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The selective catalytic reduction of nitric oxide by propylene over Pt/SiO_2

Dinyar K. Captain, Kenneth L. Roberts[1], Michael D. Amiridis*

Department of Chemical Engineering, The University of South Carolina, Columbia, SC 29208, USA

Abstract

Kinetic and in situ infrared measurements were utilized in the investigation of the selective catalytic reduction (SCR) of nitric oxide (NO) by propylene (C_3H_6) over a Pt/SiO_2 catalyst. The results of these studies indicate the presence of two kinetically distinct regions at temperatures above and below the temperature of maximum NO reduction. They further suggest that the activation of the hydrocarbon by molecular oxygen is the kinetically significant step in the low temperature region. Similar results were previously obtained with a Pt/Al_2O_3 catalyst, suggesting that the mechanism of the reaction is the same in both cases. The in situ infrared spectra of these two catalysts indicate the presence of surface isocyanate and cyanide groups in both cases, suggesting that one or both of these species may be involved in the reaction. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Selective catalytic reduction; NO; Propylene; Platinum

1. Introduction

The selective catalytic reduction of nitric oxide by ammonia (NH_3-SCR) over vanadia-based catalysts and the non-selective reduction of NO by carbon monoxide (CO) and unburned hydrocarbons over noble metal-based three-way catalysts, are currently used for the control of NO_x emissions from stationary and mobile sources, respectively. The potential use of hydrocarbons as reducing agents in the selective catalytic reduction of NO (hydrocarbon-SCR) has certain advantages over both processes [1,2], and this is why this reaction has received considerable attention since it was first introduced in 1991 [3,4].

Cu-containing ion exchanged zeolites, and in particular Cu-ZSM-5, have been studied extensively as potential hydrocarbon-SCR catalysts due to their high initial activity [2]. The commercial application of these catalysts, however, is problematic because of their low hydrothermal stability [5], hydrocarbon slip and undesirable selectivities towards CO [5–8], and lower activity in the presence of H_2O and SO_2 [4,9].

Supported noble metals, and in particular platinum-based catalysts, are also active for hydrocarbon-SCR but at lower temperatures [10–14], and are not significantly affected by the presence of H_2O in the exhaust stream [11,13,15]. These catalysts are not without their limitations, in that they exhibit a narrow temperature window of operation [10–14] and show

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*Corresponding author. Fax: +1 803 777 8265; e-mail: amiridis@sun.che.sc.edu

[1] Current address: Department of Chemical Engineering, North Carolina A&T University, Greensboro, NC 27411, USA.

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significant selectivities towards N_2O [11–14,16], which is considered a "greenhouse-effect" gas [17].

Given the commercial potential of platinum-based hydrocarbon-SCR catalysts, more attention has recently been focused on their performance [12–14,18–26]. Still, however, a clear understanding of the fundamental surface chemistry involved in this reaction has not been developed. This is in part due to the lack of in situ spectroscopic measurements to complement the plethora of the available activity data. On the contrary, in situ infrared spectroscopy has been frequently used in the past to study the performance of platinum-based catalysts for the non-selective reduction of NO by CO [27–32]. These studies are relevant to hydrocarbon-SCR since the same surface species may be involved in both reactions. More recently, Bamwenda et al. [19,33] have used infrared spectroscopy to study the reduction of NO by propylene over supported noble metals, but only briefly examined platinum-based catalysts.

In our effort to develop a clear understanding of the surface chemistry involved in hydrocarbon-SCR when platinum-based catalysts are used, we have been combining detailed kinetic and in situ infrared measurements. Previously, we have reported the results of these studies for an alumina-supported platinum catalyst [14,34]. In this work, we report results obtained with a silica-supported catalyst and compare them to our previous work.

2. Experimental

The catalysts utilized in this study were prepared by incipient wetness of hydrogen hexachloroplatinum hydrate ($H_2PtC_{16}\times4H_2O$ – Aldrich Chemical) onto the silica (Davison Syloid 74) and γ-alumina (Vista Chemical) supports. Prior to impregnation the supports were calcined overnight at 500°C in air. Following impregnation the catalysts were dried under vacuum at 120°C for 2 h and then calcined in air for 5 h at 500°C. The calcined Pt/SiO_2 catalyst had a BET surface area of 280 m^2/g, a Pt loading of 0.9 wt% (ICP-Galbraith Laboratories), and a Pt dispersion of 35% (determined via hydrogen chemisorption). The Pt/Al_2O_3 catalyst had a BET surface area of 150 m^2/g, a Pt loading of 0.8 wt%, and the Pt was fully dispersed on the alumina support.

Kinetic experiments were carried out in a stainless steel, single pass, fixed bed, flow reactor. Certified analyzed mixtures of 1.0% NO in He, 1.0% C_3H_6 in He, 10.0% O_2 in He and a 99.9999% He carrier gas were used to prepare the reacting mixture. Gases were mixed at the appropriate amounts (by the use of a system of needle valves and flow meters) and preheated prior to introduction to the reactor. The volumetric flow rate of the reacting mixture was held constant at 200 cm^3/min. Prior to the kinetic measurements the catalyst was calcined in situ at 500°C for 1 h in a 5% O_2 in He mixture.

Both inlet and outlet gas mixtures were analyzed using a gas chromatograph (Hewlett-Packard 5890) equipped with a thermal conductivity detector and a three-column system (Molecular Sieve 5A, Porapak Q, and Graphpac GC) for analysis of N_2, N_2O, CO, CO_2, and C_3H_6. Calibration curves were obtained for each of these species, and the reproducibility of the measurements in each case was within ±5%. Since no direct measurements of the NO concentration were made, NO conversions were calculated based on the amounts of N_2 and N_2O measured in the outlet stream and the amount of NO introduced in the inlet stream. A thermocouple placed in the catalyst bed was used to monitor the temperature of the catalyst. Each run utilized approximately 100 mg of the Pt/SiO_2 catalyst in the form of 60/85 mesh particles. "Blank" experiments were performed with the empty reactor and did not result in any measurable NO reduction in the temperature range examined. Similarly, no significant propylene oxidation was observed in the "blank" runs at temperatures below 350°C.

Infrared spectra were collected with a Nicolet 740 FT-IR spectrometer equipped with an MCT-B detector. Transmission spectra were collected in the single beam mode with a resolution of 2 cm^{-1}. Reference spectra of the clean surfaces in flowing He were collected separately; difference spectra between the spectra of the samples and the corresponding references are shown herein. A stainless steel cell, with a 10 cm path length and NaCl windows cooled by flowing water was used. A heating element wrapped around the cell allowed collection of in situ spectra at 250°C. The temperature was monitored through a thermocouple located in the cell and in close proximity with the catalyst sample. Catalyst samples were prepared as self-supported wafers, 12 mm in diameter and with a thickness of about 20 mg/cm^2. Prior to each experiment the samples were calcined in situ at 250°C for 2 h in a 2% O_2 in He mixture. The reacting mixtures were prepared using the same gases utilized in the kinetic measurements.

3. Results and discussion

Temperature-activity profiles for the reduction of NO and the oxidation of C_3H_6 are shown in Fig. 1. For comparison purposes, results obtained previously [14] with a Pt/Al_2O_3 catalyst of similar Pt loading are also shown in the same figure. The NO reduction reaches a sharp maximum – characteristic of the presence of the two competing oxidation reactions of propylene with NO and O_2 – of approximately 65% at around 285°C. Both N_2 and N_2O were detected as products of NO reduction. Nitrogen selectivities ranged between 50% and 70% depending on the conditions.

Propylene oxidation starts at around 250°C and closely matches the NO reduction curve up to the temperature of maximum NO conversion. At approximately this point, propylene conversion reaches 100%. The catalyst oxidizes propylene completely to CO_2 and H_2O, and no traces of CO or other partial oxidation products or N-containing organics were observed within our detection limits (20 ppm). These results are very similar to the ones obtained with Pt/Al_2O_3, the only difference being that in the case of Pt/SiO_2 the maximum in NO conversion and the hydrocarbon light-off are reached at a slightly lower temperature.

As can be seen in Fig. 2, the presence of NO in the reacting gas mixture delays the activation of propylene by 40–50°C. We have reported similar results for other platinum-based catalysts, but the shift observed in the hydrocarbon light-off curve in this case is of smaller magnitude than what we have previously observed with Pt/Al_2O_3 and Pt supported on a dealuminated Y zeolite [13,14]. These results suggest that at low temperatures NO blocks the catalyst sites responsible for the oxidation of the hydrocarbon. The smaller shift in the case of Pt/SiO_2 is consistent with our infrared results, which show that smaller amounts of adsorbed NO_x species are present on the surface of this catalyst as compared to Pt/Al_2O_3.

The effect of the concentrations of NO and O_2 on SCR activity was examined next at the two temperature regions below and above the temperature of maximum NO reduction. The effect of NO concentration on the NO reduction rate is shown in Fig. 3. The

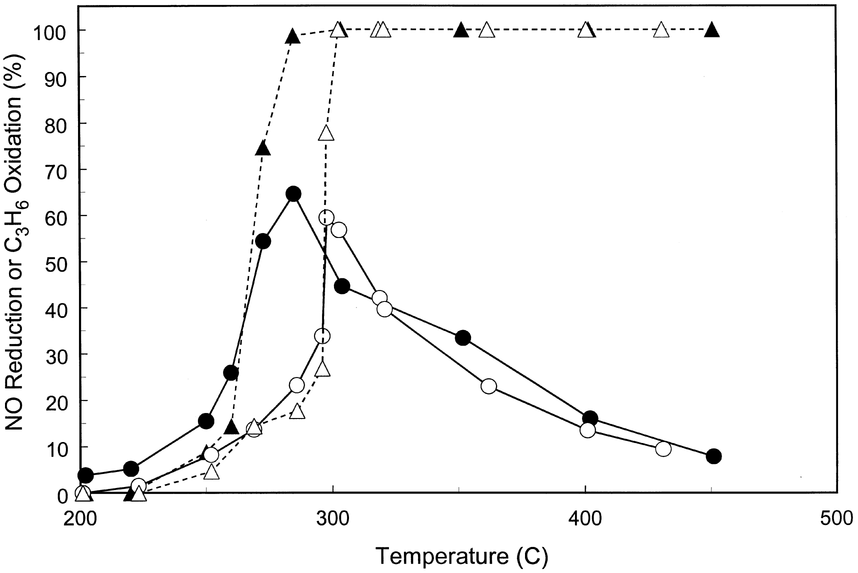

Fig. 1. NO reduction and C_3H_6 oxidation as functions of temperature for 0.8% Pt/Al_2O_3 (NO: ○, C_3H_6: △) and 0.9% Pt/SiO_2 (NO: ●, C_3H_6: ▲) catalysts (1000 ppm NO, 1000 ppm C_3H_6, 1% O_2).

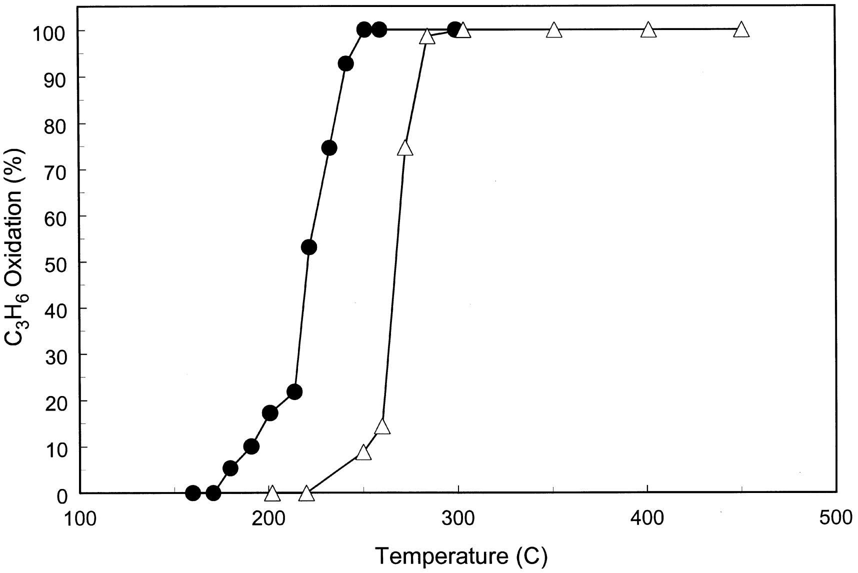

Fig. 2. C_3H_6 oxidation as a function of temperature in the absence and presence of NO (●: 1000 ppm C_3H_6, 1% O_2; △: 1000 ppm C_3H_6, 1% O_2, 1000 ppm NO).

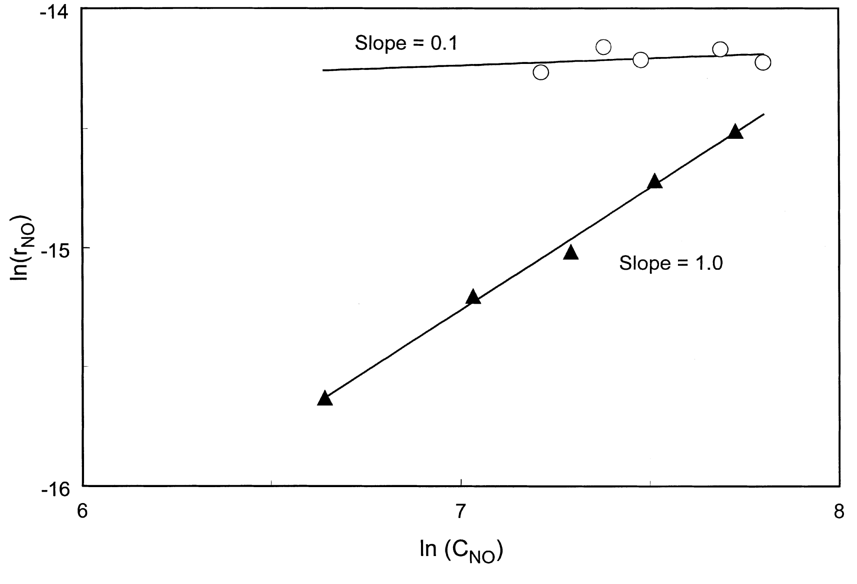

Fig. 3. Effect of NO concentration on the NO reduction rate (1000 ppm C_3H_6, 1% O_2; ○: 267°C, ▲: 402°C).

NO reduction rates shown in this figure were calculated from measurements of differential (i.e. below 30%) NO conversions, according to the following equation:

$$r_{NO} = F_{NO}x/m_{cat}, \quad (1)$$

where r_{NO} is the NO reduction rate (mol/g s), F_{NO} the molar feed rate of NO to the reactor (mol/s), x the fractional conversion of NO in the reactor, and m_{cat} is the mass of the catalyst in the reactor (g).

In the low temperature region (267°C) the rate of NO reduction is almost independent of the

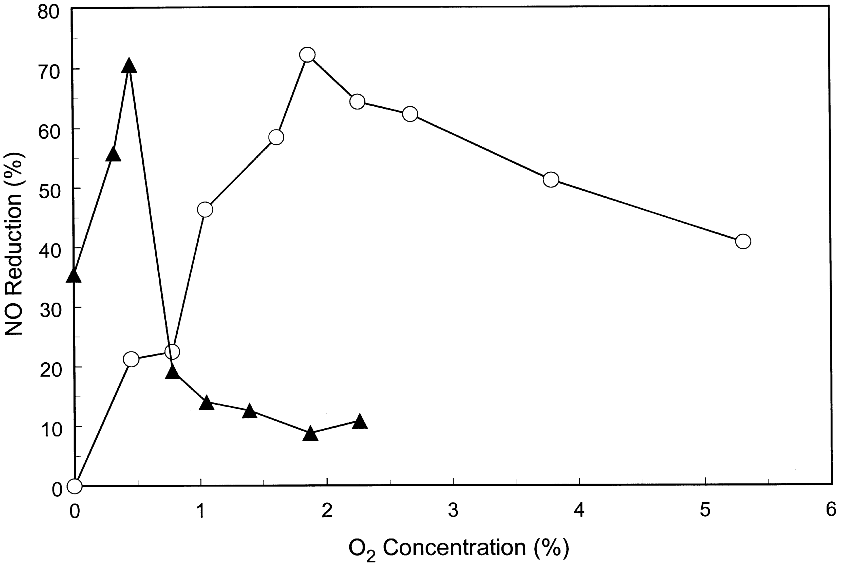

Fig. 4. Effect of O_2 concentration on NO reduction (1000 ppm NO, 1000 ppm C_3H_6; ○: 267°C, ▲: 402°C).

concentration of NO (approximately 0.1 order). On the contrary, the rate in this region is significantly affected by the concentration of oxygen (Fig. 4); at low oxygen concentrations the NO reduction increases with the oxygen concentration and reaches a maximum at approximately 2%. The corresponding hydrocarbon oxidation curve (Fig. 5) closely matches the ascending part of the NO reduction curve and reaches complete conversion at the point of maximum NO reduction. A further increase in O_2

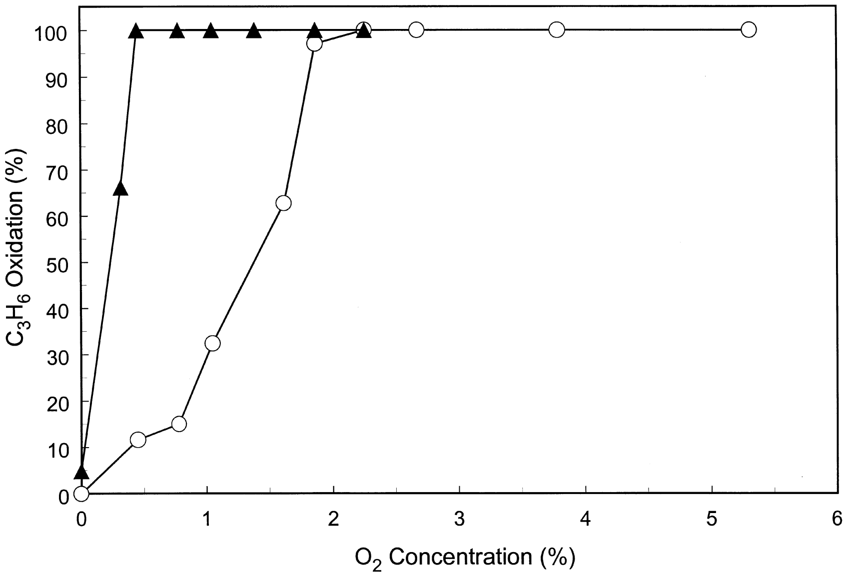

Fig. 5. Effect of O_2 concentration on C_3H_6 oxidation (1000 ppm NO, 1000 ppm C_3H_6; ○; 267°C, ▲: 402°C).

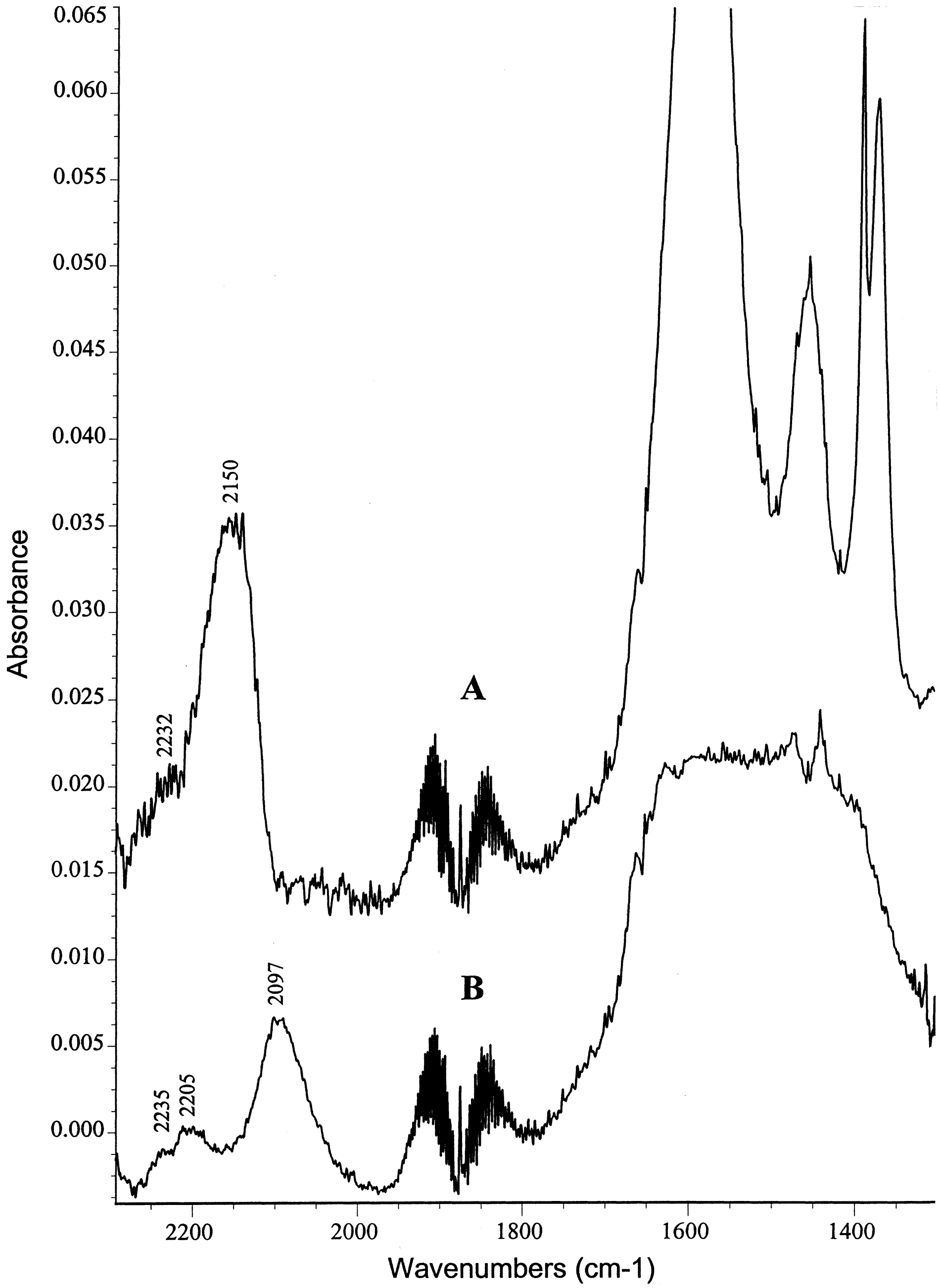

Fig. 6. In situ FTIR spectra of (a) 0.8% Pt/Al_2O_3 and (b) 0.9% Pt/SiO_2 catalysts at 250°C following exposure to a mixture of 2000 ppm NO, 2000 ppm C_3H_6 and 1% O_2 in He for 25 min.

concentration beyond the maximum results in the consumption of propylene via the non-selective C_3H_6–O_2 reaction, and therefore, a decrease in NO reduction.

At the high temperature region (402°C) the rate becomes first order with respect to NO. A maximum is again observed with oxygen concentration, but this time it is sharper and it occurs at lower oxygen levels

(0.5%). The corresponding hydrocarbon oxidation curve also rises sharply and, once again, reaches complete conversion at the point of maximum NO reduction. At this temperature region smaller amounts of oxygen are sufficient to fully activate the hydrocarbon. The NO–C_3H_6 reaction, however, becomes less selective, and a further increase in O_2 concentration strongly favors the C_3H_6–O_2 reaction, hence the sharp maximum observed.

Infrared spectra collected at 250°C under reaction conditions over the Pt/Al_2O_3 and Pt/SiO_2 catalysts are shown in Fig. 6. Both spectra show absorbance bands at 2150 and 2297 cm^{-1} – for Pt/Al_2O_3 and Pt/SiO_2, respectively – characteristic of surface cyanide groups, and poorly defined shoulders at 2235 cm^{-1} characteristic of surface isocyanate groups. The spectrum of the silica-supported catalyst further shows an additional peak at 2205 cm^{-1}, whose assignment is unclear at present. Finally, the spectrum of the alumina-supported catalyst shows significant amounts of adsorbed surface nitrates and carbonates, with characteristic peaks in the 1300–1700 cm^{-1} region. On the contrary, the spectrum of the silica-supported catalyst shows a lower intensity and very broad band in the same region. Our detailed infrared studies of the Pt/Al_2O_3 catalyst [34] suggest that the majority of the surface nitrates and carbonates are associated with the alumina support. Furthermore, the absence of the nitrates (as indicated by infrared spectra of the two catalysts following adsorption of NO) and the low surface concentration of the carbonates on the silica-supported catalyst do not have any effect on the catalytic activity of the two samples (Fig. 1), suggesting that these are spectator species which are not involved in the reaction.

Some useful information regarding the reaction mechanism can be extracted from the results of this study. The kinetic results clearly demonstrate the presence of two kinetically distinct regions at temperatures above and below the temperature of maximum NO reduction. In the lower temperature region the activation of the hydrocarbon appears to be the kinetically significant step. Such a claim is supported by the observed delay in the hydrocarbon light-off in the presence of NO, the close proximity of the ascending part of the NO reduction curves and the corresponding hydrocarbon oxidation curves, and the coupling between the points of maximum NO conversion and complete hydrocarbon oxidation. It has been proposed previously that NO_2 may be involved in the activation of the hydrocarbon (see [2] and references therein). The results presented in this study, however, appear to support the idea that over platinum-based catalysts the activation of the hydrocarbon is primarily done by molecular oxygen. The almost zero order dependence of the rate on the concentration of NO suggests that either the surface of the catalyst is saturated by the N-containing reactive intermediate (which is clearly not the case with the Pt/SiO_2 catalyst) or that the reaction between the hydrocarbon and the N-containing species (NO or NO_2) takes place after the kinetically significant step. Furthermore, if NO_2 was indeed involved in the activation of the hydrocarbon, one would expect a sharper maximum with oxygen concentration in the low rather than high temperature region, since the formation of NO_2 by the NO–O_2 reaction is favored at lower temperatures.

In the high temperature region the activation of the hydrocarbon is fast and its oxidation is complete. The kinetic results (first order with respect to NO) suggest that under these conditions the N-containing species (NO and/or NO_2) is involved in the kinetically significant step. This step is believed to be the reaction of the N-containing species with the activated hydrocarbon (or its fragments) and is in direct competition with the further reaction of the same hydrocarbon species with molecular oxygen.

4. Conclusions

Two kinetically distinct regions were observed with a Pt/SiO_2 catalyst for the selective catalytic reduction of NO by propylene at temperatures above and below the temperature of maximum NO reduction. The activation of the hydrocarbon by molecular oxygen is believed to be the kinetically significant step in the low temperature region giving rise to zero order kinetics with respect to NO. In the high temperature region the activation of the hydrocarbon is fast and NO (and/or NO_2) participates in the kinetically significant step resulting to first-order kinetics.

The activity and kinetic parameters of the Pt/SiO_2 catalyst are similar to those observed previously with a Pt/Al_2O_3 catalyst of comparable Pt loading, indicating that the reaction proceeds in both cases through the same mechanism. The observed maximum in NO reduction and the corresponding hydrocarbon light-off curve are slightly shifted towards lower temperatures in the case of Pt/SiO_2, suggesting a higher activity of this catalyst in the activation of the hydrocarbon. Given that the two catalysts had different Pt dispersions, it is not clear at this point if this effect is due to the support or the platinum morphology. In situ infrared spectra of the two catalysts indicate the presence of surface isocyanate and cyanide groups in both cases, suggesting that one or both of these species are involved in the reaction.

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