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In situ FTIR study on NO reduction by C_3H_6 over Pd-based catalysts

M. Huuhtanen [a,*], T. Kolli [a], T. Maunula [b], R.L. Keiski [a]

[a] *Department of Process and Environmental Engineering, University of Oulu, P.O. Box 4300, FIN-90014, Oulu, Finland*
[b] *Kemira Metalkat Oy, Catalyst Research, P.O. Box 171, FIN-90101, Oulu, Finland*

Abstract

The reaction mechanism of the reduction of NO by propene over Pd-based catalysts was studied by FTIR spectroscopy. It was observed that the reaction between NO and propene most probably goes via isocyanate (2256–2230 cm^{-1}), nitrate (1310–1250 cm^{-1}) and acetate (1560 and 1460 cm^{-1}) intermediates formation. Other possible intermediates such as partially oxidized hydrocarbons, NO_2, and formates were also detected. The reaction between nitrates and acetates or carbonates reduced nitrates to N_2 and oxidized carbon compounds to CO_2. In situ DRIFT provides quick and rather easily elucidated data from adsorbed compounds and reaction intermediates on the catalyst surface. The activity experiments were carried out to find out the possible reaction mechanism and furthermore the kinetic equation for NO reduction by propene. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NO reduction; Propene; Palladium; FTIR spectroscopy; Reaction mechanism

1. Introduction

Selective catalytic reduction (SCR) of NO_x by hydrocarbons is a very important field of environmental catalysis research. The use of catalysts, including noble metals (e.g., Pt, Pd, Rh), reduces considerably environmental problems caused by unburned and partially oxidized hydrocarbons, carbon monoxide, and nitrogen oxides in exhaust gas purification. The harmful emissions are converted to less hazardous compounds like N_2, CO_2 and H_2O with the help of a catalyst. NO_x reduction reactions on the catalyst surface are very complex. Research groups in industry and at universities have paid a lot of interest to investigate the possible reaction mechanisms. Many research groups have used FTIR spectroscopy to investigate the reaction intermediates in NO reduction by hydrocarbons, like CH_4 and C_3H_6 [1–6], CO [7,8], and H_2 [9] over different catalysts. In these studies NO reduction by hydrocarbons is observed to go via isocyanate species formation. This reaction path is seen to be well recognized but there are still some uncertainties about the importance of isocyanate species in the reactions [10].

According to published research results oxygenated organic intermediates like alcohols, aldehydes and carboxylates have a role in NO reduction [11]. NO is observed to be adsorbed molecularly but only a fraction of NO dissociates at low temperatures. The formation of N_2O is due to the reaction between adsorbed NO and N atom [11,12]. Moreover, palladium has been found out to be a relatively inefficient metal for dissociative chemisorption of NO [13].

In this study, the reaction intermediates during NO_x reduction by propene on Pd/Al_2O_3-based catalysts

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* Corresponding author.
E-mail address: mika.huuhtanen@oulu.fi (M. Huuhtanen).

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were investigated in lean and rich conditions by in situ DRIFT spectroscopy. FTIR spectroscopy was also used to detect the gaseous reaction products in activity experiments [10]. The proposed reaction mechanism was derived by analysis of the surface intermediates and gaseous products formed in reactions. The mechanism will be used to build the kinetic equations, the parameters of which are determined by laboratory experiments.

2. Experimental

The studied porous catalyst material was mounted on a thin (50 μm) flat metal foil. The catalysts represented real commercial catalysts by the coating method. Palladium content was 1 and 3% on the Al_2O_3 support. In addition, the support contained Ce, La, and Zr oxides.

2.1. DRIFT experiments

The spectra were measured on a Perkin Elmer 1760× FTIR with a heated reaction chamber (Environmental Chamber, Specac 19930) at a resolution of 4 cm^{-1} accumulating 20 scans. The pre-treatment of the catalyst (1 or 3% Pd on Al_2O_3 on Ø 8 mm flat foil) was started by heating the catalyst from room temperature to 400 °C in vacuum ($\sim 10^{-3}$ mbar) for 25 min after which the reaction chamber was evacuated for 15 min at 400 °C. This procedure is done to ensure that the surface is clean enough and the adsorbed species have desorbed. The catalyst was oxidized for 20 min at 400 °C and cooled to room temperature under a small oxygen flow to prevent self-reduction. Finally, the catalyst was evacuated at 25 °C for 20 min to clean the chamber from oxygen species.

The reaction gas mixture was inserted to the reaction chamber at 25 °C and the experiment was started. The NO gas flow rate was kept constant (10 $cm^3\,min^{-1}$) during the experiments. The inlet gas contained NO from 5.7 to 8.2% depending on the conditions (lean, stoichiometric, rich) Experiments were done in rich, stoichiometric and lean conditions at 25, 220, and 260 °C. Because the IR beam goes through the laboratory air the measurement does not indicate the CO_2 formation in the cell.

2.2. Activity experiments

The reaction gases mixed from 10% NO/N_2, 0.5% C_3H_6/N_2, and 0.5% O_2/N_2 were used in the activity studies. The monolith catalyst (500 cpi) pre-treatment started by heating the catalyst to 500 °C in nitrogen flow and after that the catalyst was oxidized at 500 °C for 20 min. After cooling the reactor to room temperature under oxidizing conditions the reaction chamber was purged with N_2. The reaction gases were inserted to the reactor at 25 °C and the reactor was heated to 500 °C at the rate of 10 °C/min. The total flow rate of the reaction mixture (NO 5000 ppm, C_3H_6 and O_2 variable, N_2 as carrier gas) was 1000 $cm^3\,min^{-1}$. The FTIR spectra were recorded for the following components: NO, NO_2, N_2O, NH_3, CH_4, C_3H_6, CO, CO_2, and H_2O. The analysis of the gas phase was carried out by a GASMET^{TM} FTIR Gas Analyzer.

3. Results and discussion

3.1. DRIFT experiments

Simultaneous adsorption of NO + C_3H_6(+O_2), and NO + O_2 on 1% Pd-catalyst at 260 °C is presented in Fig. 1. Formation of isocyanates can be seen at 2253–2233 cm^{-1} when the gas mixture contains propene [2,10]. The amount of isocyanates formation is small in stoichiometric conditions compared to rich conditions.

The adsorption bands from partially oxidized hydrocarbons like formates (1393 and 1379 cm^{-1}) and acetates (1567 and 1463 cm^{-1}) are also detected [3,4,14]. These surface intermediates are most probably attached to aluminum [3,4,14]. In rich conditions strong adsorption bands caused by formates are seen on the surface. The intensity of the band decreases while the mixture is switched to lean conditions. More formate species were formed in the reaction between NO and propene in the absence than in the presence of oxygen (Fig. 1).

In the beginning of the experiment a lot of nitrates and nitrites were detected in the region from 1300 to 1250 cm^{-1}. These bands disappeared in the rich condition at 260 °C, but these bands can still be observed in lean and stoichiometric conditions. It seems quite evident that NO and oxygen react to nitrate species

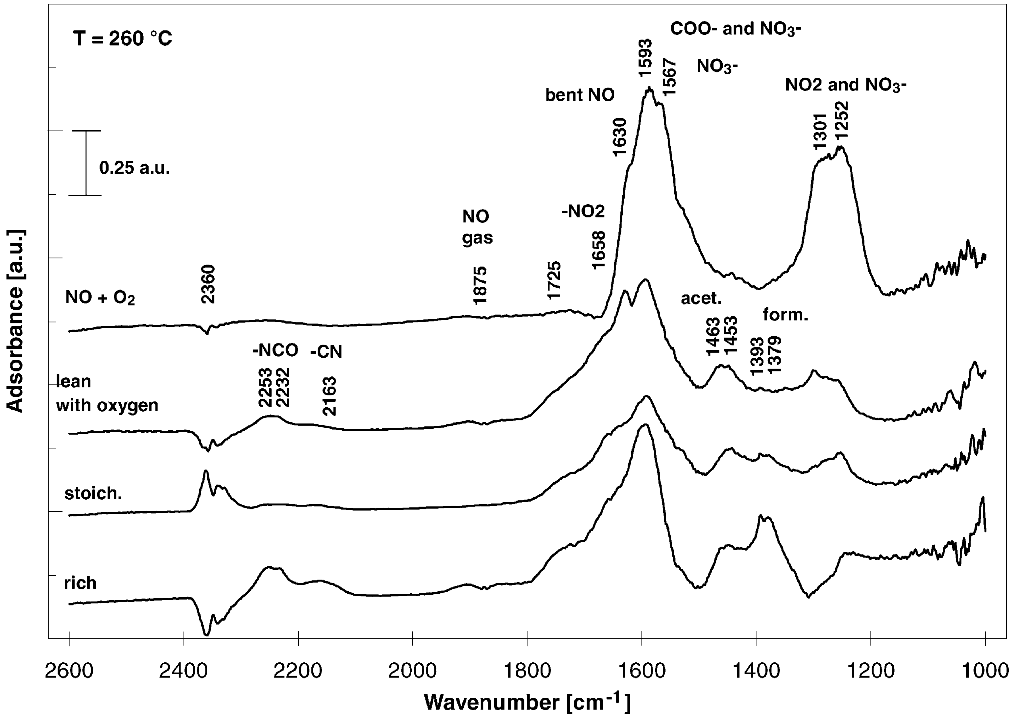

Fig. 1. FTIR spectra of NO–C_3H_6 reaction on 1% Pd/Al_2O_3 catalysts at 260 °C in rich, stoichiometric, and lean (+O_2) conditions. Also NO + O_2 spectra is shown.

at the surface when the amount of reductant is very small or it is absent.

NO on palladium probably causes the band at around 1630 cm^{-1} when the reaction gas contains propene as a reductant [15]. In NO + O_2 reaction gas mixture, the bent NO band is also present. The band at 1658 cm^{-1} can be assigned to an organic nitrite compound (R–ONO) [5,16]. According to the literature linear NO adsorption, Pd–N=O (ca. 1750 cm^{-1}), on Pd for the oxidized catalyst is not evident [15]. Our experimental results are in agreement with the literature. In reducing conditions (NO + C_3H_6) probably adsorbed COO^- causes a band observed at 1600 cm^{-1}. The analysis of observed surface intermediates is presented in Table 1.

The acetates and formates detected on catalyst surface give an evidence for the reaction mechanism that goes via the reaction between partially oxidized hydrocarbons and NO [11,16]. Also the formation of isocyanate as a reaction intermediate is observed in our

Table 1
Adsorption of NO + C_3H_6 and NO + O_2 over the Pd-catalysts (1 or 3%) at 260 °C (M=Al or La)[a]

	$Pd-N{=}O^-$	M–NO_3^-	M–CO_3^{2-}	Al–NCO	M–$HCOO^-$	M–CH_3COO^-
Rich	–	1593, 1252	1452	2253–2233	1393s, 1379s	1567, 1463
Stoichiometric	–	1593, 1252	1453	2253–2233	1393, 1379	1567, 1463
Lean	1630	1593, 1301, 1252	1453	2253–2233	1393w, 1379w	1567, 1463
NO + O_2	1630sh	1593, 1567, 1297, 1285, 1252	–	–	–	–

[a] w: weak, sh: shoulder, s: strong. λ = [oxidant]/[reductant].

studies. The other possible reaction route goes via formation of isocyanate and cyanide species by the reaction with NO to N_2 [11].

3.2. Activity experiments

The conversion of NO was near to 100% in rich and stoichiometric conditions, and in lean conditions (oxygen present or absent) conversions up to 80% were obtained in the light-off experiments. The high NO_x conversion in lean conditions can be explained by the conditions, when there is only NO as an oxidant. Therefore C_3H_6 reacts totally with NO in the absence of oxygen. In the real exhaust gases the O_2/NO ratio is, however, much more than 1.

The formation of different kind of harmful byproducts like ammonia (NH_3), carbon monoxide (CO), and nitrous oxide (N_2O) are not desired products and therefore the amount of these compounds after the catalyst should be as low as possible. According to our experiments (Fig. 2) it is possible that those components are formed but the amount of CO and NH_3 are rather small (65–120 ppm CO, 30–60 ppm NH_3) except in rich conditions (1100 ppm CO, 1700 ppm NH_3). The formation of NH_3 and CO started at 200 °C and the maxima was observed at the light-off temperature (∼250 °C). These byproducts are due to incomplete oxidation of hydrocarbons. NH_3 is formed in reactions between hydrocarbons with nitrogen oxides. It is also possible that on γ-Al_2O_3 surface intermediates like Al–NCO and H–NCO are converted to NH_3 and CO_2 [10,17].

The formation of N_2O began at 200 °C and the formation was at maximum at around 300 °C. The formation of N_2O was significantly smaller in rich than in lean or stoichiometric conditions. Nitrous oxide was expected to be formed in reactions between cyanides or isocyanates and nitrates or nitrites at the surface. NO can react with surface nitrogen atoms to N_2O. N_2O formation can also take place via isocyanate complexes and NO or NO_2. The amount of N_2O formation was the biggest in lean conditions and it could be detected in all experiments.

The total oxidation of propene seemed to be quite effective because no evidence of lighter hydrocarbons was detected. It is possible that in rich conditions also self-poisoning of the catalyst may occur and therefore

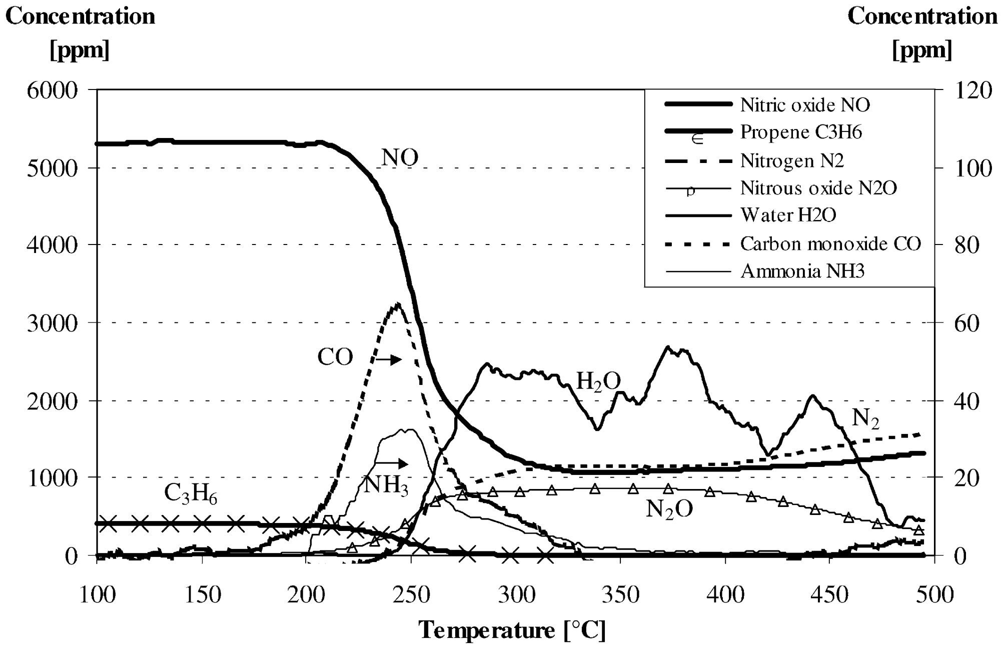

Fig. 2. An example of the concentrations of reactants and products as a function of temperature in lean conditions (5000 ppm NO, 400 ppm C_3H_6), 1% Pd/Al_2O_3 (the N_2 concentration is a calculated value).

Table 2
The observed reaction intermediates and products for NO, C_3H_6, and/or O_2 reactions (on 1 and 3% Pd-catalysts); reaction mechanism approach

Suggested reaction		Supporting literature	Observed at/by
NO adsorption and reactions			
1	$NO + * \leftrightarrow NO^*$	[12,19,20]	
2	$NO^* + * \rightarrow N^* + O^*$	[12,19,20]	
3	$NO^* + N^* \rightarrow N_2O$	[11,12,18]	Gas analysis
4	$NO^* + O^* \leftrightarrow NO_2{}^*$	[20]	$1320–1250\,cm^{-1}$
5	$NO^* + O_2 \rightarrow NO_3{}^*$	[4]	$1300–1250\,cm^{-1}$
Propene adsorption and reactions			
6	$C_3H_6 + * \rightarrow C_xH_y{}^*$	[3,21]	$3200–2900\,cm^{-1}$
7	$C_xH_y{}^* + O_2/O^* \rightarrow C_xH_yO_z{}^*$	[21]	1565 and $1395\,cm^{-1}$
8	$C_xH_y{}^* + NO^* \rightarrow –CH_2–NO^*$		$1658\,cm^{-1}$
9	$–CH_2–NO^* \rightarrow –C{\equiv}N^* + H_2O$	[5]	$2160\,cm^{-1}$
10	$C_xH_y{}^* + NO_2{}^* \rightarrow –CH_2–NO_2{}^*$	[5,17]	$1658\,cm^{-1}$
11	$C_xH_yO_z + NO^* \rightarrow –CH_2–NO_2{}^*$	[5]	$1658\,cm^{-1}$
12	$–CH_2–NO_2{}^* \rightarrow –CH_2–C{=}N{=}O^*$	[5]	$2252–2230\,cm^{-1}$
13	$–CH_2–C{=}N{=}O^* \rightarrow –CH_2–N{=}C{=}O^*$	[5]	$2252–2230\,cm^{-1}$
Cyanide/isocyanate reactions			
14	$–NCO^* + NO_x{}^* \rightarrow N_2 + CO_2 + N_2O$	[2,17,20]	Gas analysis
15	$–C{\equiv}N^* + NO_x{}^* \rightarrow N_2O + N_2 + CO_2$	[21]	Gas analysis
16	$N_2O^* + CO^* \rightarrow N_2 + CO_2$	[12]	Gas analysis
17	$–NCO^* + H_2O \rightarrow NH_3 + CO_2$	[17]	Gas analysis
18	$–C{\equiv}N^* + H_2O \rightarrow NH_3 + CO$	[22]	Gas analysis

the reduction of NO is lower than in stoichiometric conditions [18].

3.3. Mechanism

The experimental data was used to build reaction mechanisms for the reduction of NO and for oxidization of propene in lean to rich conditions. The possible reaction mechanisms of NO reduction by propene over pre-oxidized Pd-surface are presented in Table 2.

In the rich reaction conditions the formations of ammonia and carbon monoxide were significant. It could be due to the isocyanates and cyanides reaction between water when the reaction products are ammonia and CO or CO_2.

4. Conclusions

It was observed that the reduction of NO by propene goes via intermediates like NCO, acetates, formates, and nitrates. The reactions between surface and gaseous intermediates of NO and propene give very large number of varieties for the reaction routes. The most probably reaction route is initiated by adsorption of NO and propene and then adsorbed propene reacts with the surface oxygen to partially oxidized hydrocarbons ($C_xH_yO_z$). These compounds can react with NO or oxygen forward and compose organic nitro compounds, acetates, formates, and isocyanates, which were detected as surface intermediates in the DRIFT measurements. The reaction between nitrates and isocyanates or cyanides produces nitrous oxide and the desired final products (N_2 and CO_2).

It can be concluded that palladium is a good catalyst for the oxidation reaction of propene and at the same time for the reduction of NO_x in the examined conditions. Kinetic studies will be done to determine the kinetic parameters and to verify the proposed kinetic equation and reaction mechanism.

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