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Kinetic studies of selective catalytic reduction of nitric oxide by propylene on Pt/MCM-41 catalyst

S.-C. Shen, S. Kawi*

Department of Chemical and Environmental Engineering, National University of Singapore,
10 Kent Ridge Crescent, Singapore 119260, Singapore

Abstract

Reaction kinetics for selective catalytic reduction (SCR) of nitric oxide (NO) over 1% Pt/MCM-41 catalyst has been investigated at temperatures ranging 150–500°C under steady and transient state conditions. The reduction of NO is found to be promoted by a small amount of oxygen when the concentration of oxygen is less than that of the critical oxygen concentration required for stoichiometric oxidation of C_3H_6. Above the critical oxygen concentration, an optimal reaction temperature for optimal NO conversion is observed and the optimal NO conversion decreases with the increase of oxygen concentration. Two distinct kinetic regions are observed: one at the reaction temperature below and the other one above that required for optimal NO conversion. The NO reduction rate is suggested to be controlled by the activation rate of C_3H_6 at low temperatures and by the external diffusion rate of reactants at high temperatures. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Kinetic; De-NO_x; SCR; Supported platinum; MCM-41

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1. Introduction

Selective catalytic reduction of NO_x ($NO + NO_2$) by hydrocarbon (HC-SCR) is a challenging subject that has attracted much attention in recent years due to its importance for emission control applications. Ever since Iwamoto et al. [1,2] reported that transition metal ion exchanged zeolites, in particular Cu-ZSM-5, showed high HC-SCR activity, a number of work has been published reporting the catalytic behavior of those catalysts [3–8]. However, due to the poor hydrothermal stability and low activity of transition metal ion exchange zeolites in the presence of H_2O and SO_2, they are unlikely to be practical catalysts for lean NO_x abatement.

Continuing the search for the suitable HC-SCR catalyst, Pt-based catalysts were then found to be more active than Cu-ZSM-5 at low temperatures and stable in real diesel exhaust [9–11]. Since Pt supported catalysts showed high resistance to SO_2 and H_2O vapor [12–15], they appear to be the most promising catalyst for selective catalytic reduction of NO_x. However, it has been reported that different supports and Pt precursors have remarkable effects on the HC-SCR activity of Pt supported catalysts [16,17]. Burch and Watling [18] found that the NO reduction activity of Pt/SiO_2 was higher than that of Pt/Al_2O_3. Among different supports, MCM-41 is of interest due to its high surface area, uniform mesoporous structure and high hydrothermal stability in an air stream containing water vapor at high temperatures [19]. The high surface area of MCM-41 provides a better dispersion of active metal components on its surface. Due to the highly dispersed active components on its

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* Corresponding author. Tel.: +65-874-6312; fax: +65-779-1936.
E-mail address: chekawis@nus.edu.sg (S. Kawi).

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surface, MCM-41 containing metals or metallic ions (prepared either by impregnation, ion exchange or substitution) have been reported to have outstanding catalytic activities [20–26]. MCM-41 supported Pt catalyst has also been reported to have high activity for NO reduction by propene and provided the highest specific NO reduction rates for Pt as compared with Pt supported on all other conventional supports, such as Al_2O_3, SiO_2 and ZSM-5 [27].

Due to the potential application of Pt-based catalysts for HC-SCR, attention has been focused recently on the performance and reaction mechanism of these catalysts. A fundamental understanding of the reaction kinetics of NO HC-SCR is essential for the development of a catalyst having a practical application. Here, we report the results of our investigation on the kinetics of selective catalytic reduction of NO over Pt/MCM-41 using steady and transient state methods.

2. Experimental

Purely siliceous MCM-41 was prepared by hydrothermal synthesis using cetyltrimethylammonium bromide (CTMABr) as a template. An amount of 6 g aerosol silica was added to 90 g of NaOH solution (containing 2 g of NaOH and 88 g of H_2O) under stirring and heating. Meanwhile, 9.1 g of CTMABr was dissolved in 50 g of H_2O and this solution was then slowly mixed with the silica gel under stirring. After being stirred at room temperature for 6 h, the mixture gel was transferred into a polypropylene bottle and statically heated at 100°C for 72 h. The resulting solid product was recovered by filtering, washed with deionized water, and dried at 50°C for 24 h. In order to remove the organic surfactant in the pores of MCM-41, the as-synthesized samples were calcined in air at 600°C for 10 h (using a heating rate of 1°C/min).

Pt/MCM-41 catalysts (having 1 wt.% Pt loading) were prepared by incipient wetness impregnation method using tetraamineplatinum(II) nitrate (Aldrich) as the Pt precursor. After MCM-41 supported Pt catalysts were dried at 100°C and calcined at 500°C for 5 h in air, the samples were pressed and crushed to 40–60 mesh for catalytic activity measurement.

Steady state kinetics were performed on 0.03–0.45 g of catalyst packed in a micro-catalytic reactor (o.d. 1/4 in.) using a single pass, steady-state plug flow mode. The total gas flow rate was 200 ml/min. The reaction mixture was prepared from mixing a certified analyzed mixture gas of 2500 ppm of NO in He (Soxal), 25 vol.% of O_2 in He (Soxal), 1 vol.% propene in He (Soxal) and a 99.999% He (Messer) carrier gas. The concentration of C_3H_6, CO_2, N_2O and H_2O at the reactor inlet and outlet was analyzed by a gas chromatograph (Shimadzu GC-17A) equipped with a Porapak Q column and a TCD detector, and that of NO_x and O_2 was measured by a Chemiluminescent NO_x/O_2 analyzer (Shimadzu NOA-7000). NO_x conversion was calculated from the difference of NO_x concentration between the reactor inlet and outlet.

The transient kinetic was performed in a micro-flow reactor system, consisting of a small quartz tube (o.d. 1/4 in.) connected to a mass spectrometer (HP 6890). An abrupt switch in the reactant feed concentration was performed by means of a four-port valve positioned at the reactor inlet.

The pore size distribution and surface area of Pt/MCM-41 were measured by nitrogen physisorption at 77 K using a Quantachrome Auto-Sorb1 analyzer. Prior to nitrogen adsorption–desorption measurements, the sample was outgassed at 300°C under vacuum for 2 h. Powder X-ray diffraction patterns of Pt/MCM-41 samples were recorded by a SHIMADZU XRD-6000 powder diffractometer, where Cu target Kα-ray was used as the X-ray source.

3. Results and discussion

Fig. 1 shows the effect of catalyst particle size on the reduction of NO on Pt/MCM-41 catalysts. The C balance is above 92% in this work. By varying the catalyst particle size from 20 to 100 standard meshes, the effect of internal diffusion on selective catalytic reduction of NO was investigated. Although the average catalyst particle size has been reduced more than three times (from 20 to 100 standard meshes), however, the overall NO conversion is almost the same on these catalysts throughout the whole range of temperatures (150–400°C). The catalytic activity is found to be relatively independent of the catalyst particle size, implying negligible effect of internal pore diffusion on NO reduction by C_3H_6 over Pt/MCM-41 catalyst. The uniform mesoporous structure of MCM-41 support, thus, facilitates the mass transfer of reactants to

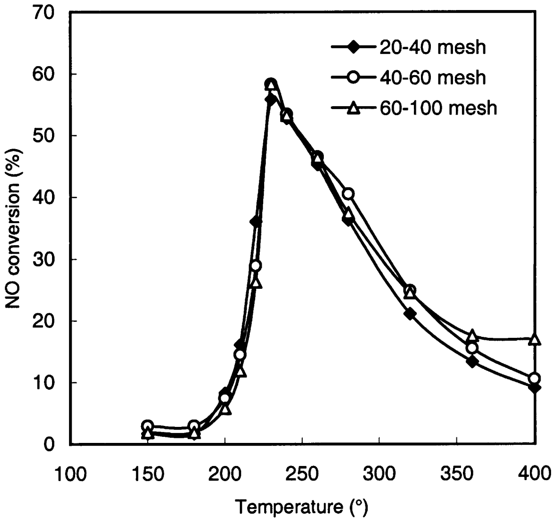

Fig. 1. Effect of catalyst particle size on reduction of NO by C_3H_6 on Pt/MCM-41 catalysts (1000 ppm NO, 1000 ppm C_3H_6, 5% O_2, VHSV = 10,000 h^{-1}).

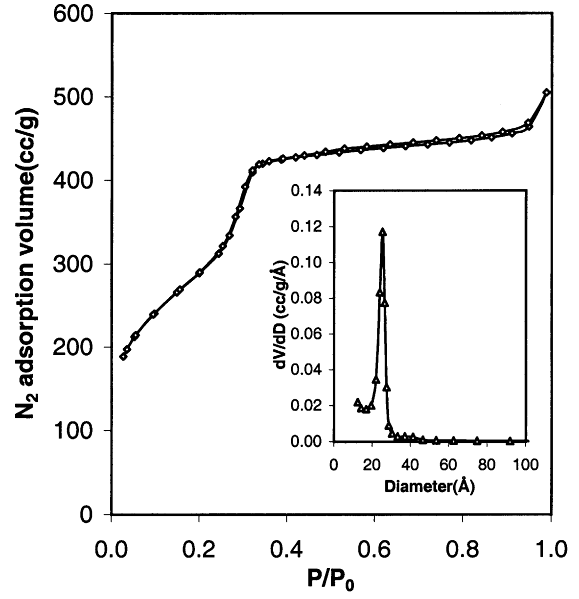

Fig. 2. N_2 adsorption–desorption isotherm and pore size distribution of Pt/MCM-41 catalyst.

reach the active catalytic sites on the internal surface of mesopores, eliminating the effect of inter diffusion on the catalyst activity for SCR reaction. However, pore diffusion limitation has been reported to be an important factor for SCR reaction on various microporous catalysts [28,29].

Fig. 2 shows the N_2 adsorption–desorption isotherm and the narrow pore size distribution of Pt/MCM-41 catalyst. The specific surface area and pore diameter (calculated based on BJH method) of the catalyst is 1053 m^2/g and 25.5 Å, respectively. The pore size of MCM-41, which is much larger than that of traditional molecule sieve, such as ZSM-5 or Y-zeolite, is believed to be responsible for the elimination of the effect of internal pore diffusion. The mesoporous structure of Pt/MCM-41 catalyst is confirmed by XRD measurement, as shown in Fig. 3. The XRD pattern of Pt/MCM-41 catalyst is similar to that of MCM-41, showing that the uniformly arranged mesoporous framework of MCM-41 can still be well maintained even after it has gone through the processes of solution impregnation, drying and high temperature calcination.

Fig. 4 shows the effect of oxygen concentration on the conversion of NO reduction and C_3H_6 oxidation. The concentration of C_3H_6 and NO at the reactor inlet was set at 1000 ppm. When C_3H_6 concentration is 1000 ppm, the critical oxygen concentration (defined as the stoichiometric oxygen concentration required for the complete oxidation of C_3H_6) is 0.45%. The effect of oxygen concentration on NO reduction is

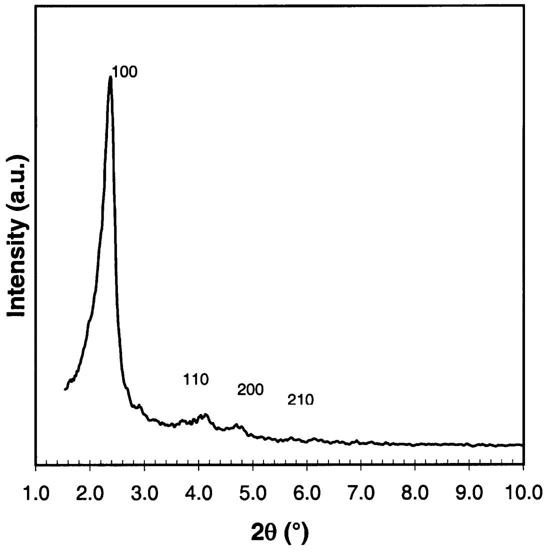

Fig. 3. Powder XRD pattern of Pt/MCM-41.

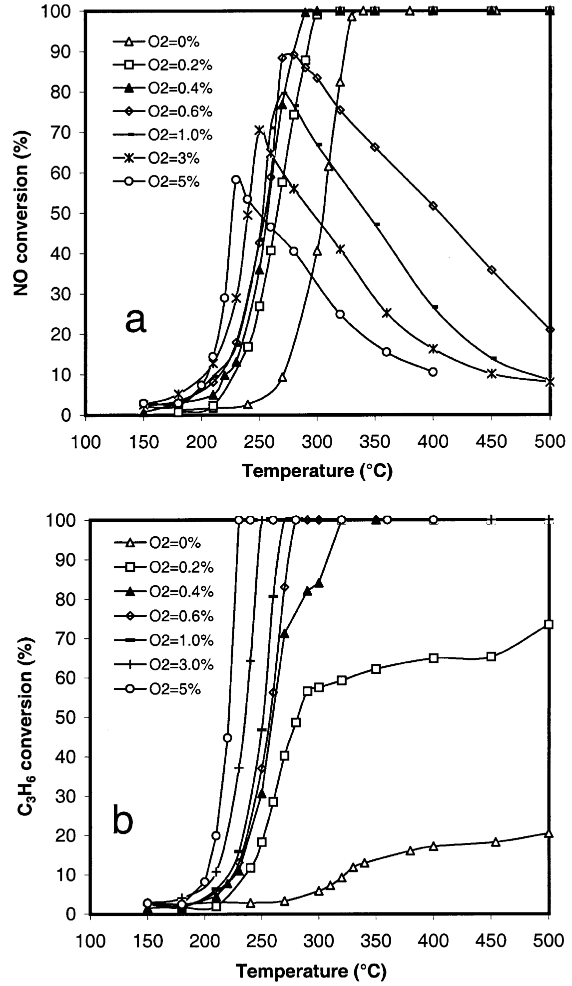

Fig. 4. Effect of oxygen concentration on (a) the conversion of NO reduction, and (b) the conversion of C_3H_6 oxidation on Pt/MCM-41 catalyst at different temperatures (VHSV = 10,000 h^{-1}, 1000 ppm NO, 1000 ppm C_3H_6).

different at oxygen concentration below or above the critical oxygen concentration. Fig. 4a shows that without having oxygen in the reaction mixture, NO conversion is very low when the temperature is below 250°C. Long and Yang [27] similarly reported that NO conversion on Pt/MCM-41 was close to zero when oxygen was not introduced into the reaction system, and they claimed that the catalyst was almost inactive even in the absence of oxygen. However, those results are only limited at the low temperature region (below 250°C). In our study, when the reaction temperature is above 270°C, NO conversion increases rapidly with the increase of temperature; in fact, it reaches 100% at 340°C and from 340 to 500°C, the complete NO conversion can be maintained.

A small increase of the oxygen concentration at the reactor inlet is found to decrease the reaction temperature required for complete NO conversion. For example, under 0.2% oxygen concentration, NO conversion reaches 100% at 300°C and maintains at this complete conversion up to 500°C. When the oxygen concentration in the reaction mixture is increased to 0.4%, NO conversion reaches 100% at even lower temperature and complete NO conversion is observed from 290 to 500°C. The results indicate that the activity of NO reduction on Pt/MCM-41 catalyst is promoted by the presence of a small amount of oxygen in the reaction system, lowering the reaction temperature required for maximum NO conversion. Because the amount of oxygen is not enough for complete oxidation of C_3H_6, the overall environment in the reaction mixture is still under reducing condition, making complete NO conversion possible.

However, when the oxygen concentration in the reaction system is further increased to a level exceeding the critical concentration, the effect is significantly different from those observed under low oxygen concentration. In the case of high oxygen concentration, an optimal operation temperature (T_m) required for maximum NO conversion is observed. With the increase of reaction temperature, NO conversion first increases to reach the maximum conversion, after which it decreases. It should be noted that NO conversion is always less than 100% at all range of temperatures when the oxygen concentration exceeds the critical one. Although the catalyst activity for NO reduction at low temperature range is improved with the increase of oxygen concentration, however, the maximum NO conversion decreases with increasing oxygen concentration in the reaction system. Above T_m, NO reduction is found to be seriously depressed with the increase of oxygen concentration. The different effects of oxygen concentration on the reduction of NO at temperatures below or above that required for maximum NO conversion are believed to be attributed to the activation and competitive oxidation of C_3H_6 at different range of temperatures.

Fig. 4b shows the effect of oxygen concentration on the conversion of C_3H_6 during NO reduction. In the absence of oxygen, NO is the only oxidant for the oxidation of C_3H_6; the conversion of C_3H_6 is less than 20% for 100% NO conversion. With 0.2% oxygen in the reaction mixture, the conversion of C_3H_6 is substantially increased. A further increase of the oxygen concentration to 0.4% results in a complete oxidation of C_3H_6 above 320°C. As the amount of oxygen is still not enough for complete C_3H_6 combustion, some oxidation is contributed by NO during the reaction. The result indicates that both NO and O_2 simultaneously react with C_3H_6 over the catalyst.

When the oxygen concentration is below the critical concentration (below 0.45%), the reaction system is under a reducing environment, yielding a complete NO conversion. The reducing environment is suggested to be helpful to maintain the reduced states of Pt species. It is known that the reduced Pt species play an important role for NO conversion [30,31]. According to the redox mechanism proposed by Burch and Millington [17], NO is reduced by C_3H_6 over Pt oxide via a redox process. The adsorption of propene on the catalyst surface reduces the available active sites made up of essentially isolated metal particles. Meanwhile, when the adsorbed C_3H_6 is in contact with surface oxygen species, it may be activated or oxidized, producing reaction hydrocarbon intermediates that can react with NO. On these reduced sites with reaction hydrocarbon intermediates, NO reduction is facile and the surface becomes oxidized and deactivated during NO reduction. However, re-reduction of the active site by propene completes the catalytic cycle. Based on this mechanism, the catalytic cycle for the selective catalytic reduction of NO by propene is suggested to occur on the reduced Pt species as it has also been reported that NO did not convert to N_2 on a completely oxidized supported Pt catalyst [16,18].

When the oxygen concentration is above the critical concentration (above 0.45%), C_3H_6 combustion is fast due to the oxidizing environment. The light-off temperature decreases with the increase of oxygen concentration. Similar to that observed on other supported Pt catalysts, the maximum NO conversion observed on Pt/MCM-41 always coincides with the temperature required for complete combustion of C_3H_6. At the lower range of temperature, the activation of hydrocarbon is believed to be important for the reduction of NO. The surface hydrocarbon intermediates resulting from partial oxidation of hydrocarbon react with N-containing compounds to form N_2 or N_2O and CO_2. Below 240°C, an increase in the concentration of oxygen increases the conversion of C_3H_6, which in turns increases the conversion of NO (Fig. 4a). Meanwhile, the temperature required for maximum NO conversion is lowered by increasing O_2 concentration. However, above the temperature required for maximum NO conversion, C_3H_6 is completely oxidized, causing the concentration of C_3H_6 to be not enough on the surface to maintain most of Pt species in the reduced states. This competitive effect is proportional to the concentration of oxygen in the reaction system, with higher oxygen concentration resulting in lower NO conversion. The results show that the presence of oxygen in the reaction system produces contrary effects on the reduction of NO over Pt/MCM-41 under two different temperature ranges, causing different reaction kinetics at the temperature region above or below those required for the maximum NO conversion.

Fig. 5 shows the effect of oxygen concentration on the catalyst selectivity to N_2 at the reaction temperature required for maximum NO conversion. Without having oxygen in the reaction system, the catalyst selectivity to N_2 is 100%. However, with the increase of oxygen concentration from 0 to 0.6%, N_2 selectivity decreases substantially to around 50%. A further increase of the oxygen concentration from 0.6

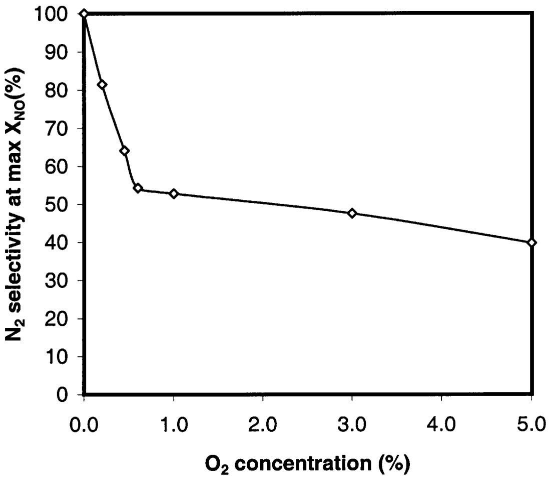

Fig. 5. Effect of oxygen concentration on N_2 selectivity at the temperature required for maximum NO conversion (VHSV = 10,000 h^{-1}, 1000 ppm NO, 1000 ppm C_3H_6).

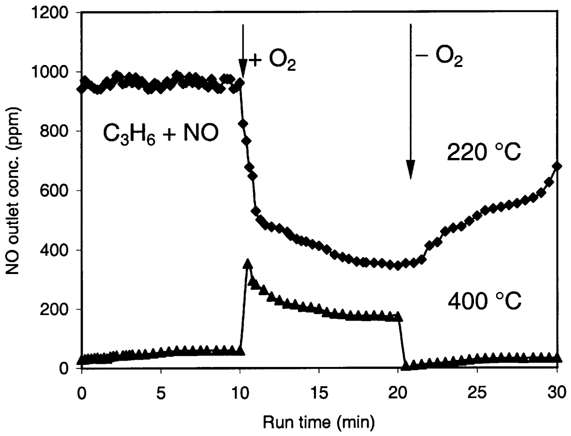

Fig. 6. Dynamic response of NO concentration at the outlet stream upon step feed and shut-off of O_2 (5 vol.%) in the reaction system at different temperature (0.2 g catalyst, VHSV = 10,000 h^{-1}, 1000 ppm C_3H_6, 1000 ppm NO).

up to 5% results in a slight decrease of the catalyst selectivity to N_2. The result indicates that the catalyst selectivity to N_2 decreases with the presence of more oxygen in the reaction system. In addition, with the increase of oxygen concentration, it is found that the corresponding T_m decreases. At lower temperature, the molecularly adsorbed NO may recombine with N atom, or surface nitrite to form N_2O [16,32], which is the main by-products for NO-SCR over Pt-based catalyst. Consequently, the selectivity to N_2 at T_m decreases with the increase of oxygen concentration in the reaction system.

The effect of oxygen on the reduction of NO over Pt/MCM-41 catalyst is further studied by transient measurement. Fig. 6 shows the transient response of NO concentration (recorded by $m/e = 30$) with or without O_2 in the reaction feed at different temperatures. At a low temperature of 220°C, the presence of O_2 in the reaction feed causes the outlet NO concentration decreases quickly at the beginning and then slowly toward a steady state value. This result confirms the steady state measurement results (shown in Fig. 4) that the low temperature reactivity of Pt/MCM-41 is significantly improved by the presence of O_2. Once O_2 is removed from the reaction system, NO concentration increases slowly with time towards the initial value. The reason why NO concentration does not increase immediately to the initial value may be explained by the fact that depending on the range of the reaction temperature, there is some effect due to the adsorption of O_2 on the catalyst surface. At the low temperature of 200°C, some oxygen species might still adsorb on the catalyst surface and participate in the reaction even after O_2 has been removed from the reaction feed. The selective catalytic reduction of NO is still promoted by the presence of adsorbed surface oxygen species. The concentration of NO slowly increases to the initial value while the surface oxygen is gradually consumed during SCR reaction without any gas phase oxygen. However, at the high temperature of 400°C, the effect of O_2 on the reduction of NO is reversed as the outlet NO concentration increases or decreases fast once O_2 is introduced into or out of the reaction system, respectively. At a high temperature of 400°C, it has been shown previously in Fig. 4 that the presence of oxygen in the reaction system prevents the reduction of NO by C_3H_6. Thus, the introduction of oxygen into the reaction system results in the immediate increase of outlet NO concentration. Compared with that of lower temperature, the outlet NO concentration decreases very fast upon removal of oxygen from the feed stream. This is because the amount of O_2 adsorbed on the catalyst surface is very low at high temperatures. In addition, the trace amount of surface oxygen can be consumed very fast by reacting with C_3H_6 at high temperature. Consequently, the removal of oxygen from the reactant feed yields a reducing environment on the catalyst, restoring the reduction of NO to the initial value fast.

Fig. 7 shows the effect of space velocity (from 10,000 to 150,000 h^{-1}) on NO reduction over Pt/MCM-41 in the presence of 5% oxygen. There are two temperature regions at which space velocity shows different effect on NO reduction. When the reaction temperature is below T_m, an increase of space velocity results in the decrease of NO conversion. However, above T_m, the increase of space velocity (from 10,000 to 150,000 h^{-1}) has little effect on NO conversion. In addition, conversion of C_3H_6 is always complete above T_m. Similar results have been observed for NO reduction over other novel metal catalysts, such as Rh/Al_2O_3 or Rh/SiO_2 [33]. The reduction rate of NO is calculated based on the measurements of differential conversion of NO as follows:

$$r_{NO} = \frac{F_{NO}X}{M_{cat}}$$

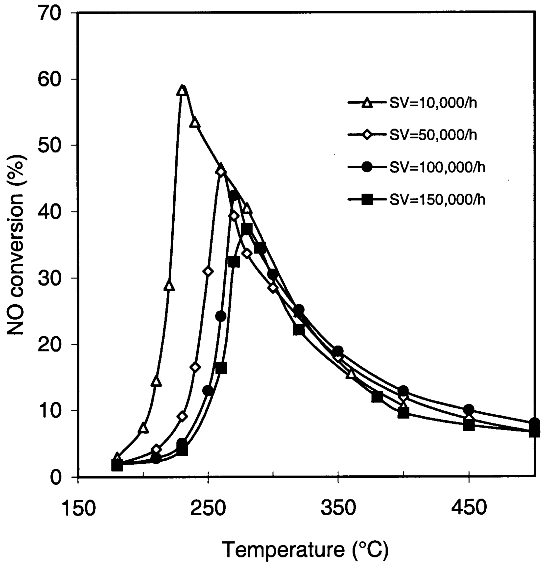

Fig. 7. Effect of space velocity on the conversion of NO reduction by C_3H_6 over Pt/MCM-41 (1000 ppm NO, 1000 ppm C_3H_6, 5 vol.% O_2).

where F_{NO} is the inlet molar rate of nitric oxide, X the NO conversion, and M_{cat} the weight of catalyst used. As shown in Fig. 8, at the low temperature of 220°C, the specific reaction rate is almost unaffected by the variation of space velocity due to the obvious decrease of NO conversion with the increase of space velocity. However, at higher temperatures above T_m (400°C), the specific reaction rate is strongly dependent on the space velocity because the conversion of NO is kept constant with the increase of space velocity.

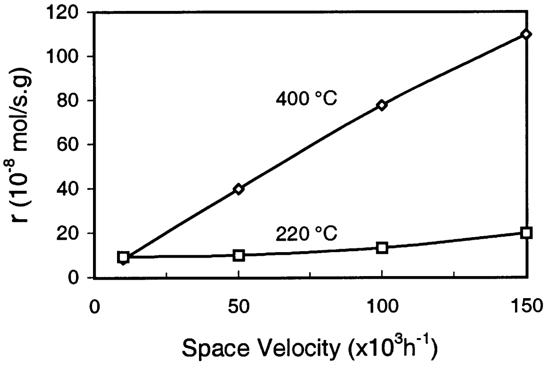

Fig. 8. Effect of space velocity on the specific reaction rate at different temperatures (1000 ppm NO, 1000 ppm C_3H_6, 5 vol.% O_2).

These results imply that the SCR-NO reaction is controlled by the surface reaction below T_m and by the external mass transfer above T_m. Below T_m, the surface reaction is suggested to be slow and becomes the controlling step for the overall NO conversion reaction. Using the fact that the overall NO conversion is found to be simultaneously increased with the conversion of C_3H_6, the activation of C_3H_6 is believed to be significant for the selective catalytic reduction of NO [34]. Above T_m, the activation of C_3H_6 is very fast and reaches complete oxidation. Although the mass transfer rate is faster at higher temperature, however, the rate of surface reaction may exceed the rate of external mass transfer of reactant. Thus, the overall reaction rate becomes controlled by the external mass transfer of reactants.

The above kinetic model for the selective reduction of NO by hydrocarbon is further supported by the different reaction order of NO observed under different reaction temperature region. Fig. 9 shows the effect of NO concentration on the reduction rate of NO. The slope of $\ln(r_{NO})$ versus $\ln(C_{NO})$ plot gives the reaction order with respect to NO concentration. As shown in Fig. 9a, at the high temperature region (above 320°C), the overall reduction rate of NO has an NO reaction order close to one (the NO reaction order is 0.91 and 1.03 at 320 and 400°C, respectively). This confirms our results that external mass transfer at high temperature controls NO reduction by C_3H_6 in the presence of excess oxygen over Pt/MCM-41. Since the reaction is controlled by external mass transfer, the driving force for the reaction is contributed by the difference in the concentration between those in the bulk gas and those on the catalyst surface, consequently making the overall reaction to be first order.

On the contrary, Fig. 9b shows that in the low-temperature region, the NO reaction order becomes negative, with a value of −0.8 at 220°C. The NO reaction order is observed to increase with the increase of reaction temperature, with a value close to zero at 260°C. The result shows that high NO concentration has a negative effect on the reduction rate of NO at low temperature as the reaction is mainly controlled by competitive adsorption and surface reaction of both reactants of NO and C_3H_6 on the catalyst surface. The competitive adsorption between the reactants may cause the negative reaction order of NO at low temperatures.

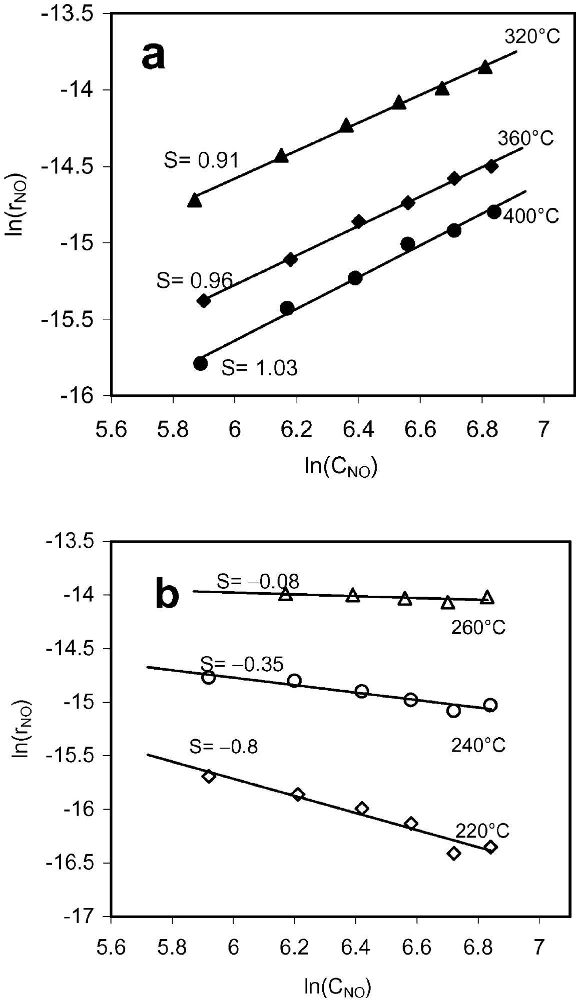

Fig. 9. Effect of NO concentration on the reduction rate of NO over Pt/MCM-41 at (a) high temperatures, and (b) low temperatures (1000 ppm C_3H_6, 5 vol.% O_2, VHSV = 10,000 h^{-1}).

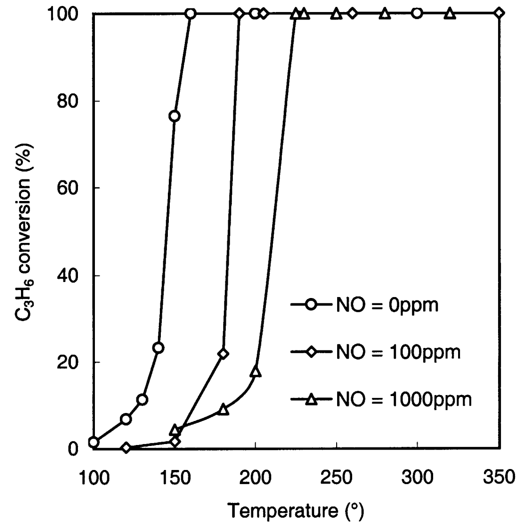

Fig. 10. Effect of NO concentration on the oxidation of C_3H_6 on Pt/MCM-41 (VHSV = 10,000 h^{-1}, 5 vol.% O_2).

The competitive adsorption of NO and propylene is studied by comparing the conversion of propylene oxidation in the absence and presence of NO. As shown in Fig. 10, a complete oxidation of propylene is achieved at 160°C when NO is not present in the reaction stream. However, when 100 ppm of NO is introduced into the reaction system, propylene is completely oxidized at higher temperatures, above 190°C. A further increase of NO concentration to 1000 ppm causes the reaction temperature required for complete oxidation of C_3H_6 to go higher to 230°C. Generally, the presence of NO is found to retard the complete oxidation of propylene by 30–50°C. The result suggests that NO blocks the active sites responsible for the oxidation of propylene at low temperature, showing that NO and propylene both adsorb on the same type of active sites. Thus, the higher concentration of NO in the reaction system prevents the adsorption and activation of propylene. Since the activation of propylene is believed to be important for NO reduction over Pt/MCM-41, the overall reduction rate of NO is adversely affected by the higher concentration of NO at low temperature. Above 230°C, the retarding effect of NO on activation of C_3H_6 is less serious as all C_3H_6 can be completely oxidized. Hence, above 230°C, the reaction order increases with the increase of reaction temperature.

The results of reaction kinetics clearly demonstrate the presence of two distinct kinetic regions at temperatures below or above T_m for NO reduction over Pt/MCM-41 catalyst. The transformation of reaction kinetics for NO reduction at different temperature region has also been reported for Pt/SiO_2 or Pt/Al_2O_3 catalysts [34,35], with the values of NO reaction order close to zero and one at 270 and 400°C, respectively. The results show that transformation of reaction kinetics for selective reduction of NO with reaction temperature is a common characteristic for Pt-based catalyst. The reaction is basically controlled by the surface reaction in the low temperature region as the adsorption and activation of hydrocarbon on the catalytic sites is suggested to be an important step for NO reduction. This observation is supported by the close proximity of ascending part of NO reduction curve and the corresponding hydrocarbon curves, and the coupling between the point of maximum NO conversion and complete hydrocarbon oxidation. However, when the reaction temperature is increased above T_m, the process is then controlled by external mass transfer of reactants even at a space velocity of 150,000 h^{-1}. Similar reaction results obtained at different space velocities and the near first order with respect to NO give further evidence for this hypothesis.

Fig. 11 shows the effect of C_3H_6 concentration on the conversion of NO and C_3H_6 on Pt/MCM-41 catalyst at different temperatures under the space velocity of 150,000 h^{-1}. At 240°C, C_3H_6 can be completely oxidized at low C_3H_6 concentration, however, the conversion of C_3H_6 decreases with the increase of C_3H_6 concentration, with a further increase in the concentration of C_3H_6 above 1000 ppm almost has no significant effect on C_3H_6 conversion. The results indicate that when the concentration of C_3H_6 exceeds 1000 ppm, the catalyst surface lacks oxidative species as the catalyst surface may be saturated with hydrocarbon species and the adsorption of either NO or O_2 on the catalyst surface is necessary for C_3H_6 oxidation. In other words, the results indicate that at the low temperature region, only a small amount of C_3H_6 is completely oxidized for NO reduction and a high C_3H_6 concentration appears to have a negative effect on both the reduction of NO and the oxidation of C_3H_6. When the reaction temperature is increased to 300°C, C_3H_6 is completely oxidized at a higher concentration of up to 1000 ppm. However, at this temperature, a slight increase of the concentration of C_3H_6 from 1000 to 2000 ppm can still increase NO reduction. A further increase of C_3H_6 concentration above 2000 ppm retards NO reduction as the catalyst surface is being saturated with hydrocarbon species. At higher temperatures above 350°C, NO conversion is found to be proportional to propylene concentration as a higher concentration of C_3H_6 (up to 4000 ppm) can be completely activated. The result shows that the rate of reduction of NO increases with the increase of C_3H_6 concentration as long as all C_3H_6 can be completely oxidized but the increase of C_3H_6 concentration can decrease the rate of reduction of NO when C_3H_6 cannot be fully oxidized by the catalyst.

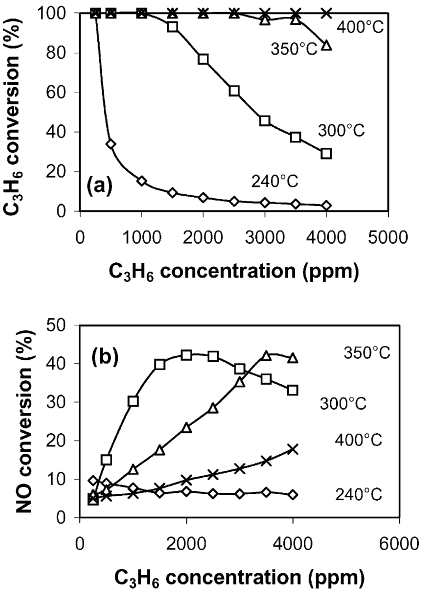

Fig. 11. Effect of C_3H_6 concentration on (a) the conversion of C_3H_6 oxidation, and (b) the conversion of NO reduction on Pt/MCM-41 at different temperatures (VHSV = 10,000 h^{-1}, 1000 ppm NO, 5 vol.% O_2).

4. Conclusions

Internal diffusion is found to be negligible for selective catalytic reduction of NO over 1% Pt/MCM-41 catalyst due to its mesoporous structure. Complete NO conversion can only be reached when the concentration of oxygen is less than the critical oxygen concentration required for stoichiometric oxidation of C_3H_6. Above the critical oxygen concentration, an optimal reaction temperature exists for the maximum NO conversion, which occurs at the temperature required for complete oxidation of C_3H_6. Both the maximum NO conversion and N_2 selectivity decrease with the increase of oxygen concentration. Below the temperature required for maximum NO conversion (T_m), the activation of C_3H_6 is believed to be an important step for the selective reduction of NO. The reaction kinetic is transformed from surface reaction control to external mass transfer control once the reaction temperature is increased above T_m. At the high temperature, the overall reaction rate of NO reduction is found to be first order with respect to NO concentration and proportional to the concentration of C_3H_6 in the inlet mixture.

Acknowledgements

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