



# Novel Pd promoted Ag/Al<sub>2</sub>O<sub>3</sub> catalyst for the selective reduction of NO<sub>x</sub>

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## Abstract

A novel palladium promoted Ag/Al<sub>2</sub>O<sub>3</sub> catalyst (denoted Ag-Pd/Al<sub>2</sub>O<sub>3</sub>) has been developed for the selective catalytic reduction of NO by C<sub>3</sub>H<sub>6</sub>. The Ag-Pd/Al<sub>2</sub>O<sub>3</sub> shows a higher NO<sub>x</sub> conversion than Ag/Al<sub>2</sub>O<sub>3</sub>, especially at the temperatures ranging from 300 to 450 °C. The addition of a small amount of Pd (0.01 wt.%) to Ag/Al<sub>2</sub>O<sub>3</sub> is considered to be favorable for the partial oxidation of C<sub>3</sub>H<sub>6</sub>. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) suggest that the presence of Pd catalyzes the formation of enolic species which is converted from C<sub>3</sub>H<sub>6</sub>. The enolic species is very active towards NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>, resulting in the formation of -NCO species which is the key reaction intermediate in the selective catalytic reduction of NO.

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*Keywords:* Ag-Pd/Al<sub>2</sub>O<sub>3</sub>; Selective catalytic reduction of NO<sub>x</sub>; Enolic species; In situ DRIFTS; Catalytic reaction mechanism

## 1. Introduction

Since Iwamoto and co-workers [1,2] and Held et al. [3] first reported that Cu-ZSM-5 is an effective catalyst for the selective catalytic reduction (SCR) of NO by hydrocarbons in the presence of excess oxygen, the SCR of NO<sub>x</sub> has received much attention as a kind of potential technology for cleaning NO<sub>x</sub> in various oxygen-rich exhausts of diesel engine, lean burn gasoline engine and gas engine. In the recent studies [4–12], alumina-supported silver catalysts (denoted Ag/Al<sub>2</sub>O<sub>3</sub>), which are relatively durable and inexpensive, are considered to be a candidate for practical use. However, the NO<sub>x</sub> conversion over Ag/Al<sub>2</sub>O<sub>3</sub> is quite low at low temperature range of 300–400 °C, which is a major disadvantage. On

the other hand, catalysts based on platinum-group metals, such as well-known three-way catalysts, can eliminate NO<sub>x</sub>, CO and unburned hydrocarbons all together in an exhaust of gasoline engines which operate close to stoichiometric condition. Unfortunately, those catalysts are almost all ineffective for the selective reduction of NO<sub>x</sub> in the presence of excess oxygen when the temperature is over 400 °C [13,14].

We first reported on 69th Annual Meeting of JCS [15] that the selective reduction of NO with C<sub>3</sub>H<sub>6</sub> over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was effectively enhanced by co-impregnating a small amount of Pd, and the negative additive effect of Pt and Au. The additive effect of Pd on Ag/mordenite was also reported by Masuda et al. [16] using (CH<sub>3</sub>)<sub>2</sub>O as a reductant although the durability of Ag/Pd/mordenite was decreased in the presence of water vapor. Seker et al. [17] showed the negative effect of Au on Ag/Al<sub>2</sub>O<sub>3</sub> for the NO<sub>x</sub> reduction with C<sub>3</sub>H<sub>6</sub>. However, the mechanism of additive

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effect of platinum-group metals on Ag based catalysts is still unclear.

In this study, we prepared and investigated a novel Ag-Pd/Al<sub>2</sub>O<sub>3</sub> for the SCR of NO by C<sub>3</sub>H<sub>6</sub>. We have made in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) observation of surface species formed on Ag-Pd/Al<sub>2</sub>O<sub>3</sub> and Ag/Al<sub>2</sub>O<sub>3</sub> to investigate the mechanism of Pd additive effect during the SCR of NO.

## 2. Experimental

### 2.1. Catalyst preparation

The Ag/Al<sub>2</sub>O<sub>3</sub> (Ag metal loading: 5 wt.%) and Pd-Ag/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by an impregnation method. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder (200 m<sup>2</sup> g<sup>-1</sup>) was dissolved in an appropriate amount of silver nitrate or silver nitrate and palladium nitrate mixed in aqueous solution. This was followed by evaporation to dryness in a rotary evaporator at 60 °C under reduced pressure. The resulting paste was dried at 120 °C overnight, and then calcined in air at 600 °C for 3 h. Before catalytic test, the catalysts were sieved into 20–40 meshes.

### 2.2. Catalytic tests

The catalytic test was measured with a fixed-bed quartz flow reactor (10 mm i.d.) by passing a mixture of 800 ppm NO, 1714 ppm C<sub>3</sub>H<sub>6</sub>, and 10 vol.% O<sub>2</sub> in high pure N<sub>2</sub> at a rate of 4000 cm<sup>3</sup> min<sup>-1</sup> over 1.2 g catalyst ( $W/F = 0.018 \text{ g s cm}^{-3}$ , GHSV =  $\sim 50,000 \text{ h}^{-1}$ ). H<sub>2</sub>O vapor (10 vol.%) was supplied with a syringe pump and vaporized by a coiled heater set at inlet of the reactor. Water was removed from the reactor effluent gas by passing a condenser instrument before reaching on line analyzers. After reaching steady state, the effluent gas was analyzed by AVL Di Gas, 4000 light for HC conversion analyses and a chemiluminescence NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer (42C-HL, Thermo Environmental) for NO<sub>x</sub> conversion analyses.

### 2.3. In situ diffuse reflectance infrared Fourier transform spectroscopy procedure

In situ DRIFTS spectra were recorded in a NEXUS 670-FTIR equipped with a smart collector and a

MCT/A detector cooled by liquid N<sub>2</sub>. The sample for studies (ca. 30 mg) was finely ground and placed in a ceramic crucible. Prior to each experiment, the catalyst was firstly heated in the flow of 10 vol.% O<sub>2</sub> + N<sub>2</sub> for 60 min at 300 and 600 °C, respectively, then cooled to 400 °C and exposed to 10 vol.% O<sub>2</sub> + N<sub>2</sub> for 30 min, and a spectrum of the catalyst in the flow of N<sub>2</sub> + O<sub>2</sub> served as the background was recorded. All spectra were measured under real reaction conditions with a resolution of 4 cm<sup>-1</sup> and accumulation of 100 scans.

## 3. Results and discussion

### 3.1. Activity measurements

Fig. 1(a) shows the NO<sub>x</sub> reduction activity of Ag/Al<sub>2</sub>O<sub>3</sub> and Ag-Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, respectively, at various temperatures. Both NO<sub>x</sub> conversions increased with the increase of reaction temperature and reached a maximum at 437 °C for Ag-Pd/Al<sub>2</sub>O<sub>3</sub> and at 470 °C for Ag/Al<sub>2</sub>O<sub>3</sub>, then decreased with the further increase of reaction temperature. The highest rate of NO<sub>x</sub> conversion was 82% over Pd-Ag/Al<sub>2</sub>O<sub>3</sub>, higher than that of 73% over Ag/Al<sub>2</sub>O<sub>3</sub>. Obviously, a trace amount of Pd added into Ag/Al<sub>2</sub>O<sub>3</sub> could enhance the NO<sub>x</sub> conversion in the presence of excess oxygen and water vapor. This metal additive effect is considered to be favorable for activating reductant molecule; for example, scission of a C–C bond and partial oxidation.

Fig. 1(b) shows the conversions of propene into CO<sub>x</sub> over Pd-Ag/Al<sub>2</sub>O<sub>3</sub> and Ag/Al<sub>2</sub>O<sub>3</sub>. Similar to the NO<sub>x</sub> conversion, the curve of C<sub>3</sub>H<sub>6</sub> conversion for Ag/Al<sub>2</sub>O<sub>3</sub> was shifted to lower temperature by Pd addition. This result suggests that Ag-Pd/Al<sub>2</sub>O<sub>3</sub> can activate C<sub>3</sub>H<sub>6</sub> to react with NO + O<sub>2</sub>.

### 3.2. In situ steady-state DRIFTS of the NO<sub>x</sub> reduction over Ag-Pd/Al<sub>2</sub>O<sub>3</sub> and Ag/Al<sub>2</sub>O<sub>3</sub>

For directly investigating the effect of Pd addition under real catalytic reaction conditions, we carried out experiments using in situ DRIFTS. Conditions for in situ DRIFTS are the same as those in Fig. 1, namely, 800 ppm NO + 10 vol.% O<sub>2</sub> + 1714 ppm C<sub>3</sub>H<sub>6</sub>. All in situ DRIFTS spectra shown in Fig. 2 are recorded in the steady state at various temperatures of 200,

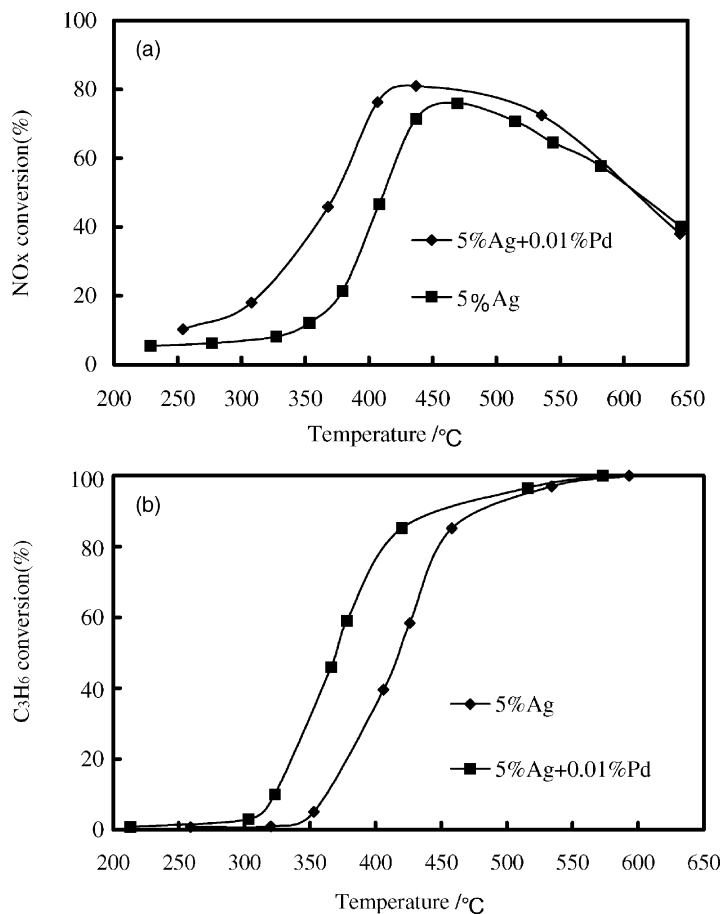


Fig. 1. (a) The catalytic activity for NO<sub>x</sub> reduction by C<sub>3</sub>H<sub>6</sub> over Ag/Al<sub>2</sub>O<sub>3</sub> and Ag-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, respectively, at various temperatures in the presence of water vapor. Reaction conditions: 800 ppm NO, 1714 ppm C<sub>3</sub>H<sub>6</sub>, 10 vol.% O<sub>2</sub>, 10 vol.% water vapor, W/F = 0.018 g s cm<sup>-3</sup>, GHSV = ~50,000 h<sup>-1</sup>, N<sub>2</sub> balance, total flow rate = 4000 ml/min. (b) Conversions of propene into CO<sub>x</sub> over Ag-Pd/Al<sub>2</sub>O<sub>3</sub> and Ag/Al<sub>2</sub>O<sub>3</sub>, respectively, at various temperatures in the presence of water vapor. Reaction conditions: the same as in (a).

250, 300, 350, 400 and 450 °C. After an exposure of the catalyst to NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> mixture gas for 60 min at 200 °C, as shown in Fig. 2, many IR peaks appeared in the region between 1700 and 1300 cm<sup>-1</sup>. According to the previous literatures [12,18,19], the strong bands at 1651, 1591, and 1392 cm<sup>-1</sup> were attributed to ν(-ONO), ν(-NO<sub>2</sub>) and δ(-CH<sub>3</sub>), respectively, which suggested that the organic compounds C<sub>x</sub>H<sub>y</sub>NO<sub>z</sub> (R-ONO and R-NO<sub>2</sub>) were largely formed on the catalyst surface at 200 °C. The peaks at 1300 and 1580 cm<sup>-1</sup> were assigned to the bidentate nitrates and monodentate nitrates, respectively [7,12,20]. The peaks at 1562 and 1454 cm<sup>-1</sup> are assigned to ν<sub>as</sub>(COO) and ν<sub>s</sub>(COO) of the adsorbed

acetate [20–23]. When we increased the reaction temperature, as shown in Fig. 2, the strong band at 1651 cm<sup>-1</sup> disappeared gradually, while the weak band at 2239 cm<sup>-1</sup> can still be observed. This feature has been observed in our previous works [11,12] and assigned to isocyanate (-NCO) species, which is a key intermediate species, reported by many researchers [7–9,14].

Fig. 3 shows the IR spectra of Ag-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst in the flow of NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> in the steady state at various temperatures. Based on the comparison between Figs. 2 and 3, the bands at 1300, 1580, 1572, 1460 (1460–1475), 1597 and 1394 cm<sup>-1</sup> are similarly assigned to bands of adsorbed nitrates, acetate and

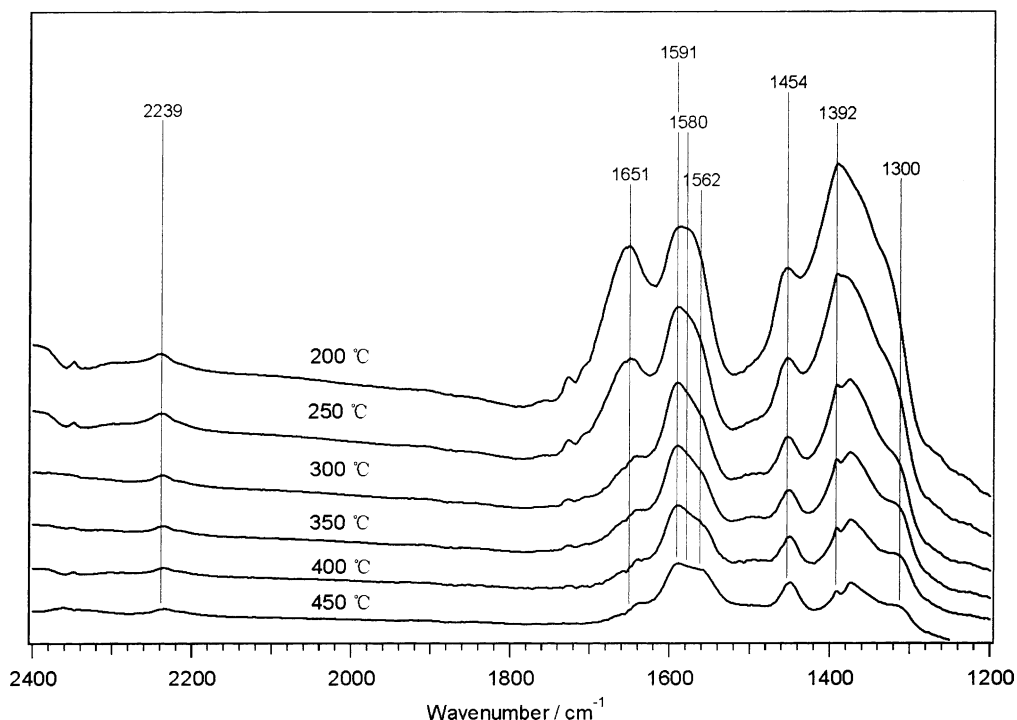


Fig. 2. In situ DRIFTS spectra of Ag/Al<sub>2</sub>O<sub>3</sub> in a steady state at various temperatures in a flow of C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> + NO. Feed: the same as in Fig. 1.

R-NO<sub>2</sub> species. The principle difference between Figs. 2 and 3 is the new peak on Ag-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst at 1637 cm<sup>-1</sup>, along with the missing peak at 1651 cm<sup>-1</sup> which has been assigned to the band of R-ONO in Fig. 2. Another new band at 2158 cm<sup>-1</sup> can be assigned to -CN surface species [12,24]. Similar peak at 1630 cm<sup>-1</sup> was also observed on Ag/Al<sub>2</sub>O<sub>3</sub> in the flow of *n*-hexane + NO + O<sub>2</sub> and assigned to carbonate species [20]. Turek et al. [25] reported that when CO<sub>2</sub> chemisorbed on the surface of γ-Al<sub>2</sub>O<sub>3</sub>, main adsorbed species was carbonate. We studied the adsorption of CO<sub>2</sub> on Ag-Pd/Al<sub>2</sub>O<sub>3</sub> at 200 °C, but no peak at 1630 cm<sup>-1</sup> was observed. The peak at 1637 cm<sup>-1</sup> in Fig. 3 may be associated with the frequency of double bond stretching vibration, such as ν(C=C), ν(C=O). In general, the stretching vibration frequencies of isolate C=C and C=O should both be higher than 1637 cm<sup>-1</sup>. When exposing Ag/Al<sub>2</sub>O<sub>3</sub> to the flow of C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub>, it is possible to form a surface enolic structure (H<sub>2</sub>C=CH-O...M<sup>+</sup>) on the surface by partial oxidation of C<sub>3</sub>H<sub>6</sub>. The

conjugation of H<sub>2</sub>C=CH-O<sup>-</sup> group may induce the vibrational mode of C-C-O to shift to a frequency which is lower than ν(C=C) and higher than ν(C-O) [26]. As a consequence, the peak at 1637 cm<sup>-1</sup> in Fig. 3 could be tentatively assigned to stretching vibration mode of C=CH-O<sup>-</sup>. With increasing temperature, the bands of nitrate (1300 cm<sup>-1</sup>) and enolic species (1637 cm<sup>-1</sup>) decreased promptly, while the -NCO band (2233 cm<sup>-1</sup>) progressively appeared. This indicates that the enolic surface species is reactive towards nitrate to form -NCO species. As a result, Ag-Pd/Al<sub>2</sub>O<sub>3</sub> has a higher -NCO surface concentration than Ag/Al<sub>2</sub>O<sub>3</sub> during the SCR of NO by C<sub>3</sub>H<sub>6</sub>. This result is in good agreement with activity of Ag/Al<sub>2</sub>O<sub>3</sub> and Ag-Pd/Al<sub>2</sub>O<sub>3</sub>.

### 3.3. Reaction mechanism on Ag-Pd/Al<sub>2</sub>O<sub>3</sub>

The reaction mechanism of the SCR of NO by C<sub>3</sub>H<sub>6</sub> over Ag/Al<sub>2</sub>O<sub>3</sub> has been proposed with R-ONO, R-NO<sub>2</sub> and -NCO as the key intermediates

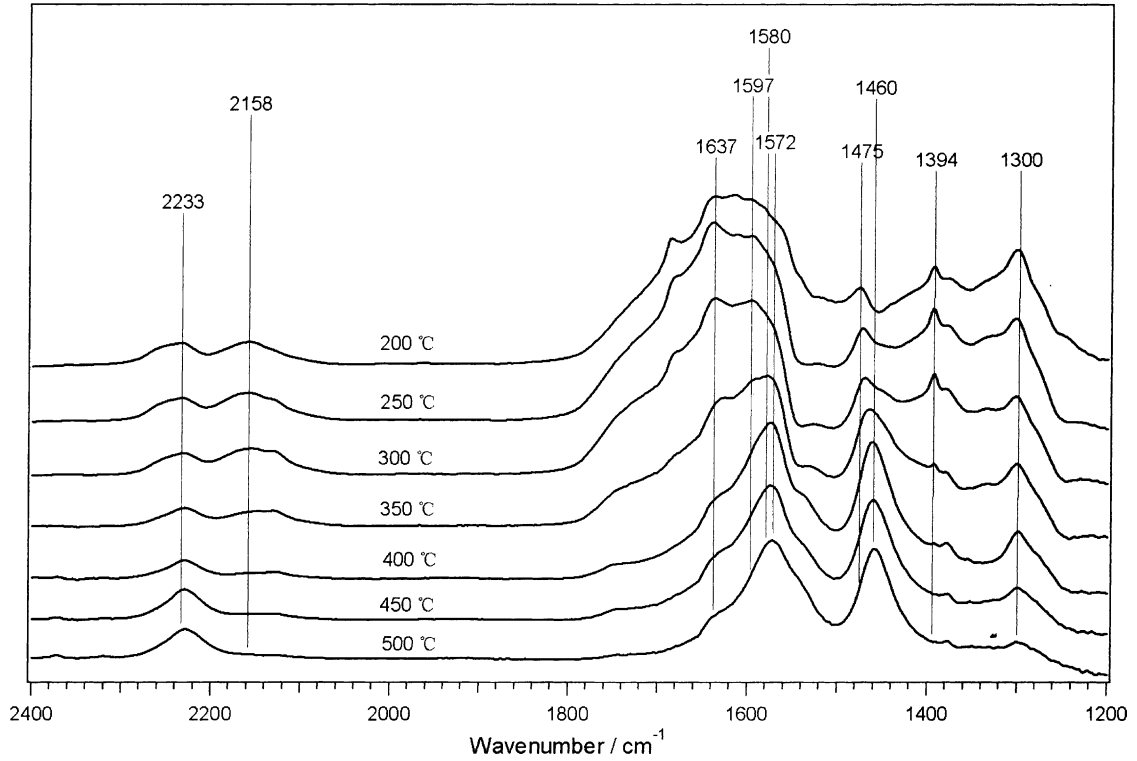
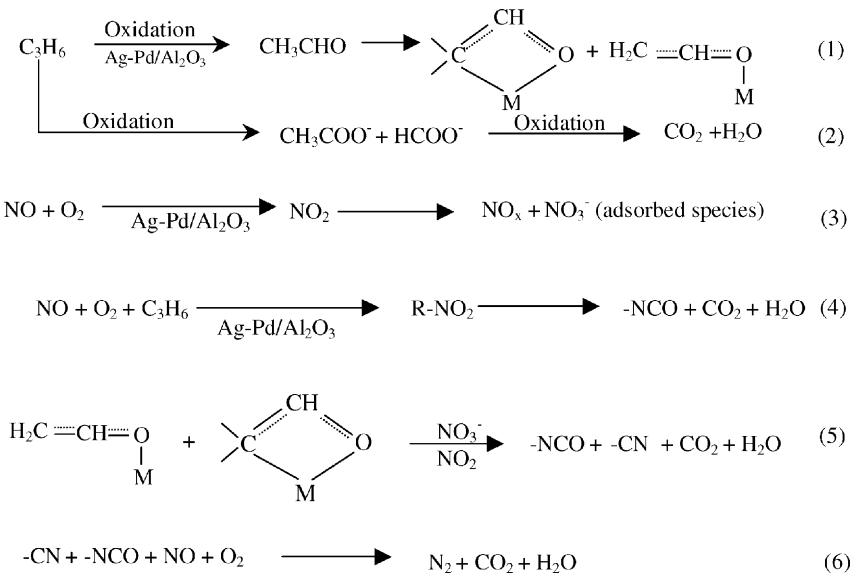


Fig. 3. In situ DRIFTS spectra of Ag-Pd/Al<sub>2</sub>O<sub>3</sub> in a steady state at various temperatures in a flow of C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> + NO. Feed: the same as in Fig. 1.



Scheme 1. The proposed reaction mechanism for the SCR of NO by C<sub>3</sub>H<sub>6</sub> over Ag-Pd/Al<sub>2</sub>O<sub>3</sub>.

[10,12,20]. Burch et al. [14] extended a similar reaction mechanism to all oxide catalysts in a review, approximately,  $\text{NO} + \text{O}_2 + \text{C}_3\text{H}_6 \rightarrow \text{NO}_x + \text{C}_x\text{H}_y\text{O}_z \rightarrow \text{R-NO}_2 + \text{R-ONO} \rightarrow \text{R-NCO} + \text{R-CN} + \text{NO} + \text{O}_2 \rightarrow \text{N}_2$ . Our in situ DRIFTS in Fig. 2 also support this mechanism. R-ONO, R-NO<sub>2</sub> and -NCO are observed on Ag/Al<sub>2</sub>O<sub>3</sub> during reaction, and high coverage R-ONO formed at a low temperature of 200 °C. However, the mechanism is dramatically altered with adding a trace quantity of Pd to Ag/Al<sub>2</sub>O<sub>3</sub>. In the case of Ag-Pd/Al<sub>2</sub>O<sub>3</sub>, R-ONO band at 1651 cm<sup>-1</sup> cannot be observed at all reaction temperatures, replaced with the enolic species band at 1637 cm<sup>-1</sup> (Fig. 3). It can be considered that the presence of Pd catalyzes the formation of enolic species, which undergoes a reaction with NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> to convert into -NCO and -CN, and subsequently into N<sub>2</sub>. Summarizing the mentioned discussion, the proposed reaction pathway of the SCR of NO by C<sub>3</sub>H<sub>6</sub> over Ag-Pd/Al<sub>2</sub>O<sub>3</sub> is illustrated in Scheme 1.

Much additional knowledge will be required before reliable reaction mechanism can be made. Further studies are under way in order to test some of the hypotheses made above.

#### 4. Conclusion

We have developed a novel Ag-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst for the NO<sub>x</sub> reduction by C<sub>3</sub>H<sub>6</sub> under lean burning conditions. According to catalytic tests over Ag-Pd/Al<sub>2</sub>O<sub>3</sub> and contrastive Ag/Al<sub>2</sub>O<sub>3</sub>, we find that loading trace amounts of Pd on Ag/Al<sub>2</sub>O<sub>3</sub> leads to a significant improvement of NO<sub>x</sub> conversion during the SCR of NO by C<sub>3</sub>H<sub>6</sub>, especially at low reaction temperature. In situ DRIFTS results suggest that Pd addition catalyzes the partial oxidation of C<sub>3</sub>H<sub>6</sub> into surface enolic species, and the surface enolic species is quite reactive towards NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub> to form surface NCO species. Based on these results, a new reaction mechanism is proposed with enolic species and NCO species as the key reaction intermediates.

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