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Activity and temperature-programmed adsorption/desorption behavior of Pd–TiO_2 catalysts in NO/CH_4 reduction and NO decomposition reactions

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Abstract

Reduction and decomposition of nitric oxide using methane as a reducing agent has been studied in the presence and absence of oxygen over Pd/TiO_2 catalysts. Temperature-programmed adsorption/desorption and reduction/oxidation behavior has been examined. Prereduced catalysts have shown significant reduction as well as decomposition activity. Isotopic labelling studies using $^{13}CH_4$, $^{15}N^{18}O$, ^{15}NO, and $^{18}O_2$ have also been performed to investigate the interaction of NO and methane with the catalytic sites.

Keywords: Reduction; Nitric oxide; Pd/TiO_2 catalysts

1. Introduction

Hydrocarbons have recently attracted much attention as possible reducing agents for NO_x in exhaust streams from stationary sources. Use of hydrocarbons as reducing agents offers many advantages since problems associated with ammonia, such as salt formation and ammonia slip are not relevant for the hydrocarbons. Reduction with higher hydrocarbons such as C_2s and C_3s has been the subject of several recent studies [1-3]. Although methane is the most readily available hydrocarbon, the difficulty of activating this highly stable molecule continues to pose a challenge. Most of the work on NO reduction with methane has been on zeolite-based catalysts, including Co–ZSM-5, Ga–H–ZSM-5, Ga–H–Y [4,5], Cu–ZSM-5, Rh/ZSM-5, Pt/ZSM-5 [6], and Pd–ZSM-5 [7]. Although fewer in number, there have been studies focusing on non-zeolite catalysts for NO/CH_4 reaction as well. Among these catalysts are rare earth oxides [8], metal exchanged ferrites [9] and Rh/Al_2O_3 [10].

There is ample evidence in the literature that indicates that palladium can activate methane and form active methyl species on the surface. In this study we have investigated the interaction of CH_4–NO system with Pd on TiO_2 support. Direct decomposition of NO was also examined over these catalysts. Temperature-programmed adsorption/desorption and oxidation behavior has been investigated. These studies have been combined with our recent work where we have used isotopic labelling under steady-state and transient conditions [11] to elucidate a

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model for the catalytic steps taking place over Pd/TiO_2 surfaces.

2. Experimental

2.1. Catalyst preparation

Pd-acetate was used as the precursor for palladium on the catalyst. The promotion of TiO_2 was done using a wet impregnation technique. The catalyst slurry was then dried overnight in an oven at 95°C followed by calcination at 500°C in oxygen flow. The surface area of the catalyst was measured using the BET technique with a Micromeritics 2100E Accusorb instrument. The catalysts were reduced in situ at 200°C in hydrogen for 30 min prior to reaction.

2.2. Temperature-programmed characterization

The TPR/TPD system used for these studies has been described previously [12]. A U-shaped quartz sample cell was used which measured 6 mm o.d. by 4 mm i.d. The cell was heated by a furnace (TECO Model F-6-1100-VH-2-SR), which was mounted on a height-adjustable lab lift. A chromel–alumel type-K thermocouple (Omega) was used for temperature reading. The temperature was controlled and displayed by TECO-Sigma temperature controller. Products were analyzed by a thermal conductivity detector (TCD), a gas chromatograph-mass spectrometer (Hewlett-Packard, MS Engine, 5989A) or both.

Prior to all the experiments the catalyst was calcined in situ in O_2 flow at 500°C for 2 h. This is to ensure that all the carbonaceous species deposited on the surface because of exposure to ambient air are oxidized. Subsequently the surface was cleaned by evacuation at 200°C for 2 h. This was followed by adsorption of the adsorbate gas at room temperature for 2 h. The catalyst surface was then flushed with He for another hour at room temperature before starting the temperature program.

2.3. $NO + CH_4 + O_2$ reaction experiments

The system used for reaction studies has been described previously [13]. The feed gases consisted of 0.5% NO in He (Linde), 10% CH_4 in He (Matheson), 10% O_2 in He (Linde), and He (Linde). The catalytic reduction reaction of nitric oxide was performed using a feed mixture consisting of 2000 ppm of NO and oxygen concentrations of 1200 and 3000 ppm. CH_4 to NO ratio was maintained at 11. The reaction temperature was 500°C. The weight of the catalyst was maintained at 75 mg. The catalyst was reduced in situ at 200°C in hydrogen stream for 30 min and then flushed with helium for 1 h at 200°C prior to the reaction. The total flowrate of the feed mixture was around 60 cc/min. Blank reactor runs were also performed over quartz wool bed. The feed and product analyses were done using a combination of gas chromatography, mass spectrometry, chemiluminescence, and wet chemistry techniques.

2.4. NO decomposition experiments

The NO decomposition reaction was also performed over a reduced catalyst as in the steady-state reactions. The feed mixture contained 2335 ppm of NO with balance being helium. The decomposition reaction was carried out at 500°C. The flowrate was maintained at 60 cc/min.

2.5. Temperature-programmed oxidation

Temperature-programmed oxidation was performed over Pd/TiO_2 catalysts. The catalyst was calcined in situ before the experiment. The surface was cleaned further by evacuation at 200°C. After the evacuation step the catalyst was reduced in a stream of hydrogen at 200°C for 30 min followed by flushing with He for 1 h at 200°C. The catalyst was cooled to room temperature. The reduced catalyst was then oxidized as a function of temperature in 1% NO flow at 50 cc/min. The temperature of the catalyst was raised from 25°C to 600°C at a rate of 5°C/min and held at 600°C for 30 min. The effluent products were monitored with a mass spectrometer. The weight of the catalyst was 200 mg.

3. Results and discussion

The promotion of the catalyst by Pd had significantly altered the nature of the surface. Experiments examining temperature-programmed desorption (TPD) of methane and nitric oxide were performed by combining a thermal conductivity detector and a mass spectrometer in series. Desorption profiles obtained following NO adsorption are presented in Fig. 1. NO was seen to adsorb both reversibly and irreversibly over the Pd/TiO_2 surface. There were two unresolved desorption features observed for NO profile below 500°C. N_2O desorption profile had three main features. The first feature was at fairly low temperatures below 200°C. The second feature was a broad unresolved peak which ranged from 400 to 500°C.

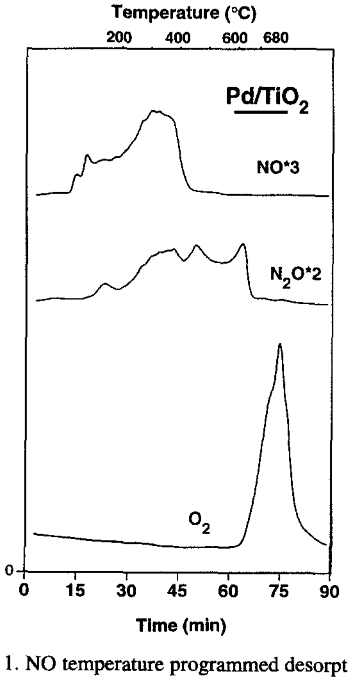

Fig. 1. NO temperature programmed desorption.

The third high temperature feature was observed at around 650°C. One of the most important observations was a strong desorption peak for oxygen at 680°C.

Significant differences were observed when a similar TPD experiment was performed on the bare TiO_2 support. The only species that desorbed from the surface was nitric oxide. The desorption maximum was around 600°C [14]. This result indicates that the irreversible adsorption of NO is associated with the Pd sites.

The other major difference observed was the absence of any oxygen peaks during NO TPD over TiO_2. This clearly indicates that the oxygen associated with palladium on the surface is more mobile or more accessible than oxygen on titania. The absence of a high temperature NO desorption peak around 600°C over Pd/TiO_2 (similar to that observed on TiO_2) indicates that the sites available for NO adsorption on titania are completely blocked after promotion with palladium.

Methane TPD experiments were also performed over Pd/TiO_2 and bare TiO_2 support (Fig. 2). Carbon dioxide, methane and oxygen desorption profiles were observed over Pd/TiO_2 catalyst. Since the catalyst was calcined in situ in oxygen flow at 500°C prior to the experiment, it can safely be assumed that the CO_2 profiles are from the adsorbed methane reacting with the surface. There were three unresolved features in the CO_2 desorption profile. The low temperature feature was around 200°C. The second peak was broad and ranged from 400 to 500°C. The third feature was in the high temperature range around 600°C. There was only one peak observed for methane desorption around 450°C. The other important observation was the occurrence of a strong O_2 peak at 680°C similar to that observed in nitric oxide TPD. This again confirms the fact that the oxygen associated with palladium on the surface of the catalyst is very mobile irrespective of the gas adsorbed.

NO and CH_4 TPD studies showed that the supported Pd catalyst was capable of adsorbing

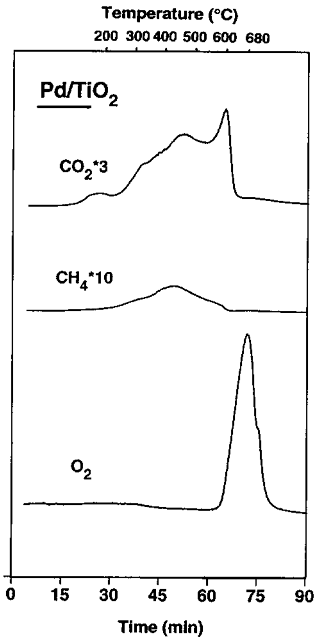

Fig. 2. CH_4 temperature programmed desorption.

both methane and nitric oxide and was able to convert CH_4 to CO_2 and NO to N_2O.

A similar TPD experiment performed after exposing the bare TiO_2 support surfaces to CH_4 at room temperature showed no desorption features of methane or any other oxidation products. This indicates that it is the palladium that has the essential surface sites for methane adsorption and activation.

Steady-state reactions over Pd/TiO_2 have indicated almost 100% conversion of NO with a very high selectivity for nitrogen (Table 1). The selectivity towards nitrogen was seen to decrease with the increase in oxygen concentration. Nonnegligible amounts of ammonia formation were also observed. No nitrous oxide was detected in the product stream in the presence of oxygen in the feed. The methane conversion increased with increase in oxygen concentration in the feed stream. The selectivity towards carbon monoxide was seen to increase with increase in oxygen concentration in feed. These results have demonstrated that Pd/TiO_2 can be a viable catalyst for NO reduction with methane in the presence of oxygen.

Table 1
$NO + CH_4 + O_2$ reaction results (NO conc. = 2000 ppm, $CH_4/NO = 11$, temperature = 500°C)

O_2 conc. (ppm)	C_{NO} (%)	C_{CH4} (%)	S_{N2} (%)	S_{N2O} (%)	S_{NH3} (%)	S_{CO2} (%)	S_{CO} (%)
1200	> 99	9.27	95.1	0	4.9	80.4	19.6
3000	> 99	19.40	92.1	0	7.9	73.3	26.7

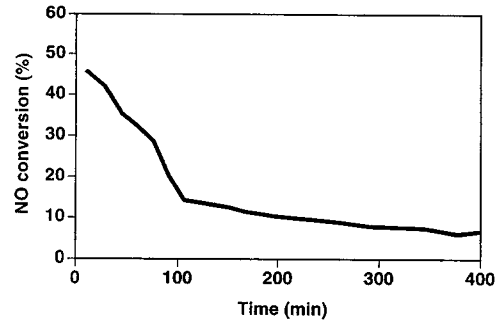

Fig. 3. NO conversion in NO decomposition.

A set of experiments were also performed examining the NO decomposition behavior of these catalysts. Prior to the decomposition experiments, the catalyst was pretreated with hydrogen at 200°C for half an hour and then flushed with helium for 1 h at the same temperature. The feed stream consisted of 2335 ppm of NO with the balance being helium. The reaction temperature was maintained at 500°C. The NO conversion was seen to decline from 47% to around 12% within the first 100 min after the beginning of the reaction (Fig. 3). The activity remained steady at around 8–9% for 24 h. N_2

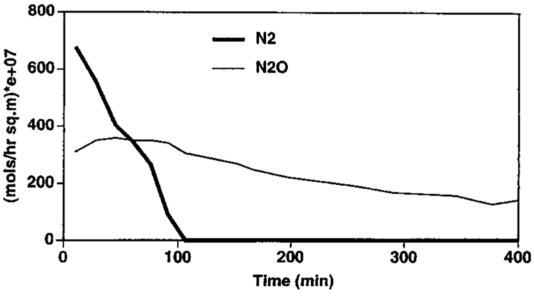

Fig. 4. N_2 and N_2O production rates in NO decomposition.

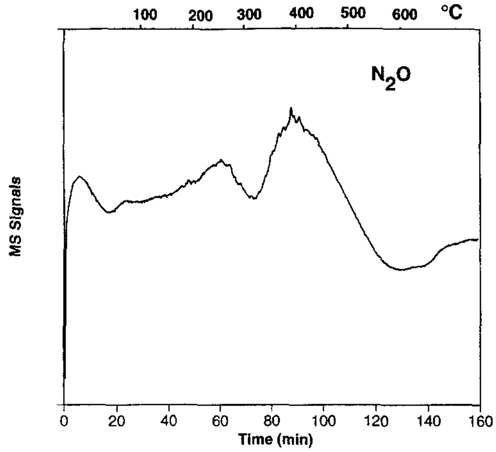

Fig. 5. Temperature programmed oxidation with NO.

production rate went down from around 70 μmol h^{-1} m^{-2} to almost zero in 100 min. N_2O production rate went through an "S" shaped curve as a function of time (Fig. 4).

These results indicate that a highly reduced catalyst promotes NO decomposition to N_2. As the surface gets oxidized with the O atom from NO, the selectivity towards N_2O increases. These results are complimented by our isotopic tracer studies in which we have seen a slow rise in N_2O formation when the feed stream of $^{13}CH_4 + NO$ was switched to NO maintaining the same space velocity.

Temperature-programmed oxidation of reduced TiO_2 with nitric oxide has also given some relevant information regarding the mechanism of the CH_4–NO reaction on the Pd/TiO_2 surface (see Fig. 5). Nitrous oxide was the only product observed in the TPO profiles. There were two prominent features observed in this experiment. The low-temperature feature was around 270°C and the second high temperature feature observed was around 400°C. As the temperature slowly increased, nitric oxide oxidized the surface and hence the only product obtained was N_2O.

Isotopic labelling studies performed under steady-state or transient conditions provided additional clues about the interaction of NO and CH_4 with the catalyst surface [11]. The NO–CH_4 reaction was investigated by observing the carbon oxide transients (CO and CO_2) in switches such as $^{13}CH_4 + NO \rightarrow NO$, and $^{13}CH_4 \rightarrow NO$. It was clearly seen that $^{13}CO_2$ profile relaxed more slowly as compared to ^{13}CO, suggesting that the intermediates responsible for $^{13}CO_2$ formation resided on the surface for a longer time. The difference in the relaxation profiles of ^{13}CO and $^{13}CO_2$ also indicates that there are at least two types of sites available for methane adsorption. It was also observed that CH_4 can be activated over prereduced Pd–TiO_2 catalysts in the absence of NO, forming stable carbonaceous surface species, that need the presence of an oxidizing agent such as NO or O_2 to oxidize and desorb.

The NO–CH_4 interaction was also investigated by observing nitrogen and nitrous oxide transients in switches such as $CH_4 + {}^{15}NO \rightarrow CH_4$ and $^{13}CH_4 + NO \rightarrow He$. A comparison of the surface residence times showed that the surface species that lead to N_2 formation appear to be short-lived, whereas N_2O forms through some stable surface intermediates. These intermediates can desorb spontaneously to give N_2O even when there is no reducing agent present. However, the presence of carbon species appear to enhance the desorption rate [11].

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