Table 2
Wavenumber and assignment of DRIFTS bands of nitrate species

Adsorbed species	Wavenumber (cm^{-1})		References
	Literature	This wok	
 bridging bidentate nitrate	1650–1600	1613–1610	[44,45]
	1225–1170	1247–1240	
 chelating bitentate nitrate	1565–1500	1584–1574	[44,46]
	1300–1260	1294–1285	
 monodentate nitrate	1530–1480	1500–1484	[44,45]
	1290–1250	1296–1285	
 bridging monodentate nitrate	1530–1480	1500–1484	[44,45]
	1290–1250	1296–1285	

reported that NO adsorption on titania resulted in its disproportionation to NO, $N_2O_2^{2-}$, and nitrates [17]. This observation accounts for the results obtained here on G5.

Fig. 2 shows bands at 1911, 1621, 1582, 1552, 1363, 1286, and 1238 cm^{-1} when the adsorption was performed using a gas containing 1000 ppm NO_2. The band at 1490 cm^{-1} observed for NO adsorption is missing. The band at 1911 cm^{-1} exhibits a low intensity and has been ascribed to nitrosyls (NO^+) adsorbed at Ti atoms. The bands at 1615 and 1245 cm^{-1}, assigned to bidentate nitrate species, are observed after treatment by NO, $NO + O_2$, or NO_2 (Fig. 3). This formation of nitrosyls and nitrates by adsorption of NO_2 is consistent with the disproportionation of NO_2 into NO^+ and $NO_3{}^-$ proposed by Hadjiivanov et al. [16]. These bidentate nitrate species are stable under helium at 523 K. However, a comparison of the spectra obtained in Fig. 3 reveals a slightly different spectrum for the adsorption recorded using a mixture $NO + O_2$, with the loss of several bands at 473 K. This can be attributed to the lower stability of some nitrate species. These weakly adsorbed species are characterized by two bands at 1500 and 1280 cm^{-1}, assigned to monodentate nitrates [17].

Using a mixture composed of 1000 ppm C_3H_6 and 9% O_2 in He produced different behaviours as a function of temperature, as illustrated in Fig. 4. At room temperature, the band of sulfates was modified, reflecting the interaction of olefin and the acid sites. The bands relative to propene are weak, but a band at 1622 cm^{-1}, corresponding to C=C vibration, is observed. This band disappears at 473 K with the development of a band at 1674 cm^{-1}, in the zone of carbonyls. In the gas phase, this band appears at 1732 cm^{-1} but can be shifted to 1657 cm^{-1} after adsorption at Lewis acid sites [18–20]. Small bands at 1455 and 1437 cm^{-1} correspond to $\delta_{as}(CH_3)$ and $\delta_s(CH_3)$ vibrations, suggesting the formation of acetaldehyde, such as the bands at 2980 and 2942 cm^{-1} in the range of $\nu(CH_3)$ modes [21]. The band at 1674 cm^{-1} has also been assigned to acrolein [12], which has strong bands at the same position. However, titania is not selective for allylic oxidation and catalyses mainly the attack at the C=C bond [22]. Band assignments reported in the literature are listed in Table 3. The tentative attribution of the carbonyl band to acetaldehyde therefore fits better with the known catalytic properties of titania. At 573 K, propene oxidation is important and produces water detected by the band at 1640 cm^{-1}. At 673 K, the band of carbonyls vanishes, and new bands appear at 1519 and

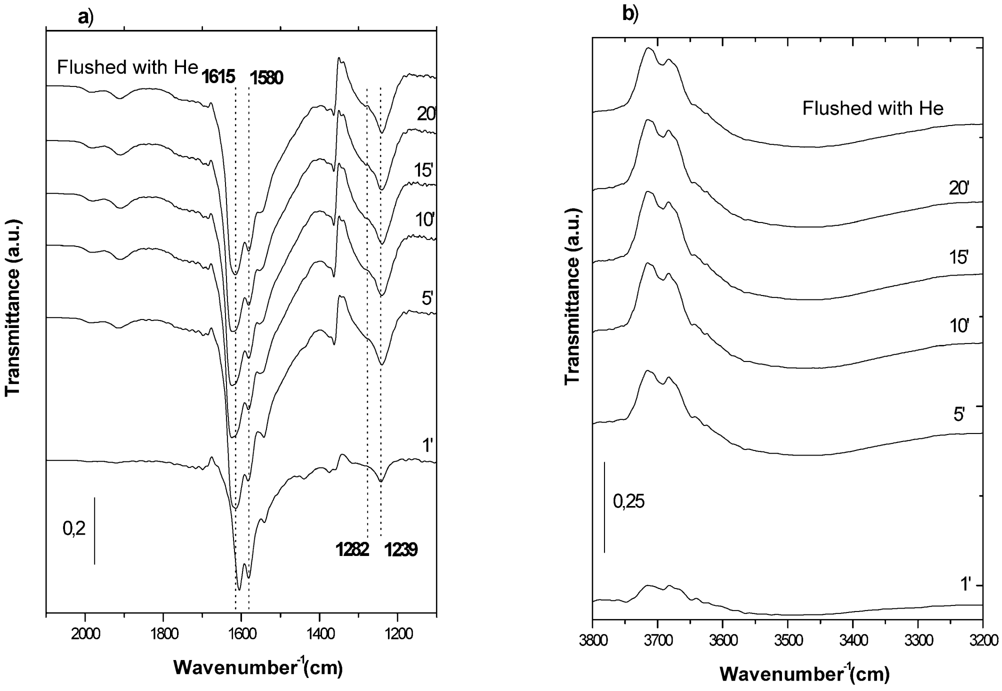


Fig. 2. DRIFTS spectra of adsorbed species during the exposure of G5 to a flow of 1000 ppm NO_2 in He at 523 K.

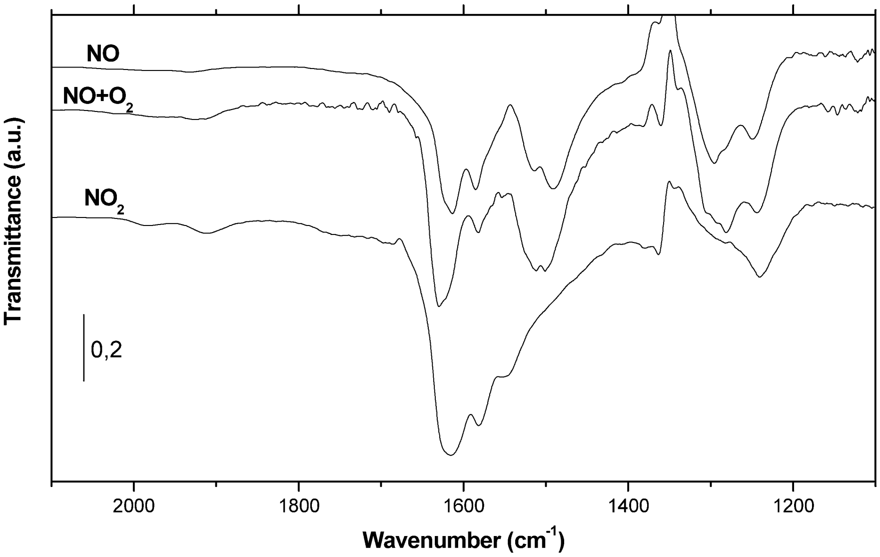


Fig. 3. DRIFTS spectra of the G5 support at 298 K, under different atmospheres.

Table 3
Wavenumbers and assignment of the infrared bands observed upon interaction of G5 with a flow of C_3H_6 and O_2 in helium

Wavenumber (cm^{-1})	Assignment	References
1449	$\nu_s(CO_3^-)$ carbonate	[47]
1519	$\nu_{as}(COO^-)$ carboxyle	[23]
1549	$\nu_s(COO^-)$ formiate	[48]
1370	$\nu_{as}(COO^-)$ formiate	
1622	$\nu(C{=}C)$ propene	[49]
1674	$\nu(C{=}O)$ acrolein	[19,50]
1455	$\delta(CH_3)$ acrolein	
1640	$\delta(OH)$ H_2O	[47]
2980	$\nu(CH_3)$	[21]

1449 cm^{-1}. These bands have been assigned to surface carbonate for the band at 1449 cm^{-1} and to carboxylate for the band at 1519 cm^{-1} [23].

Finally, spectra were recorded at 523 and 573 K in the presence of the standard reaction mixture including 1000 ppm NO, 1000 ppm C_3H_6, and 9% O_2 (Fig. 5). These spectra also contain the bands at 1673 and 1659 cm^{-1} attributed to acetaldehyde, which disappear at 573 K, with the appearance of bands at 1517 and 1440 cm^{-1} assigned to carboxylates and carbonates. In addition, new bands not observed in the other cases, at 2317, 2289, 2267, and 2192 cm^{-1}, are seen. The first two bands are absent at 573 K, where only the band at 2267 cm^{-1} is observed. The band at 2317 cm^{-1} has been attributed to a ν(CN) vibration of

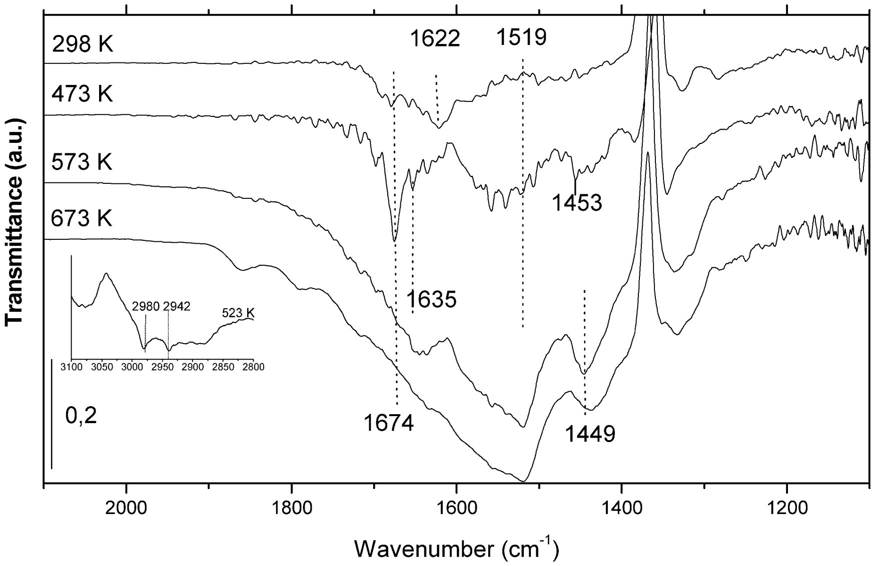


Fig. 4. DRIFTS spectra of the adsorbed species for G5 exposed to a flow of $C_3H_6 + 9\%\ O_2$ in He at different temperatures.

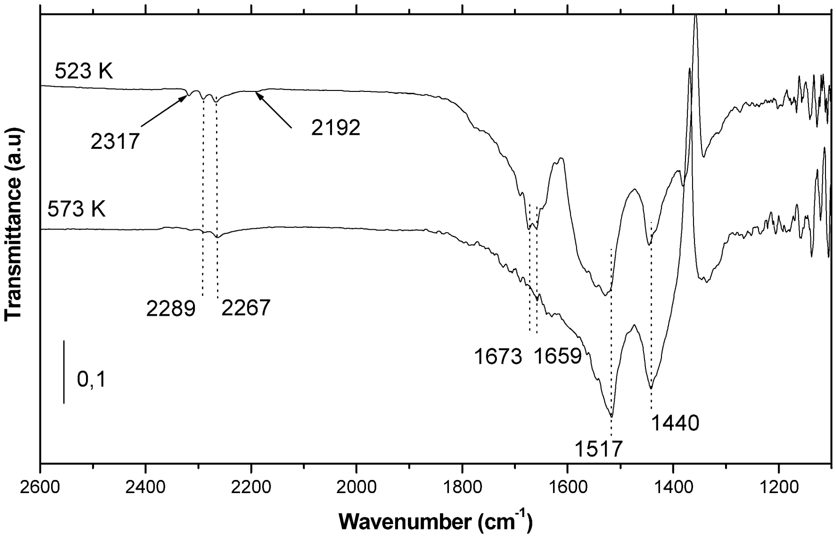


Fig. 5. DRIFTS spectra of the species adsorbed on G5 submitted to the standard reaction mixture at different temperatures.

a RCN species adsorbed at a Lewis acid Ti^{4+}. The existence of anionic vacancies is well accepted on TiO_2, leading to the formation of Ti^{3+} sites [24], and the band at 2289 cm^{-1} has thus been attributed to the adsorption of RCN species at Ti^{3+} sites; however, this band can also be attributed to the adsorption at strong acid sites, such as those modified by sulfates. The band at 2267 cm^{-1} can be attributed to the adsorption of RCN at Bronsted acid sites. The very weak band at 2192 cm^{-1} has been assigned to isocyanate compounds RNCO [25–29]. The nitrile must result from the reaction of NO or NO_2 with propene or acetaldehyde.

3.2. *Adsorptions and co-adsorptions on Rh/G5*

The adsorption of NO on Rh/G5 has been reported to yield a $Rh–NO^+$ species and nitrates [10]. The spectra recorded on the interaction with a NO–O_2 mixture, reported in Fig. 6, show the formation of two species adsorbed on Rh, one species with a band at 1925 cm^{-1} assigned to $Rh–NO^+$ (Table 4) and another species with bands at 1612 and 1577 cm^{-1} corresponding to nitrates adsorbed at the support surface. These species are formed rapidly and retained in pure helium at 523 K.

The spectra recorded on the interaction of G5 and Rh/G5 with the reaction mixture at 523 K are reported in Fig. 7. More intense bands are observed in the second case, showing the participation of Rh oxide in the process. The band at 1916 cm^{-1} is assigned to $Rh–NO^+$ species, and new bands appear at 2186, 2160, and 2112 cm^{-1}. The band at 2192 cm^{-1} observed in Fig. 5 has been assigned to isocyanates; in the presence of Rh, its intensity increases, suggesting catalysis by Rh. Several authors have suggested that NCO moieties are formed on Rh and migrated on the support [30–32]. The band at 2160 cm^{-1} has been attributed to Rh–NCO [30], and that at 2112 cm^{-1} to acetonitrile coordinated on Rh. Finally, a small band is observed at 1776 cm^{-1} that could correspond to the $Rh–NO^-$.

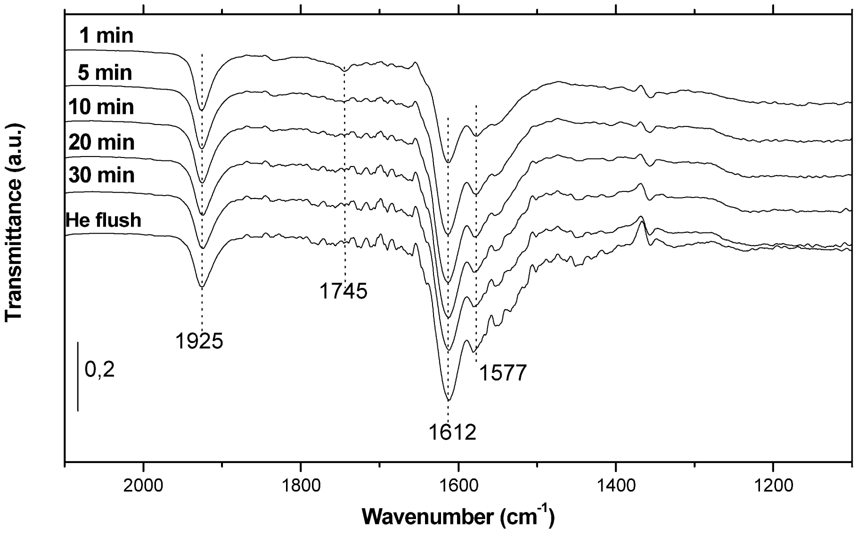


Fig. 6. Time dependence of the DRIFTS spectra recorded with Rh/G5 submitted at 523 K to a flow of 1000 ppm NO + 9% O_2 in He.

Table 4
Wavenumbers and assignments of the adsorbed species formed by interaction of Rh/G5 with a flow containing $C_3H_6/NO/O_2$ in helium

Adsorbed species	Wavenumber (cm^{-1})	Description	References
Rh–NO^-	1665	High coverage	[12,51]
	1770	Low coverage	
Rh–NO	1820	Neutral	
$(Rh^0)_2$–CO	1860–1885	Bridging	[51,52]
Rh–NO^+	1910–1930	Positively charged	[53]
$(Rh^+)_2$–CO	1995	Bridging	[51]
$(Rh^{2+})_2$–CO	2004	Bridging	[51]
Rh^0–CO	2030–2050	Linear	[51]
	2070		[54]
Rh^+–CO	2075–2093	Linear	[51,54]
$Rh^+(CO)_2$	2093	Bridging	[51]
	2029		
Rh^{2+}–CO	2114	Linear	[51]
Rh^{3+}–CO	2140–2146	Linear	[51]
	2137		[54]
Rh–NCO	2203	Covalent isocyanate	[51]
	2269		[55]
$(NCO)^-$	2175	Ionic isocyanate	
Rh–CN	2147–2154		[54]
Ti–NCO	2192		[56]
Ti–CN	2317	Adsorbed at different sites	[57]
	2289		
	2267		

We consequently conclude that cyanates, isocyanates, and nitriles are formed during the reaction. To precisely characterize the mechanism, the reactivities of the different species formed at the surface were investigated.

3.3. *Reactivity of NO_y species in the presence of propene*

In this approach, the catalyst was first submitted to a mixture composed of 1000 ppm NO–9% O_2 in He to form the nitrates, then to a flow of 1000 ppm C_3H_6 in He. The results reported in Fig. 8 show the spectra of the original surface covered with nitrates, denoted as NO_y, and also the spectra obtained after different intervals at 523 K. The first spectrum is identical to that reported above. The solid, flushed by pure helium for 60 min and retaining a large fraction of the adsorbed species, was then submitted to the C_3H_6/He flow, and the surface was analyzed at different times. The main features after 4 min are the erosion of the band of sulfates, the growth of a band at 1675 cm^{-1}, the higher intensity of the band at 1925 cm^{-1}, and decreased intensity of the band at 1612 cm^{-1}. After 1 h, a broad band centred at 1530 cm^{-1} develops.

These evolutions suggest that C_3H_6 reacts with the nitrates localised at the support surface. This reaction corresponds to NO formation, which can account for the increase of the Rh–NO^+ band at 1925 cm^{-1} and of acetaldehyde with the growth of the band at 1675 cm^{-1} [12]. After 1 h, the nitrates are consumed, and acetaldehyde remains untransformed (such as the nitrates linked to Rh), so that acetaldehyde is formed exclusively by reaction of the nitrates from the support.

3.4. *Interaction of NO + O_2 with the oxygenated species formed with propene*

The oxygenated species formed earlier were further reacted with a mixture containing 1000 ppm NO and 9% O_2 in He, to compare the products formed with those formed by interaction with propene. The resulting spectra are reported in Fig. 9, in which the spectral zones corresponding to nitrates and to isocyanates/nitriles have been separated. When the NO–O_2 mixture is admitted over the solid, the carbonylic band at 1675 cm^{-1} disappears immediately and the 1912 cm^{-1} band of Rh–NO^+ reaches maximum intensity after 180 min. Simultaneously, bands at 2187, 2161, and 2122 cm^{-1} appear in the spectrum, assigned respectively to acetonitrile, NCO adsorbed at the Rh surface, and the support. They reach a maximum after 30 min for the 2161 cm^{-1} band of isocyanate and after 3 h for acetonitrile. It is noteworthy that stable CN or NCO species appear only in the second introduction of NO, suggesting that they

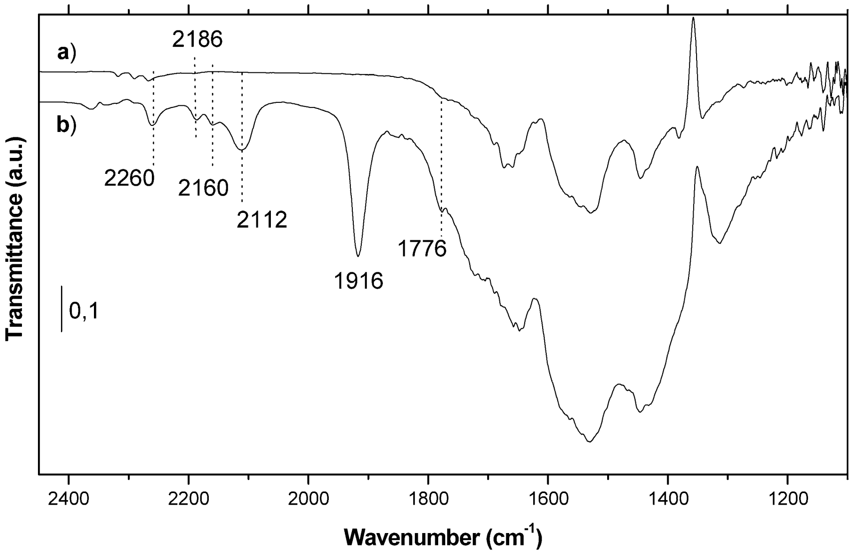


Fig. 7. DRIFTS spectra of adsorbed species for (a) G5 and (b) Rh/G5 submitted to the standard reaction mixture at 523 K.

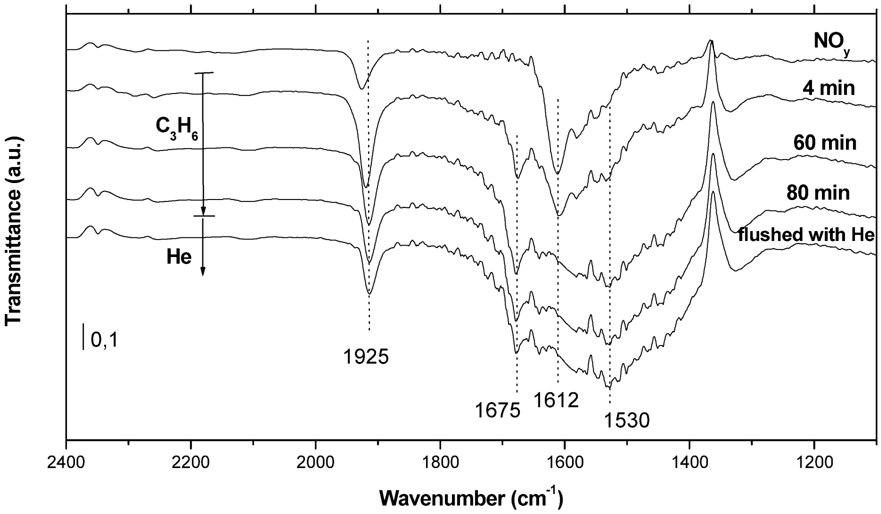


Fig. 8. Reactivity of NO_y species towards C_3H_6: evolution as a function of time of the spectra recorded at 523 K for Rh/G5 maintained in a flow of 1000 ppm C_3H_6 in He.

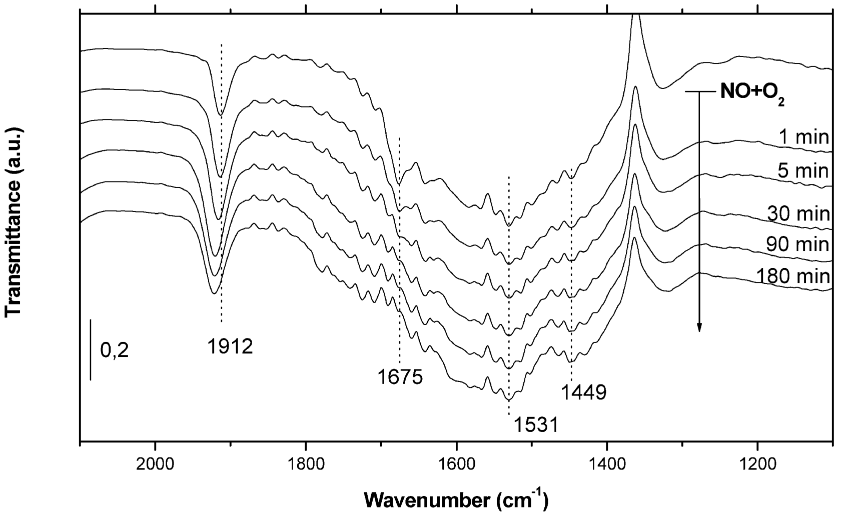
do not result from the direct interaction of NO and propene, but rather involve oxygenated intermediates.

3.5. Reactivity of adsorbed species in successive cycles

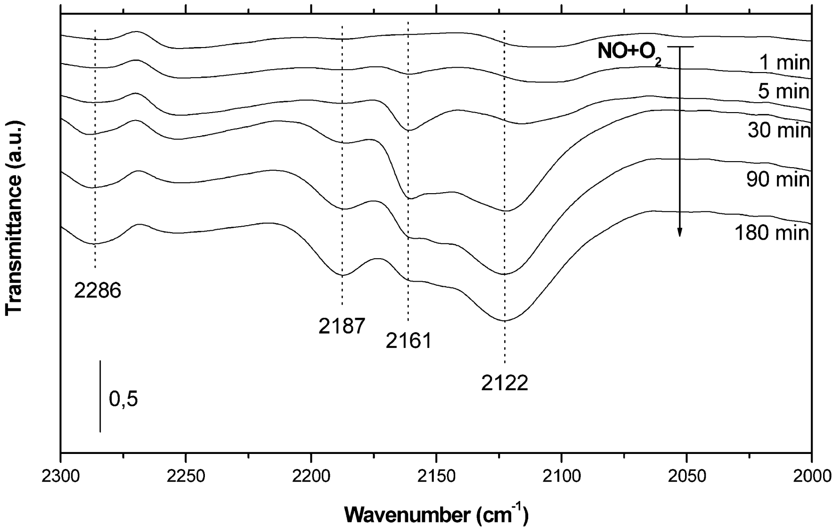
The solid was submitted to a flow of 1000 ppm C_3H_6 in He after adsorption of $NO + O_2$, followed by adsorption of C_3H_6 and then readsorption of $NO + O_2$. The spectra are reported in Fig. 10. In this case, $Rh–NO^+$ is restored very rapidly (about 7 min) but is consumed and disappears after 1 h. Acetaldehyde is hardly detected, and the spectrum in the zone 2300–2000 cm^{-1} is very similar to that observed earlier. Nevertheless, on propene introduction, the nitrile band shifts from 2122 to 2115 cm^{-1}, demonstrating the activation of the nitrile species by reduced rhodium species. This different behaviour indicates that the stationary state is not the same when the pretreatment is changed. To check this point, the pretreatment conditions were changed.

3.6. Reactivity of a surface pretreated by $C_3H_6 + O_2$

The spectra obtained at different times for Rh/G5 submitted to a flow of 1000 ppm C_3H_6 + 9% O_2 in He are reported in Fig. 11. These spectra show the formation of Rh^+–CO (band at 2092 cm^{-1}), acetaldehyde (1675 cm^{-1}), formiates (1530 cm^{-1}), and carbonates (1439 cm^{-1}). The solid equilibrated in this reaction mixture was then submitted to a flow $NO + O_2$ in He at 523 K. The resulting spectra, reported in Fig. 12, show the immediate consumption of acetaldehyde and the formation of CN and NCO species (range 2230–2100 cm^{-1}). The behaviour here is quite different from that observed with the pretreatment $NO + O_2$, then C_3H_6. In the previous case there was no CO; therefore, the results suggest that CN and NCO are formed by reaction of CO and NO on rhodium oxide. This is also suggested by the fact that $Rh–NO^+$ is formed before the appearance of nitriles and isocyanates.



(a)



(b)

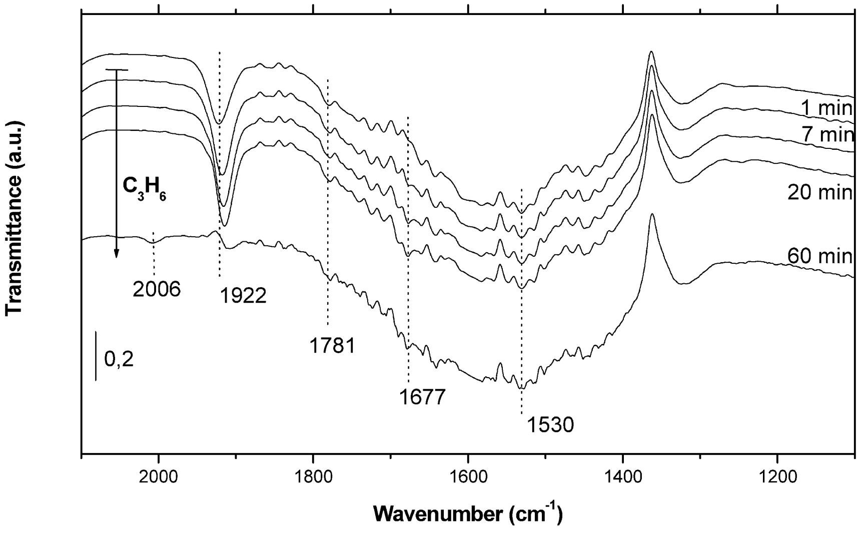
Fig. 9. Reactivity at 523 K towards NO + O_2, of the species formed by successive treatments of Rh/G5 by NO + O_2/He, then C_3H_6/He: DRIFTS spectra in the zone of (a) carbonyls and (b) NCO and CN bands.

The spectra recorded in the presence of the reaction mixture at different temperatures are reported in Fig. 13. At 373 K, the bands of nitrates are predominant, the band of Rh–NO^+ species is very weak, and the bands of CN at 2118 cm^{-1} and of NCO 2160 cm^{-1} start to appear. At 473 K, the bands of nitrates are eroded, the intensity related to Rh–NO^+ increases, and a band at 2260 cm^{-1}, attributed to a nitrile adsorbed at a Bronsted site, is observed. At 523 K, the same situation is observed with a maximum intensity of the bands at 1918 and 2160 cm^{-1}. At 573 K, the band at 2260 cm^{-1} disappears, indicating the loss of protonic acid sites. At 623 K, the band at 2184 cm^{-1}, of isocyanate adsorbed on TiO_2, is at its maximum intensity, and two new bands appear at 3141 and 3048 cm^{-1}. These bands can be assigned to ν(NH) vibrations of NH_3 adsorbed on the support. At 673 K, the bands corresponding to ammonia increase, the band of Rh–NO^+ is still high, and carboxylates/carbonates are formed in large amounts. It is interesting to note that the growth of the isocyanate band at 2118 cm^{-1} parallels that of the reaction rate. Above 673 K, NO_2 is formed in significant amounts, and the conversion of NO to N_2 decreases.

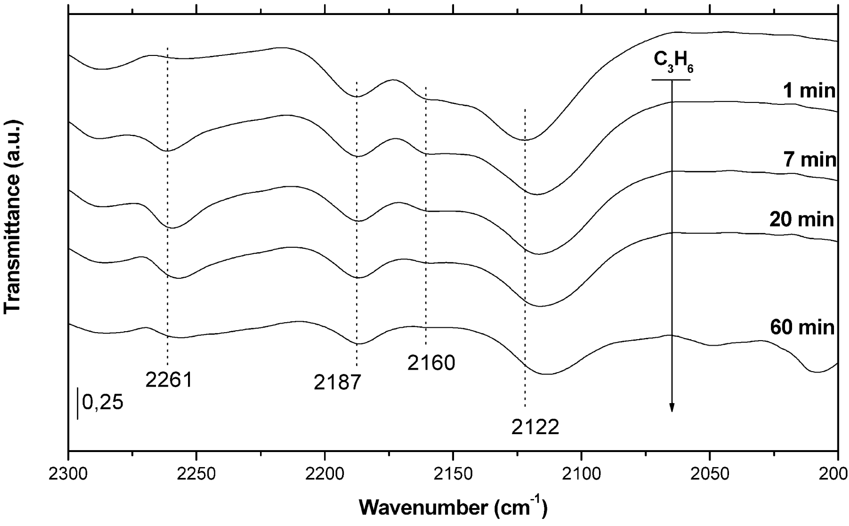
4. Discussion

The numbers of acid sites of G5 derived using three different methods agree reasonably well. The higher number of acid sites measured with NH_3 can probably be related to the higher basicity of this probe. This number of acid sites can be compared with that reported for zeolites: about 0.7 mEq/g for H-BEA (Si/Al = 13) or 0.38 mEq/g for an amorphous silica-alumina [33] and about 1.5 mEq/g for Y zeolites [34]. Increasing the S amount on that sample to 2.2% does not significantly increase the acidity, suggesting that 0.3% S is sufficient to promote acidity. Therefore, despite a relatively low S content, G5 is a solid acid and must be considered a partially sulfated titania.

The adsorption of NO–NO_2 on titania and sulfated titania has been investigated by infrared spectrometry by several groups. Ramis et al. [35], Dines et al. [36], and Hadjiivanov



(a)



(b)

Fig. 10. Reactivity at 523 K towards C_3H_6, of the species formed by successive exposures of Rh/G5 to NO + O_2/He followed by C_3H_6/He, then again NO + O_2/He: DRIFTS spectra in the zone of (a) carbonyls and (b) –CN and –NCO bands.

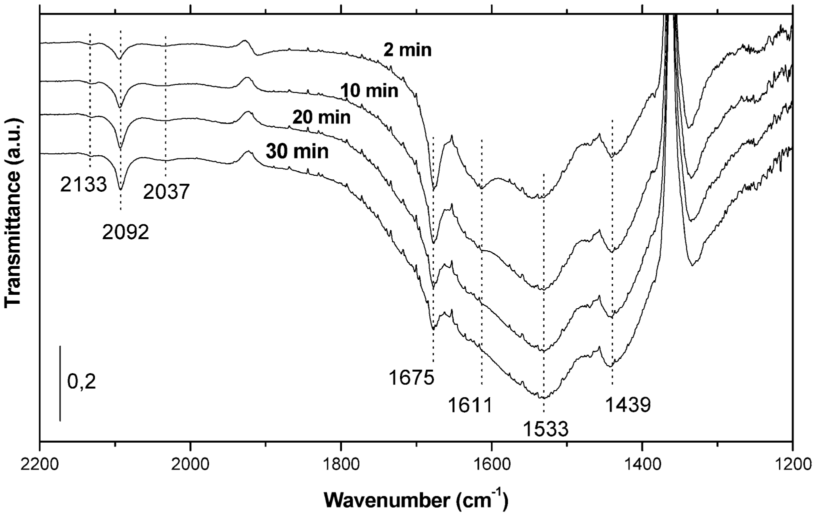


Fig. 11. DRIFTS spectra of the adsorbed species formed at 523 K on Rh/G5, maintained in a flow of 1000 ppm C_3H_6 + 9% O_2 in He.

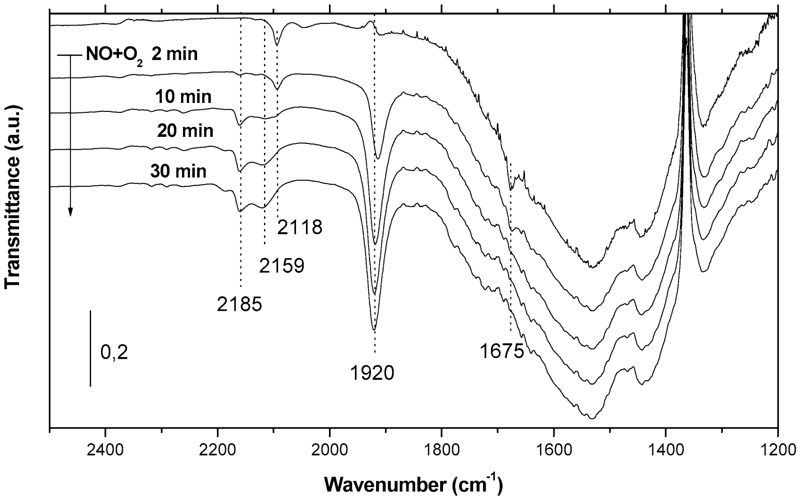


Fig. 12. Spectra, recorded at 523 K, showing the reactivity towards NO–O_2, of the species formed by the treatment of Rh/G5 in a flow of 1000 ppm $C_3H_6 + 9\%$ O_2 in He.

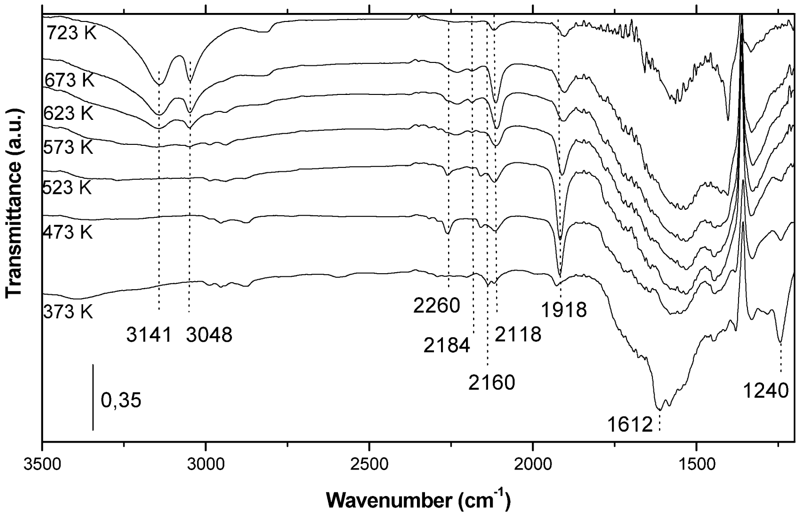
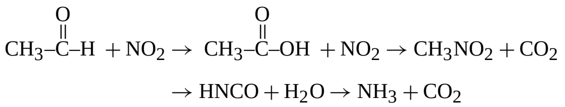


Fig. 13. DRIFTS spectra, recorded at different temperatures, for Rh/G5 maintained in the standard reaction mixture.

et al. [16] have reported the formation of nitrates on S-free anatase by adsorption of NO_2. The stability of these species differed; both bridge and bidentate species were formed at the lower temperatures, and more stable monodentate species were retained above 500 K [16]. Another important conclusion was that nitrates could decompose to NO^+, so that the same type of species are obtained when starting from NO or NO_2. Yang et al. [37] pointed out the effect of sulfation of titania on the stability of nitrates; in the absence of O_2 in the gas phase, NO was reversibly adsorbed on sulfated titania. In the presence of O_2, nitrates were formed, monodentates being more labile than bidentates. The results reported here for sulfated titania agree with these results, with the lower stability of monodentate species illustrated in Fig. 3. When the catalyst contains Rh, the bands are more intense, so that the oxidation of NO to NO_2 favours the building of nitrates at the TiO_2 surface and nitrosyls on Rh atoms.

As has been suggested by many authors, selective reduction of NO_x occurs with the participation of a carbonylic intermediate species formed by oxidation of propene. Identifying this carbonylic compound is difficult because it is formed in very small amounts. The same spectrum is observed for the interaction of propene with G5 and Rh/G5, suggesting that Rh is not strictly required in the formation of this intermediate. The results of the interaction of propene with a sample containing nitrate species suggest that this carbonylic compound is formed by the reaction with nitrates adsorbed on the support, not on Rh. This reaction of oxidation of propene not by oxygen, but rather by nitrates, is consistent with the report by Ueda et al. [38] that metal oxides such as TiO_2, MgO, and ZrO_2, pretreated with NO_2, can catalyze the partial oxidation of propene, yielding oxygenates, whereas the fresh oxides afforded mainly CO and CO_2. Titania pretreated with NO_2 led to the highest yield of oxygenates among the metal oxides tested. Such a catalytic performance disappeared when the desorption and/or reduction of adsorbed nitrogen oxides occurred at temperatures above 673 K. A fast reaction between adsorbed nitrates and propene was also reported by Haneda et al. [13] in their DRIFTS study



$$CH_3\text{–}\overset{\overset{O}{\|}}{C}\text{–}H + NO_2 \rightarrow CH_3\text{–}\overset{\overset{O}{\|}}{C}\text{–}OH + NO_2 \rightarrow CH_3NO_2 + CO_2 \rightarrow HNCO + H_2O \rightarrow NH_3 + CO_2$$

Scheme 1. Possible mechanism for the reduction of NO_x from acetaldehyde.

of the SCR of NO with propene over Ga_2O_3–Al_2O_3. Both catalysts are acidic, and the kinetic study of this reaction over Rh/sulfated titania [10] demonstrated that NO_2 reacted faster on acidic supports and was not desorbed in the gas phase below 623 K. NO_2 was then captured by propene in an acid-catalysed reaction. The role of Rh in the process may be to provide NO_2 to form nitrates. However, a second role can be proposed related to the catalytic properties of Rh for propene oxidation [39]. Between 450 and 550 K, the oxidation of olefins by O_2 gives acrolein, acetone, acetic acid, and acetaldehyde on reduced Rh/SiO_2 catalyst and acetone and propanal on RhO_2/Al_2O_3 [40]. The consecutive reactions of the products on Rh/SiO_2 have also been reported; propanal was converted to acetaldehyde, whereas acrolein was oxidized to acids and carbon oxides. Anderson and Rochester [41] also observed that acrolein was decomposed to carbonyls over Rh/SiO_2. Therefore, whatever the initial products of propene oxidation, the use of Rh catalysts results in the formation of acetaldehyde, which is the most stable product in the conditions of the reaction. On these Rh catalysts, allylic oxidation probably leads to the concurrent side reaction of combustion.

The experimental results demonstrate that the carbonylic species further reacts with the nitrates fixed on the support to yield cyanates, isocyanates, and nitriles, which are hydrolysed to ammonia above 573 K. Sachtler et al. [8,9,42] recently proposed a mechanism for the reduction of NO_2 by acetaldehyde on BaY based on pure acido–basic reactions, which can be applied here. This reaction is rapid on BaY and reaches 90% conversion at 473 K and $HSV = 35\,000\ h^{-1}$. It is represented in Scheme 1.

These reactions of acetaldehyde and NO_2 are catalyzed by acid–base mechanisms and do not require any transition metal. All of the intermediates have been detected by in situ DRIFT spectroscopy, and the sequence can be catalyzed by sulfated titania. Rh oxide is required here to provide NO_2. This mechanism explains the particularity of Rh compared with Pt and Pd; on Rh and Ru, the partial oxidation of propene at about 473 K occurs in successive steps, and the products can be isolated, whereas Pt and Pd demonstrate a lower selectivity to carbonylic compounds at 360 K, rapidly burning the intermediates [43]. Whatever the mechanism of propene oxidation, the reductant is then totally oxidized at low temperature, and SCR stops. With Rh, the lower activity for complete oxidation favors the SCR process, because the intermediates are not immediately combusted.

5. Conclusion

This in situ DRIFTS study of different reaction steps of the SCR of NO by propene provides evidence that the oxidation of propene occurs by the reaction of the nitrates formed on TiO_2. The reaction is proposed to form acetaldehyde and not acrolein, readily oxidized to CO_2 in the conditions of reaction. Rh oxide is found to promote the transformation of acetaldehyde to isocyanate. The conjunction of these steps gives a bifunctional mechanism, as observed from the kinetic study.

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