

The Nature of Surface Species on Modified Pt-Based Catalysts for the SCR of NO by C₃H₆ Under Lean-Burn Condition

Piyasan Praserttham, Choowong Chaisuk[†] and Tharathon Mongkhonsi

Center of Excellence on Catalysis and Catalytic Reaction Engineering,
Department of Chemical Engineering, Chulalongkorn University, Bangkok 10330, Thailand
(Received 22 February 2002 • accepted 8 August 2002)

Abstract—The catalytic activity behavior for the selective catalytic reduction of NO by C₃H₆ under excess oxygen and the nature of surface species on the active sites of Pt/Al₂O₃ catalyst after adding a second metal (Fe, Sn, Co, Cr or W) were investigated. It has been found that an important role of second metals is on TONs of C₃H₆ and NO conversions and the nature of surface species produced on the catalyst surface at low temperature instead of the catalytic activity behavior towards the temperature programmed reaction. Although the introduction of each second metal distinctly disturbs the characteristic of surface species, the reaction mechanism is presumably similar. The observation of few surface species and the investigation about their reactivity indicate that few mechanisms are simultaneously proceeding at the same reaction condition.

Key words: Pt/Al₂O₃, Second Metal, SCR of NO by C₃H₆, Lean-Burn Condition, Surface Species

INTRODUCTION

At the present time, the development and design of catalysts for the selective catalytic reduction (SCR) of NO with hydrocarbons in the exhaust gas from diesel or lean-burn engines are being extensively investigated. Numerous materials, such as ion exchanged zeolites, metallosilicates, single metal oxides, mixed oxides, perovskites, supported transition metals and supported noble metals, have been tested [Fritz et al., 1997]. Among these materials, a platinum catalyst has received much interest due to a good stability under the real condition where the presence of H₂O and SO₂ exists [Zhang et al., 1992; Obuchi et al., 1993] and a promising activity in a low temperature region. However, the remarkable disadvantages for this catalyst are that it is not adequate for the very demanding challenge of providing high activity and good selectivity. The high rates of N₂O formation and the narrow temperature window of the catalytic activity are crucial problem for application in practice. Hence, an attempt to overcome these limitations has been made. For example, other metals are added on monometallic Pt catalyst. The effect of metal oxides (Ba, Ce, Co, Cs, Cu, K, La, Mg, Mo, Ti) or noble metals (Ag, Au, Pd, Rh) on the catalytic activity of Pt/Al₂O₃ for the NO reduction by C₃H₆ under lean-burn condition was reported by Burch et al. [Burch et al., 1997]. They found that these promoters had a significant influence (both positive and negative) on the activity and temperature range of operation of Pt/Al₂O₃, but had no significant effect on the N₂/N₂O selectivity. Bensaddik et al. [Bensaddik et al., 1997] found that the presence of Zn on Pt/Al₂O₃ affected the increase of NO conversion in parallel with the N₂ formation and the wider range of temperature in which N₂ was formed for DeNO_x reaction under excess oxygen. Tanaka et al. [Tanaka et al., 1998] observed that the temperature window on the SCR of NO on trimetallic Pt-Mo-Na/SiO₂ catalyst was found to be wider and

to shift at higher temperature than that on monometallic Pt/SiO₂ catalyst under lean static condition. Although the improvement of the catalytic performance through such procedure is fairly successful, the outstanding knowledge about the role of promoters on the reaction mechanism or the active intermediate species is still ambiguous.

Reaction mechanisms over Pt-based catalyst have been proposed by employing various characterization techniques, such as in situ Fourier transform infrared (FTIR) spectroscopy [Tanaka et al., 1994; Bamwenda et al., 1995; Xin et al., 1997; Captain et al., 1999], temporal analysis of products (TAP) [Burch et al., 1994; Rottlander et al., 1996; Lacombe et al., 1997] and steady-state isotopic transient kinetic analysis (SSITKA) [Burch et al., 1999]. However, the influencing parameters, e.g., types of noble metal [Nikolopoulos et al., 1999], reaction conditions [Captain et al., 1998] and types of reductant [Burch et al., 1998], may be carefully taken into account for considering in details about the reaction mechanism as well. In general, using C₃H₆ as a reductant for the SCR of NO under excess oxygen on Pt-based catalyst, the overall reaction mechanism is proved to occur exclusively on the Pt surface [Okuhara et al., 1997; Xin et al., 1997; Burch et al., 1998]. However, two main different mechanisms have been proposed in the literature, i.e., the NO decomposition mechanism [Burch et al., 1994; Eckhoff et al., 1997; Xin et al., 1997] and the NO reduction mechanism [Bamwenda et al., 1995; Okuhara et al., 1997; Captain et al., 1999]. The first mechanism mentions that the hydrocarbons are contributed for removing the surface oxygen poisoning the active sites, while N₂ product is dominantly formed via NO dissociation. Hence, the complex surface species, such as organic nitro species, are distinctly neglected and either N atom or NO molecule is addressed as the intermediate species for this mechanism [Burch et al., 1994]. On the other hand, according to the NO reduction mechanism the significant concept is the complex surface species playing an important role for producing N₂, although its pathway may be different in details. For example, the hydrocarbons react with O₂ to partially oxidize hydro-

[†]To whom correspondence should be addressed.
E-mail: gnwoohc@hotmail.com

carbons, which are reactive by NO or NO₂ to form N₂ [Sasaki et al., 1992; Engler et al., 1995]. Additionally, the hydrocarbons may first react with NO₂ produced by NO oxidation to organic nitro species leading to the formation of N₂ [Okuhara et al., 1997]. Thus, there are many types of surface species, e.g., oxygenated organic complex [Bamwenda et al., 1995], organic nitro compound [Okuhara et al., 1997] and isocyanate species [Captain et al., 1999], independently assigned as the intermediate species for this mechanism.

In this work, the role of surface species on the reaction mechanism in the SCR of NO by C₃H₆ over Pt/Al₂O₃ was studied. In addition, a second metal (Fe, Sn, Co, Cr or W) was added over monometallic Pt/Al₂O₃ catalyst in order to disturb the operation of active sites in this reaction, and the catalytic activity behavior as well as the nature of surface species after adding a second metal were observed in comparison with those of monometallic Pt/Al₂O₃ catalyst as well.

EXPERIMENTAL

1. Catalyst Preparation and Characterization

1%wt Pt/Al₂O₃ and 1%wt Pt-2%wt M/Al₂O₃ (M=Fe, Sn, Co, Cr, W) were prepared by an incipient wetness impregnation method. The Al₂O₃ support used in this study was obtained from Sumitomo Aluminum Smelting (type NKH-3) and the metal salt precursors were H₂PtCl₆ (from Wako Pure Chemical Industries), Fe(NO₃)₃ (from Carlo Erba), SnCl₂ (from Fluka Chemie A.G.), Co(CH₃COO)₂ (from Carlo Erba), Cr(NO₃)₃ (from Fluka Chemie A.G.) and (NH₄)₁₀H₂(W₂O₇)₆ (from Fluka Chemie A.G.). For the second metal-doped Pt/Al₂O₃ catalysts, the Al₂O₃ was co-impregnated with the platinum and the second metal precursors. After co-impregnation, each sample was dried at 110 °C overnight and calcined in air at 500 °C for 3 h. The dispersion of a selected sample was measured by CO chemisorption after reduction at 500 °C for 1 h.

2. Catalytic Evaluation

The aim of this catalytic test was to investigate the catalytic activity behavior and the nature of surface species on the catalyst surface in the SCR of NO by C₃H₆. All experiments were conducted by using a quartz tubular downflow reactor with 0.6 cm inside diameter. The effluent gases were analyzed by two on-line gas chromatographs (SHIMADZU GC 8A) equipped with molecular sieve 5A column for separating O₂, N₂ and CO and porapak QS column for separating CO₂, N₂O and hydrocarbons. Prior to the catalytic test, 0.1 g of sample was reduced in H₂ flow at 500 °C for 1 h and subsequently treated under 10% O₂ in He at 500 °C for 1 h. The catalytic activity behavior was tested by the temperature programmed reaction technique. The reactant gas mixture contained 1,000 ppm NO, 1,000 ppm C₃H₆ and 5% O₂ diluted in He at a total flow rate of 200 ml/min (GHSV of 60,000 h⁻¹). The observation of surface species was performed by an experimental set of three continuous steps, i.e., 1st-SCR of NO by C₃H₆ step to produce the surface species, 2nd-temperature programmed desorption (TPD) step to remove the weakly adsorbed surface species and 3rd-temperature programmed oxidation (TPO) step to remove the remaining deposits. During the first step, the sample was exposed to the reactant gas mixture containing 1,000 ppm NO, 1,000 ppm C₃H₆ and 5% O₂ diluted in He at 225 °C for 2 h. It was noted that the steady state C₃H₆ and NO conversions at 225 °C were obtained by this step. TPD experiment

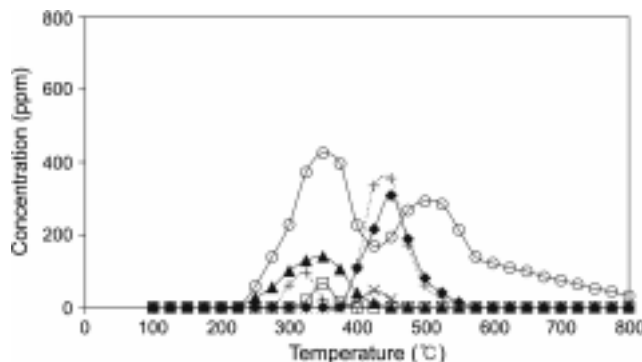


Fig. 1. The temperature programmed desorption profiles of Pt/Al₂O₃ after dosing 1,000 ppm C₃H₆+1,000 ppm NO+5% O₂ at 225 °C for 2 h: (○) CO₂, (×) CH₄, (◆) CO, (▲) N₂, (□) N₂O, (+, dashed line) O₂.

on the second step was subsequently carried out under 50 ml/min He flow with the heating rate of 5 °C/min from 100 °C to 800 °C. Afterwards, deposits were removed by heating the sample under 1% O₂ in He at a flow rate of 50 ml/min with the heating rate of 5 °C/min from 100 °C to 800 °C. The surface species formed upon the reaction were indirectly monitored by analyzing the effluent gases released during TPD and TPO steps.

RESULTS AND DISCUSSION

1. The Nature of Surface Species on Monometallic Pt/Al₂O₃ Catalyst

The characterization of surface species on monometallic Pt/Al₂O₃ catalyst in the SCR of NO by C₃H₆ was investigated by an experimental set consisting of three steps as described in the experimental section. Fig. 1 illustrates the traces of outlet gases released during TPD step from Pt/Al₂O₃ after dosing the gas mixture of C₃H₆, NO and O₂ in the first step at 225 °C. These outlet gases contain CO₂, CH₄, CO, N₂, N₂O and O₂. It is significantly remarked that most of the surface species are released during TPD step, whereas the amount of outlet gases by TPO step is extremely small. Hence, it is suggested that the surface species can easily decompose themselves on Pt/Al₂O₃.

Considering the TPD profile, it is found that there are two CO₂ peaks and two O₂ peaks, while the other gases give only one peak. N₂ and N₂O peaks exist at low temperature, whereas CH₄ and CO peaks are located at higher temperature. The deconvolution of this TPD profile indicates that there are at least three types of surface species occurring on the catalyst surface. They are addressed as C_xH_y-O_zN_w, (C_iH_jO_k)_{LTB} and (C_iH_mO_n)_{HIT} species decomposing themselves at low temperature region (200 °C to 400 °C), at moderate one (350 °C to 550 °C) and at high one (400 °C to 800 °C), respectively. The existence of these surface species is in agreement with the observation by IR technique in several references [Tanaka et al., 1994; Bamwenda et al., 1995; Xin et al., 1997; Captain et al., 1999]. For example, Captain et al. [Captain et al., 1999] noticed cyanide, isocyanate, acetate and formate species on Pt/Al₂O₃ in C₃H₆+NO+O₂ system by the use of in situ Fourier transform infrared spectroscopy and also found that only isocyanate species disappeared by flushing with He at 250 °C. In addition, only isocyanate and acetate spe-

cies were observed when increasing the reaction temperature at 350 °C and again only the intensity of isocyanate peak was essentially affected after the reactor was flushed with He.

In fact, the obtained surface species may possibly play a role to be either the intermediate species or the spectator species depending on the reaction condition as reported in some literatures. Tanaka et al. [Tanaka et al., 1994] proposed that nitro, nitrite and carbonyl surface species were key reaction intermediates for the SCR of NO by C_3H_6 on Pt/SiO₂ at 120 °C. Whereas, Xin et al. [Xin et al., 1997] suggested that nitro, nitrite and isocyanate species were not the catalytic active intermediates for the SCR of NO by C_3H_6 on Pt/ZSM-5 at 250 °C. On the other hand, Captain et al. [Captain et al., 1999] concluded that carboxylates, nitrates and cyanide species were probably the spectator byproducts of the SCR of NO by C_3H_6 on Pt/Al₂O₃ at 250 °C, whereas the surface isocyanate species could be a potential reaction intermediate in such reaction. With the above-mentioned reason, the reactivity of $C_xH_yO_zN_w$, $(C_iH_jO_k)_{LT}$, and $(C_iH_mO_n)_{HT}$ species with the oxidizing reactant gas in the reaction temperature range was also studied. The reactivity test was conducted by using TPO technique after producing the surface species in the SCR of NO by C_3H_6 on Pt/Al₂O₃ at 225 °C for 2 h. Three oxidizing gases were used in the TPO experiment: 1) 1,000 ppm NO, 2) 1% O₂ and 3) a gas mixture of 1,000 ppm NO and 1% O₂. Figs. 2-4 illustrate

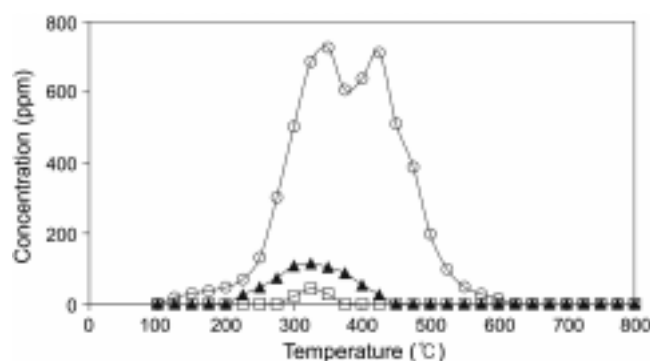


Fig. 2. The temperature programmed oxidation profiles of Pt/Al₂O₃ by using 1% O₂ as the oxidizing gas after dosing 1,000 ppm C_3H_6 +1,000 ppm NO+5% O₂ at 225 °C for 2 h: (○) CO₂, (▲) N₂, (□) N₂O.

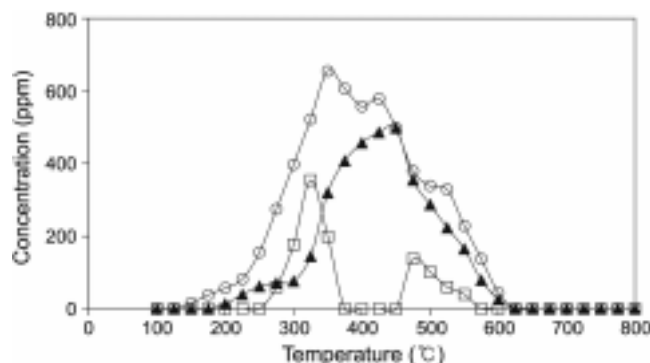


Fig. 3. The temperature programmed oxidation profiles of Pt/Al₂O₃ by using 1,000 ppm NO as the oxidizing gas after dosing 1,000 ppm C_3H_6 +1,000 ppm NO+5% O₂ at 225 °C for 2 h: (○) CO₂, (▲) N₂, (□) N₂O.

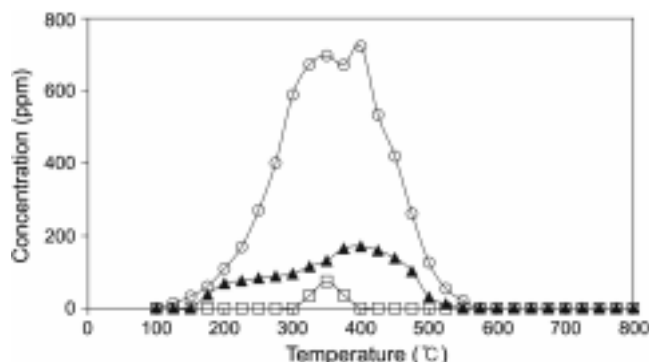


Fig. 4. The temperature programmed oxidation profiles of Pt/Al₂O₃ by using 1,000 ppm NO+1% O₂ as the oxidizing gas after dosing 1,000 ppm C_3H_6 +1,000 ppm NO+5% O₂ at 225 °C for 2 h: (○) CO₂, (▲) N₂, (□) N₂O.

the concentrations of CO₂, N₂ and N₂O during TPO experiment by using NO, O₂ and NO+O₂ as the oxidizing gas, respectively. It is noted that neither CH₄ nor CO is detected when each oxidizing gas is used for removing the surface species. It is found that the position of CO₂ peak addressed as $C_xH_yO_zN_w$ species is unaffected with changing oxidizing gas (NO, O₂ or NO+O₂). Furthermore, the N₂O peak is not shifted under either O₂ or NO+O₂ atmosphere. The observation of N₂ peak at 350 °C is rather difficult under NO or NO+O₂ atmosphere because N atoms in the oxidizing gas can possibly interact with other surface species to produce N₂. However, the introduction of only O₂ during TPO step does not influence the position of the N₂ peak. These results reveal that $C_xH_yO_zN_w$ species can decompose themselves under the oxidizing gas at the same temperature at which they decompose under He flow. Therefore, neither NO nor O₂ is involved in the decomposition of $C_xH_yO_zN_w$ species at any temperature. This is also in agreement with the work by Captain et al. [Captain et al., 1999] who reported that the surface cyanide on Pt/Al₂O₃ was not reacting in NO, NO₂, O₂ and NO+O₂ environments at 250 °C.

A larger amount of CO₂ released at low temperature and the disappearance of the CO₂ peak at high temperature (525 °C) in the presence of O₂ or NO+O₂ as the oxidizing gas indicate that the surface species decomposing at high temperature, $(C_iH_mO_n)_{HT}$ species, are easily removed by these oxidizing gases. However, the existence of CO₂ peak at 525 °C in case that only NO is used as the oxidizing gas shows that O₂ is a more potential oxidizing gas than NO to be reactive with $(C_iH_mO_n)_{HT}$ species. This corresponds with the work by Tanaka et al. [Tanaka et al., 1994] who suggested that on Pt/SiO₂ the carbonyl species reacted rapidly with NO₂ and O₂ at 120 °C, while these species were inactive to NO. Considering the reactivity of $(C_iH_jO_k)_{LT}$ species to the different oxidizing gas, the relatively small shift to lower temperature of the peak of $(C_iH_jO_k)_{LT}$ species for all oxidizing gases manifests that these species are slightly reactive with NO, O₂ and NO+O₂.

On the basis of our results, the reaction mechanism of the SCR of NO by C_3H_6 on Pt/Al₂O₃ is deduced. Although there are two different mechanisms, most researchers propose that the SCR of NO by C_3H_6 occurred only on Pt sites for both mechanisms. From our results, the observation of three types of surface species indicates the complication in formation of surface species. Each surface spe-

cies plays an independently different role on the overall reaction mechanism. It is postulated that there are at least three pathways in the overall reaction mechanism depending on the reaction temper-

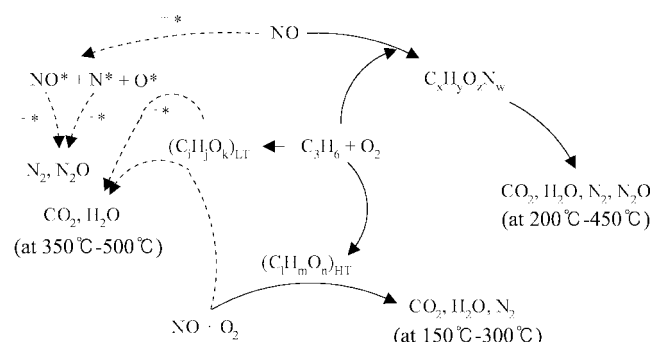


Fig. 5. A proposed reaction mechanism scheme for the SCR of NO by propene under lean-burn condition over Pt/Al₂O₃ (* is given as the vacancy Pt sites).

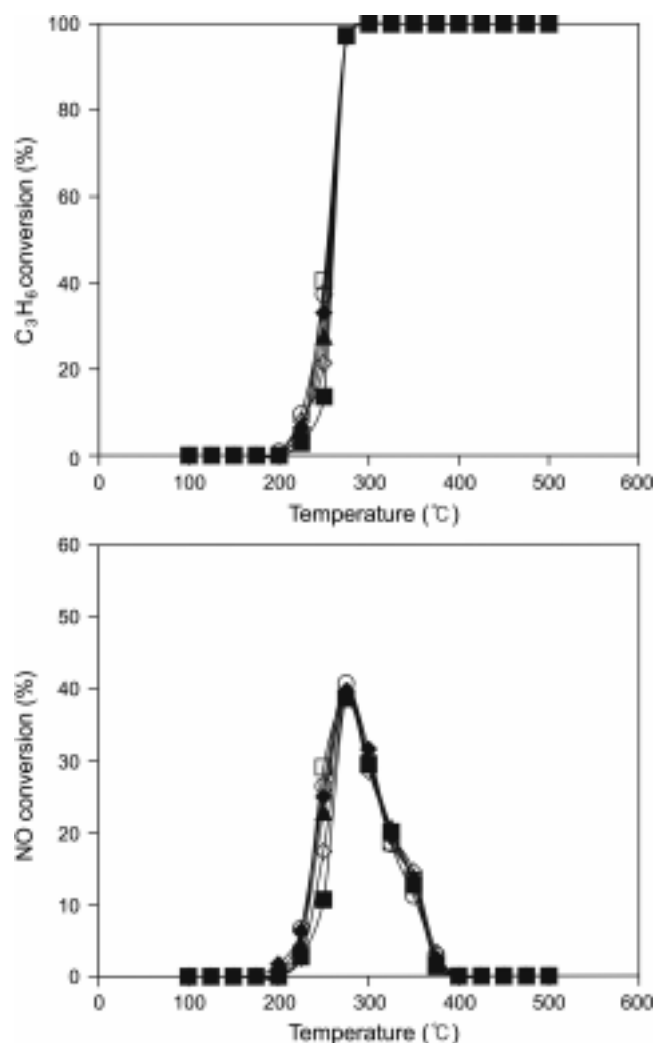


Fig. 6. The effect of the second metal on C₃H₆ and NO conversions over Pt/Al₂O₃ for the SCR of NO by C₃H₆: (▲) Pt/Al₂O₃, (□) Pt-Fe/Al₂O₃, (◇) Pt-Sn/Al₂O₃, (○) Pt-Co/Al₂O₃, (■) Pt-Cr/Al₂O₃, (◆) Pt-W/Al₂O₃.

ature range. At low temperature range (150 °C to 300 °C), the NO reduction mechanism is mainly observed. (C₃H₅O)_{HT} species on the catalyst surface easily react with NO+O₂ and O₂ to produce N₂ and CO₂. The decomposition of C₃H₅O₂N_w species occurs at moderate temperature range (200 °C to 450 °C). Significantly, the decomposition of C₃H₅O₂N_w species is an only mechanism pathway attributed to produce N₂O product. At high temperature range (350 °C to 500 °C), NO₂ and O₂ slightly assist to remove (C₃H₅O)_{LT} species. However, the N₂ production at this temperature range is still unclear. Two aspects should presumably explain this behavior. In the first case, NO can adsorb and decompose to N₂ on vacant sites, which occur by the removal of (C₃H₅O)_{LT} species. In the second case, N₂ product is generated by the reaction between NO+O₂ and (C₃H₅O)_{LT} species. Hence, the mechanism for the SCR of NO by C₃H₆ under lean-burn condition on Pt/Al₂O₃ is proposed as shown in Fig. 5.

2. The Nature of Surface Species on Modified Pt/Al₂O₃ Catalyst

Fig. 6 illustrates the catalytic activity for the SCR of NO by C₃H₆ on modified Pt/Al₂O₃ compared to that on monometallic Pt/Al₂O₃. It is observed that the addition of a second metal (Fe, Sn, Co, Cr or W) over Pt/Al₂O₃ catalyst hardly affects the catalytic activity behavior, viz., the C₃H₆ light-off temperature, the maximum NO conversion and the temperature of maximum NO conversion for such reaction. It is noted that a large amount of N₂O is detected at all temperature ranges where NO conversions appear for all catalysts. The N₂O selectivity of each catalyst at temperature of its maximum NO conversion was approximately in the range of 65-75%. By the way, Pt-W/Al₂O₃ and Pt-Sn/Al₂O₃ gave the lowest and highest selectivity of N₂O (64.5 and 74.7%, respectively), whereas Pt/Al₂O₃ provided the 69.9% selectivity towards N₂O. Similar N₂O selectivities of the modified catalysts and unmodified Pt/Al₂O₃ correspond with the work by Burch et al. [Burch et al., 1997]. Because the narrow temperature window of their catalytic activity results in the consideration in details, the turnover numbers (TONs) of C₃H₆ and NO conversions at 225 °C are obtained as given in Table 1. It is obvious that although the similarity in catalytic activity behavior towards the temperature programmed reaction of the modified catalysts and unmodified Pt/Al₂O₃ is pronounced, the different TONs of these catalysts definitely indicate the disturbance in some function of active sites over Pt/Al₂O₃ by the second metal.

From the different TONs of these catalysts, it is also interesting to study the influence of the second metal on the nature of surface species on the catalyst surface because these surface species may

Table 1. The metal active sites, the metal dispersion and the turnover number of C₃H₆ and NO conversions at 225 °C for various catalysts

Catalyst	Metal active sites (× 10 ¹⁹ molecules of CO/g cat)	Dispersion (%)	TON of C ₃ H ₆ (× 10 ⁻² /s)	TON of NO (× 10 ⁻² /s)
Pt/Al ₂ O ₃	2.55	83	0.67	0.41
Pt-Fe/Al ₂ O ₃	1.98	64	1.50	0.74
Pt-Sn/Al ₂ O ₃	1.25	41	1.33	0.77
Pt-Co/Al ₂ O ₃	2.04	66	1.16	0.72
Pt-Cr/Al ₂ O ₃	2.30	75	0.26	0.15
Pt-W/Al ₂ O ₃	2.19	71	0.87	0.49

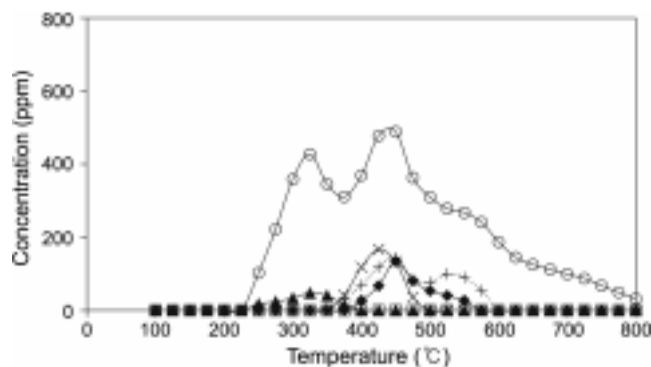


Fig. 7. The temperature programmed desorption profiles of Pt-Fe/Al₂O₃ after dosing 1,000 ppm C₃H₆+1,000 ppm NO+5% O₂ at 225 °C for 2 h: (○) CO₂, (×) CH₄, (◆) CO, (▲) N₂, (□) N₂O, (+, dashed line) O₂.

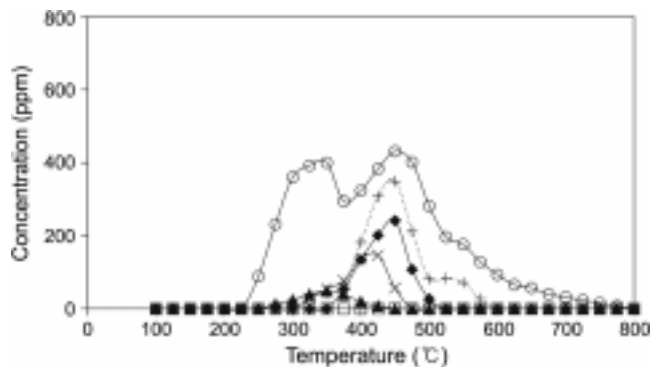


Fig. 10. The temperature programmed desorption profiles of Pt-Cr/Al₂O₃ after dosing 1,000 ppm C₃H₆+1,000 ppm NO+5% O₂ at 225 °C for 2 h: (○) CO₂, (×) CH₄, (◆) CO, (▲) N₂, (□) N₂O, (+, dashed line) O₂.

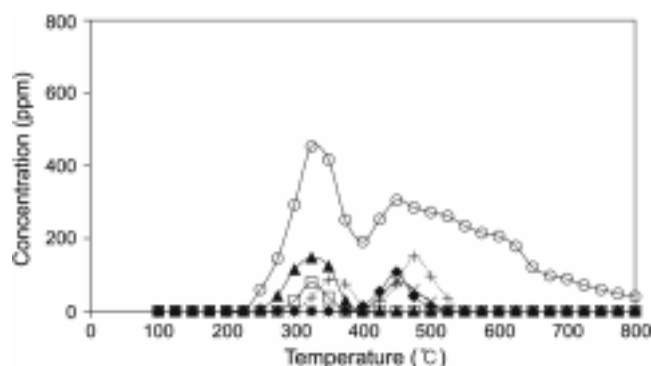


Fig. 8. The temperature programmed desorption profiles of Pt-Sn/Al₂O₃ after dosing 1,000 ppm C₃H₆+1,000 ppm NO+5% O₂ at 225 °C for 2 h: (○) CO₂, (×) CH₄, (◆) CO, (▲) N₂, (□) N₂O, (+, dashed line) O₂.

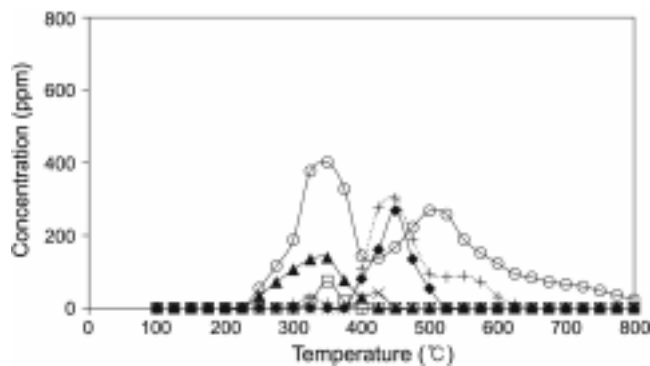


Fig. 11. The temperature programmed desorption profiles of Pt-W/Al₂O₃ after dosing 1,000 ppm C₃H₆+1,000 ppm NO+5% O₂ at 225 °C for 2 h: (○) CO₂, (×) CH₄, (◆) CO, (▲) N₂, (□) N₂O, (+, dashed line) O₂.

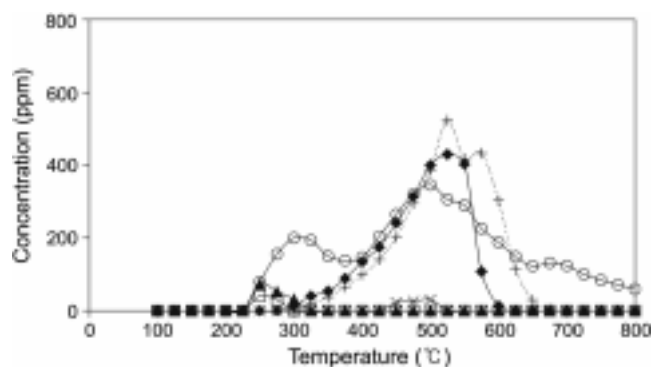


Fig. 9. The temperature programmed desorption profiles of Pt-Co/Al₂O₃ after dosing 1,000 ppm C₃H₆+1,000 ppm NO+5% O₂ at 225 °C for 2 h: (○) CO₂, (×) CH₄, (◆) CO, (▲) N₂, (□) N₂O, (+, dashed line) O₂.

play an important role in the determination of the reaction mechanism pathway as discussed in the above section. The presence of the second metal on Pt/Al₂O₃ can intrinsically result in the difference of TPD pattern as shown in Figs. 7-11. It is obvious that the nature of surface species on Pt/Al₂O₃ catalyst modified by any second metal is different from that on the monometallic Pt/Al₂O₃ ca-

talyst, although the similar composition of surface species involving C, H, O and N atoms, which are released in form of CO₂, CH₄, CO, N₂, N₂O and O₂, is observed. Pt-W/Al₂O₃ giving the TONs of C₃H₆ and NO conversions close to Pt/Al₂O₃ seems to provide rather similar characteristic of surface species. However, it should be noted that there is an additional O₂ peak at high temperature (550 °C) after the addition of W. In the case of Pt-Sn/Al₂O₃, the outlet gases released by the decomposition of C_xH_yO_zN_w species show the same behavior with those of Pt/Al₂O₃. Interestingly, an additional CO₂ peak and a lower amount of the outlet CO and O₂ at moderate temperature (450 °C) and a broader CO₂ peak at high temperature (500 °C) indicate a little change in the nature of (C_xH_yO_z)_{LT} and (C_xH_mO_n)_{HT} species on the catalyst surface. The nature of surface species on Pt-Fe/Al₂O₃ and Pt-Cr/Al₂O₃ is rather similar. Compared to the surface species on Pt/Al₂O₃, an additional CO₂ peak at moderate temperature (450 °C), the tiny shift to higher temperature of a CO₂ peak from (C_xH_yO_z)_{LT} species being coincident with the appearance of O₂ peak at the same temperature (525 °C) and the disappearance of N₂O peak from C_xH_yO_zN_w species are clearly observed on both Pt-Fe/Al₂O₃ and Pt-Cr/Al₂O₃ catalysts. The nature of surface species on Pt-Co/Al₂O₃ is rather a unique behavior. (C_xH_yO_z)_{LT} and (C_xH_mO_n)_{HT} species observed on Pt/Al₂O₃ become the particular surface species showing the new characteristic on Pt-Co/Al₂O₃. The lowest amount

of outlet gases released by the decomposition of C_xH_yO_zN_w species and the largest amount of CO and O₂ are clearly observed on the catalyst surface compared to the others.

From the above-proposed mechanism, the reaction between (C_iH_mO_n)_{HT} species and NO+O₂ and the decomposition of C_xH_yO_zN_w species are speculated to be the significant cooperative mechanism pathway for the SCR of NO by C₃H₆ on Pt/Al₂O₃ in the operating temperature range (200 °C to 400 °C) (see Fig. 6) and (C_iH_jO_k)_{LT} species should therefore be negligible in this temperature range. However, it is believed that (C_iH_jO_k)_{LT} species may be indirectly involved with the reaction mechanism as seen from the different nature of (C_iH_jO_k)_{LT} species after the addition of Fe, Sn, Co or Cr resulting in the different TONs of C₃H₆ and NO conversions. The cooperation of few mechanisms at the same reaction condition indicates the difficulty to control the required reaction mechanism over Pt/Al₂O₃ catalyst. Hence, the overall reaction mechanism is unaffected by the different nature of surface species after a second metal is added.

CONCLUSION

The introduction of the second metal (Fe, Sn, Co, Cr or W) on monometallic Pt/Al₂O₃ has no significant effect on the catalytic activity pattern, viz., the C₃H₆ light-off temperature, the maximum NO conversion and the temperature of maximum NO conversion, for the SCR of NO by C₃H₆ under excess oxygen. The similarity in the catalytic activity behavior towards the temperature programmed reaction of the modified Pt/Al₂O₃ and unmodified one suggests that the reaction mechanism is similar for all the catalysts tested. However, various second metals used have a significant influence on TONs of C₃H₆ and NO conversions and the nature of surface species produced on the catalyst surface at low temperature. The study of the role of surface species on the reaction mechanism over Pt/Al₂O₃ indicates the complexity of the reaction mechanism pathway. The reaction may possibly proceed via a few cooperative mechanisms at the same reaction condition; therefore, it is difficult to control the required reaction mechanism over this catalyst.

ACKNOWLEDGMENTS

The authors would like to thank Thailand Research Fund (TRF) and National Science and Technology Development Agency (NSTDA) for the financial support of this project.

REFERENCES

- Bamwenda, G. R., Ogata, A., Obuchi, A., Oi, J., Mizuno, K. and Skrzypek, J., "Selective Reduction of Nitric Oxide with Propene over Platinum-group Based Catalysts: Studies of Surface Species and Catalytic Activity," *Appl. Catal. B*, **6**, 311 (1995).
- Bensaddik, A., Mouaddib, N., Krawczyk, M., Pitchon, V., Garin, F. and Maire, G., "Promoting Effect of Zinc in DeNO_x Reaction over Pt/Al₂O₃," *Stud. Surf. Sci. Catal.*, **116**, 265 (1998).
- Burch, R., Millington, P. J. and Walker, A. P., "Mechanism of the Selective Reduction of Nitrogen Monoxide on Platinum-based Catalysts in the Presence of Excess Oxygen," *Appl. Catal. B*, **4**, 65 (1994).
- Burch, R., Shestov, A. A. and Sullivan, J. A., "A Transient Kinetic Study of the Mechanism of the NO/C₃H₆/O₂ Reaction over Pt-SiO₂ Catalysts," *J. Catal.*, **182**, 497 (1999).
- Burch, R., Sullivan, J. A. and Watling, T. C., "Mechanistic Considerations for the Reduction of NO_x over Pt/Al₂O₃ and Al₂O₃ Catalysts under Lean-burn Conditions," *Catal. Today*, **42**, 13 (1998).
- Burch, R. and Watling, T. C., "The Effect of Promoters on Pt/Al₂O₃ Catalysts for the Reduction of NO by C₃H₆ under Lean-burn Conditions," *Appl. Catal. B*, **11**, 207 (1997).
- Captain, D. K. and Amiridis, M. D., "In Situ FTIR Studies of the Selective Catalytic Reduction of NO by C₃H₆ over Pt/Al₂O₃," *J. Catal.*, **184**, 377 (1999).
- Captain, D. K., Roberts, K. L. and Amiridis, M. D., "The Selective Catalytic Reduction of Nitric Oxide by Propylene over Pt/SiO₂," *Catal. Today*, **42**, 93 (1998).
- Eckhoff, S., Hesse, D., van den Tillaart, J. A. A., Leyrer, J. and Lox, E. S., "Mechanistic Investigation on the Selective Reduction of NO with Propene in the Presence of Oxygen over Supported Platinum," *Stud. Surf. Sci. Catal.*, **116**, 223 (1997).
- Engler, B. H., Leyrer, J., Lox, E. S. and Ostgathe, K., "Catalytic Reduction of Nitrogen Oxides in Diesel Exhaust Gas," *Stud. Surf. Sci. Catal.*, **96**, 529 (1994).
- Fritz, A. and Pitchon, V., "The Current State of Research on Automotive Lean NO_x Catalysis," *Appl. Catal. B*, **13**, 1 (1997).
- Lacombe, S., Hoebink, J. H. B. J. and Marin, G. B., "Platinum Catalyzed Reduction of Nitric Oxide by N-butane in the Presence of Oxygen: Role of the Hydrocarbon," *Appl. Catal. B*, **12**, 207 (1997).
- Nikolopoulos, A. A., Stergioula, E. S., Efthimiadis, E. A. and Vasalos, I. A., "Selective Catalytic Reduction of NO by Propene in Excess Oxygen on Pt- and Rh-supported Alumina Catalysts," *Catal. Today*, **54**, 439 (1999).
- Obuchi, A., Ohi, A., Nakamura, M., Ogata, A., Mizuno, K. and Ohuchi, H., "Performance of Platinum-group Metal Catalysts for the Selective Reduction of Nitrogen Oxides by Hydrocarbons," *Appl. Catal. B*, **2**, 71 (1993).
- Okuhara, T., Hasada, Y. and Misono, M., "In Situ Diffuse Reflectance IR of Catalytic Reduction of Nitrogen Oxides by Propene in the Presence of Oxygen over Silica-supported Platinum," *Catal. Today*, **35**, 83 (1997).
- Rottlander, C., Andorf, R., Plog, C., Krutzsch, B. and Baems, M., "Selective NO Reduction by Propane and Propene over a Pt/ZSM-5 Catalyst: a Transient Study of the Reaction Mechanism," *Appl. Catal. B*, **11**, 49 (1996).
- Sasaki, M., Hamada, H., Kintaichi, Y. and Ito, T., "Role of Oxygen in Selective Reduction of Nitrogen Monoxide by Propane over Zeolite and Alumina-based Catalysts," *Catal. Lett.*, **15**, 297 (1992).
- Tanaka, T., Okuhara, T. and Misono, M., "Intermediacy of Organic Nitro and Nitrite Surface Species in Selective Reduction of Nitrogen Monoxide by Propene in the Presence of Excess Oxygen over Silica-supported Platinum," *Appl. Catal. B*, **4**, L1 (1994).
- Tanaka, T., Yokota, K., Isomura, N., Doi, H. and Sugiura, M., "Effect of the Addition of Mo and Na to Pt Catalysts on the Selective Reduction of NO," *Appl. Catal. B*, **16**, 199 (1998).
- Xin, M., Hwang, I. C. and Woo, S. I., "FTIR Studies of the Reduction of Nitric Oxide by Propene on Pt/ZSM-5 in the Presence of Oxygen," *J. Phys. Chem.*, **101**, 9005 (1997).
- Xin, M., Hwang, I. C. and Woo, S. I., "In Situ FTIR Study of the Selective Catalytic Reduction of NO on Pt/ZSM-5," *Catal. Today*, **38**, 187

- (1997).
Zhang, G., Yamaguchi, T., Kawakami, H. and Suzuki, T., "Selective Reduction of Nitric Oxide over Platinum Catalysts in the Presence of Sulfur Dioxide and Excess Oxygen," *Appl. Catal. B*, **1**, L15 (1992).