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Low temperature NO_x removal from diesel exhaust by coupling ethylene glycol reforming with SCR

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Abstract

The reduction of NO_x at 185 °C on Pd supported on Ti–pillared clay was studied using H_2 and CO generated by reforming of ethylene glycol (EG) over a Na–Pt/γ-Al_2O_3 catalyst. It was found that for a stream containing 490 ppm NO, 5.8% O_2, and 2.9% H_2O, at a space velocity of ~24,000 h^{-1}, a stable NO_x conversion of ~55% was obtained when a stream of 1.36% EG was reformed under a condition that the EG conversion was complete and sufficient H_2 and CO was produced. However, if the EG conversion was incomplete, the unreacted EG deactivated the deNO_x catalyst, possibly by coking, that could not be regenerated by O_2 treatment at reaction temperature. H_2O suppressed the deNO_x activity, but the effect was reversible and the activity could be recovered after removal of H_2O. The deNO_x activity was found to be higher on catalysts containing more highly dispersed Pd.

Keywords: Ethylene glycol; Oxidative reforming; NO_x removal; Hydrogen; Palladium; Pillared clay; Titania

1. Introduction

The recent tightening of permissible NO_x release from combustion engines has intensified the search for a catalytic system that can effectively remove NO_x under challenging diesel exhaust conditions. While direct decomposition or reduction of NO_x using residual hydrocarbons present in the exhaust is the most ideal, these reactions do not show sufficient activities at the diesel exhaust conditions, especially the low temperatures. Investigations over the last decade have eventually led to the implementation of a selected number of promising NO_x technologies, such as lean NO_x traps (LNTs) and urea selective catalytic reduction (urea-SCR). Although LNTs have been implemented, issues such as deactivation of these systems due to sulfur poisoning and thermal aging remain to be solved. Furthermore, LNTs require advanced control systems for their periodic regeneration. As for urea-SCR, implementation of this technology in the US would need a non-existing infrastructure for urea distribution as well as devices in vehicles to prevent ammonia release in the tail gas.

In a recent review, hydrogen-assisted NO_x removal was suggested as a promising method to meet diesel emission standards with the potential to overcome the drawbacks associated with the current technologies for diesel exhaust NO_x removal [1]. The suggestion was based on studies showing that H_2 is one of the few reductants effective for NO_x reduction at low temperatures [2]. These studies also showed that co-feeding H_2 with hydrocarbons resulted in considerable improvement in the NO_x conversion, particularly in the low temperature region [3], and hydrogen is very effective in regenerating LNTs of stored NO_x [4]. Although H_2-assisted SCR offers significant promises for lean NO_x treatment, the concentration of H_2 in the diesel exhaust is too low for effective diesel cleanup. Therefore, a practical source of H_2 needs to be available on-board a vehicle.

Although reforming or partial oxidation of diesel fuel might seem to be an obvious on-board source of hydrogen, this method would incur a fuel penalty. Previously, we have demonstrated that vapor phase reforming of ethylene glycol (EG) is possible under conditions amenable to vehicle applications [5]. One significant advantage of EG compared to fossil fuel as a H_2 source is that EG can be readily manufactured from sources such as sugars or sorbitol, thus making EG a renewable reductant. The objective of this work is

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to couple the EG reforming process to a lean NO_x reduction process to demonstrate the effect on NO_x removal using reductants (H_2/CO) derived from EG. As supporting information, NO_x reduction using a simulated feed of H_2 and CO mixture was also conducted.

Since CO is a product from EG reforming under most conditions and also present in low concentrations in diesel exhaust, the deNO_x catalyst needs to be resistant to any negative impact of CO. We chose Pd catalyst for this purpose. Unlike Pt-based catalysts for which the activities are significantly suppressed by CO, CO promotes H_2-SCR of NO over some Pd catalysts [6]. It has been suggested that the reaction proceeds by NO dissociation on Pd. Then CO reacts with the nitrogen atom to form isocyanate, which is then hydrolyzed to NH_3 for NO_x reduction [7]. The activity of Pd catalysts, however, depends on the support and the Pd precursor [8], and there is a wide variation in the activities reported by different research groups. Unfortunately, the origin of the variation is not entirely understood. We chose Pd supported on titania–pillared clay (Pd/Ti–PILC) as the deNO_x catalyst because of its high activity as well as high selectivity to N_2 [9]. The effects of Pd particle size and the reforming condition were investigated.

2. Experimental

2.1. Catalysts preparation

A Na–Pt/γ-Al_2O_3 catalyst (1.4 wt.% Na and 1 wt.% Pt), identical to the one used previously [5], was used for EG reforming. The BET area of the γ-Al_2O_3 support was 235 m^2/g, and the Pt was introduced by incipient wetness using an aqueous solution of tetraamine platinum(II) nitrate ($Pt(NH_3)_4(NO_3)_2$, Alfa Aesar). The solid was dried at 110 °C overnight and then calcined at 260 °C for 2 h. Na was added as an aqueous solution of Na_2CO_3 to the calcined sample by incipient wetness. The final solid was dried at 110 °C overnight, then calcined to 400 °C.

For the Pd/Ti–PILC catalysts, the Ti–PILC support was prepared in a similar manner as that described by Sterte [10]. Two batches of Ti–PILC prepared with different amounts of Ti were made and used. To prepare the pillaring solution, $TiCl_4$ (Aldrich) was first added to a 2 M HCl solution, and then deionized distilled (DDI) water was added slowly while the solution was vigorously stirred until the final Ti concentration reached 0.82 M for one sample (Ti–PILC-A) and 0.66 M for the other (Ti–PILC-B), and the final HCl concentration was 0.11 M. The partially hydrolyzed Ti-polycation solution was aged for 12 h at room temperature before use. Meanwhile, 4 g of a purified montmorillonite powder (Bentonite, Fisher) was dispersed in 1 l of DDI water for 5 h with vigorous stirring. Then, the Ti pillaring solution (10 mmol Ti/g clay) was added slowly with vigorous stirring to the clay suspension. Intercalation was allowed to take place for 18 h after which the mixture was suction-filtered. The solid was washed with DDI water and resuspended in DDI H_2O repeatedly until the filtrate was free of chloride ions. The sample was dried at 120 °C overnight and calcined at 300 °C for 12 h. The clay was ground and sieved before being impregnated with Pd.

Table 1
Chemical compositions of bentonite and Ti–PILC determined by XRF

Oxides (wt.%)	Bentonite	Ti–PILC-B
SiO_2	69.5	42.0
TiO_2	0.1	39.4
Al_2O_3	20.3	12.9
Fe_2O_3	3.7	3.2
MgO	2.5	1.3
K_2O	0.4	0.2
Na_2O	2.6	0
CaO	1.0	0.2

The chemical compositions of the starting clay and the Ti–PILC-B samples as determined by XRF are listed in Table 1.

The loss of Na_2O upon pillaring is an indication that successful intercalation of Ti has taken place since intercalation occurs by the exchange of the Na cations located between the layers by the Ti polycations. The large increase in the BET surface area of the clay material upon pillaring (from 30 m^2/g to 279 m^2/g) further confirms the incorporation of Ti into the clay structure.

Pd was added to the Ti–PILC by incipient wetness using aqueous solutions of palladium(II) nitrate (Aldrich). A batch of catalysts of 0.1 wt.%, 0.2 wt.%, and 0.5 wt.% Pd loading was prepared with Ti–PILC-B, and another batch of 0.1 wt.% Pd was prepared with Ti–PILC-A. After impregnation, the solids were dried at 120 °C overnight and then calcined at 500 °C for 6 h.

2.2. Catalytic reaction

EG reforming and deNO_x were carried out in two independently controlled but connected reforming and deNO_x reaction units, such that the products from the reforming unit could be fed to the feed stream of the deNO_x unit. The reactions were carried out in a flow system at near atmospheric pressure using quartz tubular reactors that were placed in electric furnaces. The powder catalyst samples were held in place between plugs of quartz wool in the reactors. The tips of the thermocouples were placed outside the reactors but in contact with the middle section of the catalyst beds to monitor the catalyst temperature during reaction, which were also used to control the electric furnaces. All reactor lines were heated to 100 °C to prevent condensation.

All EG reforming reactions were conducted at 230 °C. EG (Alfa Aesar) and DDI H_2O were injected directly into the quartz wool upstream of the catalyst bed in the reforming unit using a Harvard syringe pump. N_2 (ultra high purity, Airgas) and O_2 (20% O_2/N_2, Matheson) were used as purchased. The feed composition was adjusted using the liquid injection rate and the gas flow rates (controlled using mass flow controllers), while maintaining the total flow rates within the range of 30–77 ml/min, unless otherwise stated [5].

For SCR of NO_x using a simulated H_2/CO feed, H_2 (2% H_2/Ar, Airgas), CO (5% CO/Ar, Matheson), and NO (1% NO/He, Matheson) were used as purchased. The flow rates of these gases were adjusted to form a 200 ml/min feed stream containing 500 ppm NO, 3000 ppm H_2, 1200 ppm CO, 5% O_2 and when present, 4% H_2O. For NO_x reduction using EG reformate in the coupled system, the reformate stream leaving the reforming reactor was combined with a simulated exhaust stream containing NO, O_2, and N_2, such that the 200 ml/min stream entering the NO_x reactor was composed of 3640–14,000 ppm H_2, 0–3200 ppm CO, 2.9–6.8% H_2O, 500 ppm NO, and 5–5.8% O_2.

The compositions of the feed and product streams were analyzed with four separate columns in two gas chromatographs as described previously [5]. EG conversions were calculated from conversions to CO and CO_2, and H_2 production efficiency was defined as moles of H_2 produced per mole of EG reacted. The NO and NO_2 concentrations were measured by a chemiluminescence analyzer. All NO_x conversions reported here are steady state values obtained after at least 1 h of reaction.

The Pd dispersions were 27% for 0.2 wt.% Pd/Ti–PILC-B and 40% for 0.1 wt.% Pd/Ti–PILC-B, as determined by pulse O_2 (5% O_2 in helium) chemisorption at room temperature followed by pulse H_2 titration (5% H_2 in N_2) at 100 °C to avoid H_2 absorption by palladium [11]. Before chemisorption, the catalysts were first cleaned in a stream containing O_2 at 300 °C, purged with helium briefly, and then reduced in flowing H_2 at 150 °C and purged with He at 400 °C. Metal dispersions were calculated assuming one O atom adsorbs on one Pd surface atom.

3. Results and discussion

3.1. Effect of Pd loading on SCR of NO_x using simulated feed

The reduction of NO by H_2 and CO was conducted over Pd/Ti–PILC-B catalysts containing 0.1–0.5 wt.% Pd. The amount of catalyst used for each catalytic testing was equivalent to 0.0005 g Pd in every case. Fig. 1 shows the NO conversion as a function of reaction temperature.

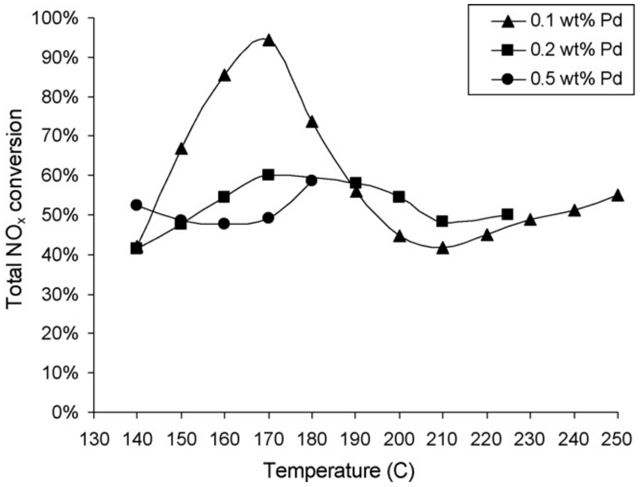

Fig. 1. NO_x reduction with Pd/Ti–PILC-B catalysts as a function of temperature. Reaction conditions: 500 ppm NO, 3000 ppm H_2, 1200 ppm CO, 5% O_2, total flow rate 210 ml/min. In each case, the amount of catalyst used (50 mg, 25 mg, and 10 mg for the 0.1 wt.%, 0.2 wt.%, and 0.5 wt.% sample, respectively) corresponds to 0.0005 g Pd.

The 0.1 wt.% Pd catalyst was the most active, and the maximum NO_x conversion was observed at 170 °C. These results differ somewhat from those reported by Qi et al. [9] that showed a higher maximum activity that occurred at a lower temperature. The cause of the difference was not investigated in detail, and could be due to differences in Pd dispersion (ref. [9] did not provide dispersion information) since the surface areas of the Ti–PILC supports were different between the two studies. Minor differences in catalytic behavior for the clay samples are not unusual since the final characteristic of the intercalated clay is known to be modified by slight variations in the preparation procedure [12].

The NO conversion, H_2 and CO consumptions, N_2 selectivity, and NO_x reduction efficiency for the various Pd catalysts at 140 °C and 170 °C are reported in Table 2. The data show that as the Pd loading increases (Pd dispersion decreases), the NO_x reduction efficiency decreases while the corresponding rates of H_2 and CO oxidation increase. As shown in Fig. 1, this effect is evident only for reaction temperatures below about 200 °C, in agreement with what was observed by Qi et al. [13]. As was observed by McCarthy et al. [14], we also found that H_2 chemisorption was suppressed on highly dispersed Pd samples during our preliminary dispersion measurements (which led to our decision to use titration measurements instead). It is possible that NO adsorption is more competitive on these samples due to the lower coverage of H_2. In addition, NO decomposition on Pd has been proposed to be the initial step of the reduction reaction [7], and dissociation of NO is a structure sensitive reaction, one that occurs more extensively on smaller Pd particles [15]. Thus, taking all these together, it appears that

Table 2
Effect of Pd loading on NO_x reduction, CO and H_2 conversions, N_2 selectivity, NO_x reduction efficiencies

Catalyst	Temperature									
	140 °C	170 °C	140 °C	170 °C	140 °C	170 °C	140 °C	170 °C	140 °C	170 °C
	NO conv. (%)		CO conv. (%)		H_2 conv. (%)		N_2 selectivity (%)		NO_x eff.[a]	
0.1Pd/Ti–PILC-B	44	94	5	91	23	100	76	88	0.30	0.15
0.2Pd/Ti–PILC-B	42	61	15	61	46	90	79	87	0.14	0.11
0.5Pd/Ti–PILC-B	52	49	44	100	85	100	84	90	0.10	0.08

Reaction conditions: 3000 ppm H_2, 1200 ppm CO, 500 ppm NO, 5% O_2, total flow rate 200 ml/min.

[a] NO_x efficiencies = NO converted/H_2 consumed.

Pd particle size is an important factor for NO_x activity, and is likely the principal differences observed in the deNO_x catalytic activity observed over Pd catalysts on different supports as well as catalysts prepared using different precursors.

Unlike NO_x reduction efficiency, N_2 selectivity improved as the temperature increased from 140 °C to 170 °C. Within error, the N_2 selectivity did not depend on the Pd particle size. This is in agreement with the literature report for H_2-SCR with Pt where the N_2 selectivity was found not to depend on the active metal properties, but on the acidity of the support, being higher on more acidic supports due to a higher concentration of adsorbed NH_4^+ ions that could reduce NO as in NH_3-SCR [16]. This would explain the higher selectivity observed with the Pd/Ti–PILC compared to Pd supported on oxide supports such as alumina. Other than the influence of the support, addition of alkali elements such as potassium has been reported to promote the N_2 selectivity of Pd-based catalysts for NO_x reduction by CO + H_2 [17].

3.2. Effect of H_2O on NO_x reduction activity using simulated feed

The effect of water on the NO_x reduction activity at 185 °C is shown in Table 3. Addition of 4% H_2O caused the NO_x conversion to drop from 73% to 44%, most likely due to competitive adsorption by water. This loss in NO_x activity is fully reversible and can be recovered once water is removed from the feed as shown in Fig. 2. The lower NO_x conversion in the presence of water is accompanied by a marked decrease in CO conversion, while the H_2 conversion remained high. This suggests that H_2 oxidation is more facile than CO oxidation, and in the absence of added H_2O, H_2 is likely nearly completely consumed in the early part of the catalyst bed. Then, CO reduction of NO_x would be the primary process in the latter part of the bed.

3.3. Coupled EG reforming and deNO_x reactions

All experiments with the coupled systems were carried out using the 0.1 wt.% Pd/Ti–PILC catalyst for deNO_x, and the Na–Pt/γ-Al_2O_3 catalyst for EG reforming. The gas composition was adjusted so that feed to the deNO_x unit always contained ~500 ppm NO, ~5.5% O_2, with variable amounts of H_2, CO, and H_2O depending on the EG reforming condition. Fig. 3 shows the NO conversion for a 2.2% EG feed to the reformer. As expected, there was significant NO_x conversion. However, the activity declined with time-on-stream, and 1/3 of the activity was lost in an hour. The NO conversion increased with higher EG concentration used (Table 4), which is expected because of higher concentrations of H_2 and CO produced.

Table 3
Effect of H_2O on the NO_x reduction activity at 185 °C

Water conc. (%)	NO conversion (%)	CO conversion (%)	H_2 conversion (%)	N_2 selectivity (%)
0	73	42	98	85
4	44	14	97	85

Reaction conditions: 3000 ppm H_2, 1400 ppm CO, 470 ppm NO, 5% O_2, total flow rate 200 ml/min, 0.5 g 0.1 wt.% Pd/Ti–PILC-A.

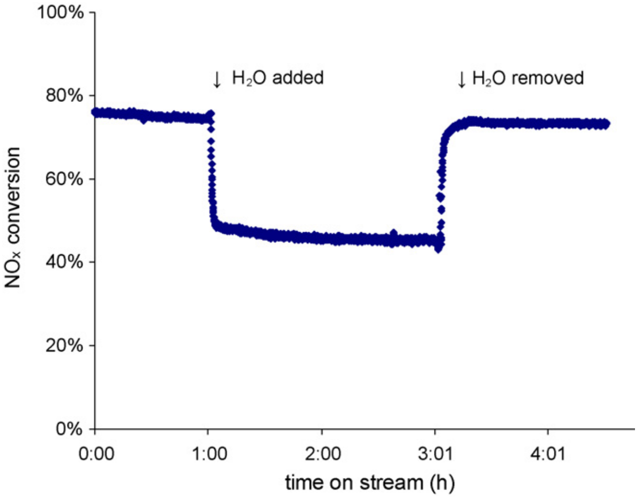

Fig. 2. Effect of water on NO_x reduction at 185 °C. Reaction conditions: 3000 ppm H_2, 1400 ppm CO, 470 ppm NO, 5% O_2, 4% H_2O, total flow rate 200 ml/min, 0.5 g 0.1 wt.% Pd/Ti–PILC-A.

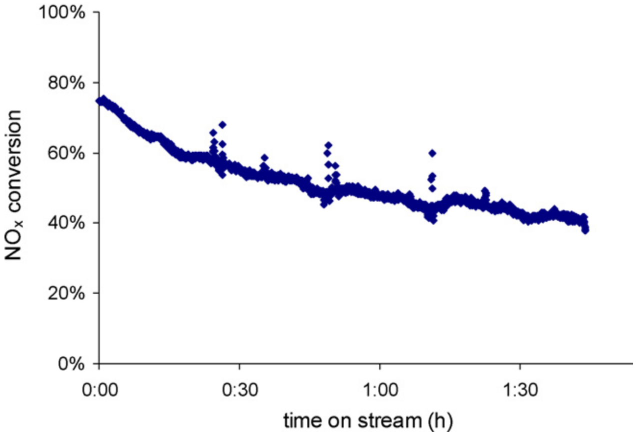

Fig. 3. Coupled EG reforming-deNO_x reduction reaction. Reaction conditions for EG reforming: a feed of 2.2% EG, 2.65% O_2, 13.7% H_2O, total flow rate 77 ml/min, 0.1 g Na–Pt/Al_2O_3 catalyst, 230 °C. Reaction conditions for coupled-deNO_x: a feed of 1.4% H_2, 3200 ppm CO, 1100 ppm EG, 500 ppm NO, 5.3% O_2, 5.3% H_2O, total flow rate 200 ml/min, 0.5 g 0.1 wt.% Pd/Ti–PILC-B, 170 °C.

Since the Pd catalyst did not deactivate when a simulated reforming feed was used, we reasoned that the observed deactivation must be associated with the small amounts of unconverted EG, which was detected in these experiments. To determine if exposure to EG deactivates the catalyst and if the deactivation is reversible, a Pd catalyst was first tested with a simulated reforming feed containing H_2 and CO. Then it was used with a EG reformate the same as that shown in Fig. 3, such that the deNO_x feed containing 0.1% EG would passed over the catalyst for 3 h. Afterwards, the sample was purged with 150 ml/min gas mixture containing 6.7% O_2 balance N_2 for 5 h at 170 °C to remove any material condensed in the pores and the deNO_x activity was tested again using the simulated reforming feed. The results (Table 5) show that exposure to unreacted EG

Table 4
Effect of EG concentration in the reformer on NO_x conversion at 170 °C in the coupled reactor unit

EG reforming unit			deNO$_x$ unit		
EG feed conc. (ppm)	O_2/EG	EG conv. (%)	H_2 conc. (ppm)	CO conc. (ppm)	NO conv. (%)
3630	1.6	78	3640	390	48
4700	1.5	75	5600	520	70

Other reaction conditions for the deNO$_x$ unit: 6.8% H_2O, 470 ppm NO, 5% O_2, total flow rate 200 ml/min, 0.3 g Na–Pt/Al_2O_3.

deactivates the catalyst irreversibly under our conditions. Along with the decrease in the NO_x activity, the catalyst sample also changed color from yellow to gray, suggesting deposition of carbonaceous compounds as a possible cause of deactivation.

Experiments were then conducted to find conditions where EG conversion is complete in the reforming unit by changing the EG and O_2 concentrations in the feed. Table 6 shows the results of changing EG concentration. Increasing the EG concentration from 3.5% to 8.2% did not affect the EG conversion significantly. On the other hand, increasing the O_2/EG ratio increased the EG conversion, eventually attaining 100% conversion for a ratio of 2.0 (Table 7).

Using the conditions derived from these experiments, the deNO$_x$ reaction using the coupled reaction unit was tested again, and the results are shown in Fig. 4. Unlike the previous tests, a stable activity was attained for the duration of the test.

Table 5
Effect of exposure to ethylene glycol on the NO_x activity of Pd/Ti–PILC at 170 °C

	NO conversion (%)	CO conversion (%)	H_2 conversion (%)	N_2 selectivity (%)
Before EG	94	91	100	88
After EG	21	49	83	86

Reaction conditions: 3000 ppm H_2, 1400 ppm CO, 490 ppm NO, 5% O_2, total flow rate 200 ml/min, 0.5 g 0.1 wt.% Pd/Ti–PILC-B.

Table 6
Effect of EG concentration on the EG conversion and H_2 efficiency in EG reforming. Reaction conditions: 0.1 g Na–Pt/Al_2O_3, O_2/EG = 1.0, H_2O/EG = 6.2, total flow rate = 30–49 ml/min, 230 °C

EG concentration (%)	EG conversion (%)	H_2/EG	CO/CO_2
3.5	71	1.85	0.30
5.0	68	1.84	0.31
8.2	68	1.68	0.55

Table 7
Effect of O_2/EG ratio on EG reforming over 0.3 g Na–Pt/Al_2O_3, total flow rate 45 ml/min, 230 °C

EG concentration (%)	O_2/EG	H_2O concentration (%)	H_2 formed (%)	CO formed (%)	EG conversion (%)
0.89	1.2	16.5	2.3	0.105	86
0.73	1.5	13.7	1.8	0.026	93
0.57	2.0	10.7	0.87	0	100

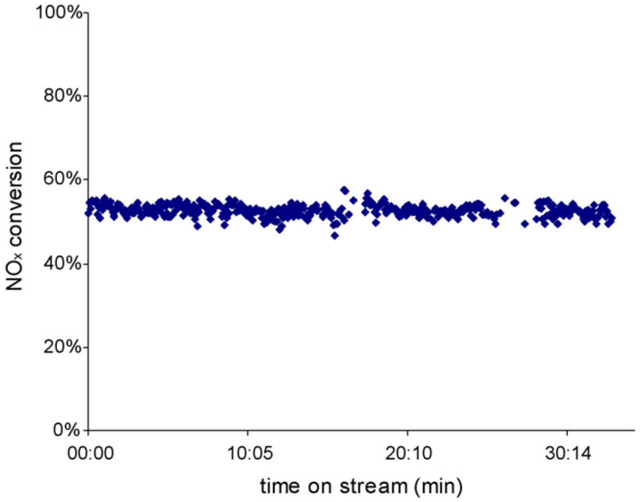

Fig. 4. Coupled EG reforming-deNO$_x$ reduction reaction. Reaction conditions for EG reforming: a feed of 1.36% EG, 2.8% O_2, 8.5% H_2O, total flow rate 71 ml/min, 1.0 g Na–Pt/Al_2O_3 catalyst, 230 °C. Reaction conditions for coupled-deNO$_x$: a feed of 5400 ppm H_2, 960 ppm CO, 490 ppm NO, 5.8% O_2, 2.9% H_2O, total flow rate 200 ml/min, 0.5 g 0.1 wt.% Pd/Ti–PILC-A, 185 °C.

Under these conditions, 450 ppm unreacted H_2 and 300 ppm unreacted CO were detected in the effluent from the deNO$_x$ unit.

4. Conclusions

We have investigated NO_x reduction over Pd/Ti–PILC catalysts using H_2 and CO derived from the reforming of EG over a Na–Pt/Al_2O_3 catalyst. A condition was found where stable, effective reduction of NO_x was achieved at 185 °C. The deNO$_x$ catalyst was found to be deactivated by unreacted EG from the reforming unit. Thus, it is important that the reforming condition results in complete EG conversion while generating sufficient concentrations of H_2 and CO. In addition, using a simulated reforming feed, the catalytic activity of Pd was found to depend on the Pd dispersion. Further improvement of hydrogen yield in EG reforming and in NO_x conversion would make commercialization of this demonstrated concept more attractive.

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