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Bifunctional mechanism for the selective catalytic reduction of NO_x on Rh/sulfated titania

F. Figueras [a,*], J.L. Flores [a], G. Delahay [b], A. Giroir-Fendler [c], A. Bourane [a], J.-M. Clacens [a], A. Desmartin-Chomel [a], C. Lehaut-Burnouf [d]

[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
[c] Laboratoire d'Application de la Chimie à l'Environnement, UMR 5634 CNRS-UCB Lyon 1, 43, boulevard du 11 novembre 1918, 69622 Villeurbanne cedex, France
[d] Millennium Chemicals, Rueil-Malmaison, France

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Abstract

The selective catalytic reduction of NO by propene has been investigated on a series of Rh catalysts supported by sulfated titanias. The dispersion of Rh oxide was measured by FTIR, from the observation of NO adsorption, and the number of acid sites by gravimetry, from the observation of NH_3 adsorption. The addition of sulfated titania to Rh/SiO_2 as a mechanical mixture increased the rate of N_2 formation, and a higher rate was observed when Rh was supported on sulfated titania. A quantitative analysis of the influence of the acidity of the support shows that the activity for N_2 increases with the number of acid sites. An increase in the surface of Rh oxide also leads to an increase in rate up to a plateau, at which point the rate is limited by an acid-catalysed reaction. This behaviour is attributed to a bifunctional mechanism for the reaction. In the presence of 25 ppm of SO_2 and 3% water, these catalysts reach 40% yield in N_2 at a GHSV $= 35{,}000\ h^{-1}$ with no loss of properties.

Keywords: Selective catalytic reduction; Propene; Rhodium; Sulfated titania; Sulfur dioxide; Bifunctional catalysis; Dispersion of oxides

1. Introduction

The selective catalytic reduction (SCR) of NO to N_2 by hydrocarbons in the presence of a large excess of O_2 has been extensively studied as a potential process in NO_x emission control for diesel and lean-burning engines [1]. The mechanism of this process is complex and depends on the catalyst [2], the type of hydrocarbon, and reaction conditions [3]. Different reaction schemes have been proposed: a redox mechanism involving Cu^I, generated through reduction by hydrocarbon [4]; a bifunctional mechanism in which NO is oxidised first to NO_2 on the metal oxides or cationic sites and then NO_2 reacts with an adsorbed hydrocarbon activated by the acid function [5]; and a bifunctional mechanism in which hydrocarbons are converted to some carbonyl intermediates, which then interact with NO_x in an acid-catalysed reaction [6,7]. The promoting effect of acidity on activity and N_2 selectivity has been reported by several authors. Loughran and Resasco [8] first showed that a mechanical mixture of sulfated zirconia (SZ) and Pd/SiO_2 was effective in promoting the activity in SCR of NO by methane. The same phenomenon was observed with mechanical mixtures of sulfated zirconia with MnO_2 or Cu manganite, with a large increase in NO reduction to N_2 in a large temperature range [9]. When the Cu/ZrO_2 catalyst was promoted by sulfate, the conversion of NO by decane

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[*] Corresponding author. Fax: +33 47244 5399.
E-mail address: figueras@catalyse.cnrs.fr (F. Figueras).

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became selective for N_2 [10]. This effect corresponds to the capture of NO_2 by the acid reaction.

Indeed solid acids exhibit some activity in SCR of NO at temperatures at which radical oxidations in the gas phase provide the intermediates [11]. In such a model, in which different reactions are coupled, the rate can be limited either by the oxidation or by the acid-catalysed reaction. The variations in the turnover number with acidity can give an answer to this question. In the case of Cu/sulfated ZrO_2 the rate per surface Cu atom at 573 K was found to be independent of acidity [12]. Therefore, in that case oxidation limited the rate, and any improvement of the catalyst required a change in the oxidising function for a more active one. The best catalysts for oxidation at low temperature are the noble metals. Pt and Pd are known to form N_2O, which is also not desired, so the best candidate is Rh, which has been studied here, with sulfated titanias as supports. In the presence of nitrogen oxides and oxygen, Rh is oxidised to its oxide after adsorption of nitric oxide [13]. It is most probably present as oxide under the conditions of the reaction, and hydrogen adsorption cannot be used to determine the dispersion. Rh catalysts strongly adsorb NO in a variety of forms detectable by infrared spectroscopy, which offers the possibility of selecting species of simple stoichiometry [14]. A band at 1910–1930 cm^{-1} has been assigned by several authors [15,16] to a linear Rh^+–NO species adsorbed on an oxidised Rh species, and the area of the band can then be used to measure the dispersion of the oxide.

2. Experimental

Rh was supported on a mesoporous silica from Grace Davison (GD 432) and a series of titanias commercialised or developed by Millennium Chemicals. Titanias can be prepared by hydrolysis either of sulfates (G5 and DT51), in which case they contain sulfur in amounts depending on the final pH of the process, or chlorides (GP350), giving sulfur-free TiO_2. Sulfation was made by bringing the support into contact with a H_2SO_4 solution: G5-S-1N-773 stands for a G5 support treated with a 1 N H_2SO_4 solution and calcined at 773 K in air for 2 h. A nonporous S-free titania obtained by flame hydrolysis of the chloride (designated FHTi) of low surface area was also used for comparison. The different supports used are listed in Table 1. Since calcination induces partial desulfatation of the solid, the amount of sulfur is reported before and after calcination.

Rh/TiO_2 catalysts containing 0.6–1.7 wt% Rh were prepared from the supports by incipient wetness impregnation, with $RhCl_3 \cdot xH_2O$ as precursor. Rh/SiO_2 was prepared by cation exchange from ammonia solutions of $(Rh(NH_3)_6)Cl_3$. The catalyst was dried at oven temperature and then calcined in flowing air at 773 K for 10 h, reached with a ramp of 5 K/min. 1Rh-G5-1N stands for a sample containing 1 wt% Rh, deposited on G5-1N and calcined at 773 K. In a few cases the sample was calcined at 973 K, in which case it is referred to as 1Rh-G5-1N-973.

Table 1
Amount of sulfur retained by the solid and acidity after calcinations at 773 K

Sample	Non-calcined S (wt%)	Calcined S (wt%)	Calcined S_{BET} (m^2/g)	Calcined Acidity (meq/g)
GP350	< 0.1	< 0.1	50	0.32
GP350-S-0.1N	1.32	1.08	69	0.30
GP350-S-1N	2.6	2.44	91	0.74
G5		0.32	63	0.36
G5-S-1N	2.37	2.24	100	0.40
DT51	0.56		74	0.23
DT51-S-0.1N	1.08	0.74	74	0.26
DT51-S-1N	2.44	0.86	80	0.30
DT52	–	0.26	89	–
FHTi	< 0.1		55	0.23
FHTi-S-0.01N	0.23			
FHTi-S-0.1N	0.59			
FHTi-S-1N	2.98	0.93	50	0.26
Al_2O_3-S-1N	–	3.55		0.52

The chemical analyses were performed by ICP on the solutions obtained by acid attack of the solid. Surface areas were determined from the isotherms of N_2 adsorption at 77 K. The dispersion of Rh oxide on the supports was estimated by infrared spectrometry with NO as a molecular probe and a Bruker FTIR spectrometer. Self-supported wafers mounted in a glass cell were used for this purpose. The catalysts were calcined at 773 K in air, brought into contact with NO at room temperature, and then evacuated at different temperatures. The acid properties were determined by adsorption of ammonia at 383 K, measured by gravimetry with a SETARAM microbalance. The solid was first treated for 1 h in air at 773 K, then in helium for 1 h at the same temperature, cooled in helium to 383 K, then brought into contact 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.

X-ray photoelectron spectroscopy (XPS) experiments were carried out in a VG Escalab 200R spectrometer with a hemispherical analyser with a pass energy of 20 eV. A Mg-K_α X-ray source at 1253.6 eV was used for the analyses. The spectrometer was calibrated on the $3d_{5/2}$ line of sputter-cleaned Ag, at a binding energy of 368.20 eV. Photoelectron binding energies on Rh$3d$ signals were referenced to the C$1s$ line fixed at 285.0 eV. The normalised XPS intensities, which are proportional to the effective concentrations of the corresponding elements in the surface layer, were determined as the integrated peak area divided by their corresponding sensitivity factor [17].

The catalytic tests were performed in a flow reactor, with 0.1 g of catalyst and a reaction mixture composed of 1000 ppm NO, 1000 ppm C_3H_6, and 9% O_2 in He. The total flow rate was 120 cm^3/min, corresponding to a space velocity of about 35,000 h^{-1}. The reaction products were measured by gas chromatography for nitrogen and propene, and by infrared absorption with detectors for nitrogen oxides. The catalyst was first treated for 1 h at 773 K in a mixture of 10% O_2/He, then cooled to low temperature. A temperature-programmed reaction was then performed, and the catalyst was maintained at 773 K for 1 h in the presence of the reaction mixture; then the temperature was progressively decreased to room temperature over a 6-h period. The results reported here are those obtained when the temperature was decreasing, since the catalyst is stabilised by the procedure used.

3. Results and discussion

3.1. *Characterisations of the catalysts*

Changing the surface area of the support and the conditions of sulfation results in quite different acidities, as reported in Table 1. The acidities measured for 0.6Rh-GP350 and 0.6Rh-G5 were those of the pure supports within an error of 10–15%. The fact that Rh addition does not change the number of acid sites can be accounted for by the small Rh content.

Measuring the dispersion of supported oxides is not a trivial problem and requires selection of a probe with a known stoichiometry of adsorption at the surface. NO is readily adsorbed and is known to form different surface species such as nitrosyls or nitrates [14]. Among these species, mononitrosyls have been observed after adsorption at low temperature, characterised by a band at 1935–1908 cm^{-1} of a Rh^x–$NO^{\delta+}$ species, due to the formation of a π-bond between Rh and NO. For the adsorption of NO on alumina-supported Rh oxide at 523 K, Efthimiadis et al. [18] reported this band at 1908 cm^{-1}. The experiments were performed with a flow cell, in an oxidising atmosphere (5% O_2), to maintain the sample in the oxidised state. On a freshly reduced Rh/Al_2O_3 sample, adsorbing NO from a NO/He mixture, the band assigned to Rh–NO^+ has been reported at 1877 cm^{-1} [19]. After one night of contact at 473 K with an originally reduced sample, a unique NO band was observed near 1910 cm^{-1} that corresponded to the Rh(I)–NO^+ species [16]. The same band has been found at 1920 cm^{-1} on Rh supported by TiO_2, which was either pure or doped by W^{6+} cations [15]. Therefore the position of the band changes with the degree of oxidation of Rh, and a band in the range of 1935–1908 cm^{-1} is characteristic of the oxide [20]. This molecular adsorption corresponds to a 1:1 stoichiometry, which makes it possible to estimate the dispersion.

FTIR spectra for NO adsorbed at different temperatures appear in Fig. 1 for Rh-FHTi and in Fig. 2 for Rh-GP350 sulfated. The intensity changes with the evacuation temperature, and a slight shift is noticed after desorption at 473 K. The formation of the cationic (M–NO^+) species has been reported to be produced by donation of an electron antibonding ($p2pz^*$) of NO to a d orbital of the metal to strengthen the NO bond [21]. The shift of the band from its initial position at 1936 to 1914 cm^{-1} after evacuation at 473 K reflects a small change in the retrodonation, attributed to a slight reduction of the sample induced by vacuum treatment. Electron enrichment at the Rh site makes it possible to pump more electrons into the anti-bonding π-orbital of NO, thus weakening the N–O bond. This change in electron density at the Rh atom induces a stretching of the N–O bond and therefore a change in the dipole moment, leading to a higher intensity of the band. The results obtained at 373 K were used to estimate the dispersion of Rh oxide, since the adsorption is then more representative of the catalyst in the oxidised state. The integrated area of the band was corrected by the weight of the sample and the surface of the wafer.

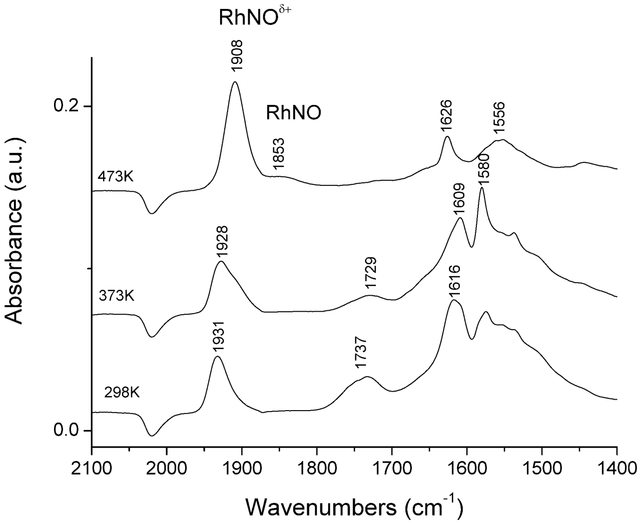

Fig. 1. Infrared spectra of NO adsorption on Rh-FHTi after evacuation at different temperatures.

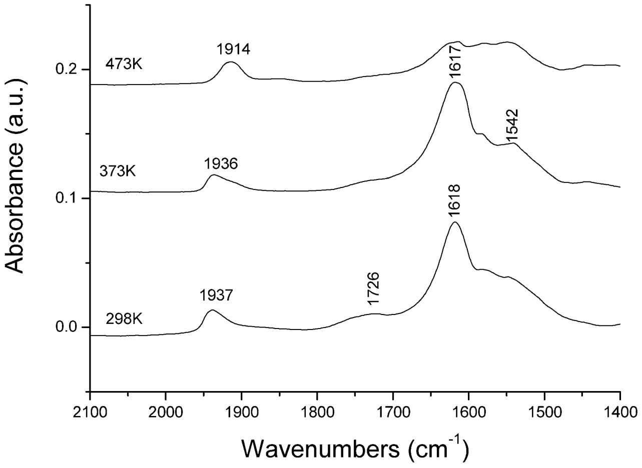

Fig. 2. Infrared spectra of NO adsorption after evacuation at different temperatures on a 0.6Rh-GP350-S-1N sample used in the SCR test.

The intensities of the bands measured on the catalyst after the reaction differ somewhat from those measured on the

Table 2
Area and position of the FTIR band (not corrected for the amount of Rh) of the mononitrosyl species measured after evacuation at 373 K for fresh and used catalysts

Sample	Fresh catalyst		Used catalyst	
	Area (a.u.)	Wavenumber (cm^{-1})	Area (a.u.)	Wavenumber (cm^{-1})
0.6Rh-GP350-S-1N	13	1926	19	1936
0.6Rh-GP350	20	1918	49	1928
0.35Rh-G5	5	1913	5	1921
0.6Rh-FHTi			50	1928
1Rh-G5	17	1924	54	1910
2Rh-G5	69	1920	138	1922
1Rh-DT51	37	1925	62.4	1920
0.6Rh-G5-S-1N			7.5	1920
1Rh-DT51(bis)	38	1913		
0.6Rh-FHTi-S-1N			13	1930

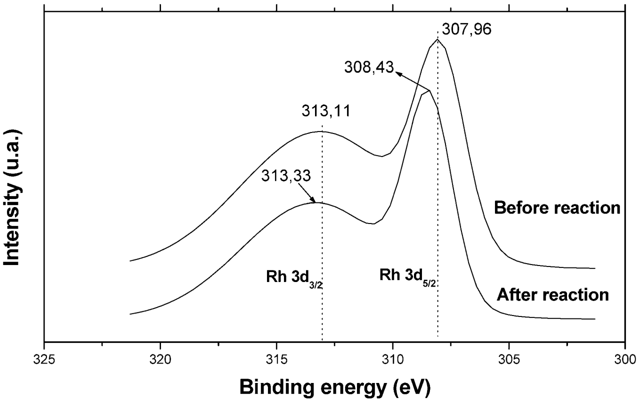

Fig. 3. XPS spectra of 1Rh-G5 before, and after reaction.

fresh catalyst (Table 2). However, taking into account the resolution of the spectrometer (4 cm^{-1}), their position varies only a little. The treatment in the reaction mixture usually leads to more intense bands, suggesting surface reconstruction in this atmosphere. Indeed, the surface migration of Rh atoms in the presence of NO was proposed earlier [16].

These areas reported in Table 3 show that significant changes in dispersion can be observed with a change in the support. If we consider the series containing 0.6% Rh on GP350, a lower dispersion is noticed on the sulfated oxide. Pure TiO_2 is basic and can exchange anions, but sulfation decreases basicity, and the interaction, if any, between the solid acid and Rh anions is very weak; Rh is then fixed not by exchange but by adsorption of small particles, the size of which depends on the concentration of the solution and rate of evaporation of the solvent [22].

The oxidation state of Rh was investigated by XPS before and after the reaction. The sample "before reaction" was pretreated in a mixture of O_2–He, and the sample "after reaction" was cooled in the reaction mixture and kept under argon for the transfer in the spectrometer. The XPS spectra, reported in Fig. 3, show two bands at 313 and 307 eV assigned to $Rh3d_{3/2}$ and $Rh3d_{5/2}$ peaks. According to the literature, the $3d_{5/2}$ band is at 309.1 eV for Rh_2O_3 and at 307.3 eV for metallic Rh [23], so that the spectra are those of a mixture of Rh^{3+} and Rh^{+} species. After reaction the peaks are shifted to higher energies and the solid is therefore more oxidised than it was originally after treatment under a O_2–He mixture. The deconvolution of the peak indeed yields about 70% Rh as Rh^{3+} after the reaction. This finding agrees with the report by Oh and Carpenter [24] that the oxidation state of Rh/Al_2O_3 changes reversibly in response to changes in the stoichiometry of the gaseous environment at the temperatures occurring in the catalytic treatment of exhaust gases. Part of the reduction of the sample can probably be ascribed to the vacuum treatment in the XPS chamber, and it can then be concluded that in the conditions of the reaction, the catalyst is indeed an oxide.

3.2. *Catalytic properties*

The catalytic properties were determined in the temperature range 523–773 K. The influence of the acidity of the support in bifunctional processes can be demonstrated with mechanical mixtures. This is illustrated in Fig. 4, which reports the catalytic properties of Rh/SiO_2, compared in Fig. 5 with those of a mechanical mixture of Rh/SiO_2 and sulfated TiO_2, and of Rh deposited on sulfated titania. As reported earlier by several authors, Rh is very selective for N_2 and forms NO_2 above 550–600 K when the support is silica, and above 700 K when an acid support is used, so that the reaction below 550 K is selective for N_2.

Table 3
Integrated intensities of NO–Rh bands at 373 K corrected for the weight of sample and activities for the selective reduction of NO by propene at 573 K

Sample	Rh (wt%)	Surface of the support ($m^2\ g^{-1}$)	Area of the IR band/g solid (a.u.)	Rate at 573 K (10^{-7} mol s^{-1} g^{-1})
0.35Rh-G5	0.36	63	519	1.07
1Rh-G5	1.12	63	1664	1.3
1Rh-G5-1N-773	1	100	2623	1.6
1Rh-G5-1N-923	1	–	2249	0.8
2Rh-G5	1.7	63	6866	1.25
1Rh-DT 51	1.04	74	3661	1.5
1Rh-DT 51(bis)	1.04	74	3774	1.8
0.6Rh-GP350-S-1N	0.6	91	2400	1.4
0.6Rh-GP350	0.6	50	4900	1.4
0.6Rh-FHTi	0.6	55	790	0.66

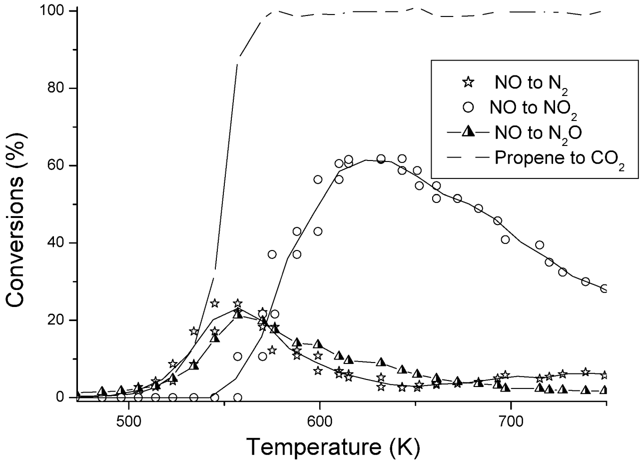

Fig. 4. Catalytic properties of Rh/SiO$_2$ at different temperatures.

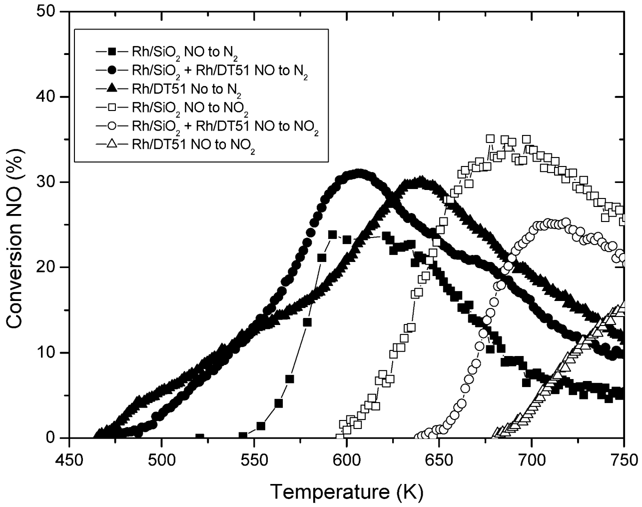

Fig. 5. Comparison of the conversions with pure Rh/SiO$_2$, a mechanical mixture of Rh/SiO$_2$ and sulfated titania, and Rh/sulfated titania.

The addition of an acid support in a mechanical mixture increases the rate of formation of N$_2$ on Rh/SiO$_2$ at low temperatures and shifts the production of NO$_2$ to higher temperatures. In the mechanical mixture, the two reactions proceed with different particles, and the process can be limited by interparticle diffusion, mainly at the higher temperatures. As predicted by the theory of bifunctional reactions, supporting Rh on the surface of the solid acid leads to a further increase of the rate at low temperature. Above 600 K, the rate is strongly limited by internal diffusion. This rate measured at 573 K with a feed containing 1000 ppm of NO and a GHSV of 34,000 h^{-1} corresponds to 10^{-7} mol s^{-1} g^{-1}. The Thiele modulus modified by Weisz [25,26]

$$\phi = vR^2/(D_{\mathrm{eff}}C_0),$$

where v is the rate (mol s g^{-1}), R is the radius of the catalyst grains (here 0.01 cm), C_0 is the concentration (3×10^{-8} mol ml^{-1}), and D_{eff} is the diffusion coefficient (10^{-4} cm^2 s^{-1}) is about 0.3. Diffusion limits the overall process when $\phi \cong 1$, and the conversion at higher temperatures is therefore limited by the size of the particles and is not representative of the mechanism.

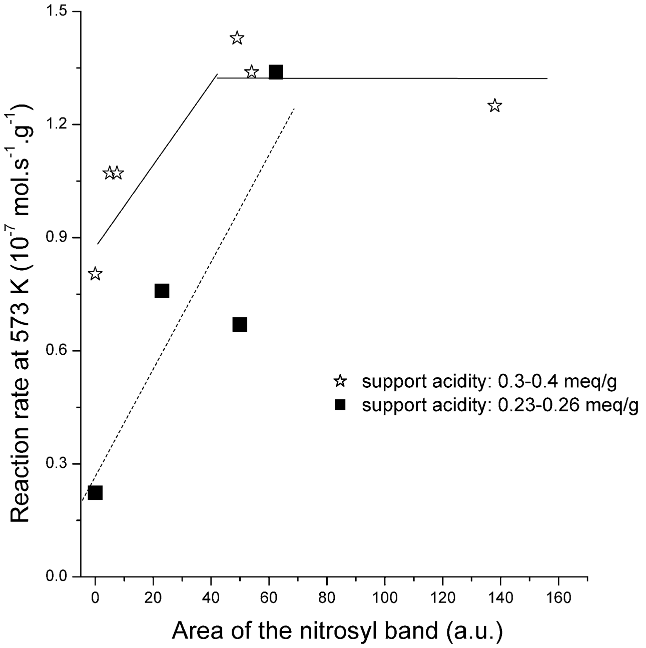

Fig. 6. Variations of the conversion at 573 K as a function of the surface of the nitrosyl infrared band measured after catalytic testing on Rh catalysts deposited on different supports.

For $\phi > 0.3$ diffusion resistance is limited, and the rate at 573 K was taken as representative of activity for the comparison of different Rh catalysts. The activity is plotted against the surface of the infrared band of the nitrosyl species in Fig. 6, for catalysts prepared from different supports and containing 0.6–1.7 wt% Rh. In this plot, the area of the infrared band was that measured after catalysis, and the supports showing acidities in the range of 0.3–0.4 meq/g (supports GP350, GP350-S-0.1N, G5, G5-S-1N, and DT51-S-1N) or 0.23–0.26 meq/g (DT51, DT51-S-0.1N, FHTi, and FHTi-S-1N) in Table 1 were considered as equivalent. The pure supports show some activity, which increases with the acidity of the support, and this activity is taken as the activity of the Rh-free support. A linear correlation is initially observed with the surface of the Rh–NO band with both acidities. The observation of parallel lines suggests the additivity of two different processes: one catalysed by pure Rh oxide, predominant at low acidity, and one involving acidity, when acid sites are numerous. It appears also that when the surface exposed by Rh oxide is high, the activity is levelled: in that case, the reaction is controlled by the acid function and increasing the amount of Rh has no effect.

The effect of the number of acid sites on the rate is reported in Fig. 7. In this figure the point at zero acidity is that measured with Rh/SiO$_2$. Activity first increases with the number of acid sites, then reaches a plateau. This behaviour is expected for a bifunctional reaction in which the rate-limiting step would be the acid-catalysed reaction at low acidity, and oxidation on the most acidic catalysts. Therefore

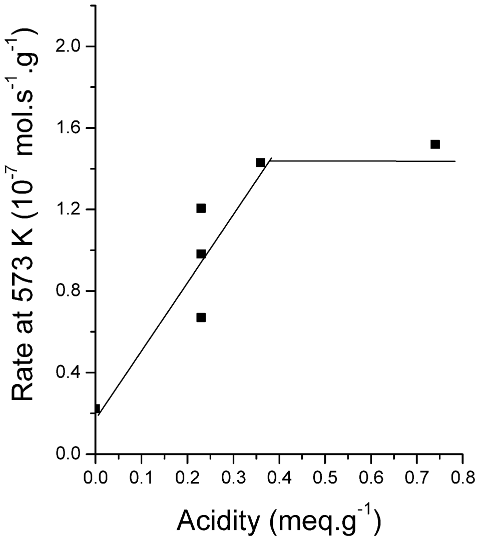

Fig. 7. Variation of the activity at 573 K as a function of acidity for catalysts containing 0.6% Rh supported on different acidic supports.

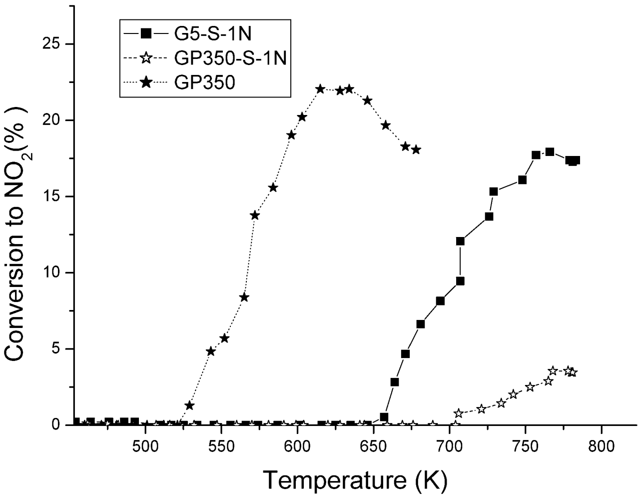

Fig. 8. Effect of the acidity of the support on the selectivity into NO_2 for Rh catalysts containing 0.6% Rh.

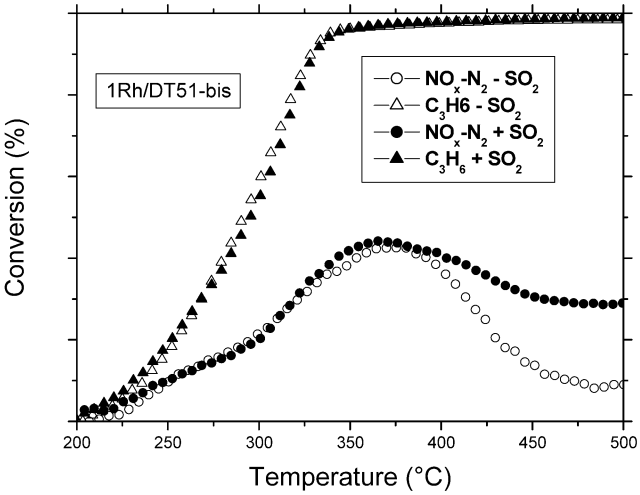

Fig. 9. Conversion of NO (○, ●) and propene (△, ▲) as a function of temperature using a reaction mixture containing 1000 ppm NO, 1000 ppm C_3H_6, 25 ppm SO_2 and 9% O_2, GHSV = 35,000 h^{-1}.

this kinetic analysis supports the hypothesis of a complex mechanism, reduced to a redox on a silica support, but assisted by acidity when the number of sites is sufficiently high. This effect of acidity is indicated by the samples 1Rh-G5 calcined at 773 or 923 K (Table 3): in that case the surface of the IR band of nitrosyls does not change appreciably, but calcinations induce a loss of sulfur and a decrease in activity by a factor of 2. The changes in selectivity for N_2/NO_2 also vary in the direction predicted for a bifunctional mechanism in which NO_2 is consumed by an acid-catalysed reaction: increasing the acidity of titanias shifts the temperature at which NO_2 is formed to higher values (Fig. 8). At low acidity, the rate of production of NO_2 is too high compared with the rate of the acid-catalysed reaction and NO_2 appears in the gas phase.

Because of the protocol of activation including a calcination at 773 K before the reaction, the operation in oxygen-rich conditions in the presence of N oxides, we assume that the working catalyst is a supported Rh oxide, as indicated by XPS. In a neutral atmosphere and with reduced catalysts, the formation of both N_2 and N_2O requires the presence of reduced surface sites [27], which are unlikely to exist in our experimental oxidising conditions. A detailed mechanism has been proposed by Adelman et al. [28] for the SCR of NO by propene on Cu/ZSM5. This proposal supposes the formation of nitrosoalkanes by reaction of alkyl radical with NO or NO_2 to form nitrosoalkanes. Nitrosoalkanes with an α-hydrogen are not stable and would spontaneously isomerise to form oximes [29]. Indeed, Beutel et al. have shown that on Cu/ZSM-5, acetone oxime, the isomerisation product of nitrosopropane, reacts fast with NO to form N_2 and N_2O [30]. Isotopic labelling shows that N–N bonds are formed between two nitrogen atoms with different histories: an impinging NO molecule and an adsorbed oxime complex. This mechanism does not involve any step catalysed by acids and cannot be strictly applied here. However, oximes can be converted to nitriles or hydroxylamines by an acid catalytic process [29], and this path through nitriles could account for the role of acid supports [31,32]. Rh catalyses partial oxidation of propene to acrolein, acetone, and ethanol [33]; therefore a path similar to that recently described by Yeom et al. [34] for the reaction of acetaldehyde with NO_2 on BaY zeolites could also be suggested. Nitromethane was detected in the reaction products, showing that acid-catalysed reactions can convert acetaldehyde to nitromethane, which has long been reported as an intermediate of the reaction [35].

An interesting characteristic of these catalysts is their resistance to SO_2 and water: as illustrated in Fig. 9, the rate shows little sensitivity to the presence of 25 ppm of SO_2 in the reaction mixture and is retained with the addition of 3% H_2O in the feed. Toubeli [36] observed an inhibition of the formation of N_2 by the addition of SO_2 but used reduced Rh catalysts supported by a TiO_2 of low surface area, about

20 $m^2 g^{-1}$ doped by W^{6+}. It has been observed that the adsorption of SO_2 on FHTi is reversible at moderate temperatures. This reversibility shows a low interaction of sulfates with the surface and is not observed on TiO_2 with high surface areas, which appear then as much more acidic. The lack of influence of SO_2 could be a result of the oxidation state of the metal: the oxide has an acidic character and is not prone to adsorb an acid like SO_2.

In conclusion, the determination of the rate as a function of the dispersion of Rh oxide suggests a bifunctional mechanism for the selective catalytic reduction of NO by propene. At the higher acidities it appears that the rate is controlled by the oxidation of propene, so that the improvement of catalytic activity has to be focused on this step.

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