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Selective catalytic reduction of NO by propene in excess oxygen on Pt- and Rh-supported alumina catalysts

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Abstract

A comparative study of Pt/alumina and Rh/alumina catalysts was performed for the selective catalytic reduction of NO with C_3H_6 in the presence of excess oxygen. Pt/alumina was more active for NO reduction at lower temperatures compared to Rh/alumina. However, the latter exhibited clearly superior performance in terms of selectivity to N_2. This makes Rh/alumina a more suitable catalyst for the selective catalytic reduction of NO under excess oxygen conditions. Detailed kinetic studies of the SCR of NO were performed on Pt/alumina and Rh/alumina to obtain low-temperature kinetic expressions for NO reduction and C_3H_6 oxidation in the presence and absence of NO. Qualitative similarities yet quantitative differences in these kinetic expressions appear to indicate the existence of two partially similar mechanistic schemes. One is based on the indirect participation of the reductant through reduction of the active sites, followed by dissociative adsorption of NO on reduced sites (applicable for Pt/alumina). The other is based on the direct participation of the reductant (apparently by its partial oxidation) in forming an activated intermediate species, followed by its interaction with activated NO (applicable for Rh/alumina).

Keywords: Selective catalytic reduction; NO; Propene; Alumina; Pt; Rh

1. Introduction

The selective catalytic reduction of nitrogen oxides by hydrocarbons (HC-SCR) in the presence of excess oxygen is currently receiving increasing attention as a promising method for the removal of environmentally hazardous NO_x emissions from automotive engines [1,2]. This method overcomes the substantial applicability limitations of other current technologies for de-NO_x control. The use of ammonia (NH_3-SCR) requires stoichiometric control of ammonia addition, a rather complex problem due to the variable levels of NO_x in automotive exhausts. It also has serious technical limitations (on-board storage, corrosion-resistant equipment) [1]. The use of Three-Way-Catalysis (TWC) is limited by the inability of current catalytic converters to effectively reduce NO under excess oxygen (lean-burn) conditions; lean-burn gasoline or diesel engines offer considerable improvement in fuel economy (reduced cost and lower CO_2 emissions per unit distance) [1].

Since the verification of the use of hydrocarbons for NO reduction [3], a plethora of studies has been focusing on this catalytic process [1–16]. Among the various catalytic systems that have been examined (metal-exchanged zeolites, transition-metal and noble-metal-supported oxides), the noble-metal-

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supported oxide catalysts appear to be favorable for the reduction of NO. This is mainly due to their excellent hydrothermal stability and enhanced resistance to the presence of SO_2 [4–7]. Also, Pd-, Pt- and Rh-supported-oxide catalysts have been shown to exhibit enhanced NO reduction activity at low temperatures (typically lower than 300°C) [2,8–11]. This activity characteristic is of critical importance, since a major percentage of the automotive exhaust emissions is released during the initial heating period of the engine ('cold start' problem).

Bibliographical references on the selective catalytic reduction of NO by light hydrocarbons (typically propene) on Pt- and Rh-supported-oxide catalysts have also indicated some significant problems in their catalytic performance. These are a narrow temperature window and relatively poor selectivity to N_2 of the Pt-based catalysts [9–12]. Various mechanistic studies of the SCR of NO on these catalysts have proposed conflicting theories for the mechanism of NO reduction [9–16]. Is the role of the reductant to reduce the catalyst, thus, indirectly enhancing NO decomposition [9,10] or to directly reduce NO through the formation of an activated intermediate species [11–14]? Is the presence of excess oxygen assisting at low temperatures by oxidizing NO to the more easily reduced NO_2 [15], by oxidizing and thus activating the hydrocarbon into forming an activated intermediate which then carries the reduction [11–14], or both [16]? Is it inhibiting, by reoxidizing the reduced active catalyst sites [9,10]? Despite certain similarities in their catalytic behavior, could the observed differences between Pt- and Rh-supported catalysts (namely the selectivity to N_2 and the observed types of NO adsorption [13]) support a hypothesis for a different mechanism of NO reduction between them?

Bearing in mind that Pt- and Rh-supported catalysts are currently considered as among the most promising materials for the SCR of NO [2,11–16], the scope of this study is to comparatively evaluate the catalytic performance of Pt- and Rh-supported catalysts for the catalytic reduction of NO. Furthermore, it is to perform a preliminary kinetic investigation of the low-temperature activity of these catalysts for NO reduction, in an attempt to answer some of the above mechanistic questions and thus to elucidate the mechanism of this reaction on these catalytic systems.

2. Experimental

2.1. Catalysts and characterization

The incipient wetness method was used for the aqueous impregnation of a γ-alumina carrier (Engelhard), producing catalysts with nominal loading of 2.0 wt.% Pt and Rh. Impregnation of the support was performed using H_2PtCl_6 and $RhCl_3$ solutions, respectively. The catalysts were dried at 120°C and calcined in air at 600°C for 6 h prior to reaction [5,8]. Characterization of the samples included determination of the surface area by the BET method. The corresponding surface areas for Pt/ and Rh/alumina were measured to be 177 and 182 m^2/g. The actual metal loading was measured by inductively coupled plasma and atomic emission spectroscopy (ICP/AES) and was found to be 1.55 ± 0.05 wt.% and 1.86 ± 0.05 wt.% for Pt/alumina and Rh/alumina, respectively.

2.2. Reaction/analysis system

Kinetic experiments were performed in a fixed-bed quartz microreactor (7 mm i.d.). The catalyst was loaded onto a fine-quartz fritted disk and the reaction temperature was continuously monitored by a thermocouple inserted in the catalyst bed. A second thermocouple, located after the fritted disk, was used for measuring the temperature of the effluent gases. Catalyst weights of 0.15 and 0.25 g were used.

The reaction system was equipped with mass flow controllers and pressure indicators, thus offering accurate control of the flow and partial pressure of each reactant. Typical feed composition was 1000 ppm NO, 1000 ppm C_3H_6, and 5.0% O_2 in He (all ultra-high purity gases). The total feed flow to the reactor through heated transfer lines was 300–1000 cc/min ($W/F = 0.009$–0.05 g.s/cc). The oven and heated line temperatures were controlled to within ± 0.5°C.

Product analysis was performed with an on-line set of gas analyzers in series and a gas chromatograph (GC) with a thermal conductivity detector (TCD). The on-line analyzers were: a chemiluminesence $NO/NO_2/NO_x$ analyzer (42C-HL, Thermo Environmental), non-dispersive infrared (NDIR) CO and CO_2 analyzers (VIA-510, Horiba) and a magnetopneumatic O_2 analyzer (MPA-510, Horiba). The

GC (Shimadzu model 14B) had two packed columns in series for gas separation: a Porapak-N (80/100, $10' \times 1/8''$, Supelco) for separating CO_2, N_2O and C_3H_6, and a Molecular Sieve 13X (60/80, $10' \times 1/8''$, Supelco) for separating O_2 and N_2.

3. Results

Preliminary kinetic experiments were performed in order to determine the appropriate set of experimental parameters that would ensure catalyst evaluation for the reduction of NO based on intrinsic kinetics measurements. The experimental parameters in question were the space-time (expressed in terms of the ratio of catalyst weight to the total feed flow, *W*/*F*) and the catalyst particle size (expressed in terms of the average particle diameter, d_p). They were varied in order to examine the possible influence of external and internal transfer limitations on the catalytic activity, respectively. The Rh/alumina catalyst was used for the evaluation experiments. Prior to reaction, the sample was conditioned by in-situ heating with 20% O_2/He at 600°C for 1 h, in order to desorb any adsorbed compounds.

3.1. Variable space-time experiments

The variable space-time experiments were performed with a typical feed composition of 1000 ppm NO, 1000 ppm C_3H_6, and 5.0% O_2 in He, catalyst weight of 0.15/0.25 g and total flow of 300–1000 cc/min ($W/F = 0.009$–0.05 g s/cc). The effect of *W*/*F* on the catalytic activity of Rh/alumina for NO reduction and C_3H_6 oxidation at 302 ± 1°C, expressed as percent conversion, is shown in Fig. 1. *W*/*F* values higher than 0.02 g s/cc resulted in a non-proportional relationship between conversion and space-time. This indicates a clear influence of external transfer limitations on the measured activities for both NO reduction and C_3H_6 oxidation. The same behavior was also found to be valid for the oxidation of NO to NO_2. Thus, a *W*/*F* value no greater than 0.02 g s/cc is required in order to avoid the influence of external transfer limitations and obtain a true measure of intrinsic kinetics for NO reduction. A *W*/*F* value of 0.018 g s/cc (corresponding to a catalyst weight $W = 0.15$ g and a feed flow $F = 500$ cc/min) was selected for the rest of the kinetic experiments of this work.

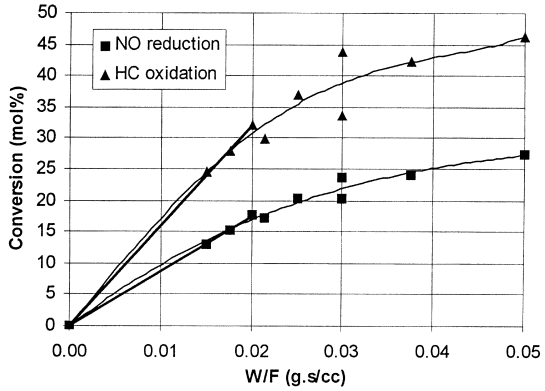

Fig. 1. Variable space-time effect on NO reduction and C_3H_6 oxidation activity of Rh/alumina. Conditions: 0.1% NO, 0.1% C_3H_6, 5.0% O_2, $W = 0.25$ g, $F = 300$–1000 cc/min, $W/F = 0.015$–0.05 g s/cc, $T = 302 \pm 1$°C.

3.2. Variable particle size experiments

Two catalyst samples of Rh/alumina were evaluated in terms of their NO reduction performance, having particle size diameters d_p in the range $106\ \mu m < d_p < 180\ \mu m$ and $180\ \mu m < d_p < 355\ \mu m$. The NO reduction experiments were performed with a feed composition of 1000 ppm NO, 1000 ppm C_3H_6, and 5.0% O_2 in He, catalyst weight of 0.15 g and total flow of 500 cc/min ($W/F = 0.0018$ g s/cc). Such conditions, as shown above, were found to ensure the absence of external transfer limitations on the catalytic activity measurements.

The particle size effect on the reduction of NO (expressed in % conversion) on Rh/alumina is shown in Fig. 2, as a function of reaction temperature. The measured NO conversions were found to be essentially the same at every temperature for the two catalyst samples of different particle size. This, therefore, indicates that there appears to be no significant influence of internal transfer limitations on the measured catalytic activities of samples with particle sizes of less than 355 μm. The same behavior was observed for the oxidation of C_3H_6 (results not shown). The slight deviations between the two samples were well within the typical uncertainty of these measurements, taking into consideration the high sensitivity of the measured activities to even small variations in reaction temperature.

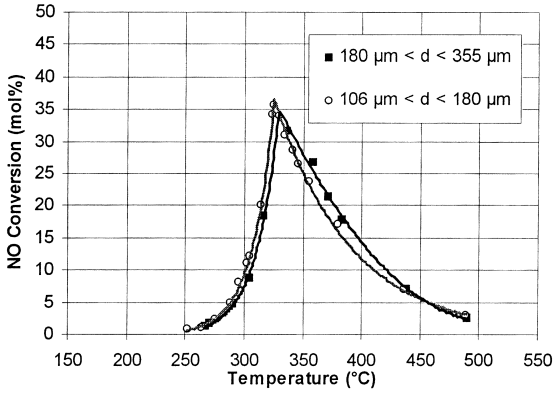

Fig. 2. Variable particle-size-distribution effect on NO reduction activity of Rh/alumina. Conditions: 0.1% NO, 0.1% C_3H_6, 5.0% O_2, $W/F = 0.018$ g s/cc, $d_p = 106$–180 μm/180–355 μm.

3.3. Activity evaluation of Pt/alumina and Rh/alumina catalysts

The catalytic performance of Pt/alumina for the reduction of NO was investigated and compared to that of Rh/alumina. The reaction conditions were the standard ones, i.e., 1000 ppm NO, 1000 ppm C_3H_6 and 5.0% O_2 in He and $W/F = 0.018$ g s/cc (GHSV = 1×10^5 h^{-1}). This space velocity is within the 0.5×10^5–1.2×10^5 h^{-1} range of practical application. The scope of this study was to evaluate the activity differences of the two noble metals (Pt and Rh) under similar catalyst formulations, i.e., nominal metal loading (2.0 wt.%), support (γ-alumina) and method of preparation and treatment.

The performance of Pt/alumina, expressed in terms of pseudo-steady-state conversions for NO reduction (squares), NO oxidation to NO_2 (diamonds) and C_3H_6 oxidation (triangles) as functions of the reaction temperature is given in Fig. 3a. The equilibrium conversion curve for the oxidation of NO to NO_2 (dashed line) is also shown for comparison. The temperature range examined was from 550°C down to 150°C. At each temperature a pseudo-steady-state was obtained before advancing to the next reaction temperature.

The Pt/alumina catalyst exhibited typical activity behavior [5,8–11], with the NO reduction curve passing through a maximum of ca. 38% conversion to reduction products at $T = 290$°C. The oxidation of C_3H_6

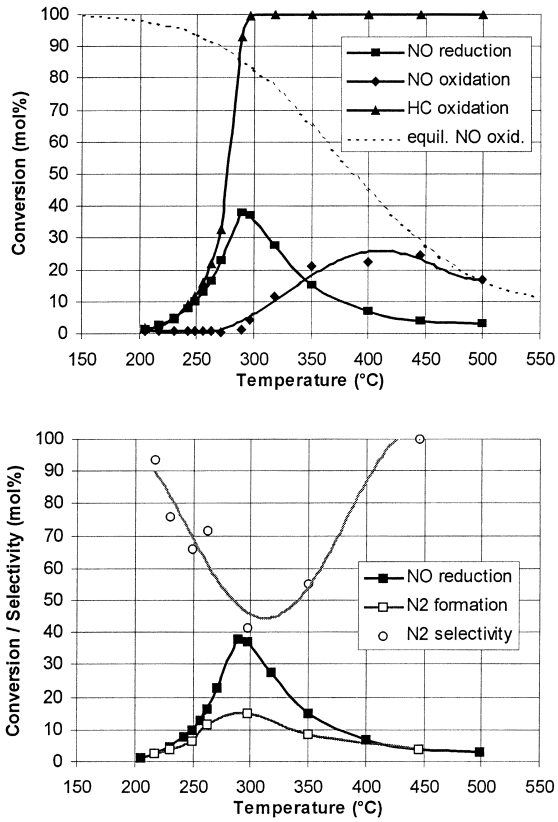

Fig. 3. (a) Temperature effect on the selective catalytic reduction of NO on Pt/alumina. (b) Temperature effect on the selectivity to N_2 on Pt/alumina. Conditions: 0.1% NO, 0.1% C_3H_6, 5.0% O_2, $W/F = 0.018$ g s/cc.

was observed to increase with temperature in parallel to the increase in NO reduction [8,10,11]. It was found to reach completion (100% conversion to CO_2) at a temperature about that of maximum NO reduction (ca. 300°C). Minimal amounts of CO (less than ca. 2%) were measured in the range of incomplete C_3H_6 oxidation. At higher temperatures the reduction of NO was found to decrease, being limited by the absence of reductant due to its complete oxidation, thus leading to increased NO_2formation [10,14]. At the highest examined temperatures, however, the NO oxidation to NO_2 was suppressed by reaction equilibrium limitations, as shown in Fig. 3a. The low-temperature (low-T) activities for NO reduction and C_3H_6 oxidation, expressed as reaction rates (μmol/g s) were observed to follow Arrhenius-type behavior. The appar-

ent energies of activation were found to be essentially equal (22 and 24 kcal/mol, respectively). The ratio of the low-T C_3H_6 oxidation rates to the NO reduction rates was found to be ca. 1.

The catalytic activity for the SCR of NO is typically evaluated in terms of conversion (or rate) of NO reduction to its reduction products, i.e., N_2 and N_2O. However, the desirable product is N_2, whereas N_2O, although not currently restricted as a pollutant, is not considered environmentally benign [17]. Thus, it is an undesirable byproduct for the SCR of NO. The evaluation of a catalyst should, therefore, be based on the NO conversion to N_2.

The N_2 formation (or yield) and the selectivity to N_2 of Pt/alumina are shown in Fig. 3b. This catalyst was found to exhibit rather poor selectivity to N_2, with a minimum value of ca. 40% (obtained at the temperature of maximum NO reduction activity). It should be noted, however, that the N_2 selectivity values have a substantially higher uncertainty compared to the NO reduction ones. This was due to the difficulty of reproducible quantitative measurement of small concentrations of N_2O (less than 50 ppm).

The catalytic activity of Rh/alumina for NO reduction, NO oxidation and C_3H_6 oxidation is presented in Fig. 4a. The obtained activity curves followed qualitatively the same behavior with reaction temperature as those for Pt/alumina. A maximum in NO reduction activity (ca. 39% conversion at ca. 315°C) was obtained, in close agreement with the completion of the C_3H_6 oxidation (ca. 320°C) and a decrease in NO reduction (with a parallel increase in NO oxidation) at higher temperatures. The low-T NO reduction and C_3H_6 oxidation activities were also observed to follow Arrhenius-type kinetics. The measured apparent activation energies were equal (36 and 38 kcal/mol, respectively), yet clearly greater than the ones obtained for Pt/alumina. Additionally, the ratio of the low-T C_3H_6 oxidation to NO reduction rates was also found to be quite different than that of Pt/alumina (values of 1.7–2.4 were recorded from various experiments on Rh/alumina samples).

The N_2 formation and selectivity curves of Rh/alumina are shown in Fig. 4b. This catalyst was observed to exhibit significantly better selectivity to N_2 compared to Pt/alumina [13] (minimum value of ca. 80%, also obtained around the temperature of maximum NO reduction activity).

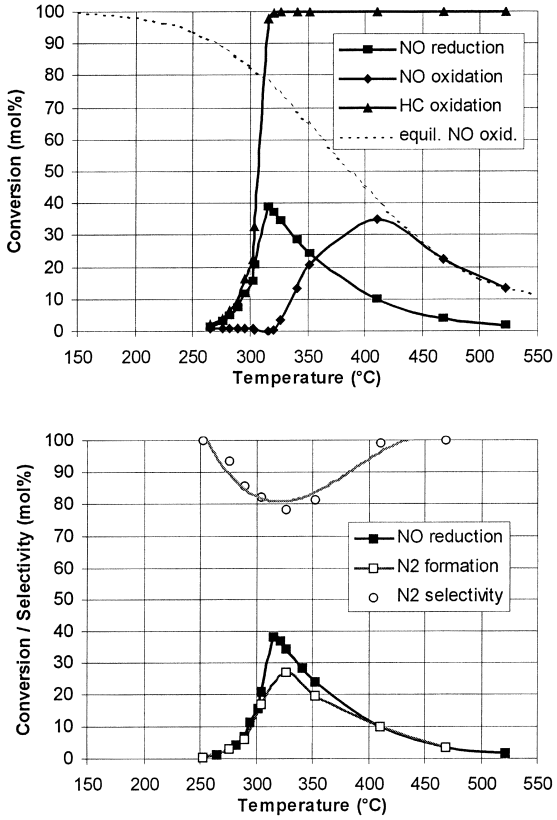

Fig. 4. (a) Temperature effect on the selective catalytic reduction of NO on Rh/alumina. (b) Temperature effect on the selectivity to N_2 on Rh/alumina. Conditions: 0.1% NO, 0.1% C_3H_6, 5.0% O_2, $W/F = 0.018$ g s/cc.

A comparison of the catalytic activities of Pt/alumina and Rh/alumina for the reduction of NO and the formation of N_2 can be made, based on the results of Figs. 3b and 4b, respectively. Pt/alumina appeared to be more active for NO reduction than Rh/alumina, exhibiting higher activity at lower temperatures. Despite the similarity between the two low-temperature activity curves, the corresponding apparent activation energies were substantially different (24 ± 3 and 37 ± 3 kcal/mol for Pt and Rh, respectively). However, Rh/alumina was found to exhibit clearly superior performance in terms of N_2 formation (max. yield of 27% as opposed to 15% on Pt/alumina), yet moderately shifted to higher temperatures (330°C versus 290°C).

The effect of the presence of NO on the C_3H_6 oxidation activity of Pt/alumina and Rh/alumina was also

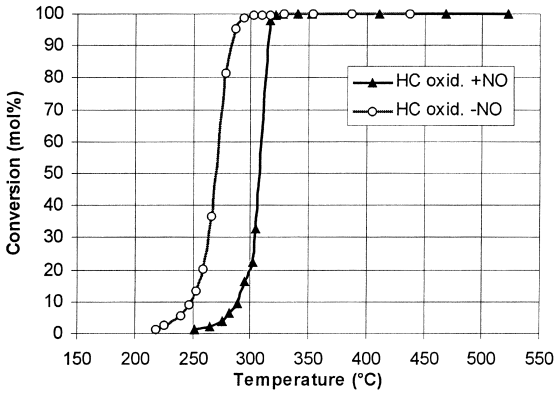

Fig. 5. Effect of the presence of NO on C_3H_6 oxidation activity on Rh/alumina. Conditions: 0.0/0.1% NO, 0.1% C_3H_6, 5.0% O_2, $W/F = 0.018$ g s/cc

examined. The C_3H_6 oxidation activity in the presence (SCR of NO) and absence of NO (C_3H_6 combustion) on Rh/alumina under typical reaction conditions is presented in Fig. 5. A downshift in the C_3H_6 oxidation activity curve (by ca. 40°C) was observed in the absence of NO. This indicates that the presence of NO has a negative effect on the activity of Rh/alumina for C_3H_6 oxidation. Interestingly, the calculated apparent energies of activation for C_3H_6 oxidation in the presence and absence of NO were found to be equal to each other (36 ± 1 kcal/mol). A qualitatively similar effect was observed for Pt/alumina, in agreement with various literature reports on Pt-supported catalysts [8,11,12].

3.4. Kinetic studies of NO reduction on Pt/alumina and Rh/alumina

The effect of varying the feed concentration of each of the reactants (NO, O_2, C_3H_6) while keeping the other concentrations constant was examined on the NO reduction and C_3H_6 oxidation activities of the Pt/alumina and Rh/alumina catalysts. Parameters such as reaction temperature and space velocity were kept constant, so that the only variation in the rates resulted form the particular concentration change. The reaction temperatures were chosen so as to approach 'differential' reaction kinetics (conversions less than ca. 20%, differential plug-flow rate expressions). The scope of this study was to obtain low-T kinetic expressions as well as to gain some

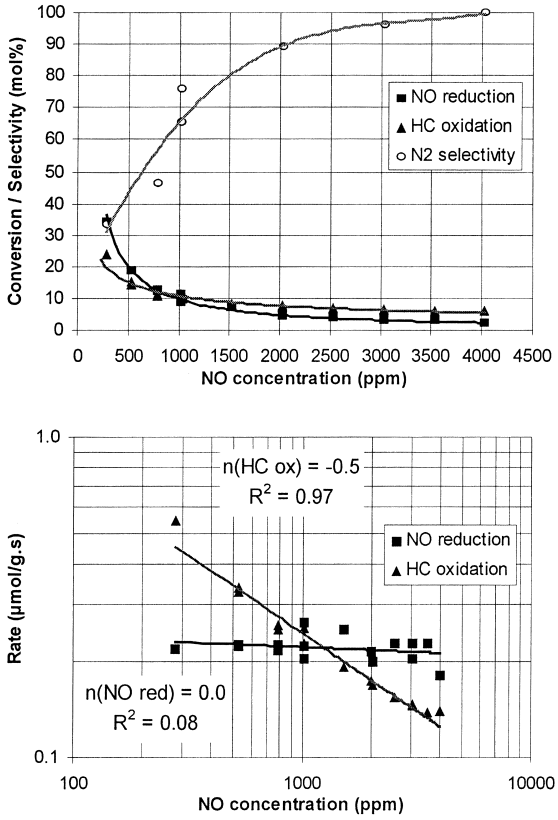

Fig. 6. (a) NO concentration effect on the SCR of NO and N_2 selectivity on Pt/alumina. (b) NO concentration effect on NO reduction and C_3H_6 oxidation on Pt/alumina. Conditions: 250–4000 ppm NO, 0.1% C_3H_6, 5.0% O_2, $W/F = 0.018$ g s/cc, $T = 236 \pm 1$°C.

insight on the mechanism of NO reduction at low temperatures.

The effect of varying NO concentration (250–4000 ppm) on NO reduction, C_3H_6 oxidation, as well as N_2 selectivity on Pt/alumina at 236 ± 1°C is shown in Fig. 6a. An increase in both the conversions and a decrease in N_2 selectivity with decreasing NO concentration was observed. The activities for NO reduction and C_3H_6 oxidation, expressed as reaction rates, were plotted versus NO concentration as shown in Fig. 6b. The apparent reaction orders were found to be zero for NO reduction and -0.5 for C_3H_6 oxidation. The zero-order dependence of NO reduction activity on NO appears to be in relatively good agreement with similar biliographical results (0.1 and 0.3 orders for Pt/silica and Pt/alumina, respectively) [11,12]. The low value of the correlation coefficient R^2 for the NO

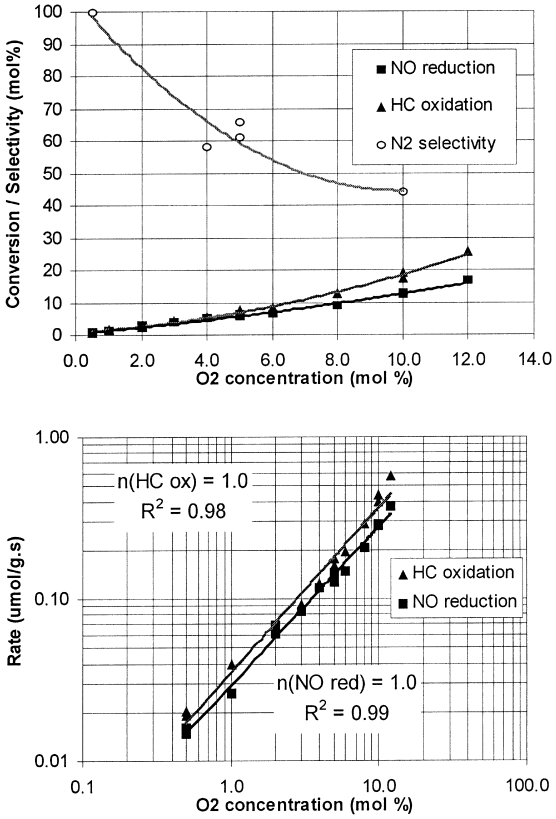

Fig. 7. (a) O_2 concentration effect on the SCR of NO and N_2 selectivity on Pt/alumina. (b) O_2 concentration effect on NO reduction and C_3H_6 oxidation on Pt/alumina. Conditions: 0.1% NO, 0.1% C_3H_6, 0.5–12.0% O_2, $W/F = 0.018$ g.s/cc, $T = 230 \pm 1$°C.

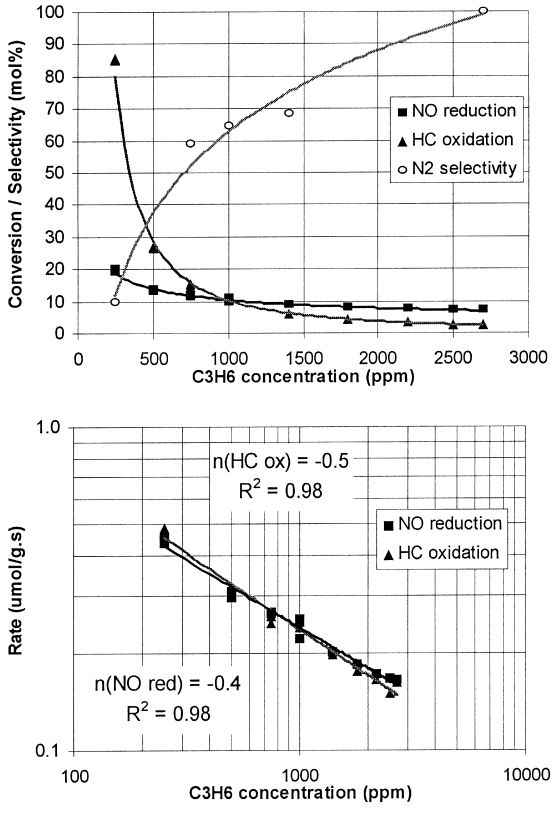

Fig. 8. (a) C_3H_6 concentration effect on the SCR of NO and N_2 selectivity on Pt/alumina. (b) C_3H_6 concentration effect on NO reduction and C_3H_6 oxidation on Pt/alumina. Conditions: 0.1% NO, 250–3000 ppm C_3H_6, 5.0% O_2, $W/F = 0.018$ g s/cc, $T = 237 \pm 1$°C.

reduction activity data is typical for linear regressions with a slope of essentially equal to zero.

The effect of varying O_2 concentration (0.5–12.0%) on the NO reduction, C_3H_6 oxidation and N_2 selectivity of Pt/alumina at 230 ± 1°C is shown in Fig. 7a. A linear increase in both the conversions was observed, as well as a decrease in N_2 selectivity with increasing O_2 concentration. The selectivity trend was qualitatively in good agreement with the literature [11]. The NO reduction and C_3H_6 oxidation activities were plotted as a function of O_2 concentration and are shown in Fig. 7b. The apparent reaction orders were found to be 1 for both the reactions and the measured reaction rates were practically equal to each other. The observed monotonic increase in NO reduction activity with O_2 would appear to be inconsistent with findings in other studies on Pt/alumina and Pt/silica, where a maximum in NO conversion with O_2 was obtained [11,12].

The effect of varying C_3H_6 concentration (250–3000 ppm) on NO reduction, C_3H_6 oxidation and N_2 selectivity on Pt/alumina at 237 ± 1°C is shown in Fig. 8a. A decrease in activity for both reactions and an increase in N_2 selectivity with increasing C_3H_6 concentration was obtained. These three curves appear to be in very good agreement with similar observations of Roberts et al. [11]. It should be noted that the activities for the lowest tested C_3H_6 concentration values of less than 500 ppm were found to deviate significantly from 'differential' kinetics. Thus, the accuracy of those data points would be questionable (and so would be the corresponding selectivity value). The rates for NO reduction and C_3H_6 oxidation are presented in Fig. 8b. The estimated orders of reaction with respect to C_3H_6 were both ca. -0.5 and

the two reaction rates were essentially equal to each other.

By combining the above (theoretically independent) observations, we obtain these overall low-T kinetic expressions for the reactions of interest on Pt/alumina:

$$r(\text{NO red}) = k_{\text{red}} \frac{[O_2]}{[C_3H_6]^{0.5}} \quad (1)$$

$$r(C_3H_6 \text{ ox}) = k_{\text{ox}} \frac{[O_2]}{[NO]^{0.5}[C_3H_6]^{0.5}} \quad (2)$$

It would be interesting to compare these rate expressions with the corresponding expression for the oxidation of C_3H_6 in the absence of NO (i.e. C_3H_6 combustion). By applying the same methodology (results not shown), the obtained rate expression was

$$r(C_3H_6 \text{ comb}) = k_{\text{comb}} \frac{[O_2]}{[C_3H_6]^{0.5}} \quad (3)$$

which appears to be essentially identical to the expression for the reduction of NO. It should be noted, however, that these kinetic experiments were performed at $158 \pm 1^\circ$C, i.e., a temperature significantly lower than the one for the experiments in the presence of NO.

The same methodology was also applied for investigating the effect of variable concentration of each of the reactants on the catalytic reduction activity of Rh/alumina. These experiments were performed at $272-274 \pm 1^\circ$C, i.e., at temperatures relatively higher than the corresponding ones for the Pt/alumina catalyst, due to the lower activity of Rh/alumina for the SCR of NO (Fig. 4a). These temperatures, however, were appropriate for ensuring 'differential' kinetic measurements.

The NO reduction, C_3H_6 oxidation and N_2 selectivity curves that were recorded as functions of the concentration of each of the reactants NO, O_2 and C_3H_6, were found to follow qualitatively the same trends that were observed for Pt/alumina (as shown in Fig. 6a, 7a and 8a, respectively). Thus the selectivity to N_2 was found to increase with increasing NO or C_3H_6 concentration or with decreasing O_2 concentration. The effect of varying NO, O_2 and C_3H_6 concentration on the NO reduction and C_3H_6 oxidation activity of Rh/alumina was compiled in Fig. 9a, 9b and 9c, respectively. The observed reaction orders were distinctly different from those of Pt/alumina in every case. The corresponding

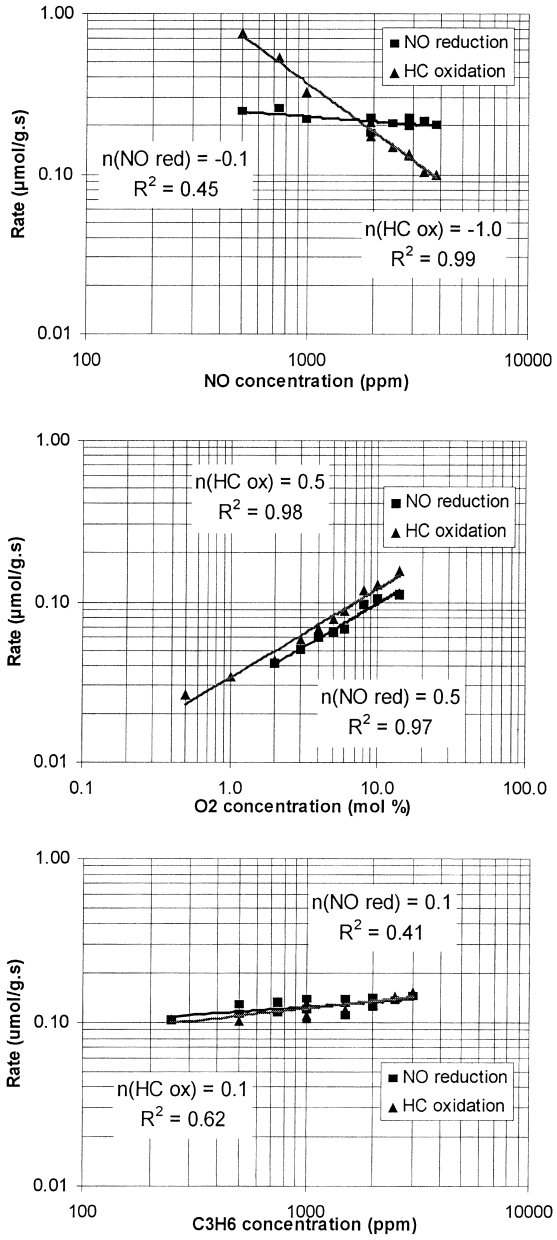

Fig. 9. (a) NO concentration effect on NO reduction and C_3H_6 oxidation on Rh/alumina. Conditions: 250–4000 ppm NO, 0.1% C_3H_6, 5.0% O_2, $W/F = 0.018$ g s/cc, $T = 274 \pm 1^\circ$C. (b) O_2 concentration effect on NO reduction and C_3H_6 oxidation on Rh/alumina. Conditions: 0.1% NO, 0.1% C_3H_6, 0.5–14.0% O_2, $W/F = 0.018$ g s/cc, $T = 272 \pm 1^\circ$C. (c) C_3H_6 concentration effect on NO reduction and C_3H_6 oxidation on Rh/alumina. Conditions: 0.1% NO, 250–3000 ppm C_3H_6, 5.0% O_2, $W/F = 0.018$ g s/cc, $T = 274 \pm 1^\circ$C.

rate expressions for the low-T activity of Rh/alumina were:

$$r(\text{NO red}) = k_{\text{red}}[O_2]^{0.5} \quad (4)$$

$$r(C_3H_6\,\text{ox}) = k_{\text{ox}}\frac{[O_2]^{0.5}}{[NO]} \quad (5)$$

and for the oxidation of C_3H_6 in the absence of NO (C_3H_6 combustion) on Rh/alumina, the kinetic results for which were obtained at 243–245 ± 1°C:

$$r(C_3H_6\ \text{comb}) = k_{\text{comb}}[O_2]^{0.5} \quad (6)$$

It is particularly interesting to note that the low-T kinetic expression for the reduction of NO appears to be essentially identical to that for C_3H_6 combustion (keeping in mind that the two sets of experiments were performed at temperatures different by ca. 30°C). The same observation was true for the Pt/alumina catalyst. Furthermore, these kinetic expressions appear to be dependent on O_2 concentration only (zero-order dependence on the reductant). In general the kinetic expressions for Pt/alumina and Rh/alumina appear to be related to each other: the expressions for the latter could be derived from the corresponding ones of the former by subtracting a half-order dependence on NO and O_2 and adding a half-order dependence on C_3H_6. Such an observation might lead to the hypothesis that the mechanisms of SCR on these two catalysts are possibly interrelated.

4. Discussion

As already noted, relatively conflicting hypotheses for the mechanism of SCR of NO on Pt-supported catalysts have been proposed in the literature [9–12]. In an insightful work, Burch et al. [9,10] supported a dissociative mechanism for NO reduction on Pt/alumina. This involves the dissociative chemisorption of NO on reduced Pt sites, followed by recombination of two neighboring Pt-N species (release of N_2) or Pt-N and Pt-NO species (release of N_2O). The formation of reduced Pt sites by reaction of oxidized Pt with the reductant was proposed as the rate-determining step of the process. On the other hand, the detailed kinetic study performed by Amiridis and coworkers on Pt/alumina [11] and Pt/silica [12] seems to favor the direct involvement of the reductant C_3H_6 in the reduction, through the reaction of an activated-hydrocarbon intermediate with activated NO. This hypothesis appears to be supported by various other investigating groups as well, for both Rh/alumina [13,14] and Pt-supported catalysts [15,16]. Based on spectroscopic investigations, various activated intermediates have been proposed to be apparently linked with the NO reduction activity, such as isocyanate (–NCO) species [13,14], or organic nitro (R-NO_2) or nitrite (R-ONO) species [15]. The formation of N_2 (or N_2O) has been visualized to take place through the reaction of these intermediate species with adsorbed NO [11–14] or, possibly, with activated NO in the form of NO_2 [15,16].

Analysis of the kinetic results of this study on both Pt/alumina and Rh/alumina indicated the practically identical low-T kinetic expressions for NO reduction and C_3H_6 combustion. In addition, the almost coinciding low-T activities and essentially equal activation energies for NO reduction and C_3H_6 oxidation clearly indicate that the reduction of NO is directly linked with the activation of the reductant. At temperatures lower than that of max. NO conversion, a temperature increase would facilitate activation of the reductant (direct NO reduction mechanism), or of the active sites by their reduction (NO decomposition mechanism), thus enhancing NO reduction. At higher temperatures, however, the limited availability of the reductant due to rapid combustion would naturally result in a decline in NO reduction.

The zero-order dependence of NO reduction on the concentration of NO for Pt/alumina Eq. (1) and Rh/alumina Eq. (4) could imply the non-participation of NO in the rate-determining step of NO reduction, in agreement with the previously described NO decomposition mechanism [9,10]. However, it would also be consistent with the direct NO reduction mechanism, provided that the rate-determining step is the formation of the activated N-containing intermediate (–NCO species, for instance), rather than the decomposition of such species by reaction with another adsorbed NO-type molecule. In the latter case the concentration of NO should then appear in the low-T kinetic expression.

The rate expression for the oxidation of C_3H_6 in the presence of NO Eq. (2) was found to differ from the other two rate expressions Eq. (1) and (3) by a nega-

tive half-order term with respect to NO. This negative dependence in NO can be interpreted by inhibition of reductant oxidation due to the presence of strongly-(and apparently dissociatively-) adsorbed NO. This was indeed observed to be the case, since the presence of NO was found to cause a significant upshift in the activity curve for C_3H_6 oxidation. The same behavior was obtained for Rh/alumina (Fig. 6), yet the dependence on NO was found to be of first order for this catalyst (Eq. (5)). The difference between these reaction orders seems to be qualitatively well-correlated with the substantially higher concentration of nitrosonium species on Rh/alumina ($Rh\text{-}NO^+$) in comparison to Pt/alumina, where enhanced NO dissociation was found to favor the presence of N-type species (i.e. –NCO, –CN) [13].

The negative half-order dependence on C_3H_6 concentration observed for all three rate expressions of Pt/alumina (Eq. (1)–(3)) appears to indicate activation of the reductant by dissociative adsorption, possibly leaving strongly-adsorbed fragments of the reductant on the active sites. At low temperatures reductant activation would be kinetically-limited. Therefore, increased formation of such strongly-adsorbed fragments by increasing reductant concentration would practically lead to a poisoning phenomenon, as clearly shown in this work (Fig. 8a) as well as elsewhere [11]. At higher temperatures, however, removal of these fragments would be expected to proceed rather quickly due to oxidation (combustion). Thus, under such conditions a zero- or positive-order dependence on the concentration of the reductant would be predicted. Consequently, the temperature window for enhanced NO reduction, as well as the influence of the reductant concentration, even under conditions of large excess of oxygen, would depend strongly on the type and adsorption behavior of the reductant.

The first-order dependence of NO reduction and C_3H_6 oxidation on O_2 for Pt/alumina could seem quite unexpected. A half-order dependence, signifying activation of oxygen by dissociative adsorption, would seem more reasonable. Certainly the possibility of direct participation of O_2 from the gas phase in the activation of the reductant or the removal of carbonaceous deposits cannot be disregarded. Other studies examining the effect of oxygen on the NO reduction activity of Pt/alumina [11] and Pt/silica [12] have indicated a maximum in the conversion of NO with O_2 for both intermediate and high temperatures. Interestingly, the location of the maximum NO reduction with respect to O_2 concentration was found to be a function of reaction temperature, being shifted to higher oxygen concentrations with decreasing temperature. In fact it was coincident with the point of complete oxidation of the reductant and not related to the stoichiometric oxygen concentration, as it might have been assumed [11,12]. This behavior was interpreted in terms of two opposing functions of oxygen on this reaction system: a positive contribution by activating the reductant (more evident at lower temperatures), and a negative effect of competing with NO for oxidizing the reductant (dominant at higher temperatures) [11,12].

The observed monotonic increase in both NO reduction and C_3H_6 oxidation with oxygen would at first sight seem to be in contradiction to the above. This result, however, was obtained at quite low temperatures, in order to ensure a 'differential' kinetic behavior. Reductant oxidation was, therefore, kept at low conversions (and certainly way below 100% completion) throughout the examined range of oxygen concentration (up to 12.0% O_2). Consequently, at low temperatures, even under excess O_2, the reductant was selectively oxidized by NO. Thus, there was no significant competitive oxidation to lead to a poisoning effect of oxygen on the NO reduction activity.

Based on the above considerations, it is evident that the observed dependence of the catalytic reduction of NO for Pt/alumina on varying NO or C_3H_6 concentration cannot undisputedly identify whether the applicable mechanism under the given conditions is based on the indirect role of the reductant in reducing the catalyst [9,10] or on the direct oxidative activation of the reductant by either activated NO or oxygen [11–16]. In fact, since both types of mechanisms involve activation of NO by dissociative adsorption at low temperatures, it would rather seem that both types of mechanistic steps are applicable. The relative strength of one over the other apparently depends on the particular state of the catalyst and the reaction conditions (temperature and reactant concentration) [9].

The first-order dependence of NO reduction on oxygen at low temperatures obtained in this study (Fig. 7a,b) appears to support the hypothesis of reactivating the catalyst active sites by removing hydrocarbon fragments formed due to strong reductant adsorption on Pt. This interpretation, along with the relatively

lower values for the apparent activation energies on Pt/alumina with respect to those on Rh/alumina, appear to more likely favor the catalyst reduction mechanism. The formation of reduced ensembles of active sites is the key step, followed by dissociative adsorption of NO and recombination of the activated N-type species to form either N_2 or N_2O.

On the other hand, the kinetic results obtained for Rh/alumina were found to be qualitatively similar yet quantitatively different to those for Pt/alumina. The absence of a kinetic term for the reductant in all kinetic expressions (Eq. (4)–(6)) is a clear indication that Rh appears to have a lower affinity for the reductant in comparison to Pt. Thus, activation of the reductant would be considered as a more critical kinetic step in the NO reduction mechanism. This reductant activation seems to take place via its partial oxidation by activated (dissociatively adsorbed) oxygen, resulting in the observed half-order dependence of all three rate expressions on oxygen. Additionally, the higher apparent activation energies obtained for Rh/alumina in contrast to Pt/alumina would seem to favor a more complicated mechanistic scheme, involving formation of an activated intermediate species.

Therefore, the obtained kinetic results on Rh/alumina appear to rather support the hypothesis of the low-temperature activation of the reductant by its partial oxidation. Then, interaction with adsorbed (either dissociatively or molecularly) NO to form an activated intermediate of type $C_xH_yO_zN$ would follow. The last step would involve decomposition of this intermediate by reaction with another activated NO-species, yielding N_2 (or N_2O) and combustion products.

It should be stressed at this point that the above mechanistic hypotheses are applicable for the particular catalytic systems and for the given set of conditions, in terms of low temperature and excess of oxygen. In fact, the two suggested mechanistic schemes seem to coexist on the examined catalysts. The relative affinity of the active sites for each of the reactants (which appears to be a strong function of temperature) is the most critical parameter in determining their relative applicability for low temperature NO reduction. It could be visualized that, upon activating Rh to lower temperatures, a more Pt-like behavior would be predicted to apply, resulting in an increasing activation of NO with respect to oxygen. This activation could lead to higher concentrations of N-type species on the catalyst sites, resulting in increasing probability of their recombination to form N_2 (or N_2O, depending on the relative stability of molecular vs. dissociated NO on the catalyst surface). Inversely, by lowering the activity of Pt (i.e. shifting the reaction window to higher temperatures), a more Rh-like performance could be expected. The higher activation of oxygen would tend to limit the direct decomposition of NO and to favor the reduction of NO by an activated (probably by partial oxidation) reductant species.

5. Conclusions

Summarizing the observations and arguments presented above, the low-temperature kinetic expressions for NO reduction and C_3H_6 oxidation in the presence and absence of NO on Pt/alumina and Rh/alumina, and their catalytic performance for the SCR of NO, have shown qualitative similarities as well as quantitative differences.

The low-temperature kinetics of NO reduction on Pt/alumina appears to be consistent with a mechanistic scheme based on the indirect participation of the reductant in the reduction process, through reduction of ensembles of active sites as the most critical (rate-determining) step. This results in dissociative adsorption of NO on the reduced Pt sites, followed by recombination of Pt-N species (formation of N_2) or of Pt-N and Pt-NO species (formation of N_2O). The strong affinity of Pt for the reductant appears to result in the formation of strongly-bound reductant fragments on the catalyst surface, apparently inhibiting the adsorption of NO. The critical role of oxygen in this case would seem to be the reactivation of the catalytic sites by oxidation of these fragments.

On the other hand, the low-temperature SCR performance of Rh/alumina could be interpreted by assuming another mechanistic scheme, based on the direct participation of the reductant in the reduction process by forming an activated intermediate species as the rate-determining step. Further interaction of this intermediate with activated (dissociatively- or molecularly-adsorbed) NO would result in its decomposition, yielding N_2 (and possibly N_2O). In this case the important role of oxygen would be to activate the reductant (apparently by partial oxidation).

The two described mechanistic hypotheses show many qualitative similarities so that they could be

visualized as being complementary, and therefore, they can essentially both be applicable for the SCR of NO on the examined catalysts. The extent of their applicability seems to be determined by the relative affinity of each catalyst for low-temperature activation of each of the reactants. As a consequence of this hypothesis, this relative affinity of a catalytic site and its ability to selectively activate NO would seem to be a critical parameter for producing superior catalyst performance for the low-temperature SCR of NO.

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