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Sulphated TiO_2 for selective catalytic reduction of NOx by n-decane

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ABSTRACT

The selective catalytic reduction of NO by n-decane ($C_{10}H_{22}$-SCR), with or without water (1.5 vol.%), has been studied over sulphated titania catalysts (~2 wt% S). Such sulphated materials have been explored as candidates for HC-SCR by decane with process temperatures >600 °C. The nature of the functional groups from residual reaction products and the thermal stability of sulphated compounds were characterized by mass spectroscopy, FTIR analysis and temperature programmed desorption experiments. It was observed that hydrocarbons (C_xH_y), aldehyde (RCHO), acid (RCOOH), ester (RCOOR) and primary and secondary amine (RNH_2, R_2NH) functional groups were present at the catalyst surface. For the sample not tested under HC-SCR reaction, the sulphate compounds ($SO_4{}^{2-}$, $SO_3{}^{2-}$) were stable up to 600 °C under He-TPD whereas for samples tested under the HC-SCR reaction, sulphate species were released above 400 °C. This might be due to the exothermic oxidation reaction of deposited carbon compounds, characterized by ex situ analysis, with oxygen supplied by the sulphated support. This effect was confirmed by mixing the catalyst with soot particles. Lastly, we propose a reaction scheme for the HC-SCR of NO by decane over sulphated titania.

1. Introduction

The removal of NOx from engine exhaust gas is highly important due to its detrimental impact on the environment resulting in acid rains, ground-level ozone, as well as degradation of the visibility and human health (i.e. lung infections and respiratory allergies) [20,48]. One solution to reduce this toxic gas is by selective catalytic reduction of NOx using hydrocarbons (HC-SCR). The most practical method is to use the unburned hydrocarbons already present in the exhaust gas. Several studies have focused on the effect of light hydrocarbons (C_1–C_4), in particular methane [39,42], ethylene [21,36], propene [3,19] and propane [23,27,43]. However, these kinds of molecules are not commonly observed in diesel engine exhaust. Moreover, the most reducing reactants are olefin, paraffin, aromatic and oxygenate compounds. Few reports deal with the catalyst reactivity in the presence of high hydrocarbons ($C > 7$) [8,29,35]. Some investigations have been carried out with decane ($C_{10}H_{22}$) [14–16]. The nature of the catalyst support (zeolitic, non-zeolitic or mesoporous oxides) and active metal (transition or platinum group metal) has been studied [5,26,28]. The most investigated supports are Al_2O_3 [45], SiO_2 [27] and ZrO_2 [13] oxides and, to a less extent, TiO_2 or sulphated TiO_2 supports [18,51]. Even without acidic treatment, TiO_2 is an interesting candidate due to its intrinsic properties for HC-SCR application [17,18].

The selective catalytic reduction of NO using hydrocarbons has been shown to be enhanced on acidic supports [2,9,32,37]. In particular, acidity created by sulphate species has shown to be superior to other acids in promoting SCR of NO [33]. The acidic component in the mechanism is considered to play a role in the oxidation of NO to NO_2 [37,53] as well as in the reduction of NO_2 to N_2 [31,33]. A basic scheme for SCR of NO proposed by Kate et al. and modified by Li et al. can be seen in Scheme 1 [31,33]. The scheme outlines how an acidic group, H^+, or noble metal, Pd, are responsible for the oxidation of NO followed by the subsequent reduction of NO_2 to N_2 using methane.

The practical and cost-effective solution for SCR would be to use fuel as the reductant. Decane is considered as a model molecule for SCR as it is found in diesel exhaust and has been shown to facilitate HC-SCR of NO [15,16,49]. The aim of this paper is to analyze n-decane as the reductant in HC-SCR over a sulphated-titania catalyst. To date, there has not been a study presenting results concerning the HC-SCR reaction of n-decane including the characterization of residual reaction products and the thermal stability of sulphate compounds over a sulphated TiO_2 catalyst. In addition, an attempt has been made to analyze qualitatively the residual reaction products involved in HC-SCR of NOx by n-$C_{10}H_{22}$ using ex situ mass-spectroscopy and FTIR analysis. The effect of these residual products on the thermal stability of sulphate species was evaluated by temperature programmed desorption and compared

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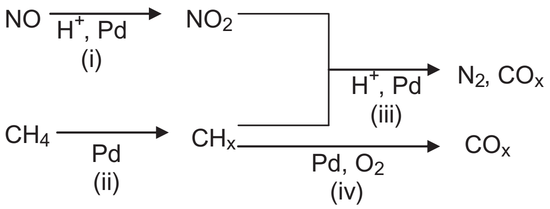


Scheme 1. Proposed three functional pathway for SCR of NO over Pd supported on sulphated-Al_2O_3 [33].

to the results obtained under inert atmosphere with or without the presence of soot. In this purpose, sulphated titania was used as the catalyst.

2. Experimental

The catalyst used in this study was a commercial TiO_2 sulphated catalyst (2 wt% S) supplied by Millennium®. After calcination at 500 °C for 10 h, the specific surface area of the sample, determined by N_2 adsorption, was measured to be 150 $m^2\,g^{-1}$.

The selective catalytic reduction of NOx by n-decane ($C_{10}H_{22}$-SCR) was carried out in a U-shaped quartz reactor containing 200 mg of catalyst. The reactor was electrically heated and the temperature of the catalyst was monitored using a K-type thermocouple. The reaction mixture was composed of 400 ppm NO, 240 ppm $C_{10}H_{22}$ and 9 vol.% O_2 in He as carrier gas in the presence or not of H_2O (1.5 vol.%). The total flow rate was 120 mL min^{-1}, corresponding to a space velocity of about 35,000 h^{-1}. Reaction products were analyzed by micro gas chromatography (μGC: TCD detector) for N_2 (molecular sieve 5A) [1,6] and CO_2 (Porapak® Q), by gas chromatography (FID detector) for $C_{10}H_{22}$ and by IR-UV for NO, NO_2 and N_2O. After stabilization, the temperature-programmed reaction was started at 25 °C by increasing the catalyst temperature at a rate of 2 °C min^{-1} until 500 °C was obtained. At the end of the ramp, the temperature was maintained 30 min and decreased at a rate of 1 °C min^{-1} down to room temperature. The light-off curves presented in this paper were recorded during the heating and cooling ramps. The N_2, N_2O, NO_2, global NO, total $C_{10}H_{22}$ yields, nitrogen balance and the experimental C_1/NO ratio were calculated by the following equations from (1)–(7):

$$Y_{NO-N_2} = 100 \times \frac{2[N_2]}{[NO]_0} \tag{1}$$

$$Y_{NO-N_2O} = 100 \times \frac{2[N_2O]}{[NO]_0} \tag{2}$$

$$Y_{NO-NO_2} = 100 \times \frac{[NO_2]}{[NO]_0} \tag{3}$$

$$Y_{NO\ global} = 100 \times \left(\frac{2[N_2]+[NO_2]+2[N_2O]}{[NO]_0}\right) \tag{4}$$

$$Y_{C_{10}H_{22}} = 100 \times \left(\frac{(1/10)[CO_2]}{[C_{10}H_{22}]_0}\right) \tag{5}$$

$$\text{N balance}: \quad [NO]_0 + [NO_2]_0 = [NO] + [NO_2] + 2[N_2] + 2[N_2O] \tag{6}$$

$$\frac{C_1}{NO} = \frac{10[C_1H_{22}]_0}{[NO]_0} \tag{7}$$

Mass spectrometry analysis using an Inficon® quadrupolar mass spectrometer equipped with a closed ion source was used to analyze the main *m/z* fragments from residual reaction products formed and adsorbed at the surface during the catalytic reduction of NOx by $C_{10}H_{22}$. The HC-SCR test conditions were similar as described above. After stabilization, the temperature-programmed reaction was started at 25 °C by increasing the catalyst temperature at a rate of 2 °C min^{-1} until 300 °C was reached. At the end of the ramp, the temperature was maintained for 10 min followed by decreasing to room temperature at the same rate, under reacting mixture. The catalyst was then removed and placed in the temperature-programmed desorption apparatus (TPD). The thermal desorption experiment was carried out under He at 10 °C min^{-1} up to 600 °C and *m/z* fragments were recorded continuously between the mass of 1 and 150. The *m/z* peak was assumed to be acceptable if its signal was higher than the detection limit, in average higher than 5×10^{-13} A, and different from the background noise. The fragment peaks detected are summarized in Table 1. The function al groups of the residual reaction products were characterized by FTIR analysis using a Vector 22 Bruker® apparatus ($T_r = I/I_0$) for the catalyst previously tested in HC-SCR test as described above. In order to carry out FTIR analysis, the catalyst was diluted in KBr powder at a ratio of 3 wt%.

For the complementary TPD experiment on sulphated TiO_2 catalyst, the production of soot particles was needed. For this purpose, soot particles were produced by means of a miniCAST (Combustion Aerosol Standard) soot generator using propane as fuel. High purity propane was used as fuel, synthetic air as oxidant and N_2 as balance. The fuel and the oxidation air flows were fixed at 60 and 1550 mL min^{-1}, respectively, to produce soot particles with a lean flame [40].

3. Results and discussion

3.1. Catalytic activity measurements

The catalytic activity of the sulphated titania catalyst was evaluated in HC-SCR using n-decane with or without water (1.5 vol.%). The water concentration in this study is lower than that observed in diesel exhaust gas (~10 vol.%). It has been reported that the activity of SCR by long chain alkanes *increases* in the presence of large concentrations of water due to the decrease in the concentration of carbonaceous species blocking adsorption sites at the surface [25]. This carbonaceous layer is due to the higher enthalpy of adsorption of heavier alkanes [46]. The reason for a lower water concentration in this work was because of the concern in the release of sulphur from the catalyst, by hydrolysis of the bond between the

Table 1
Assignment of the *m/z* fragment obtained by MS analysis to atom groups of the different families distinguished.

C compounds (Non-HC)		HC compounds		N compounds		S compounds	
m/z	Group	*m/z*	Group	*m/z*	Group	*m/z*	Group
12	C	29	C_2H_5	14, 15	N	16	O
27	CN, CHO	43	C_3H_7, CH_3CO	28	N_2, CO	32	S, O_2
28	CO, N_2	57	C_4H_9	30	NO	48	SO
29	CN, CHO	71	C_5H_{11}	44	N_2O, CO_2	64	SO_2
44	CO_2	85	C_6H_{13}	46	NO_2		
		99	C_7H_{15}	62	NO_3		
		142	$C_{10}H_{22}$	76	N_2O_3		

Table 2
Summary of the HC-SCR by $C_{10}H_{22}$ with or without H_2O over TiO_2 sulphated catalyst.

Test	Without H_2O		With H_2O	
	Heating	Cooling	Heating	Cooling
C_1/NO	7.1	8.2		
Max NO conversion/%	150	47	112	40
Max N_2 yield/%	69	18	53	17
Temperature max N_2 yield/°C	457	390	450	407
$C_{10}H_{22}$ conv. at max N_2 yield/%	>150	96	>150	98
NO–N_2 window/°C	200–500	250–500	220–500	280–490
N_2 selectivity max/%	96	82	86	81
NO_2 yield/%	5	9	7	11
N_2O yield/%	9	9	7	7

sulphate and the surface. Since the aim of this study was to check the influence of residual carbon species on the thermal stability of the sulphate compound, a compromise was established between the carbonaceous effect at low H_2O content and the release of sulphate at high H_2O content, which justifies the choice of 1.5 vol.% water. The material balance of N in the heating step without water is reported in Fig. 1. Despite the slight variation of the theoretical NO concentration (400 ppm), around ±5%, the global N balance remained constant in the temperature range of 100–500 °C. Decane was observed to be completely oxidized to CO_2 as the presence of CO was not observed. Fig. 2 displays the N_2 yield and the decane conversion during heating and cooling steps with or without water, and Table 2 summarizes the HC-SCR properties of the TiO_2 sulphated catalyst.

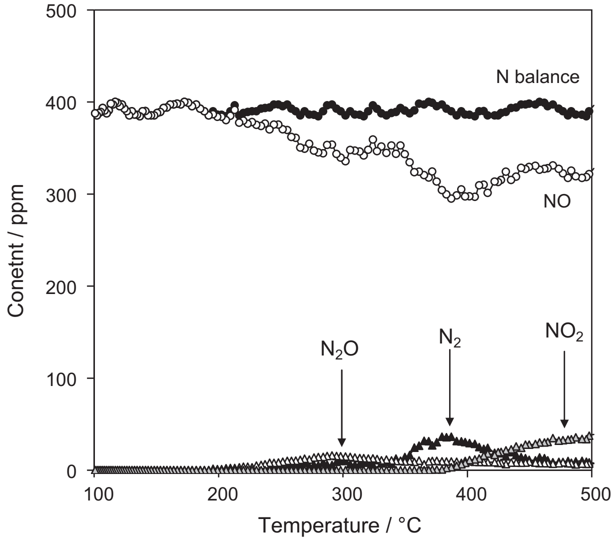


Fig. 1. Example of N balance, NO, N_2O, NO_2 and N_2 concentration trend obtained during cooling step without H_2O in HC-SCR test by $C_{10}H_{22}$ for sulphated TiO_2 catalyst.

During the heating step, the NO and $C_{10}H_{22}$ conversion started simultaneously at 250 °C. For experiments carried out without and with water at temperatures exceeding 400 °C, the NO balance is higher than 100% due to strong adsorption of NO on the catalyst at

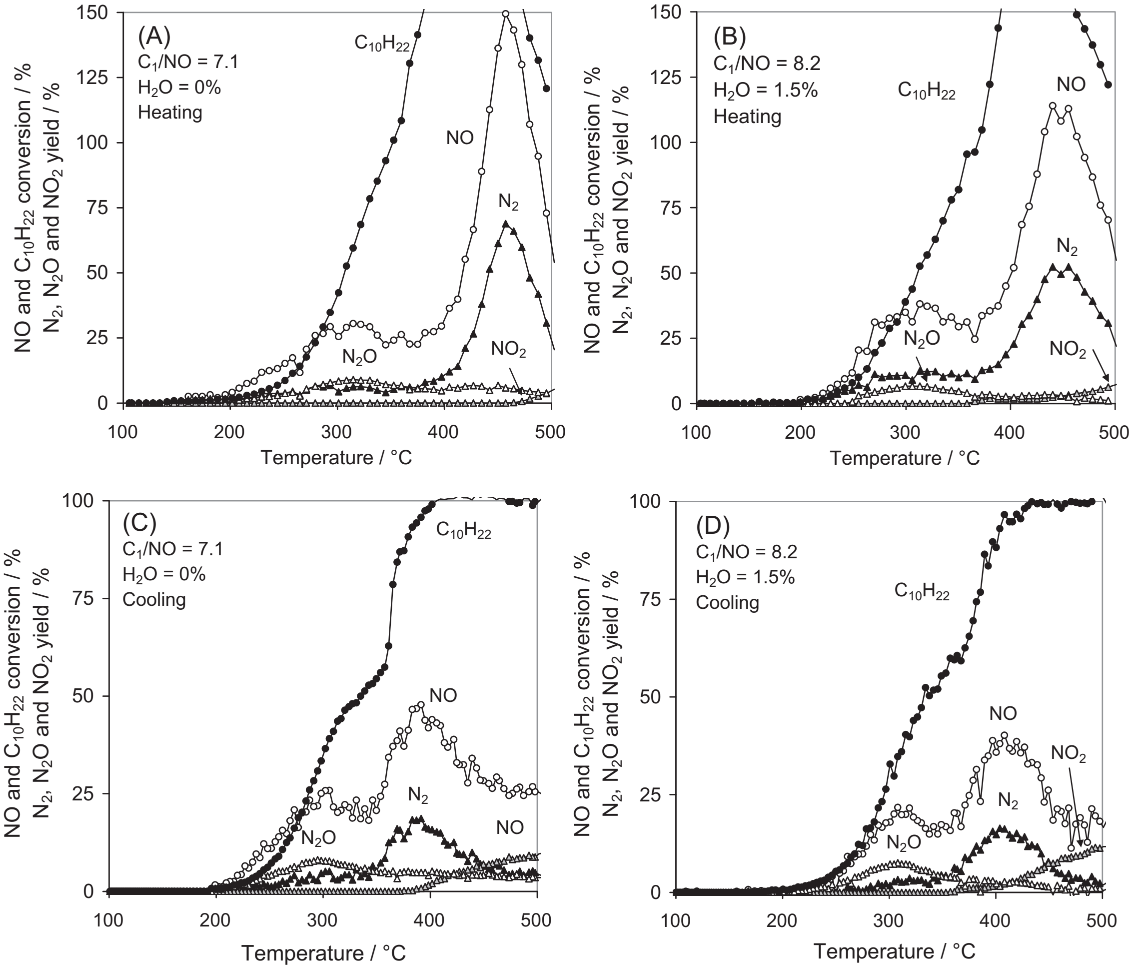


Fig. 2. NO and $C_{10}H_{22}$ conversion and N_2, N_2O and NO_2 yield obtained during heating (A and B) and cooling step (C and D) without (A and C) or with H_2O (B and D) in HC-SCR test by $C_{10}H_{22}$ for sulphated TiO_2 catalyst.

low temperatures. The adsorption can be attributed to NO forming intermediate species as observed by FTIR and discussed later in the report. The maximum N_2 yield without water (69%) and with water (53%) are reached at ∼450 °C and are shifted to higher temperature, $\Delta T \sim 20$ °C with regard to the maximum $C_{10}H_{22}$ conversion which occurs at 410 °C. The corresponding maximum N_2 selectivity is higher than 85%. At higher temperatures, the N_2 yield curve decreased until 500 °C. The N_2 yield window is the same regardless of the conditions between 220 and 500 °C. The instantaneous balance for $C_{10}H_{22}$ conversion, calculated via CO_2 formation (Eq. (5)), is higher than 100%, exceeding 150% at ∼410 °C. This phenomenon occurs during the heating step only and has been attributed to the formation of carbon compounds (C or C_xH_y) at the catalyst surface by adsorption of the hydrocarbon at low temperatures (<100 °C). At this maximum the corresponding C_1/NO ratio, ∼15, is twice as high as the value obtained during the calibration, ∼8. The enrichment of the reductant concentration on the catalyst surface improves the catalytic activity towards N_2 formation. The N_2O production starts at low temperatures (∼250 °C) and reaches a maximum of 9% at around 310 °C with or without water. The NO_2 production begins at temperatures higher than 400 °C and does not exceed 7%, even at 500 °C. The increased activity observed during the heating step, which is a transient procedure, has been observed on zeolitic catalysts [4,10,12,38,41] and the boosting effect has been attributed to (i) the carbonaceous deposit which acts as reducing agents [10,38], (ii) the ability of the catalyst to store hydrocarbon species at low temperatures [11,41] and (iii) low NOx trapping with long chain n-alkane [4].

During the cooling step, the NO and $C_{10}H_{22}$ conversion could be correctly determined as no reactant had been adsorbed at the catalyst surface at 500 °C. There are three main temperature domains where the catalyst activity changes. At the beginning, from 500 °C to 400 °C, decane is totally oxidized and the NO_2 formation is preferred with a maximum of 9–11% at 500 °C with or without water, respectively. Such results were already observed with HC-SCR by lower hydrocarbons like C_3H_6 [3]. In this temperature range, decane is very reactive with oxygen and frees surface active sites for NO adsorption. Thus NO oxidation can be achieved. At the second temperature range, between 400 °C and 340 °C, decane conversion is lower than 100% which is attributed to adsorption. Compared to the heating step, the maximum N_2 yield decreased drastically from 69 to 18% without water and from 53 to 17% with water. This maximum N_2 yield occurred only when the hydrocarbon conversion was lower than 100%. The maximum N_2 selectivity decreased slightly but is still higher than 80%. In parallel, NO conversion reaches a maximum of 47% at 390 °C and 40% at 400 °C for experiments carried out with and without water, respectively. Finally, for temperatures < 340 °C, a second N_2 peak is observed. The production of N_2O is preferred over N_2 at this temperature independent of water concentration with yielding values between 9 and 11%.

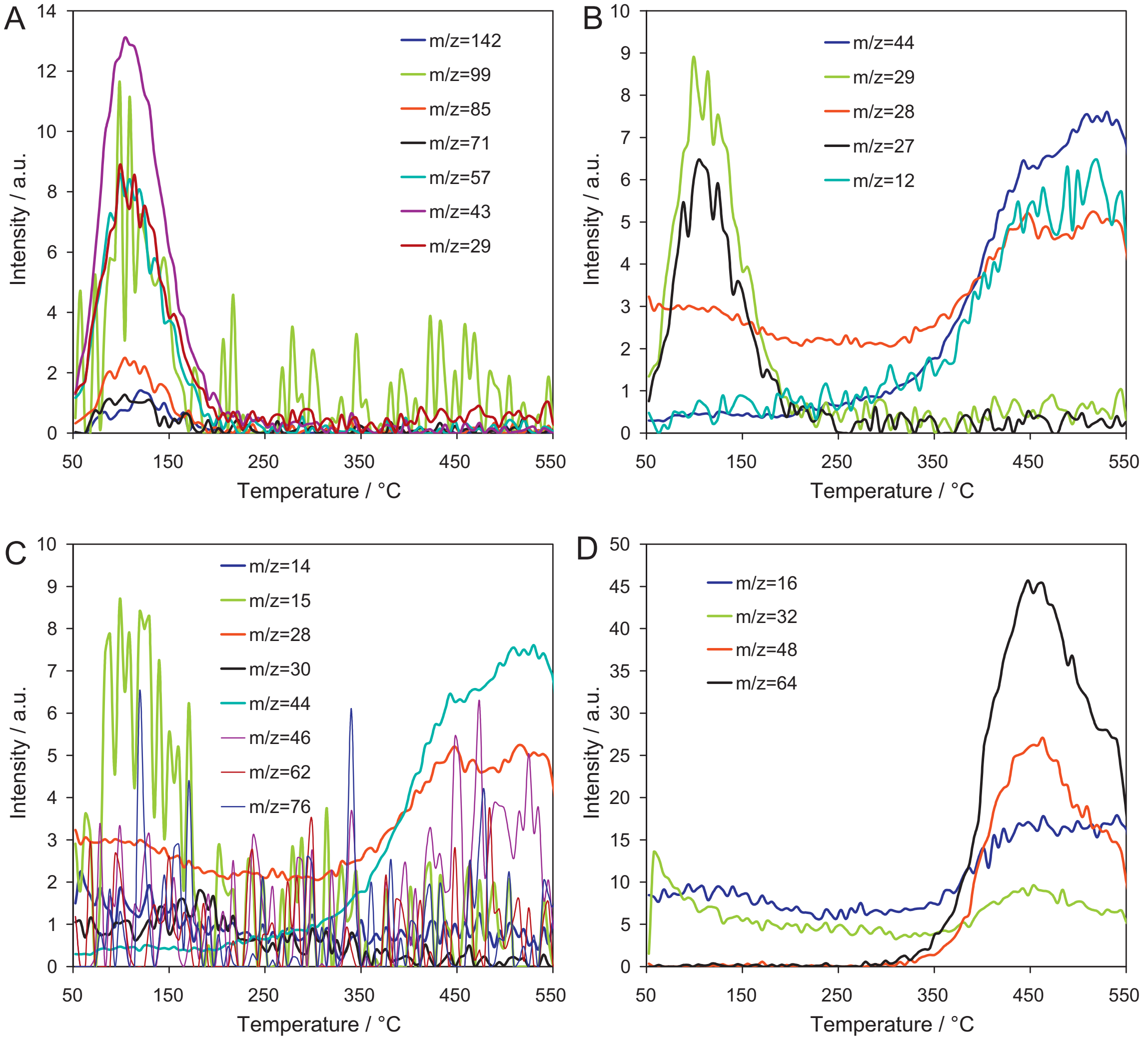


Fig. 3. Mass spectra of C (HC) (A), non-HC (B), N (C) and S (D) compounds obtained during TPD under He of TiO_2 sulphated catalyst after NOx reduction by $C_{10}H_{22}$ without H_2O stopped at 300 °C.

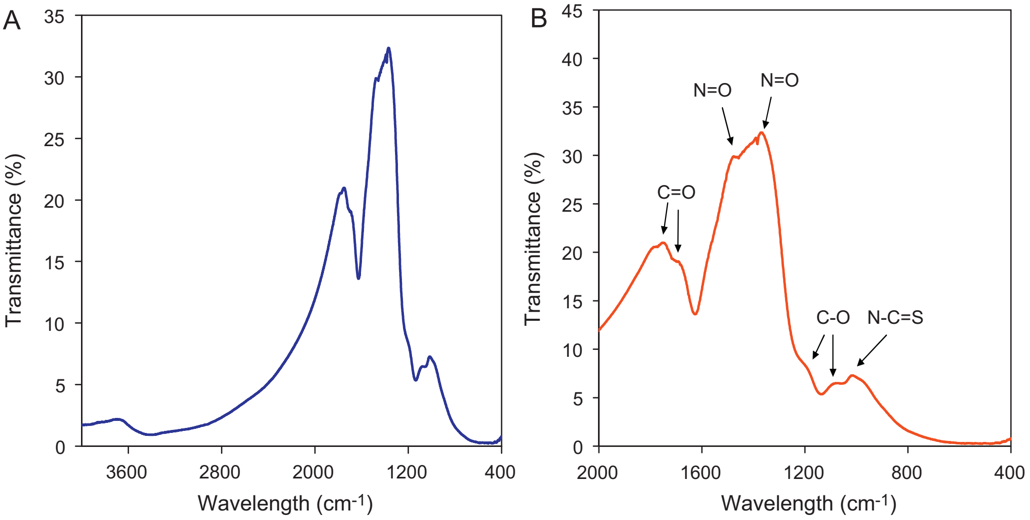


Fig. 4. FTIR spectra obtained in transmittance mode [400–4000 cm^{-1}] (A) and [400–2000 cm^{-1}] (B) for TiO_2 sulphated sample after NOx reduction by $C_{10}H_{22}$ stopped at 300 °C.

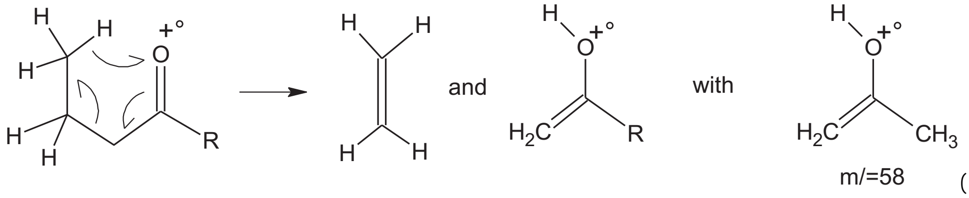
Decane has two distinct conversion peaks (~420 °C and ~340 °C) during the cooling period (i.e. two shoulders on the decane conversion curve Fig. 2C and D). The peaks signify two different mechanism pathways which decane is oxidized. The change in hydrocarbon oxidative species on the catalyst is likely to alter the mechanism that NO is reduced. In our recent study [3], the same was observed for the oxidation curve of C_3H_6 during HC-SCR over ceria/sulphated titania catalyst. The oxidation of C_3H_6 resulted in two peaks where $CO:CO_2$ molar ratio changed as a function of temperature. The CO production was observed to decrease while CO_2 production increased at a faster rate at ~410 °C. In the present study, decane undergoes a similar oxidation. In addition to decane oxidation, NOx reduction is observed to display two peaks that coincide with decane oxidation. These two peaks are associated with at least two different NO species. The lower temperature peak correlates to a high conversion of N_2O, and the higher temperature peak correlates to a high conversion of N_2. The correlation between decane oxidation and NOx reduction provides evidence that it is possible NOx is being catalyzed via two different adsorbed species; one dominate at lower temperatures and one dominate at higher temperatures. Different nitrate species have been observed to form on sulphated titania via the reaction between NO^- with one, or two sulphate species: $NO^- + SO_4{}^{2-} = NO_2{}^- + SO_3{}^{2-}$ and $NO^- + 2SO_4{}^{2-} = NO_3{}^- + 2SO_3{}^{2-}$ [30]. Further work is needed in order to quantify and attribute the desorption peaks with the multiple NOx species.

Finally, during cooling step, the presence of 1.5 vol.% H_2O shifts the N_2 peak to higher temperatures ($\Delta T \sim 20$ °C) but does not modify the maximum N_2 yield, around 18%.

3.2. Characterization of residual products in HC-SCR by n-decane

Mass spectroscopy and FTIR analyses revealed that the addition of steam had no impact on the residual reaction products (results not shown here), therefore only the results from experiments conducted without water are reported here.

Concerning mass spectroscopy experiments, the mass fragments (*m/z*) obtained can be classified into four groups as presented in Table 1: (i) HC compounds, (ii) non-HC compounds (C, CO and CO_2), (iii) N compounds and (iv) S compounds. For each group, the functional groups and the type of molecules (aliphatic, aromatic) which were present at the surface were identified in Fig. 3. There were no aromatic molecules or alcohol groups (ROH) detected; the main *m/z* fragments for aromatic molecules and alcohol groups being 65 and 31, 45, 59, 73, respectively. Furthermore, the absence in the detection of $m/z = 58$, corresponding to a McLafferty rearrangement, Eq. (8), implied that no ketone (RCOR) functional groups were present. However, the molecular mass of decane, 142, and the consecutive subtraction of $m/z = 14$ fragment (CH_2) revealed the presence of linear hydrocarbon molecules (C_xH_y) as presented in Table 1. Notably, C_7H_{15} is periodically released during the heating step (Fig. 3A) further indication of the decomposition of decane. The second significant HC species detected was ethane. The decomposition of decane is attributed to oxidation which corresponds to the reduction of NOx species. In addition, the base peak of n-decane mass spectrum was $m/z = 43$, the mass $m/z = 43$, 44 and 45 which are characteristic of aldehyde (RCHO), ester (RCOOR), acid (RCOOH) and amine (RNH_2, R_2NH) function groups.



(8)

Desorption of N_2 reached a maximum plateau at 425 °C, and remained constant until the end of the heating ramp, 550 °C. This is in contrast with the experimental catalytic tests. During the catalytic testing the formation of N_2 obtained a maximum peak at ~450 °C (Fig. 2A) followed by a steady decline corresponding to a symmetrical peak. The mass/charge ratio of N_2 is equal to CO which explains this discrepancy. Hence for the TPD beyond 450 °C, the detection of $m/z = 28$ is largely due to CO and not N_2.

The conversion of decane is observed to be >100% beginning around 350 °C during the heating ramp (Fig. 2A) which continued

$$NO + O_2 \longrightarrow NO_2 \quad \text{[on sulphate acid sites]}$$

$$NO_2 + C_{10}H_{22} \longrightarrow N_2 + CO_x + H_2O \quad \text{[on titanium sites]}$$

Scheme 2. Proposed two functional pathway for SCR of NO over sulphated titania support.

until 375 °C during the cooling step (Fig. 2C). Another significance at 450 °C is desorption of the sulphur species (Fig. 3D). Peaks corresponding to SO_2 and SO desorption reach a maximum at this temperature.

FTIR analysis was carried out in order to obtain information on functional groups. The transmittance spectra for the HC-SCR of NO by $C_{10}H_{22}$ without water are presented in Fig. 4. The overall spectra are reported between 400 and 4000 cm^{-1} (A) with a zoom between 400 and 2000 cm^{-1} (B). A reference table for infrared characteristic group frequencies was used to quantify the band vibrations [47]. As previously mentioned the NO balance exceeds 100% when the catalyst is heated above 400 °C. The FTIR data for the catalyst displays two nitrogen species, N–C=S and N=O, below 300 °C. The N=O vibration peak is the more prominent. The higher NO balance can be attributed to the release of these species at temperatures >400 °C. Other notable functional groups characterized by FTIR were C=O and C–O. The N=N, S–S and C–O–C functional groups were not observed because the attributed bands were not their strongest corresponding vibrations. However, as observed by mass spectroscopy analysis, the functional groups which appeared were linear hydrocarbon molecules (C_xH_y), aldehydes (RCHO), esters (RCOOR), acids (RCOOH) and amines (RNH_2, R_2NH).

The presence and the role of these functional groups have been outlined in the mechanisms proposed by several authors either directly for HC-SCR by hydrocarbons as propene or propane or for the chemistry of acetaldehyde or acetic acid in the presence of NOx in order to elucidate reaction pathways [24,43,44,53].

It has long been accepted that the C–H bond activation of saturated hydrocarbons can be catalyzed by solid acids, and in particular sulphate species [7,22,52]. At the same time, an alternative C–H bond activation could take place with NO_2. Kikuchi and Yogo proposed that NO is oxidized to NO_2 on Brönsted acid sites followed by their migration to an active metal site where a direct NO_2–hydrocarbon reaction would take place [32]. The presence of aldehydes, esters, acids and amines correlates to the latter reaction pathway. The results presented from FTIR correlate more to a reaction pathway where C–H bond activation is catalyzed by an NO_2 species. In this route the Brönsted sites indirectly participate in the C–H bond breaking by oxidizing NO to form the reactive species, NO_2. Upon formation of NO_2, a reaction proceeds involving adsorbed decane species. In this step the migration of NO_2 cannot be excluded. Here we propose a similar pathway (Scheme 2) to that of Kikuchi and Yogo [32]. This scheme is supported by FTIR and catalytic tests that display the conversion of NO and decane began simultaneously.

3.3. *Thermal stability of sulphate compounds*

At 300 °C under a flowing reaction mixture, it was observed that organic compounds were adsorbed at the catalyst surface. These carbon molecules influenced the thermal stability of S species. The desorption of S compounds was observed by mass spectrometry analysis (Fig. 3D) from characterizing the main *m/z* fragments (16, 32, 48 and 64). The NO reduction by CHx, producing H_2S, did not occur because the mass $m/z = 34$ and 33 were not detected (no H_2S production or quantity under the limit of detection). The sulphate desorption started at 350 °C and the same temperature was observed for non-HC compounds (Fig. 3B). This effect can be attributed to (i) a reaction between sulphated species and HC compounds like polymers, or to (ii) the oxidation of organic particles (soot, polymer, ...) with oxygen provided by $SO_3{}^{2-}$ and $SO_4{}^{2-}$ species. During TPD under He, a temperature increase was recorded at the catalytic bed level, due to the reaction of soot and oxygen provided by the sulphated species ($SO_3{}^{2-}$, $SO_4{}^{2-}$) adsorbed on the catalyst. Assuming that the partial reaction $C_{ads} + O_{ads} \rightarrow CO_g$ occurred with $\Delta H_r = -111\ kJ\,mol^{-1}$, and complete oxidation of the 2400 ppm of C (240 ppm of $C_{10}H_{22}$), the adiabatic temperature at the catalyst surface should reach about 830 °C ($nCp_{air}\Delta T = \Delta H_r$ let $\Delta T = (\Delta H(ppm/10^6)X)/(Cp_{air})$ [34], where Cp_{air} being the molar specific heat of air at constant pressure ($32\ J\,K^{-1}\,mol^{-1}$), and X being the CO yield (100%). This temperature is the range required for thermal desorption of sulphates under He. This is confirmed by TPD experiment carried out to a maximum temperature of 900 °C (Fig. 5). A fresh sulphated titania catalyst desorbed S related compounds, characterized by $m/z = 32$ (O_2) and $m/z = 64$ (SO_2), beginning at 600 °C and was completed at 860 °C. This temperature range observed for sulphate decomposition is in good agreement with those obtained for sulphates formed over different oxides (ZrO_2, MgO, BaO, Al_2O_3, $MgAl_2O_3$), between 700 and 1000 °C [50].

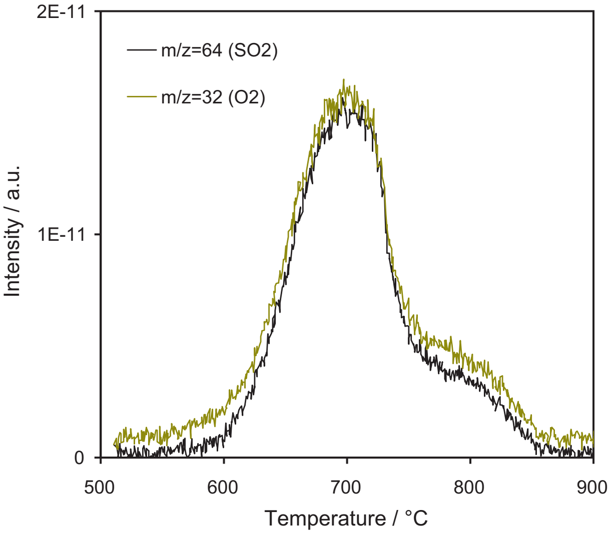


Fig. 5. TPD under He of the fresh TiO_2 sulphated sample (not tested under HC-SCR conditions).

To further investigate the effect of carbon species deposited at the catalyst surface, a mixture of TiO_2/sulphated catalyst with soot particles was prepared (~3 wt%) and analyzed under TPD of He. Soot was pre-generated by a miniCAST soot generator. Fig. 6A and B shows the evolution of the main *m/z* fragments of the non-HC compounds (12, 28 and 44) and of the S compounds (16, 32, 48 and 64) for both experiments, without (A1 and A2) and with (B1 and B2) 3 wt% of soot. The desorption of S compounds started between 400 and 450 °C with the simultaneous appearance of CO_2 ($m/z = 44$), showing that the combustion of organic compounds takes place during the TPD experiments with oxygen provided by the catalyst itself. This temperature range is slightly higher than the temperature obtained during TPD after HC-SCR test of NO by decane stopped at 300 °C. The temperature shift could be attributed to (i) the difference between the nature of the organic carbon species adsorbed during HC-SCR test compared to the nature of the soot particles or to (ii) the soot deposition route; the grind milling procedure used to mix powder and soot particles might have a consequence on the affinity between carbon and sulphate species. Some results showed that sulphate formed over oxide supports can be reduced at lower temperature (400–600 °C) than under inert atmosphere,

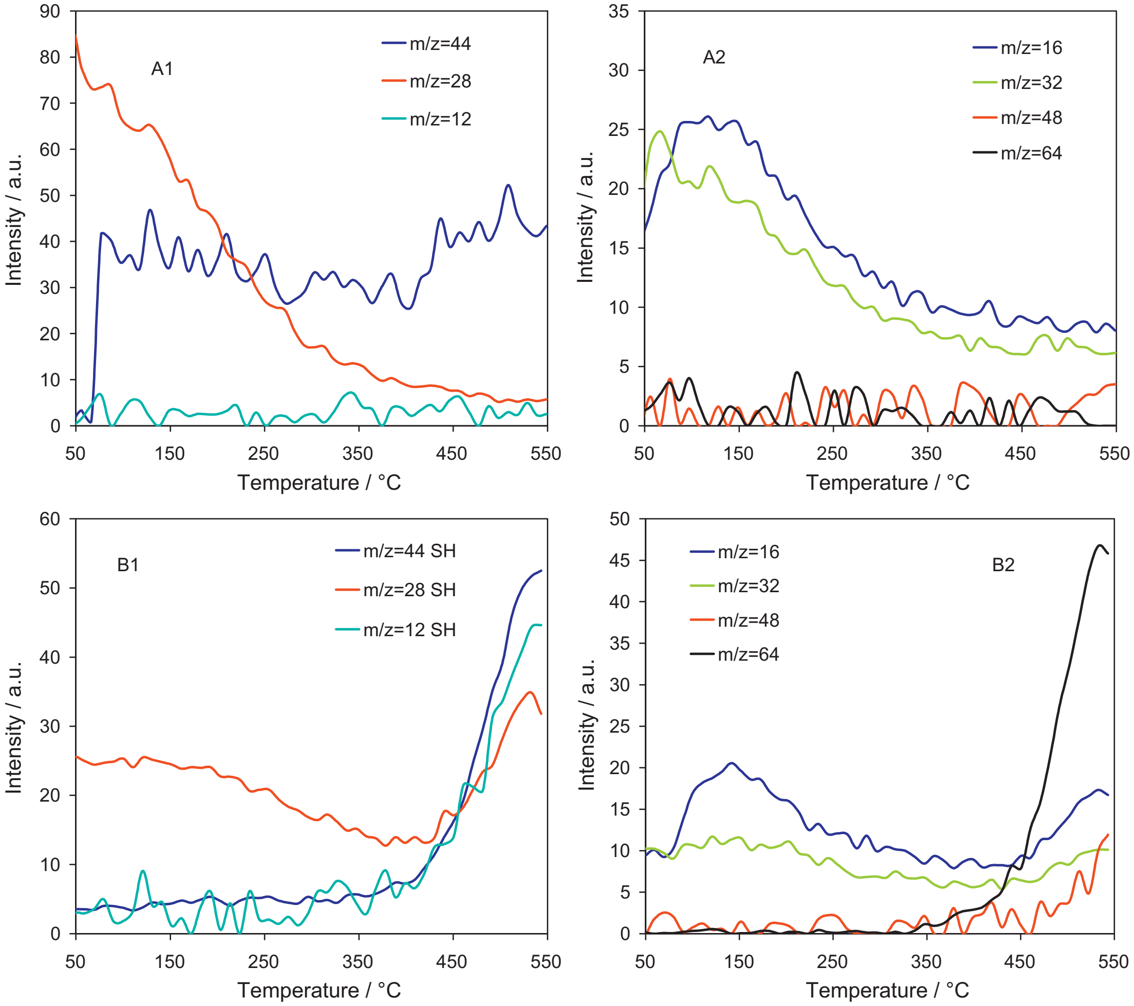


Fig. 6. Mass spectra of C (non-HC: C, CO, CO_2) and S compounds obtained after TPD under He of fresh TiO_2 sulphated sample (A1 and A2) and fresh TiO_2 sulphated sample mixed with 3 wt% soot (B1 and B2).

by different reducing agents, such as hydrogen or carbon monoxide [50].

From the TPD of the sulphated TiO_2 and soot mixture it can be concluded that carbon, formed by adsorption and dissociation of hydrocarbons, does contribute to the decomposition and desorption of sulphate compounds. The use of sulphated TiO_2 materials in HC-SCR of NOx by decane is not practical for long term applications where temperatures exceed 600 °C, due to the thermal instability of sulphates. In addition, the excess of hydrocarbons could react with the oxygen provided by sulphate species and consequently induce catalyst deactivation. This result could account for the loss of activity (N_2 yield; Fig. 2) in HC-SCR by decane during the cooling step.

4. Conclusion

This work presents the results concerning the qualitative study of the residual reaction products and the evaluation of the thermal stability of sulphated compounds on a sulphated titania catalyst during the HC-SCR reaction by n-decane. Hydrocarbons (C_xH_y), aldehydes (RCHO), acids (RCOOH), esters (RCOOR) and primary and secondary amines (RNH_2, R_2NH) where characterized at the catalyst surface by means of mass spectroscopy and FTIR analysis. Based on literature and the present work we propose a reaction scheme (Scheme 2) that outlines the SCR of NO by n-decane over sulphated titania. The stability of the sulphate species ($SO_4{}^{2-}$, $SO_3{}^{2-}$) under He-TPD, ex situ analysis, decreased after the HC-SCR reaction. Furthermore, sulphate species were observed to desorb at temperatures above 400 °C. The release of sulphur can be contributed to the exothermicity of the reaction of oxygen from sulphate compounds or from the support with carbon species, or a combination of both.

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