ELSEVIER

Catalysis Today 38 (1997) 187–192

CATALYSIS TODAY

In situ FTIR study of the selective catalytic reduction of NO on Pt/ZSM-5

Mei Xin[1], In Chul Hwang, Seong Ihl Woo*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1, Kusong-dong, Yusong-gu, Taejon, 305-701, South Korea

---

Abstract

The 'direct decomposition mechanism' is suggested for the reduction of NO over ion-exchanged Pt/ZSM-5 catalyst with propene in the presence of oxygen by in situ FTIR spectroscopy.

Keywords: In situ FTIR; Selective catalytic reduction; NO; Pt/ZSM-5

---

1. Introduction

Recently, Pt-group metals, as an alternative system to Cu/ZSM-5 in the reaction of selective catalytic reduction (SCR) of NO, have been reported to show the highest activity for NO reduction at very low temperature range (200–350°C) [1–3]. Among these catalysts, ion-exchanged Pt/ZSM-5 showed more stable performance in the presence of water vapor and/or SO_2 and has been examined in actual diesel engine exhaust [4,5].

Different intermediates have been detected and some mechanisms were then suggested for $NO + C_3H_6 + O_2$ reaction on platinum supported on inorganic metal oxides, such as organic nitro- and nitrito-compounds on Pt/SiO_2 by IR below 200°C [1]; isocyanate (–NCO) species on Pt/Al_2O_3 by FTIR at 250°C [2]; and the direct decomposition of NO molecules on reduced platinum sites to produce nitrogen on Pt/Al_2O_3 by steady-state reaction and TPA technique [3]. However, the reaction mechanisms are still not fully understood. In view of the lack of IR data as well as the study of the Pt/ZSM-5 mechanism in the literature, in the present work we used diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) for the in situ identification of the surface species formed on Pt/ZSM-5 during the $NO + C_3H_6 + O_2$ reaction.

2. Experimental

The Pt/ZSM-5 catalyst was prepared by a conventional ion-exchange procedure. The metal salt used was $Pt(NH_3)_4Cl_2$. Na/ZSM-5, having a Si/Al ratio of 30, was synthesized according to the patent [6]. Following the ion-exchange procedure in an aqueous solution at room temperature for 24 h, the solid was thoroughly washed with deionized water and dried at 393 K overnight and then calcined in air at 500°C for

---

*Corresponding author.

[1] On leave from State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, P.R. China.

PII S0920-5861(97)00065-5

1 h. The platinum loading was 2.4 wt% as determined by ICP–ES (Inductively Coupled Plasma–Atomic Emission Spectroscopy).

DRIFT spectra were recorded on a Bomem Model MB-102 FT–IR spectrometer equipped with an on-line mass spectrometer to analyze the effluent gas. Before recording IR spectra the catalyst was treated in situ IR cell in the following procedure: (1) oxidation in flowing O_2 at 400°C for 10 min; (2) flushing in the flowing He at 400°C for 30 min; (3) reduction in flowing H_2 at 350°C for 1 h; and (4) flushing in flowing He at 400°C for 30 min. The sample was then cooled to the desired temperatures in the flowing He. Gas mixtures were prepared by mixing different reactants which were 1% NO/He, 1% C_3H_6/He and 20% O_2/He before feeding into the cell. The total flow rate in most of the experiments was 30 cm^3 min^{-1}. The NO gas was passed through a dry ice trap to remove traces of NO_2 before being mixed with other gases.

In the case of NO adsorption experiment, 5% NO/He was introduced as flowing gas. Different in situ pretreatment was carried out on Pt/ZSM-5 as follows: (1) oxidization in 20% O_2/He at 400°C for 1 h and cooling in it to the desired temperatures (Pt/ZSM-5(OX)); (2) reduction in H_2 at 350°C for 1 h, flushing in He at 400°C for 30 min and cooling in He to the desired temperatures (Pt/ZSM-5(RE)); and (3) after (2), changing the flush from He to 5% NO/He at 400°C for 30 min. and then cooling in NO/He to the desired temperatures (Pt/ZSM-5(OX/NO)). IR spectra of Pt/ZSM-5 were acquired during the reaction in the flow of NO/He.

3. Results

Fig. 1 shows the IR spectra of the adsorbed species after the addition of a mixture of NO + C_3H_6 + O_2 onto Pt/ZSM-5 and Na/ZSM-5 at reaction temperatures. IR bands around 1721, 1595 and 1510 cm^{-1} are detected on Pt/ZSM-5 at 200°C as shown in Fig. 1b. At 250°C, two broad bands around 1721 and 1580 cm^{-1}, which may be deconvoluted to the bands at 1580 and 1595 cm^{-1}, exist on the surface (Fig. 1a). In addition, broad bands are observed at 2800–3000 cm^{-1}, which are attributed to asymmetric and/or symmetric C–H stretching vibrations in CH_3 and CH_2 groups of hydrocarbon fragments adsorbed on the catalyst [7] and disappear at 250°C. The absence of C–H stretching bands above 3000 cm^{-1} indicates that no olefinic or acetylenic hydrocarbon fragments are present. The band at 2098 cm^{-1} is assigned to CO adsorbed on platinum [8]. The two bands at 2358 and 2334 cm^{-1} can be assigned to gas phase CO_2 confined in the pore system of ZSM-5. Trace of –NCO band at 2235 cm^{-1} is detected on Na/ZSM-5 at 250°C as shown in Fig. 1c.

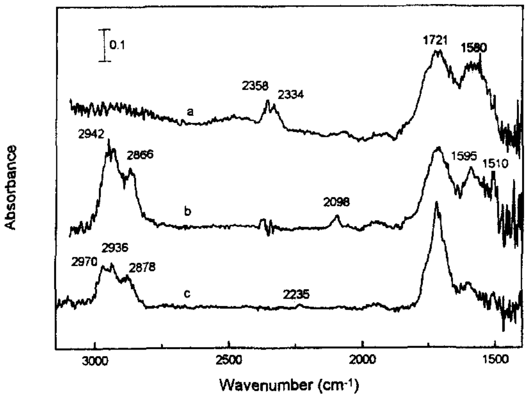

Fig. 1. DRIFT spectra recorded at 200 or 250°C of adsorbed species on Pt/ZSM-5 (a and b) and NaZSM-5 (c) obtained after the addition of NO(3300 ppm) + C_3H_6(3300 ppm) + O_2(7%) for 60 min at (a) 250°C, (b) 200°C and (c) 250°C.

Fig. 2 shows IR spectra obtained after exposing Pt/ZSM-5 to C_3H_6, $C_3H_6 + O_2$, $C_3H_6 + NO$ and $NO + C_3H_6 + O_2$ at 200°C, respectively. According

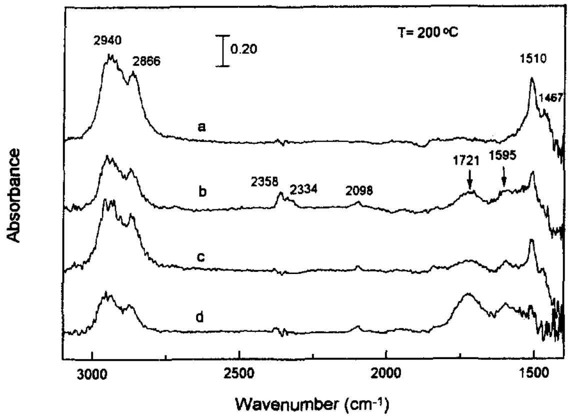

Fig. 2. DRIFT spectra recorded at 200°C of adsorbed species on Pt/ZSM-5 obtained after the addition of various mixed gases at 200°C for 90 min: (a) C_3H_6 (5000 ppm), (b) C_3H_6(5000 ppm)+ O_2(10%), (c) C_3H_6(3300 ppm) + NO(3300 ppm) and (d) NO(3300 ppm) + C_3H_6(3300 ppm) + O_2(7%).

to the literature [9–14] the sharp band at 1510 cm^{-1} is assigned to the π-allyl complexes, i.e., $C\cdots C\cdots C$, formed during the adsorption of propene on Pt/ZSM-5. The shoulder at 1467 cm^{-1} can be assigned either to deformation vibrations of C–H or to the asymmetric stretching vibration of $C\cdots C\cdots C$ in the π-allyl species. This means that the C=C bond of propene is greatly weakened by the adsorption on Pt/ZSM-5 as evidenced by the absence of IR bands in 1600–1650 cm^{-1} region arising from ν(C=C) mode. With the presence of excessive oxygen as shown in Fig. 2b, a new band at 1595 cm^{-1} along with the 1580 cm^{-1} band in Fig. 1a can be associated with the stretching vibrations of COO^- and/or CO_3^{2-} groups in carbonate and carboxylate species adsorbed on the surface. The most reasonable assignment of 1721 cm^{-1} band is the stretching of ν(C=O). Its frequency shifts with the function group that bonds directly to the carbon atom

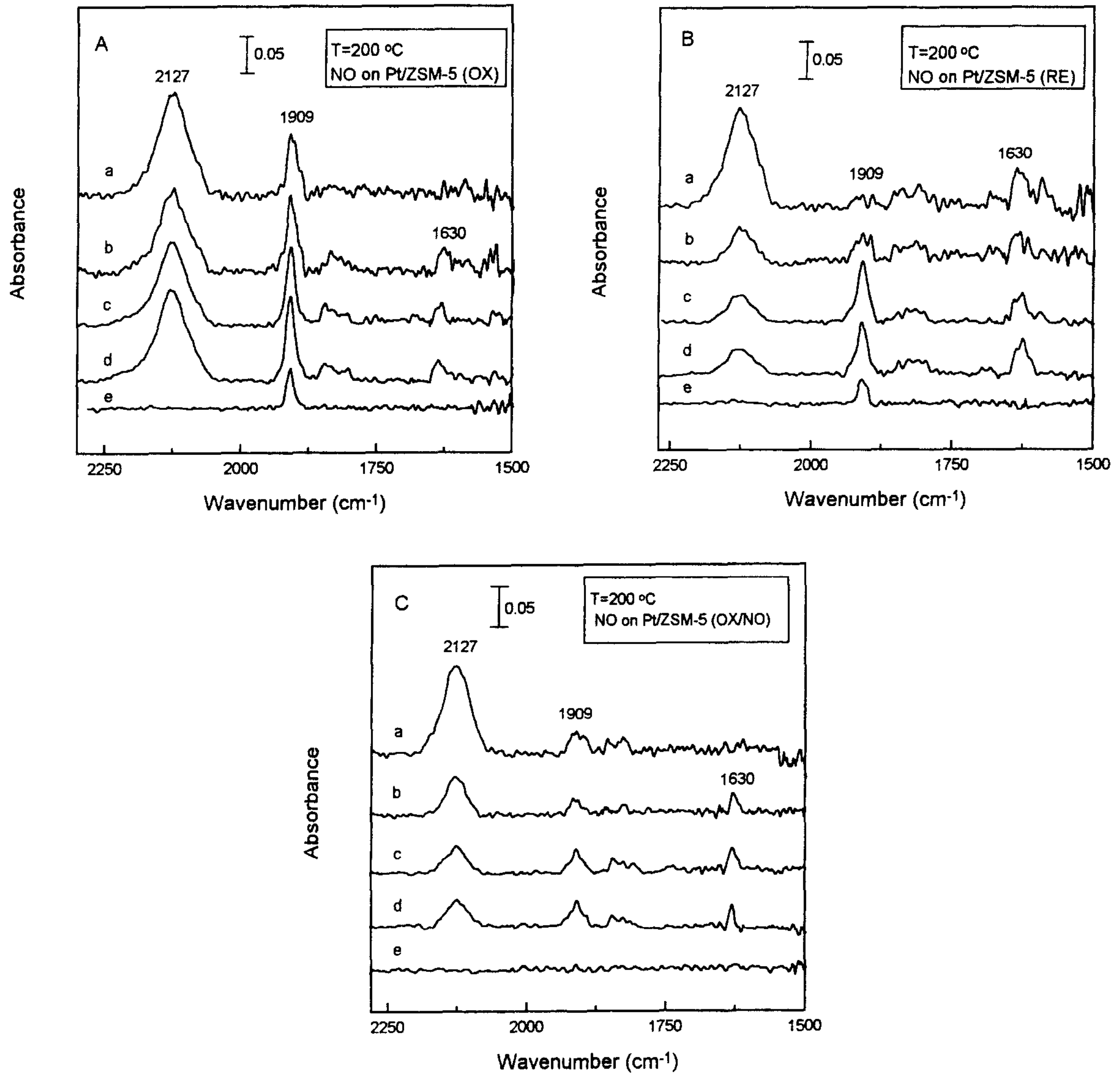

Fig. 3. DRIFT spectra taken at 200°C on Pt/ZSM-5 after the addition of 5% NO/He on (A) Pt/ZSM-5(OX), (B) Pt/ZSM-5(RE), and (C) Pt/ZSM-5(OX/NO). The time-on-stream in NO is (a) 5 min; (b) 15 min; (c) 30 min; (d) 60 min; and (e) after (d) in He for 30 min.

[13]. For comparison, IR spectrum of the coadsorption of NO and propene is shown in Fig. 2c, which exhibits a weaker band at 1721 cm^{-1} but a comparatively strong peak at 1595 cm^{-1}. It is also noticeable that CO band at 2098 cm^{-1} is observed in Fig. 2c, suggesting that the oxidation of propene is proceeded by NO on Pt/ZSM-5.

Fig. 3 illustrates the in situ IR spectra for NO adsorption at 200°C on Pt/ZSM-5 pretreated at different conditions (see Section 2). As shown in Fig. 3A, the most intense bands formed after NO adsorption on Pt/ZSM-5(OX) are at 1909 and 2127 cm^{-1}. The band around 1900 cm^{-1} has been previously assigned in the literature to molecular adsorption of NO on a partly oxidized platinum surface on Pt/SiO_2 at 1935 cm^{-1} [15], Rh-NO^+ on Rh/Al_2O_3 at 1910 cm^{-1} [16], and NO adsorption on oxidized Ir sites on Ir/Al_2O_3 at 1950 cm^{-1} [17].

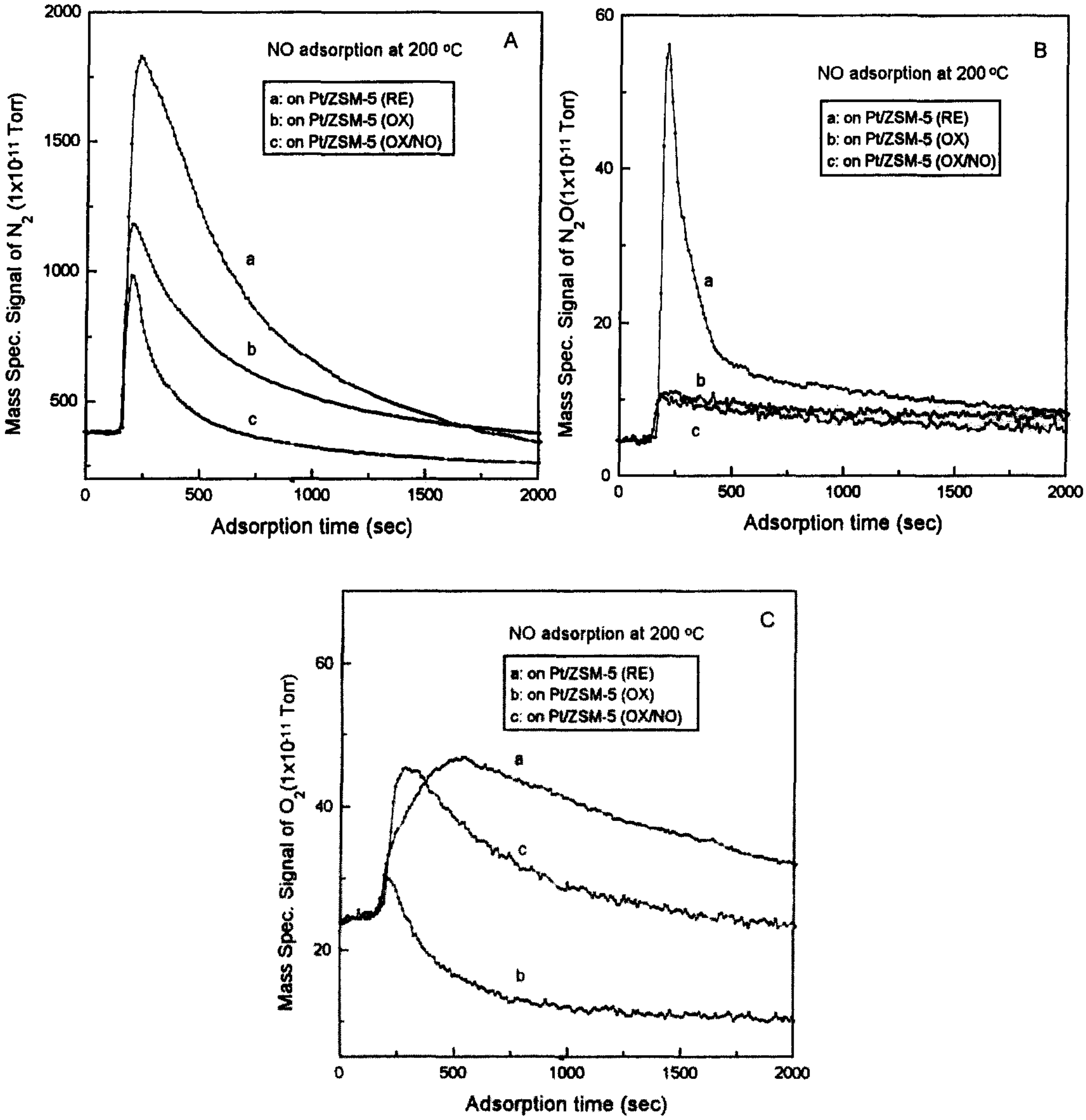

Fig. 4. On-line mass spectrometer signals of (A) N_2 ($m/e = 28$), (B) N_2O ($m/e = 44$) and (C) O_2 ($m/e = 32$) detected at outlet of in situ IR cell after Pt/ZSM-5 catalysts were brought in contact with 5% NO/He at 200°C.

We therefore assign the present 1909 cm^{-1} band to NO molecules adsorbed on oxidized platinum sites. The band at 2127 cm^{-1} has been attributed to the adsorbed NO_2^+ on ZSM-5, which may be associated with the framework hydroxyls of the zeolite [18]. When Pt/ZSM-5(RE) was brought in contact with NO, as shown in Fig. 3B, there is an obvious growth of the band at 1909 cm^{-1} with exposure time. As compared to the NO adsorption on oxidized Pt/ZSM-5, this 1909 cm^{-1} band is at lower intensity. Another significant feature in Fig. 3B is a drastic decrease in intensity of the band at 2127 cm^{-1} with exposure time, especially within the first 10 min. Fig. 3C further shows the IR spectra of NO adsorption on Pt/ZSM-5(OX/NO). A higher decrease in intensity of the 1909 cm^{-1} band is observed, which can be completely removed by flushing in He for 30 min. The other weak IR bands of low frequencies at 1630 cm^{-1} are probably attributed to bridged or bent bound NO species on platinum sites [15,19].

The on-line mass spectrometric results, as shown in Fig. 4, clearly show that reduced platinum surface is very active for NO decomposition, producing considerable amount of N_2 (Fig. 4A) and trace of N_2O (Fig. 4B) in the gas phase. But its activity quickly decreases by the adsorbed oxygen atoms remaining on the surface after the decomposition of NO (Fig. 4C). The mass spectrometric results for Pt/ZSM-5(OX) and Pt/ZSM-5(OX/NO) are very similar. Both of them show low activity for the NO decomposition, suggesting the oxidation of pre-reduced Pt/ZSM-5 in NO at 400°C.

4. Discussion

The above FTIR results have shown that the main surface species observed on Pt/ZSM-5 during the $NO + C_3H_6 + O_2$ reaction are partially oxidized compounds such as carbonyl, carbonate and/or carboxylate formed from the oxidation of propene. No other species which have been reported to be the intermediates such as the N-containing species are detected on Pt/ZSM-5 under our experiment conditions. Partial oxidation of propene is also observed proceeding in the presence of NO, leading to the formation of carbon monoxide and partially oxidized compounds on the surface. The reduced Pt/ZSM-5 shows its high activity for the decomposition of NO, while very low activity is found on oxidized surfaces. It might be expected from the present IR results that reduced platinum sites are the active sites not only for the decomposition of NO but also for the reduction of NO by propene on Pt/ZSM-5. A direct decomposition mechanism is therefore suggested for the reduction of NO on Pt/ZSM-5. According to this mechanism, NO decomposition on reduced platinum sites to generate nitrogen and adsorbed oxygen atoms, followed by the removal of adsorbed oxygen by hydrocarbon, thus produces CO_2, CO and other partially oxidized compounds which might be adsorbed on the catalyst. N_2O which has been reported as another main product during the SCR reaction on Pt-grouped metal catalysts, is yielded by the reaction between adsorbed NO molecules and N atoms on surface.

This proposed mechanism is essentially consistent with that of Burch et al. [3] who suggested that propene firstly reduced Pt-O to Pt metal active sites during the same reaction on pre-oxidized Pt/Al_2O_3. In the case of Pt/ZSM-5, Fig. 3A–C clearly indicate that on the reduced catalyst, the development of 1909 cm^{-1} band is due to NO adsorbed on platinum sites in the neighborhood of adsorbed oxygen produced by the decomposition of NO on freshly reduced surface. For the oxidized catalyst, however, NO adsorption on pre-oxidized platinum sites leads to a strong band quickly appeared at 1909 cm^{-1}. Moreover, the results on Pt/ZSM-5(OX/NO) indicate that there are differences in the characteristics of the platinum sites depending on the pretreatment condition. The comparison of the 1909 cm^{-1} bands of NO adsorption on different samples of Pt/ZSM-5 (Fig. 3A–C) indicates that the degree of the oxidation of pre-reduced platinum sites by adsorbed oxygen atoms may be different from those which are pre-oxidized either by pure oxygen or by NO at higher temperatures. From this result it can be further expected that the pre-oxidized platinum sites may be quite different in the way of getting reduced by propene from the platinum sites occupied by adsorbed oxygen atoms which may become mobile on the surface as temperature is increased. The former may be partially reduced by propene, leading to the generation of active sites for NO decomposition, while the removal of adsorbed oxygen atoms on the latter surface by propene is expected to be more effective.

5. Conclusion

The main surface species observed on Pt/ZSM-5 in the NO + C_3H_6 + O_2 reaction are carbonyl, carbonate and/or carboxylate compounds formed from the partial oxidation of propene on the surface. In contrast to the oxidized ones, reduced Pt/ZSM-5 is found to be very active for the decomposition of NO, producing N_2 in the gas phase and leaving oxygen atoms adsorbed on the surface. We therefore suggest the 'direct decomposition mechanism' for the reduction of NO on Pt/ZSM-5.

References

[1] T. Tank, T. Okuhara and M. Misono, Appl. Catal. B, 4 (1994) L1.

[2] G.R. Bamwenda, A. Ogata, A. Obuchi, J. Oi, K. Mizuno and J. Skrzypek, Appl. Catal. B, 6 (1995) 311.

[3] R. Burch, P.J. Millington and A.P. Walker, Appl. Catal. B, 4 (1994) 65.

[4] M. Iwamoto, H. Yahiro, H.K. Shin, M. Watanabe, J.W. Guo, M. Konno, T. Chikahisa and T. Murayama, Appl. Catal. B, 5 (1994) L1.

[5] H. Hirabayashi, H. Yahiro, N. Mizuno and M. Iwamoto, Chem. Lett., (1992) 2235.

[6] R.J. Araguer and G.R. Landolt, U.S. Patent, 3,702,886 (1992).

[7] L.H. Little, A.V. Kiselev and V.I. Lygin, Infrared Spectra of Adsorbed Species, New York, NY, 1966, pp. 4, 127.

[8] M. Huang, S. Kaliaguine and S. Suppiah, Appl. Surf. Sci., 90 (1995) 393.

[9] V.A. Matyshak and O.V. Krylov, Catal. Today, 25 (1995) 1.

[10] A.A. Davydov, V.G. Mikhaltchenko, V.D. Sokolovskii and G.K. Boreskov, J. Catal., 55 (1978) 299.

[11] L.C. Ivo Freriks, R. Bouwman and P.V. Geenen, J. Catal., 65 (1980) 311.

[12] A.A. Davydov, A.A. Yefremov, V.G. Mikhalchenko and V.D. Sokolovskii, J. Catal., 58 (1970) 1.

[13] E.L. Force and A.T. Bell, J. Catal., 38 (1975) 440.

[14] E. Maslowsky Jr., Vibrational Spectra of Organometallic Compounds, Wiley, New York, Ny, 1977, pp. 267–276.

[15] K.P. De Jong, G.R. Meima and J.W. Geus, Appl. Surf. Sci., 14 (1982–1983) 73.

[16] H. Arai and H. Tominaga, J. Catal., 43 (1976) 131.

[17] F. Solymosi and J. Rasko, J. Catal., 62 (1980) 253.

[18] T.E. Hoost, K.A. Laframboise and K. Otto, Catal. Lett., 33 (1995) 105.

[19] B.A. Morrow, J.P. Chevrier and L.E. Moran, J. Catal., 91 (1985) 208.