In situ Infrared Spectroscopic Studies on the Mechanism of the Selective Catalytic Reduction of NO by C₃H₈ over Ga₂O₃/Al₂O₃: High Efficiency of the Reducing Agent

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The partial oxidation of propane and the mechanism of selective catalytic reduction (SCR) of NO by propane over Ga_2O_3/Al_2O_3 in excess of O_2 have been investigated using in situ Fourier transform infrared spectroscopy. An optimized Ga_2O_3/Al_2O_3 catalyst shows high activity and efficiency of the reducing agent propane (100% conversion of NO at 623 K, GHSV: 10 000 h⁻¹). One molecule of propane converts more than 4 NO molecules to N₂. The reaction starts with the partial oxidation of C_3H_8 by O_2 and carboxylates (acetate, formate) are formed on the catalyst surface above 573 K. This oxidation represents the rate-determining step of the SCR reaction. These surface carboxylates represent a dominating intermediate and (easily) react with (adsorbed) NO forming nitrogen-containing organic species. The latter are proposed to react with NO to form N₂. Total oxidation of propane was enhanced at temperatures above 773 K leading to decreased reductant efficiency. Surface nitrite and nitrate species can also be observed, but they were found to be spectators only. This could be concluded from the electron balance (conversion of propane relative to NO) and from the relative rates of the single reaction steps. On the basis of these investigations and stoichiometric calculations, a conclusive reaction mechanism is proposed.

Introduction

It is widely accepted that selective catalytic reduction (SCR) of nitrogen oxides using hydrocarbons in an oxidizing atmosphere is a promising method to remove NO_x from lean-burn and diesel exhausts and could be an interesting cheaper alternative to ammonia SCR, e.g., for power stations.^{1,2} Although the first catalysts reported and many studies focused on SCR of NO by hydrocarbons are related to zeolite or metal ion exchanged zeolite catalysts, metal oxide or supported metal oxide catalysts are probably the best candidates for this reaction due to their high activity and stability.^{3–21} Among them, Ga₂O₃/Al₂O₃ is a promising candidate for practical applications because of its high stability and activity even in the presence of water and SO₂.^{20,21}

The most important limitation of Ga₂O₃/Al₂O₃ for practical application is that the active temperature is too high and the activity—temperature relationship shows a volcano shape which results in a small operation temperature range.^{20,21} Recently, several research groups have studied modifications of these catalysts by changing the catalyst preparation methods, adding a second or third metal oxide, or mixing different catalysts physically in order to increase the activity at lower temperature and broaden the temperature range.^{20–25} Alternatively, researchers have focused on structure—activity relationships and reaction

mechanism since this information may lead us to the design of more active catalyst systems.^{26–28}

Depending on the catalyst, the reducing agent, and reaction conditions, various reaction mechanisms for the SCR of NO by hydrocarbons have been proposed in the literature:^{26–37} On the basis of the knowledge of the mechanism of decomposition of NO over supported noble metal catalysts, a mechanism that involves dissociation of NO to $N_{(ads)}$ and $O_{(ads)}$ with subsequent desorption of $N_2 \mbox{ or } N_2 O$ and removal of $O_{(ads)}$ by the reducing agent has been proposed by Burch et al.,^{29,30} Acke et al.,³¹ Wogerbaur et al.,³² and Cho et al.³³ independently. Engler et al.³⁴ studied the mechanism of the SCR of NO by hydrocarbons on alumina-supported platinum catalysts and proposed that both NO and hydrocarbons are first activated by O₂ forming adsorbed surface species (oxygenates, nitrates). Then, these adsorbed species react with each other to give CO₂, N₂, and H₂O. Haneda et al.27 and Shimizu et al.28 investigated the mechanism of SCR of NO using C₃H₆ over Ga₂O₃/Al₂O₃ and Al₂O₃ independently. The authors suggested that NO was first oxidized to NO2 and adsorbed as NO_x^- (NO_2^- , NO_3^-) species; subsequently, the adsorbed NO_x^{-} species were reduced to N_2 by C_3H_6 or by oxygenates generated from C₃H₆. On the other hand, Obuchi et al.³⁵ proposed that carbonaceous or carbon deposits generated from partial oxidation of the reducing agents play a crucial role as intermediates in the SCR reaction in their studies on the reduction of NO using MTBE over γ -alumina. The last mechanism is further supported by Shibata et al.³⁶ and Meunier et al.³⁷ by studies of the SCR of NO using C₃H₈ and C₃H₆ over Ag/γ -Al₂O₃ and by Radtke et al. by investigations on the SCR of NO using ethene or propylene over CuO_x/γ -Al₂O₃.³⁸ To reveal the reaction mechanism of the hydrocarbon SCR reaction,

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it can be extremely important to investigate the formation and consumption of the possible intermediates and to calculate the electron balance for each reaction step. However, little detailed work focused on the stoichiometry of the reaction.

In the present work, we report a first systematic in situ Fourier transform infrared (FTIR) study including time-dependent experiments on the mechanism of the selective catalytic reduction of NO by C_3H_8 over Ga_2O_3/Al_2O_3 . The catalyst has been optimized, and its catalytic properties have been investigated extensively (conversions as function of various temperatures, detailed selectivity based on complete nitrogen and carbon balance). It is this catalyst Ga₂O₃/Al₂O₃ that is particularly interesting and suitable for mechanistic investigations for several reasons: (i) In comparison to all other systems reported, it shows the highest efficiency of the reducing agent: one propane molecule converts (more than) 4 NO molecules exclusively to N₂. This makes the system clearer, and several reaction mechanisms proposed in the literature can surely be excluded for Ga₂O₃/Al₂O₃ due to the overall electron balance. (ii) It is generally accepted that such oxide systems neither directly decompose NO nor oxidize NO to NO₂.²⁶ (iii) Neither Ga₂O₃ nor Al₂O₃ are known to be redox-active materials, i.e., partially reduced catalyst intermediates can also be excluded. On the basis of detailed in situ FTIR experiments on the oxidation of C₃H₈ in different gas atmospheres and on the consumption of surface carboxylates and nitrates and by careful correlation of the results with catalytic properties, a conclusive reaction mechanism will be presented.

Experimental Section

Catalyst Preparation. The catalysts applied in this work (10 mol % Ga₂O₃/Al₂O₃) were prepared by the impregnation method. A certain amount of γ -Al₂O₃ (specific surface area, Brunauer–Emmett–Teller: 198 m²/g) support was soaked into a solution of gallium nitrate (Merck, >99%) in a predetermined amount of H₂O and was allowed to stand at room temperature for 2 h with frequent stirring. Then the water was removed by heating under reduced pressure. The catalyst precursor thus obtained was dried at 393 K overnight, followed by calcinations at 723 K in air for 4 h.

Catalytic Activity Measurements. The catalytic activity was measured by using a fixed bed-flow reactor. The reaction mixture consisted of 1000 ppm NO, 1000 ppm C_3H_8 , and 10% O_2 (Helium as balance gas). The gas flow rate GHSV is 10 000 h^{-1} . The analysis of feed gas and products was carried out with a mass spectrometer, a CLD NO_x analyzer, a NDIR CO analyzer, and a gas micro chromatograph with a thermal conductivity detector and Porapack Q and molecular sieve A as separation columns. The catalytic activity was evaluated in terms of NO conversion to N₂, C_3H_8 conversion to CO_x (CO + CO_2), and the NO competitiveness factor.³⁹ The formation of N₂O was found negligible in the present work.

In situ FTIR Experiments. Catalyst powder (5 mg) was pressed into self-supporting wafers with a diameter of 8 mm (10 mg/cm²) and placed in a high-temperature flow cell with two pieces of CaF₂ windows. IR spectra were recorded on an FTIR spectrometer (FTS-575C, BIO-RAD) with 16 scans at a resolution of 2 cm⁻¹. Prior to each experiment, the catalyst wafer was first activated in situ by heating in a flow of O₂ (total flow: 50 mL/min) at 673 K for 2 h, followed by cooling to the desired temperature and purging in He for 30 min. Then, the spectrum of clean surface was recorded which was used as the background of the in situ experiment. The IR spectra of surface species in a flow of various gas mixtures (total flow: 50 mL/

 TABLE 1: Composition of Different Gas Mixtures Used in

 This Paper

no.	gas mixture	concentration
1	Не	pure helium (99.999%)
2	O_2	10% O ₂ /He
3	NO	1000 ppm NO/He
4	C_3H_8	3000 ppm C ₃ H ₈ /He
5	$NO + O_2$	$1000 \text{ ppm NO} + 10\% \text{ O}_2/\text{He}$
6	$C_{3}H_{8} + O_{2}$	$3000 \text{ ppm } \text{C}_3\text{H}_8 + 10\% \text{ O}_2/\text{He}$
7	$C_3H_8 + O_2 + NO$	$3000 \text{ ppm } \text{C}_3\text{H}_8 + 10\% \text{ O}_2 +$
		1000 ppm NO/He

TABLE 2: Catalytic Performance of Al_2O_3 and Ga_2O_3/Al_2O_3 in SCR of NO by C_3H_8

catalyst	temperature (K)	$X_{ m NO}{}^a$ (%)	X _{СЗН8} ^b (%)	$X_{\rm NO}$: $X_{\rm C3H8}$	NOCF ^c (%)
Al ₂ O ₃	623	10.1	1.7	5.9	59.4
	673	14.7	3.7	4.0	39.7
	723	28.4	10.1	2.8	28.1
	773	86.5	52.9	1.6	16.4
	823	93.4	95.3	1.0	9.6
	873	83.5	99.3	0.8	8.4
Ga ₂ O ₃ /Al ₂ O ₃	573	14.2	3.1	4.6	45.8
	623	28.6	8.5	3.4	33.7
	673	46.5	10.8	4.3	43.0
	723	100	24.1	4.2	41.5
	773	95.3	91.8	1.0	10.4
	823	95.0	98.5	1.0	9.6
	873	92.1	99.2	0.9	9.3

 a NO conversion: ([NO]_{inlet} - [NO]_{outlet}/[NO]_{inlet} \times 100\%. {}^b C₃H₈ conversion: ([C₃H₈]_{inlet} - [C₃H₈]_{outlet}/[C₃H₈]_{inlet} \times 100\%. {}^c NO competitiveness factor: ([NO]_{inlet} - [NO]_{outlet})/{10 \times ([C_3H_8]_{inlet} - [C_3H_8]_{outlet})} \times 100\%. {}^{39}

min) were recorded as a function of time. The composition of different gas mixtures are listed in Table 1. The short description in column two "gas mixture" is used in this paper.

In addition to the steady-state reaction, the time-dependent experiments were employed to clarify the role and reactivity of particular surface species. The catalyst was first exposed to either $C_3H_8 + O_2$ or NO + O_2 at 623 K for 120 min to accumulate the surface species. After purging in flowing He for 30 min, the feed gas was switched to various gas mixtures, and the changes in the intensity of IR bands were measured with time on the stream.

Results

1. Catalytic Performance of SCR of NO by C_3H_8 over Al_2O_3 and Ga_2O_3/Al_2O_3 . Table 2 shows the NO conversion for Al_2O_3 and Ga_2O_3/Al_2O_3 catalysts in the SCR of NO by C_3H_8 as a function of temperature in a fixed bed continuous flow reactor. Ga_2O_3/Al_2O_3 appears to be more active than Al_2O_3 over the whole temperature range. Both catalysts show a maximum in NO conversion (slight volcano shape), which is shifted to lower temperature for Ga_2O_3/Al_2O_3 for temperatures higher than the optimum value. The impregnation of Ga_2O_3 onto Al_2O_3 reduced the temperature of maximum NO conversion and broadened the temperature activity window for the reduction of NO by C_3H_8 .

Particular emphasis has been placed on the careful quantitative determination of all (by)products of the SCR reaction (complete carbon and nitrogen balance by a complex gas analysis system). In contrast to NO conversion, the conversion of C_3H_8 continuously increases for temperatures higher than an optimum value leading to a reduction of efficiency of the reducing agent (so-called NO competitiveness factor, NOCF).³⁹ At temperatures



Figure 1. IR spectra of adsorbed species under different gas atmospheres over Ga_2O_3/Al_2O_3 at 623 K after 200 min in (a) $C_3H_8 + O_2$, (b) $C_3H_8 + NO$, (c) $C_3H_8 + O_2 + NO$, and (d) $NO + O_2$.

lower than 673 K, the NOCF is ca. 40%, while at temperatures higher than 673 K, the NOCF decreased. This suggests the occurrence of side reactions at T = 673 K and higher (propane combustion). Thereby, propane is not completely oxidized, i.e., on the average 45% CO₂ and 55% CO are detected as oxidation products. On the other hand, NO is reduced nearly completely to N₂ (only 1% N₂O were detected).

2. Nature of Adsorbed Species Formed in Different Gas Atmospheres. The IR spectra of the adsorbed species on $Ga_2O_3/$ Al₂O₃ in dependence on the composition of the gas atmosphere at 623 K are shown in Figure 1. In flowing $C_3H_8 + O_2$ (spectrum a), the following bands have been observed: two strong bands centered at 1564 and 1456 cm⁻¹, two weak bands at 1392 and 1376 cm⁻¹, and a broad band at 3550 cm⁻¹. In the literature, the bands in the region between 3800 and 3200 cm^{-1} are assigned to the stretching vibration of OH groups. We assign the broad band at 3550 cm⁻¹ to bridging hydroxyl groups perturbed by interaction with C3H8 or with other organic species generated from C_3H_8 . The bands at 1564 and 1456 cm⁻¹ are in good agreement with those of acetic acid adsorbed on Ga₂O₃/ Al₂O₃ as reported by Haneda et al.²⁷ and by blank adsorption tests performed by us for all relevant species discussed here (not shown). These two bands are assigned to vibrations $v_{\rm as}(\rm COO)$ and $v_{\rm s}(\rm COO)$ of acetate formed by the reaction between C₃H₈ and O₂. The frequencies of the bands at 1392 and 1376 cm⁻¹ are in good agreement with those of formic acid adsorbed on the same catalysts (not shown) and those found in previous studies with formate adsorbed on Al₂O₃ as reported by Shimizu et al.²⁸ and Amenomiya et al.⁴⁰ Thus, the two bands at 1392 and 1376 cm⁻¹ have been assigned to $\nu_s(COO)$ and δ (CH) of adsorbed formate. They are also observed in flowing C_3H_8 + NO and C_3H_8 + NO + O₂. In comparison to the $C_3H_8 + O_2$ flow, four additional bands have been observed for flowing C_3H_8 + NO: 2230, 2180, 1716, and 1306 cm⁻¹. The bands at 2230 and 2180 cm⁻¹ are assigned to adsorbed isocyanate and cyanide, respectively.^{41–43} The bands centered at 1716 and 1306 cm⁻¹ are suggested to be due to vibrations of adsorbed carbonyl and the asymmetric vibration of nitrate according to recent literature by Meunier et al.37 and Shimizu et al.44 An additional band in the region of 1400-1360 cm⁻¹

 TABLE 3: Wavenumber and Assignment of Main

 Absorption Bands in the FTIR Spectra

wavenumber/			
cm^{-1}	surface species	vibration	ref
3768	Al ³⁺ -OH	ν(O-H)	28, 47
3755		ν(O-H)	28, 47
3686	Ga-OH-Al	ν(O-H)	28, 47
3608	hydrogen-bonded	ν(O-H)	47
	hydroxyl group		
2230	out of phase (Al-NCO)	ν (N=C=O)	42, 43
2180	cyanide (-CN)	$\nu(C \equiv N)$	27, 37, 42
1716	carbonyl		44
1590	formate	$\nu_{\rm as}(\rm COO)$	27
1580	bidentate nitrate (NO ₃ ⁻)	$\nu(N=O)$	27,36
1564	acetate	$v_{\rm as}(\rm COO)$	27
1552	unidentate nitrate	$\nu(N=O)$	
1456	acetate	$\nu_{\rm s}({\rm COO})$	27, 36
1392	formate	$\delta(CH)$	27, 36
1376	formate	$\nu_{\rm s}({\rm COO})$	27, 36
1306	nitrate		37
1294	unidentate nitrate	$v_{as}(ONO)$	36
1240	bidentate nitrate (NO ₃ ⁻)	$v_{\rm as}(\rm ONO)$	36

in a flow of NO $+O_2$ (Figure 1, spectrum d) has been assigned by Chi et al.⁴⁵ to NO₂ stretching in bidendate nitrate.

In flowing $C_3H_8 + O_2 + NO$, four strong bands at 1580, 1552, 1294, and 1240 cm⁻¹ have been observed in addition to the bands observed in flowing $C_3H_8 + NO$ and $C_3H_8 + O_2$. Couples of bands in the regions of 1650–1500 and 1170–1300 cm⁻¹ are assigned to the v_3 split stretching vibration of nitrates on metal oxides in the literature.^{28,46} Thus, the bands at 1552 and 1294 cm⁻¹ and 1580 and 1240 cm⁻¹ have been assigned to v(N=O) and $v_{as}(ONO)$ of unidentate and bidentate nitrates, respectively.

Two negative bands at 3768 and 3686 cm⁻¹ (O-H stretching region of the spectra) are observed in flowing $C_3H_8 + O_2$ and $C_{3}H_{8}$ + NO as well as $C_{3}H_{8}$ + O_{2} + NO. In flowing NO + O₂, these negative bands have been found to be slightly shifted to 3755 and 3686 cm⁻¹. Signals of OH groups of the oxide surface should not be observed in the IR spectra because of background subtraction. These OH groups are consumed by interaction with acetate and/or nitrates or by formation of acetate and/or nitrates. Thus they appear as negative bands in the spectra. The OH band around 3780-3760 cm⁻¹ has been identified as being coordinated to a terminal Al-OH group, which is generally ascribed to a basic hydroxyl group.^{46,47} Pushkar et al.46 assigned the band between 3688 and 3680 cm⁻¹ to a Ga-OH-Al bridging structure on Ga₂O₃/Al₂O₃ catalysts. Shimizu et al.²⁰ suggested that Ga-O-Al bonds observed for low gallium loadings on Ga₂O₃/Al₂O₃ catalysts exhibit high activity for SCR of NO by C_3H_6 . According to this, it can be expected that the OH groups of terminal basic Al-OH and of bridged Ga-OH-Al are reactive and removed or exchanged upon the formation of acetate and nitrates as has been observed in this work. The main observed IR bands of the adsorbed species on Ga₂O₃/Al₂O₃ in various gas atmospheres and their assignments are listed in Table 3.

3. Dynamic Changes of Surface Species under Reaction Conditions ($C_3H_8 + NO + O_2$). The results of catalytic activity measurements suggested that NO reduction to N₂ over Ga₂O₃/ Al₂O₃ was effectively catalyzed at temperatures above 623 K (Table 2). To clarify the behavior of surface species formed during the SCR reaction, the time-dependent quantitative changes of surface species formed in flowing NO + C_3H_8 + O₂ were measured at 623 K. As shown in Figure 2, the formation of formate (2908, 1392, and 1378 cm⁻¹), acetate (1465 cm⁻¹), and nitrite or nitrate (1580, 1552, and 1238 cm⁻¹) species is



Figure 2. FTIR spectra of adsorbed species in flowing NO + $C_3H_8 + O_2$ on the Ga_2O_3/Al_2O_3 catalyst surface at 623 K as a function of time: (a) 0.5, (b) 2.5, (c) 5, (d) 15, (e) 30, (f) 60, (g) 90, (h) 120, and (i) 180 min.



Figure 3. Time dependence of integrated area of the band characteristic of acetate $(1480-1420 \text{ cm}^{-1})$ under different gas atmospheres on Ga₂O₃/Al₂O₃ at 623 K: (**I**) C₃H₈ + O₂, (**O**) C₃H₈ + NO, and (**A**) C₃H₈ + O₂ + NO.

observed immediately after the gas mixture introduction, while weak bands due to nitrogen-containing organic species (-CN and -NCO) are only observed after an induction period of ca. 5 min. Obviously they are formed by the reaction between adsorbed carboxylates and NO or by species generated from NO. The IR intensity of the formate bands increases at the beginning and became constant after ca. 5 min; however, the IR intensity of acetate increases upon time on stream until 80 min. This could result from the differences in the reactivity between acetate and formate toward the other gases O₂ or NO.

Acetate is also formed in $C_3H_8 + O_2$ and $C_3H_8 + NO$ as shown in Figure 1. Figure 3 includes the change in intensity of the IR band assigned to adsorbed acetate (1480–1420 cm⁻¹) in a flow of $C_3H_8 + O_2$, $C_3H_8 + NO$, and $C_3H_8 + NO + O_2$, respectively, at 623 K. This figure illustrates that the corresponding reaction rates and the concentration of adsorbed surface acetate follows the sequence of $C_3H_8 + O_2 > C_3H_8 +$ $NO > C_3H_8 + NO + O_2$. C_3H_8 itself can hardly be adsorbed on the catalyst surface at 623 K.48 Propane should be activated by adsorbed O₂ or adsorbed species generated from NO (e.g., NO_x^{-}).⁴⁸ According to proposals from the literature, the decrease in the concentration of adsorbed acetate in an order of C_3H_8 + $O_2 > C_3H_8 + NO > C_3H_8 + NO + O_2$ is explained by the difference in the oxidizing potential of the oxidizing agents and the inhibition of propane oxidation by NO.49,50 The difference in reactivity of surface acetate to NO or O₂ also explains the relations of the surface concentrations. The initial rate of acetate formation in flowing $C_3H_8 + NO + O_2$ is higher than in flowing C_3H_8 + NO (Figure 3). After 40 min, the acetate concentration in flowing $C_3H_8 + NO + O_2$ becomes lower than the one in a flow of C_3H_8 + NO. In a flow of C_3H_8 + NO + O_2 , propane is mainly oxidized by O₂, and the acetate formed is further oxidized by NO (or other nitrites/nitrates generated from $NO + O_2$). The intensity of the IR bands characteristic of surface acetate increased very quickly at the beginning, and an equilibrium between formation and consumption of surface acetate is achieved after ca. 80 min.

4. Studies on Single Steps of the Reaction Cycle: Formation and Consumption of Surface Acetate. The IR spectra of adsorbed carbonaceous species over Ga_2O_3/Al_2O_3 in flowing $C_3H_8 + O_2$ at different temperatures are shown in Figure 4. There are only quantitative differences in the IR spectra of adsorbed species on Ga_2O_3/Al_2O_3 and Al_2O_3 (not shown). The main adsorbed species in flowing $C_3H_8 + O_2$ over both catalysts are acetate (1558, 1468 cm⁻¹) and formate (1392, 1376 cm⁻¹). The bands due to acetate and formate are observed over Ga_2O_3/Al_2O_3 starting at 523 K. Over Al_2O_3 , these bands can be observed only at 573 K and higher temperatures. Furthermore, the rate of formation of surface acetate over Ga_2O_3/Al_2O_3 is higher than the one over Al_2O_3 catalysts at the same temperature (Figure 5). These results indicate that the impregnation of Ga_2O_3 onto Al_2O_3 reduces the reaction temperature and improves the



Figure 4. IR spectra of adsorbed species on Ga_2O_3/Al_2O_3 in flowing $C_3H_8 + O_2$ at (a) 523 K, (b) 573 K, (c) 623 K, and (d) 648 K for 120 min.



Figure 5. Time dependence of the integrated area of the band due to acetate $(1480-1420 \text{ cm}^{-1})$ in flowing $C_3H_8 + O_2$ on Ga_2O_3/Al_2O_3 (solid) and Al_2O_3 (blank) at different temperatures: (\blacksquare, \Box) 523 K, (\bullet, \bigcirc) 573 K, (\bullet, \triangle) 623 K, and $(\bullet, \bigtriangledown)$ 648 K;

activity for the partial oxidation of propane. This correlates well with the increased catalytic activity in SCR of the Ga_2O_3/Al_2O_3 system at lower temperatures (Table 2).

The reactivity of adsorbed acetate over Ga₂O₃/Al₂O₃ toward different oxidizing agents was evaluated by time-dependent changes of the IR spectra at different temperatures. In these experiments, the catalyst was first exposed to a flow of $C_3H_8 + O_2$ for 120 min (Figure 6, spectrum a), followed by purging in flowing He for 30 min. Then the gas flow was switched to He, O₂, NO, and NO + O₂, respectively. Figure 6 also shows the IR spectra recorded at 623 K for 90 min after change of the gas composition. Adsorbed acetate (1564, 1456 cm⁻¹) and formate (1392, 1376 cm⁻¹) are the dominating species



Figure 6. IR spectra of adsorbed species on Ga_2O_3/Al_2O_3 at 623 K taken (a) after soaking into a flow of $C_3H_8 + O_2$ for 120 min, followed by He purge for 30 min and then changing the gas to (b) He for 80 min, (c) O_2 for 90 min, (d) NO for 90 min, and (e) NO + O_2 for 90 min, respectively.

observed in flowing $C_3H_8 + O_2$ (spectrum a). After purging in flowing He for (80 min, spectrum b) and then in O_2 for 90 min (spectrum c), no significant changes have been observed in the IR spectra. However, the intensity of the IR bands characteristic of adsorbed acetate and formate decreased significantly when the feed gas was switched to NO or NO + O_2 during 90 min. Between 2000 and 1000 cm⁻¹, the bands due to acetate (1564, 1458 cm⁻¹) disappeared completely, and bands at 1552, 1294 cm⁻¹ and 1580, 1240 cm⁻¹ assigned to ν (N=O) and ν_{as} (ONO) of unidentate and bidentate nitrates, respectively, have been observed. In the OH vibration region, negative bands were shifted from 3768 and 3686 cm⁻¹ to 3755 and 3686 cm⁻¹. The surface acetate was consumed by NO or NO + O_2 .

The time dependence of the intensity of the acetate band $(1480-1420 \text{ cm}^{-1}; \text{ normalized by initial intensity})$ in the various gas flows at different temperatures is shown in Figure 7. In a flow of He as well as O₂, a small decrease in the intensity of the acetate band has been observed. This small decrease can be interpreted by desorption of the adsorbed species (in both gases) and by slow oxidation of the adsorbed species by oxygen (in O₂). However, the intensity of IR bands due to acetate significantly decreased when the feed gas was switched to NO or NO + O₂. This can be due to (i) the reaction of acetate with NO and NO/O₂ or (ii) site competition with other species (e.g., NO_x^{-}). All experimental observations of this paper and results from the literature (e.g., of Shimizu et al.^{28,44}) support that the chemical reaction of surface oxygenates with NO (point i) is the reason for this decrease. The temperatures at which the reaction (acetate consumption) takes place correlates exactly with the catalysis results and the formation of N₂. The reaction rates as a function of temperature reflect the expectations for the reaction and not for adsorption-desorption equilibria. The small differences in the reaction rate of acetate consumption in NO and NO + O_2 , respectively, suggest that O_2 does not significantly promote the reaction between adsorbed acetate and NO. The consumption of the surface oxygenates in O₂ increased significantly with increasing temperature. At lower temperatures,



Figure 7. Time dependence of the relative intensities of the acetate band in the range $1420-1480 \text{ cm}^{-1}$ normalized by initial intensity in (**I**) He, (**O**) O_2 , (**A**) NO, and (**V**) NO + O_2 . Before the measurements, the catalyst was pretreated in $C_3H_8 + O_2$ /He for 120 min and purged by He at 623 K for 30 min: (A) 573 K; (B) 623 K; (C) 648 K.



Figure 8. IR spectra of adsorbed species on Ga₂O₃/Al₂O₃ at T = 573 K taken (a) after soaking into a flow of NO +O₂ for 120 min followed by He purge for 30 min and then change the gas to (b) He for 80 min, (c) C₃H₈ for 90 min, and (d) C₃H₈ + O₂ for 90 min, respectively.

NO is the predominant reaction partner of surface acetate (even in extreme excess of oxygen). For higher temperatures, the reaction with oxygen is enhanced. This leads to a decrease in efficiency of the reducing agent propane (competitiveness factor) and is reflected by a (slight) volcano shape (shown in Table 2). It should be mentioned that the temperatures consciously chosen for the IR experiments correspond well to the temperatures where Ga₂O₃/Al₂O₃ is active and shows measurable high NO conversions to N₂. They are below the optimum temperature with highest activity (total conversion, T = 723 K).

5. Studies on Single Steps of the Reaction Cycle: Reactivity of Surface Nitrates. The reactivity of adsorbed NO_x^- species toward propane was evaluated by transient response of the IR spectra at 573 K. First, the catalyst was exposed to a flow of $NO + O_2$ for 120 min (Figure 8, spectrum a) and then purged in flowing He for 30 min. Finally, the gas flow was switched



Figure 9. Time dependence of the nitrate concentration (left) and relative intensities of nitrate bands in the region $1330-1180 \text{ cm}^{-1}$ normalized by the intensity of 150 min in different gas flows: (\Box), NO + O₂ in helium; (\bullet) He; (\blacktriangle) C₃H₈/He; (\blacksquare) C₃H₈ + O₂/He. Temperature = 573 K.

to C_3H_8 and $C_3H_8 + O_2$, respectively, for 90 min. Figure 8 also shows the IR spectra recorded at 573 K after changing the feed gas for 90 min. Four bands centered on 1578 and 1240 cm⁻¹ as well as 1554 and 1294 cm⁻¹ assigned to surface bidentate and monodentate nitrate species were observed in flowing NO + O₂. After purging in flowing He for 80 min (spectrum b) and/or in flowing C_3H_8 for 90 min, only small quantitative changes of the IR bands are observed. That means adsorbed nitrates do not react with C_3H_8 over Ga_2O_3/Al_2O_3 at 573 K. However, after purging in flowing He and then in flowing $C_3H_8 + O_2$ for 90 min, a new band characteristic of acetate (1458 cm⁻¹) is observed. Simultaneously, the intensity of the IR bands characteristic of surface nitrates decreased.

Figure 9 shows the changes in the integrated intensity of the nitrite/nitrate bands in the range of $1330-1180 \text{ cm}^{-1}$ (normalized by initial intensity) as a function of time after the feed gas

was switched from NO + O_2 to He, C_3H_8 , or $C_3H_8 + O_2$ at 573 K. The intensity of the IR bands characteristic of surface nitrates decreased only slightly in flowing He, C₃H₈, or $C_3H_8 + O_2$. This indicates that nitrates are stable in C_3H_8 and $C_3H_8 + O_2$. In flowing He, the small decrease in the concentration of nitrates can be interpreted by desorption of adsorbed species. In flowing C_3H_8 , there is no significant difference in the consumption rate of surface nitrate compared to flowing He. This illustrates that the adsorbed NO_x^{-} species are not reactive to C₃H₈ at 573 K. Interestingly, an increase of the intensity of the IR bands due to nitrates (1330-1180 cm⁻¹) at the beginning is observed when the feed gas was switched to $C_3H_8 + O_2$. This might be due to the formation of acetate species by C₃H₈-O₂ reaction, because weak IR bands due to acetate species appear in the regions of 1200-1235 cm⁻¹ and 1290-1340 cm⁻¹.^{27,28} After 10 min, the intensity of the IR bands due to adsorbed NO_x⁻ species (1330-1180 cm⁻¹) decreased with time. Although the consumption rate of surface nitrates is also slow, it is faster than in flowing He and in flowing C₃H₈. This indicates that the surface acetate formed under these conditions $(C_3H_8 + O_2)$ acts as the active intermediate in the consumption of adsorbed NO_x^{-} species.

Discussion

1. Particular Catalytic Properties of the Optimized System Ga₂O₃/Al₂O₃. The optimized catalyst Ga₂O₃/Al₂O₃ investigated in the present work shows high activity and selectivity to N₂ for the selective catalytic reduction of nitric oxide by propane. It converts NO completely at temperatures of 723K and above (GHSV = 10 000 h⁻¹, Table 2) selectively to nitrogen (99% N₂, 1% N₂O).

The particular performance of this catalyst is, however, the high and reproducible efficiency of the reducing agent (propane), which is in general not regarded and achieved for other oxidic catalyst systems before. Yan et al.³⁹ described this efficiency by a so-called "NO competitiveness factor" (Table 2, superscript c), which is near 40% (43.0% for 673 K and 41.5% for 723 K) in the present work.

As shown in Table 2, one molecule of propane converts rather exactly four NO molecules exclusively to N2 (feed gas composition: NO:C₃H₈ = 1000:1000 ppm). The same relation and selectivity are observed for lower temperatures and lower conversions (T = 573, 623, and 673 K), i.e., at the temperatures, at which the in situ IR studies were performed (Table 2). This relation is clearly more efficient than for most other SCR catalysts reported in the literature like silver-alumina or cobaltalumina systems.^{11,39} It is this that makes the catalyst Ga₂O₃/ Al₂O₃ particularly interesting for mechanistic investigations also because of several additional reasons: (i) several reaction mechanisms proposed in the literature can be surely excluded for Ga₂O₃/Al₂O₃ due to the overall electron balance (see below); (ii) it is generally assumed that such oxide systems neither directly decompose NO nor oxidize NO to NO2;²⁶ (iii) furthermore, neither Ga₂O₃ nor Al₂O₃ are known to be redox active materials, i.e., partially reduced catalyst intermediates can also be excluded. In the following, the electron balance of the reaction system will be regarded in detail.

2. Electron Balance and Stoichiometric Calculations for Possible Reaction Pathways. There are two oxidizing agents (NO and O_2) and one reducing agent (C_3H_8) in the SCR feed (reaction eq 1), and two main competing reactions (eqs 2 and 3) must be taken into account for the overall SCR process.⁵¹

$$C_3H_8 + xNO + (10 - x)/2O_2 \rightarrow 3CO_2 + x/2N_2 + 4H_2O$$
(1)

$$C_{3}H_{8} + 10NO \rightarrow 5N_{2} + 3CO_{2} + 4H_{2}O$$
 (2)

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \tag{3}$$

For the reduction of one molecule of NO, two electrons must be delivered by propane (formal reduction from +2 for N in NO to 0 in N₂). On the other hand, one molecule C₃H₈ provides 20 electrons when it is oxidized to CO₂ and H₂O. One molecule of propane can thus formally reduce 10 NO molecules to N₂ (eq 2).

As experimentally observed (Table 2), one molecule of propane converts four NO exclusively to N₂, i.e., the overall reaction at temperatures of $T \le 673$ K can be formally described by eq 4

$$C_{3}H_{8} + 4NO + 3O_{2} \rightarrow 3CO_{2} + 2N_{2} + 4H_{2}O$$
 (4)

That means 12 electrons must be accepted by O_2 and that O_2 has been involved in the hydrocarbon SCR reaction. (More exactly, the incomplete conversion of C_3H_8 to carbon dioxide must be taken into account: 45% CO₂, 55% CO. In concern of the carbon balance, approximately 50% of the carbon compounds are not completely oxidized, i.e., in fact only 11 electrons are accepted by oxygen, or 4 NO molecules are reduced by even less than 1 C_3H_8 .)

This is still in agreement with reaction mechanisms proposed in the literature for different catalyst/reducing agent systems, according to which (i) NO initially activated (oxidized) by O_2 reacts with the hydrocarbon,^{27,28} (ii) the hydrocarbon is first partially oxidized and then reacted with NO,^{35–38} or (iii) both NO and hydrocarbon are preoxidized by O_2 and then the generated species react to each other.³⁴ If we assume however that propane is preoxidized to surface acetate (what is generally accepted by the majority of literature reports^{35–38} and also demonstrated in this work) then the reaction partner cannot be an adsorbed nitrate (* $-NO_3^-$). This reaction path (a variation of iii) can be excluded by the electron balance considerations for Ga₂O₃/Al₂O₃. In this case, only two NO molcules could be reduced by one molecule of propane in contrast to the experimental finding of NO:C₃H₈ conversion = 4:1.

Even the preoxidation of NO to NO_2 becomes less probable due to the following calculations: By assumption that propane is oxidized first to surface acetate, the following reaction fits the mechanism best

"*-CH₃COOH" + 4NO →
$$2N_2 + 2CO_2 + 2H_2O$$
 (5)

This equation reflects the highest possible efficiency for NO conversion by surface acetate and fits very well the proposed reaction mechanism presented below for the Ga_2O_3/Al_2O_3 system, i.e., NO oxidation is neither expected on Ga_2O_3/Al_2O_3 or on Al_2O_3 nor it is in agreement with the electron balance and reaction mechanism. Although these considerations do not give any information on the detailed reaction mechanism as, e.g., the role of nitrogen containing organic species or possible NO decomposition, it allows valuable conclusions to exclude some reaction pathways (the pathway iii where both reactants are first oxidized) for the Ga_2O_3/Al_2O_3 system.

3. Formation and Consumption of Surface Species. Adsorbed nitrates, oxygenates (partially oxidized hydrocarbons, mainly acetate and formate), and nitrogen-containing organic species (-CN and -NCO) have been observed on the surface of Ga₂O₃/Al₂O₃ exposed to SCR atmosphere at reaction tem-

peratures (Figures 1 and 2). The same surface species have also been reported by Sibata et al.³⁶ during SCR of NO by propane over Ag/Al₂O₃ catalysts and by Haneda et al.²⁷ during SCR of NO by propene over Ga_2O_3/Al_2O_3 . In the present work, the formation and consumption of these adsorbed species on Ga2O3/ Al₂O₃ in different gas atmospheres were investigated in order to elucidate their role in the SCR reaction. As shown in Figures 1 and 3, hydrocarbon-derived surface oxygenates (acetate, formate) can be formed in flowing $C_3H_8 + O_2$, $C_3H_8 + NO$, as well as $C_3H_8 + O_2 + NO$ at 623 K. The concentration of adsorbed surface acetate decreases in the order $C_3H_8 + O_2 >$ $C_3H_8 + NO > C_3H_8 + NO + O_2$, suggesting that only O_2 but not NO is a useful oxidizing agent for the partial oxidation of propane over Ga_2O_3/Al_2O_3 . The partial oxidation of propane is even inhibited by NO. These results are in good logical agreement with De Soete et al.49 by studies on combustion of coal char in gas atmospheres with and/or without NO and with Chambers et al.,⁵² who reported that the introduction of NO into a flow of $C_3H_8 + O_2$ caused an inhibition of propane oxidation over Pt/SiO₂ catalysts. This is explained by NO₂ formation and decomposition cycles on the catalyst surface.

In flowing $C_3H_8 + O_2$, the formation of surface acetate starts from 523 K and its concentration increases with increasing temperature until 673 K (Figure 3). The impregnation of Ga₂O₃ onto Al₂O₃ leads to an enhancement of the partial oxidation of propane. Explanations are given by Haneda et al.²⁷ according to their catalysis testing and catalyst characterization results. It is this partial oxidation of propane to acetate (formate) that represents the rate-determining step of the SCR reaction. There is a perfect correlation between this partial oxidation reaction and the activity of the Ga₂O₃/Al₂O₃ catalyst in the SCR reaction. The formation of surface nitrite/nitrate species cannot be the rate-determining step, because the rate of nitrite/nitrate formation and its surface concentration decreases with increasing temperature, whereas the NO conversion increases with increasing temperature when the reaction temperature is lower than 723 K.

Differences in reactivity of surface acetate with O₂, NO, or $NO + O_2$ are also reflected by the time dependence of the intensity of acetate IR bands in corresponding atmospheres. As shown in Figures 6 and 7, surface acetate species are stable in flowing O_2 but reactive in flowing NO or NO + O_2 . The presence of NO (and/or N-derived species) decreases the surface acetate concentration. The small differences in the rate of consumption of surface acetate in flowing NO and NO + O_2 (Figure 7) indicate that O_2 does not enhance the reaction between acetate and NO. This is an additional indication that the participation of nitrite/nitrate species in the SCR reaction mechanism over Ga2O3/Al2O3 can be neglected. The rate of acetate consumption depends on the reaction temperature. The increase in reaction rate with temperature and the absolute temperature values correlate very well with the catalytic results (NO conversion, Table 2).

Surface nitrite and/or nitrate species are observed in flowing NO, NO + O₂, as well as NO + O₂ + C₃H₈ (Figures 2 and 8). The intensity of the IR bands due to surface nitrites/nitrates decreases only slightly in flowing He and C₃H₈ at 573 K. Haneda et al.²⁷ and Shimizu et al.²⁸ suggested for C₃H₆ that this alkene can be oxidized by O₂ as well as surface nitrates. C₃H₈, however, does not react with surface nitrates on Ga₂O₃/Al₂O₃ as found in this study (as shown in Figure 8). This can be explained by the difference in the reactivity of C₃H₈ and C₃H₆. The decrease of intensity of nitrite/nitrate bands in flowing C₃H₈ + O₂ is faster than in flowing C₃H₈ suggesting that nitrates

SCHEME 1: Proposed Reaction Pathways of NO Reduction by Propane over Ga₂O₃/Al₂O₃^{*a*}



^a Pathways 1 and 4 are the main reaction pathways.

can react with hydrocarbon derivates (acetate, formate) generated from $C_3H_8 + O_2$ only. However, according to the discussion above the surface nitrite/nitrate species cannot be involved in the intrinsic SCR mechanism and we attribute them to spectators for the catalytic system under study. As discussed above, the formation of surface nitrites/nitrates cannot be the rate-determining step of the SCR reaction over Ga₂O₃/Al₂O₃. Even more, the role of oxidized NO_x surface species in the reaction mechanism is called into question at all by experimental results and electron balance considerations presented in this work.

Nitrogen-containing organic species (-CN and -NCO) are only detected in a flow of $C_3H_8 + NO + O_2$ after an induction period of about 5 min (Figure 2). Probably they are formed by the reaction between adsorbed carboxylates and NO or NO derived species only.

4. Reaction Mechanism of SCR of NO by C₃H₈ over Ga₂O₃/Al₂O₃. As discussed above and illustrated in Scheme 1, the C₃H₈-SCR of NO over Ga₂O₃/Al₂O₃ starts with the partial oxidation of C₃H₈ by O₂ to surface carboxylates such as acetate and formate (step 1). This represents the rate-determining step of the whole reaction cycle. The surface oxygenates (mainly acetate, formate) are highly reactive to (adsorbed) NO (or NOderived species) forming nitrogen-containing organic surface species (isocyanides, cyanides, step 4). The coupling of nitrogen atoms to form N₂ most probably occurs via the comproportionation reaction between NO (gas or adsorbed) and reduced nitrogen containing species (e.g., -CN, -NCO, step 5). This mechanism is in very good agreement with the catalytic results (N₂ selectivity, C₃H₈ conversion/competitiveness factor) as a function of temperature and the presence, concentration, and rate of formation and consumption of all relevant surface species observed by IR spectroscopy.

The possible oxidation of propane by NO or NO_x (oxidized NO_x species, step 2) is much slower than the main reaction (step 1 in Scheme 1; Figure 3). Nitrite and/or nitrate species, which are observed on the Ga₂O₃/Al₂O₃ surface, are found to be spectators only. Their participation in the main reaction cycle (steps 1, 4, and 5) can be excluded from considerations of the electron balance and the reaction rates. At higher temperatures surface carboxylates can be oxidized totally by oxygen (step 3 in Scheme 1; Figure 7). This side reaction is the reason for the decrease of the NO competiveness factor in the reaction at temperatures above 773 K and probably for the clearly less efficient NO reduction over other HC–SCR catalysts such as Ag/Al₂O₃ and Co/Al₂O₃ in comparison to Ga₂O₃/Al₂O₃.^{11,39}

Conclusions

The formation and consumption of surface species and the role of the adsorbed oxygenates and nitrates during SCR of NO by propane on Ga_2O_3/Al_2O_3 were investigated by in situ IR spectroscopy. The reaction starts with the formation of surface carboxylates (acetate, formate) by the reaction of $C_3H_8 + O_2$.

Carboxylates become the predominant surface species in the steady state and act as an important intermediate during the NO reduction. This propane oxidation is the rate-determining step of the whole SCR reaction. The surface carboxylates react easily with (adsorbed) NO. Nitrogen-containing organic species are believed to be intermediates in the final formation of N₂. The stoichiometry of the SCR reaction, in particular the comparison of NO and hydrocarbon conversion, allow interesting conclusions concerning the reaction mechanism. Surface nitrites/ nitrates are found to be only spectators in the system under study (propane, Ga_2O_3/Al_2O_3).

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