

# In situ DRIFTS study of the selective reduction of $\text{NO}_x$ with alcohols over $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst: Role of surface enolic species

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## Abstract

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to clarify the formation and reactivity of enolic species and its role in the formation of the isocyanate species ( $-\text{NCO}$ ) during the selective catalytic reduction of  $\text{NO}_x$  (SCR of  $\text{NO}_x$ ) by alcohols ( $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$  and isopropyl alcohol (IPA)) over  $\text{Ag}/\text{Al}_2\text{O}_3$  catalyst. The enolic species, which was derived from the partial oxidation of  $\text{C}_2\text{H}_5\text{OH}$  and IPA in the presence of  $\text{O}_2$  over  $\text{Ag}/\text{Al}_2\text{O}_3$ , had a high reactivity with  $\text{NO} + \text{O}_2$ , resulting in a high surface concentration of  $-\text{NCO}$  species and high efficiency of  $\text{NO}_x$  reduction when using  $\text{C}_2\text{H}_5\text{OH}$  or IPA as reductants. In contrast,  $\text{CH}_3\text{OH}$  was much less effective for the SCR of  $\text{NO}_x$ . The order of the facility for the formation of enolic species and  $-\text{NCO}$  species was in good agreement with the order of the activities in the SCR of  $\text{NO}_x$  process ( $\text{C}_2\text{H}_5\text{OH} > \text{IPA} > \text{CH}_3\text{OH}$ ) in the moderate temperature range of 523–623 K.

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## 1. Introduction

The SCR of  $\text{NO}_x$  in the presence of excess  $\text{O}_2$  can be applied to the removal of gaseous pollutants from diesel and lean-burn engines. In recent studies [1–10], alumina-supported silver catalysts (denoted as  $\text{Ag}/\text{Al}_2\text{O}_3$ ), which are relatively durable and inexpensive, have been considered to be a candidate for practical use. In particular,  $\text{C}_2\text{H}_5\text{OH}$  is extremely effective for the SCR of  $\text{NO}_x$  over  $\text{Ag}/\text{Al}_2\text{O}_3$  even in the presence of water and  $\text{SO}_2$  [1,4,5].

So far, several reaction mechanisms for  $\text{NO}_x$  reduction including the intermediates (such as  $\text{NO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{R}-\text{NO}_2$ ,  $-\text{CN}$  and  $-\text{NCO}$  species, etc.) have been proposed [4–7,11–18]. Among these mechanisms,  $-\text{NCO}$  species has often been proposed as a crucial intermediate. Our previous studies as well as other research works have also proved that the formation of  $-\text{NCO}$  species and its effective reaction with  $\text{NO}$  or  $\text{NO} + \text{O}_2$  are key steps in the SCR reaction [4,5,11,15,17]. We recently have proposed a novel

mechanism of the SCR of  $\text{NO}_x$  by  $\text{C}_2\text{H}_5\text{OH}$  [19], where the surface enolic species related with the high surface concentration of  $-\text{NCO}$  and the high efficiency of  $\text{NO}_x$  reduction by  $\text{C}_2\text{H}_5\text{OH}$ . However, other alcohols (such as IPA and  $\text{CH}_3\text{OH}$ , etc.) have not been proved to follow the same mechanism during the SCR of  $\text{NO}_x$ .

In this paper, we use in situ DRIFTS method to study the behavior of surface species on  $\text{Ag}/\text{Al}_2\text{O}_3$  during the SCR of  $\text{NO}_x$  using  $\text{C}_2\text{H}_5\text{OH}$ , IPA and  $\text{CH}_3\text{OH}$  as reductants. Particular attention is given to the surface enolic species, which formed from the partial oxidation of alcohols during the SCR of  $\text{NO}_x$ . The results could provide new insights into the mechanisms for the SCR of  $\text{NO}_x$  by alcohols.

## 2. Experimental

### 2.1. Catalyst preparation

$\text{Ag}/\text{Al}_2\text{O}_3$  (5 wt.%) catalyst was prepared by an impregnation method as following:  $\text{Al}_2\text{O}_3$  powder (200  $\text{m}^2/\text{g}$ ) was

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dissolved in an appropriate amount of silver nitrate aqueous solution. The sample was dried at 393 K for 3 h and calcined at 873 K for 3 h in air.

## 2.2. Activity measurements

The catalytic activity was measured in a fixed-bed reactor by passing a gaseous mixture of NO (800 ppm), reductant ( $C_2H_5OH$  1565 ppm or IPA 1200 ppm or  $CH_3OH$  2250 ppm)  $O_2$  (10%) in  $N_2$  balance at a total flow rate of 2000 mL/min.  $W/F = 0.018 \text{ g s cm}^{-3}$  (GHSV  $\sim 50,000 \text{ h}^{-1}$ ).  $NO_x$  conversion was analyzed on-line by a chemiluminescence  $NO/NO_2/NO_x$  analyzer (42C-hl, Thermo Environmental). An aqueous  $C_2H_5OH$  (or IPA or  $CH_3OH$ ) solution was supplied with a micropump into the gas stream and vaporized by a coiled heater at the inlet of the reactor. Analysis of the gas products was carried out using a NEXUS 670-FTIR spectrophotometer fitted with a gas cell of volume  $2 \text{ dm}^3$  (all spectra were measured with a resolution of  $1 \text{ cm}^{-1}$  and with an accumulation of 32 scans) and gas chromatography (Agilent 6890N GC) coupled to a mass spectrometer (Agilent 5973N MS) with a column-containing HP-PLOT Q (Agilent  $30 \text{ m} \times 0.320 \text{ mm}$ ).

## 2.3. In situ DRIFTS procedure

In situ DRIFTS spectra were recorded on a NEXUS 670-FTIR equipped with a smart collector and a MCT/A detector cooled by liquid  $N_2$ . The catalyst was finely ground and placed in a ceramic crucible. Prior to each experiment, the catalyst was firstly heated in a flow of 10 vol%  $O_2 + N_2$  for 60 min at 573 and 873 K, respectively, then cooled to the desired temperature and a spectrum of the catalyst in the flow of  $N_2 + O_2$  served as the background was recorded. All gas mixtures were fed at a flow rate of 300 mL/min. All spectra were measured with a resolution of  $4 \text{ cm}^{-1}$  and with an accumulation of 100 scans.

## 3. Results and discussion

### 3.1. Reaction activity of various alcohols for the SCR of $NO_x$ over $Ag/Al_2O_3$ catalyst

Fig. 1 shows the conversion of  $NO_x$  over  $Ag/Al_2O_3$  catalyst for the various reaction systems ( $NO-O_2$ -reductant). When using  $C_2H_5OH$  as a reductant, the maximal conversion of  $NO_x$  was up to 99.7% with a very broad active temperature window (597–747 K). In the case of IPA, it is worthwhile to note that the  $NO_x$  conversion was nearly the same as that of  $C_2H_5OH$  within the temperature range of 623–773 K. In contrast, there was a relatively lower  $NO_x$  conversion by  $CH_3OH$  in the temperature range of (547–691 K) and the highest conversion of  $NO_x$  was only 21.9%. These results indicate that the  $NO_x$  conversion is strongly influenced by the kinds of alcohols and the order of the

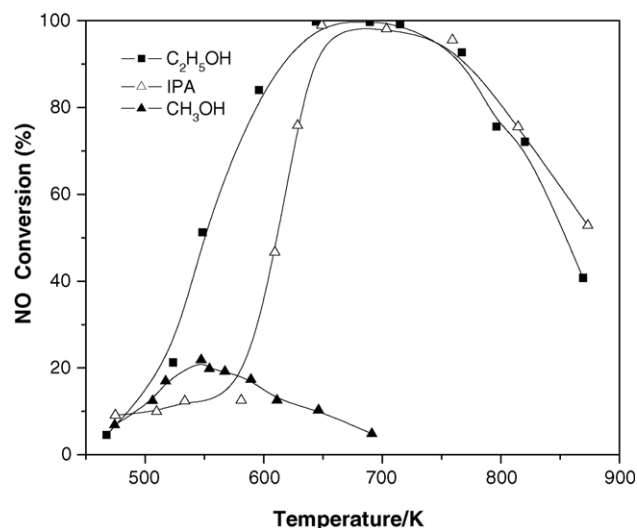


Fig. 1. Catalytic activity for  $NO_x$  reduction with different alcohols over  $Ag/Al_2O_3$  catalyst at various temperatures. Conditions:  $NO$  800 ppm;  $CH_3OH$  2250 ppm or  $C_2H_5OH$  1565 ppm or IPA 1200 ppm;  $O_2$  10% in  $N_2$  balance at total flow rate 2000 mL/min.  $W/F = 0.018 \text{ g s cm}^{-3}$  (GHSV  $\sim 50,000 \text{ h}^{-1}$ ).

effective reactivity is  $C_2H_5OH > IPA > CH_3OH$  in the moderate temperature range of 523–623 K.

The main products of the SCR of  $NO_x$  over  $Ag/Al_2O_3$  catalyst are  $N_2$  and  $CO_2$ . The diversity of by-products using different alcohols as reductants only could be seen at low temperatures, so we measure the by-product distributions at 473 K. GC-MS alone would not permit us to distinguish  $CO_2$  from  $N_2O$ ,  $N_2$  from  $CO$ ; on the other hand,  $N_2$  is not IR active, and hence could not be detected. As a result, both the two analysis systems are used in our experiments. From FTIR gas spectra, we detected small amount of  $N_2O$  ( $<30 \text{ ppm}$ ) and traces of  $HCN$  and  $NH_3$ . GC-MS analysis was used to detect other nitrogen-containing species, which were not detectable by FTIR. In the reduction of  $NO_x$  with  $C_2H_5OH$  (Fig. 2A), mainly  $N_2$  and  $CO_2$  were produced and the reduction was accompanied by side reactions leading to the formation of acetaldehyde ( $CH_3CHO$ , 200 ppm) along with 120 ppm unreacted  $C_2H_5OH$  and small amount of nitrogen-containing compounds such as  $N_2O$  and  $CH_3NO_2$ . During the reduction of  $NO_x$  by IPA, acetone ( $CH_3COCH_3$ ) was the main side product, together with other minor by-products such as  $C_2H_5OH$ ,  $CH_3CHO$ ,  $N_2O$  and  $CH_3NO_2$ . Traces of  $HCN$  and  $C_3H_6$  were also present (Fig. 2B). As for  $CH_3OH$  (Fig. 2C), the main products were  $CO_2$  and  $N_2$ , accompanied by small amount of unreacted  $CH_3OH$ . No by-products could be detected at 473 K and higher temperatures.

### 3.2. In situ DRIFTS study of the SCR of $NO_x$ by different alcohols over $Ag/Al_2O_3$ catalyst

The difference of these three alcohols for the SCR of  $NO_x$  over the  $Ag/Al_2O_3$  was investigated by DRIFTS method. Fig. 3 shows the in situ DRIFTS spectra of  $Ag/Al_2O_3$

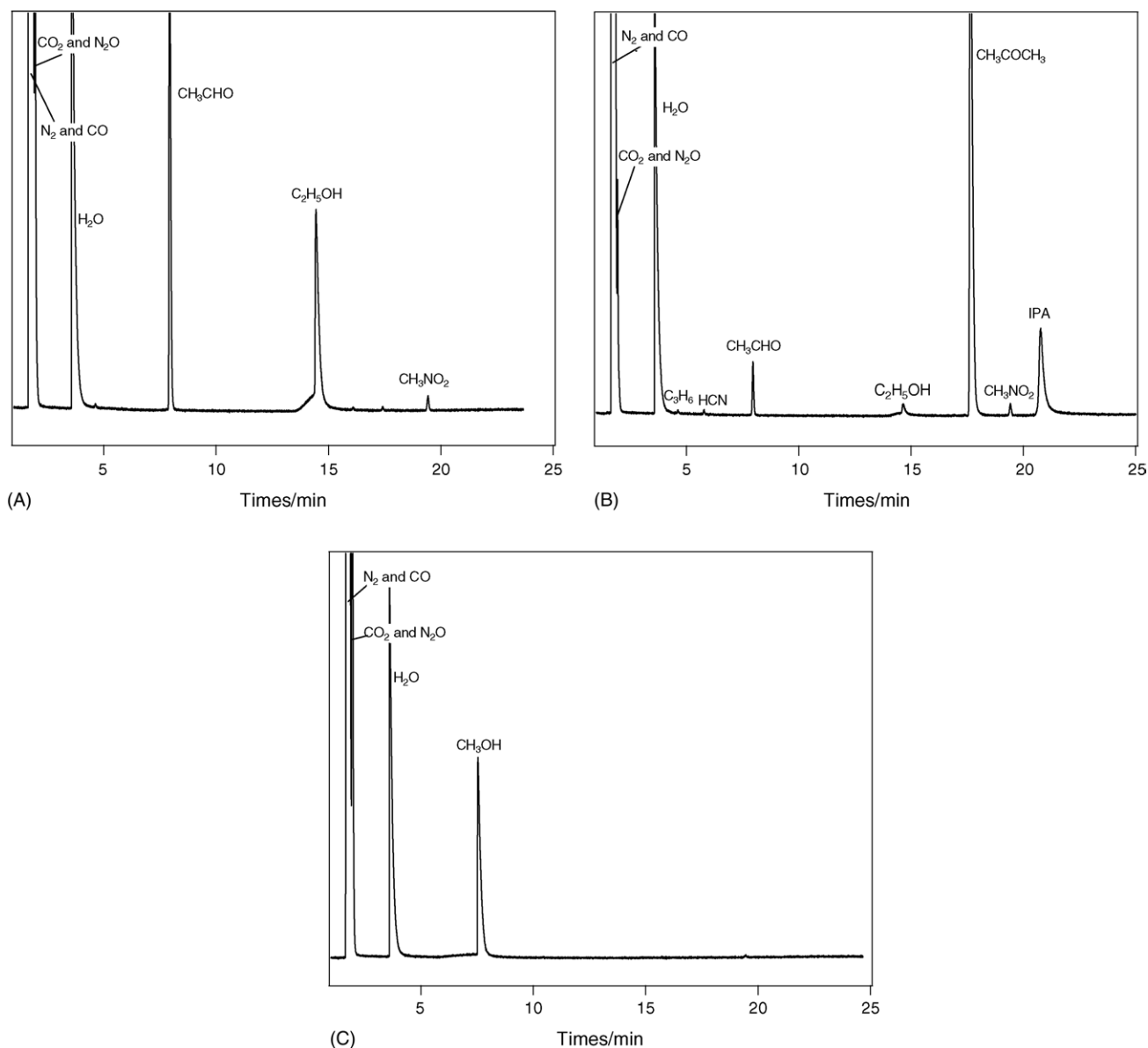


Fig. 2. (A) GC–MS chromatogram of gas products of  $C_2H_5OH/NO/O_2$  reaction at 473 K on  $Ag/Al_2O_3$  catalyst. Conditions:  $NO$  800 ppm;  $C_2H_5OH$  1565 ppm;  $O_2$  10%. (B) GC–MS chromatogram of gas products of  $IPA/NO/O_2$  reaction at 473 K on  $Ag/Al_2O_3$  catalyst. Conditions:  $NO$  800 ppm;  $IPA$  1200 ppm;  $O_2$  10%. (C) GC–MS chromatogram of gas products of  $CH_3OH/NO/O_2$  reaction at 473 K on  $Ag/Al_2O_3$  catalyst. Conditions:  $NO$  800 ppm;  $CH_3OH$  2250 ppm;  $O_2$  10%.

catalyst in the flow of  $NO + C_2H_5OH + O_2$  in steady state at various temperatures. Based on the previous study [19], the bands at 1633, 1416 and  $1336\text{ cm}^{-1}$  are assignable to the enolic species and the peaks at 1578 and  $1464\text{ cm}^{-1}$  are associated with acetate species, whereas the bands at 1585 and  $1304\text{ cm}^{-1}$  are due to adsorbed nitrates. In addition, a very strong peak appeared at  $2233\text{ cm}^{-1}$ , which is assignable to  $-NCO$  species. During  $NO + IPA + O_2$  reaction over  $Ag/Al_2O_3$  catalyst (Fig. 4), the characteristic peaks are similarly assigned to enolic species ( $1633$ ,  $1412$  and  $1338\text{ cm}^{-1}$ ), acetate species ( $1579$  and  $1468\text{ cm}^{-1}$ ) and nitrates ( $1585$  and  $1302\text{ cm}^{-1}$ ). The shoulder peak at  $1612\text{ cm}^{-1}$  was also assigned to bridge adsorbed surface nitrate species [7,15,19]. The obvious difference is the

appearance of the formate bands at  $1591$  and  $1382\text{ cm}^{-1}$ , while the peak at  $1392\text{ cm}^{-1}$  could be associated with  $\delta(C-H)$  [13,17,19,22]. In the case of  $NO + CH_3OH + O_2$  reaction (Fig. 5), very weak  $-NCO$  peak at  $2233\text{ cm}^{-1}$  and strong formate peaks at  $1595$  and  $1379\text{ cm}^{-1}$  were observed. Whereas the bands at  $1300$ ,  $1589$  and  $1612\text{ cm}^{-1}$  are similarly assigned to adsorbed nitrates and the band at  $1390\text{ cm}^{-1}$  is associated with  $\delta(C-H)$ , as shown in Fig. 4. The bands at  $1639$ ,  $3732$ ,  $3697$  and  $3589\text{ cm}^{-1}$  are considered to relate with the formation of  $H_2O$  by dehydration of  $CH_3OH$  and it disappeared by increasing temperature to 623 K. According to the literature [20,21],  $CH_3OH$  was selectively dehydrated to dimethyl ether (DME) over  $\gamma-Al_2O_3$  and promoted  $\gamma-Al_2O_3$  in the

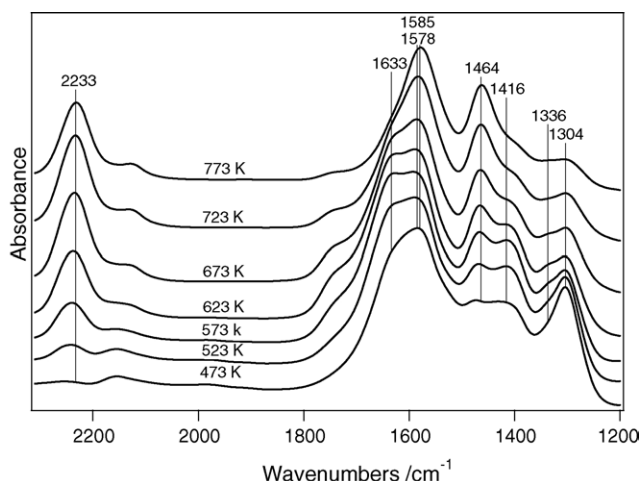


Fig. 3. In situ DRIFTS spectra of adsorbed species in steady state on Ag/Al<sub>2</sub>O<sub>3</sub> in a flow of C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> + NO at various temperatures. Conditions: NO 800 ppm; C<sub>2</sub>H<sub>5</sub>OH 1565 ppm; O<sub>2</sub> 10%.

temperature of 423–573 K, accompanied by the formation of H<sub>2</sub>O.

As shown in Figs. 3–5, the formation of –NCO species in the NO–O<sub>2</sub>–C<sub>2</sub>H<sub>5</sub>OH is similar to that in the NO–O<sub>2</sub>–IPA system, which is different from that in the NO–O<sub>2</sub>–CH<sub>3</sub>OH system. When the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was exposed to a NO–O<sub>2</sub>–CH<sub>3</sub>OH mixture under the same experimental conditions, very weak band of –NCO species was observed compared with the cases using C<sub>2</sub>H<sub>5</sub>OH or IPA as reductants. We have proposed the mechanism of the SCR of NO<sub>x</sub> by C<sub>2</sub>H<sub>5</sub>OH over Ag/Al<sub>2</sub>O<sub>3</sub>, as shown in Scheme 1 [19]. It has been widely accepted that –NCO species is a crucial intermediate in the SCR of NO<sub>x</sub> over Ag/Al<sub>2</sub>O<sub>3</sub> and its high productivity results in a high efficiency of NO<sub>x</sub> reduction. The linkage between the formation tendency of –NCO species and enolic species was clearly observed in Figs. 3–5. As for Ag/Al<sub>2</sub>O<sub>3</sub>, the order of the facility for the formation of –NCO species was in good agreement with the

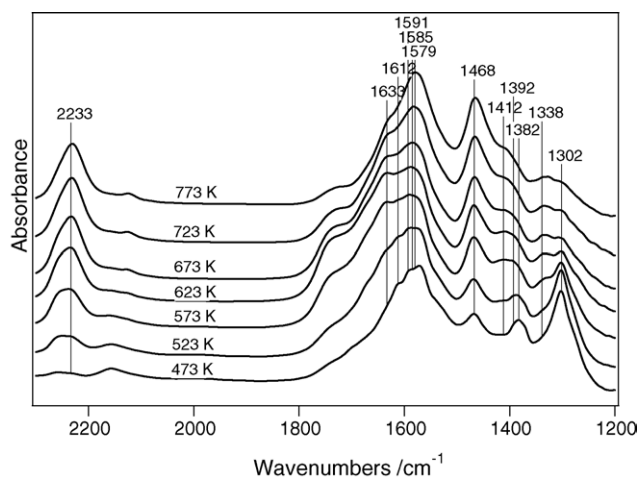


Fig. 4. In situ DRIFTS spectra of adsorbed species in steady state on Ag/Al<sub>2</sub>O<sub>3</sub> in a flow of IPA + O<sub>2</sub> + NO at various temperatures. Conditions: NO 800 ppm; IPA 1200 ppm; O<sub>2</sub> 10%.

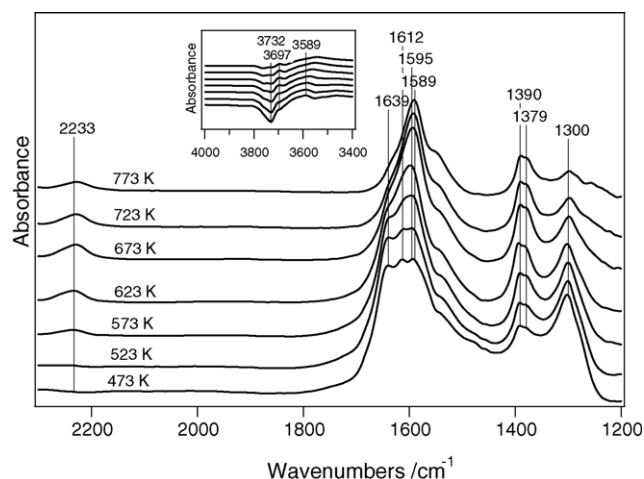


Fig. 5. In situ DRIFTS spectra of adsorbed species in steady state on Ag/Al<sub>2</sub>O<sub>3</sub> in a flow of CH<sub>3</sub>OH + O<sub>2</sub> + NO at various temperatures. Conditions: NO 800 ppm; CH<sub>3</sub>OH 2250 ppm; O<sub>2</sub> 10%.

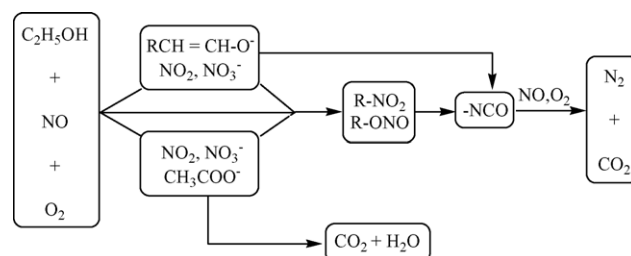
order of the activities in the SCR of NO<sub>x</sub> process (Fig. 1: C<sub>2</sub>H<sub>5</sub>OH > IPA > CH<sub>3</sub>OH) in the moderate temperature range of 523–623 K.

GC–MS and FTIR experiments indicated the formation of nitrogen-containing molecule (such as CH<sub>3</sub>NO<sub>2</sub>) and oxygen-containing molecules (such as CH<sub>3</sub>CHO and CH<sub>3</sub>COCH<sub>3</sub>) during the SCR of NO<sub>x</sub> by C<sub>2</sub>H<sub>5</sub>OH or IPA over Ag/Al<sub>2</sub>O<sub>3</sub>. Nitrogen-containing molecules and oxygen-containing molecules have been proposed to be the key intermediates in the reduction of NO<sub>x</sub> [3,4,15,19]. The analysis of gas products together with in situ DRIFTS spectra proved the similar mechanisms of the SCR of NO<sub>x</sub> by C<sub>2</sub>H<sub>5</sub>OH and IPA over Ag/Al<sub>2</sub>O<sub>3</sub>, whereas CH<sub>3</sub>OH was not found to follow the similar mechanism. More evidences for the different reaction mechanisms will be discussed below.

### 3.3. Formation of adsorbed enolic species in the partial oxidation reaction over Ag/Al<sub>2</sub>O<sub>3</sub>

To elucidate the differences among the reductants for the SCR of NO<sub>x</sub> over Ag/Al<sub>2</sub>O<sub>3</sub>, we investigated the surface species formed on the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst during the oxidation reaction of different alcohols.

Fig. 6 shows the in situ DRIFTS spectra of Ag/Al<sub>2</sub>O<sub>3</sub> at various temperatures in steady state after the exposure to



Scheme 1. The mechanism of the SCR of NO<sub>x</sub> by C<sub>2</sub>H<sub>5</sub>OH over Ag/Al<sub>2</sub>O<sub>3</sub>.

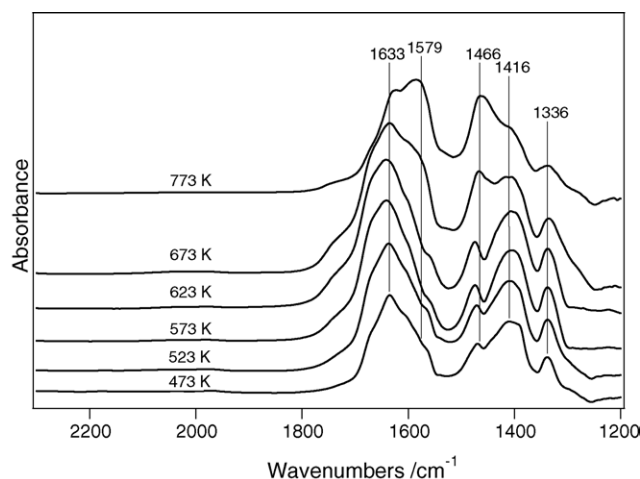


Fig. 6. In situ DRIFTS spectra of adsorbed species in steady state on Ag/Al<sub>2</sub>O<sub>3</sub> in a flow of C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> at various temperatures. Conditions: C<sub>2</sub>H<sub>5</sub>OH 1565 ppm; O<sub>2</sub> 10%.

C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> mixture gas, where the five peaks appeared at 1633, 1416, 1336, 1579 and 1466 cm<sup>-1</sup>. The peaks at 1633, 1416 and 1336 cm<sup>-1</sup> are attributed to the enolic species and the peaks at 1579 and 1466 cm<sup>-1</sup> are assigned to acetate species. As shown in Fig. 6, the enolic species is dominantly formed from the partial oxidation of C<sub>2</sub>H<sub>5</sub>OH in the temperature range of 473–673 K, whereas at 773 K, the enolic species was further oxidized into the acetate species.

The same set of experiment was conducted after exposing the catalyst to a flow of IPA + O<sub>2</sub>. As shown in Fig. 7, within the temperature range of 573–723 K, a very strong peak at 1633 cm<sup>-1</sup> due to the enolic species was also observed, which accompanied by the appearance of the peaks at 1408 and 1335 cm<sup>-1</sup>. The bands at 1595 and 1379 cm<sup>-1</sup> are assigned to formate species, the bands at 1581 and 1468 cm<sup>-1</sup> are attributed to acetate species and the peak at 1392 cm<sup>-1</sup> can be associated with δ(C–H), as the same as in Fig. 4. At low temperatures, the formate species was

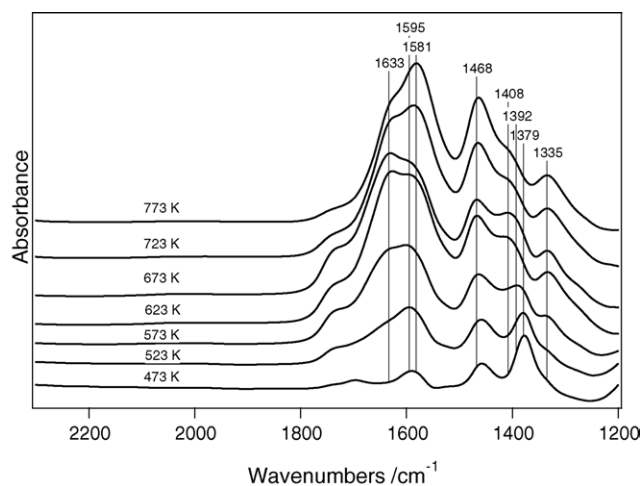


Fig. 7. In situ DRIFTS spectra of adsorbed species in steady state on Ag/Al<sub>2</sub>O<sub>3</sub> in a flow of IPA + O<sub>2</sub> at various temperatures. Conditions: IPA 1200 ppm; O<sub>2</sub> 10%.

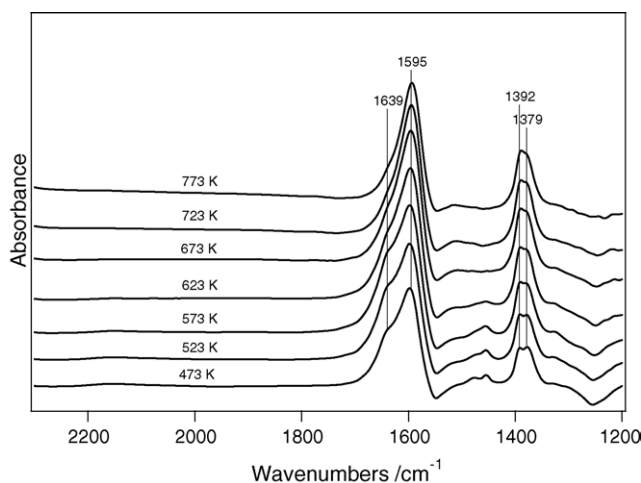


Fig. 8. In situ DRIFTS spectra of adsorbed species in steady state on Ag/Al<sub>2</sub>O<sub>3</sub> in a flow of CH<sub>3</sub>OH + O<sub>2</sub> at various temperatures. Conditions: CH<sub>3</sub>OH 2250 ppm; O<sub>2</sub> 10%.

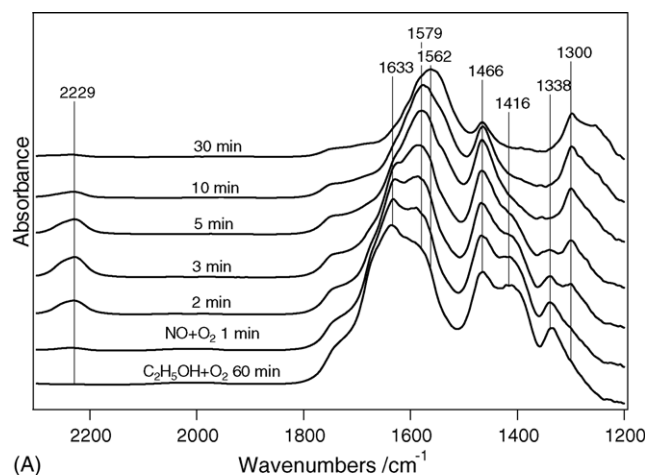
predominant, while within the temperature range of 623–673 K, the enolic species became predominant, indicating that the partial oxidation occurs preferentially on Ag/Al<sub>2</sub>O<sub>3</sub>. However, the acetate species resulted from further oxidation of the enolic species is dominant at temperatures above 723 K.

Exposing Ag/Al<sub>2</sub>O<sub>3</sub> catalyst to a flow of CH<sub>3</sub>OH + O<sub>2</sub> resulted in the appearance of four peaks (1639, 1595, 1392 and 1379 cm<sup>-1</sup>). As can be seen from Fig. 8, the band at 1595 and 1379 cm<sup>-1</sup> are assigned to the formate species and the very weak band at 1639 cm<sup>-1</sup> is due to the formation of H<sub>2</sub>O by dehydration of CH<sub>3</sub>OH, as discussed in Fig. 5. While the peak at 1392 cm<sup>-1</sup> is associated with δ(C–H). Apparently, the deep oxidation of CH<sub>3</sub>OH occurred preferentially above 573 K on Ag/Al<sub>2</sub>O<sub>3</sub>, because the formate species is predominant during the oxidation reaction and the characteristic bands of the enolic species were not detected in this study. Comparative studies show that partial oxidation of CH<sub>3</sub>OH is different from that of other alcohols. As a fact, while the enolic species was the dominant surface species on Ag/Al<sub>2</sub>O<sub>3</sub> during the partial oxidation of C<sub>2</sub>H<sub>5</sub>OH and IPA, it is not the case for CH<sub>3</sub>OH, which may account for the relatively low efficiency in the SCR of NO<sub>x</sub>.

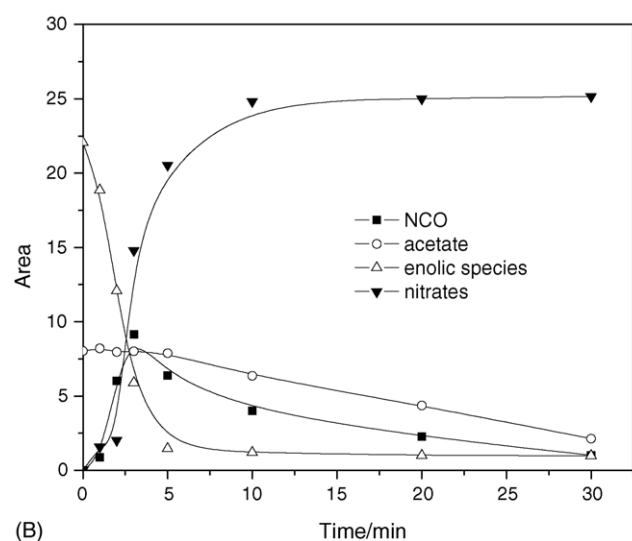
### 3.4. Reactivity of the surface enolic species over Ag/Al<sub>2</sub>O<sub>3</sub>

To obtain further information on the reactivity of the surface enolic species, the reactivity of the enolic species toward NO + O<sub>2</sub> was studied by the transient response of DRIFTS method.

Fig. 9A shows the dynamic changes of in situ DRIFTS spectra of the adsorbed species in a flow of NO + O<sub>2</sub> on Ag/Al<sub>2</sub>O<sub>3</sub> at 673 K. The integrated areas of these peaks in Fig. 9A are displayed as a function of time in Fig. 9B. When the catalyst was exposed to C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> for 60 min, very strong enolic species peaks appeared at 1633, 1416 and



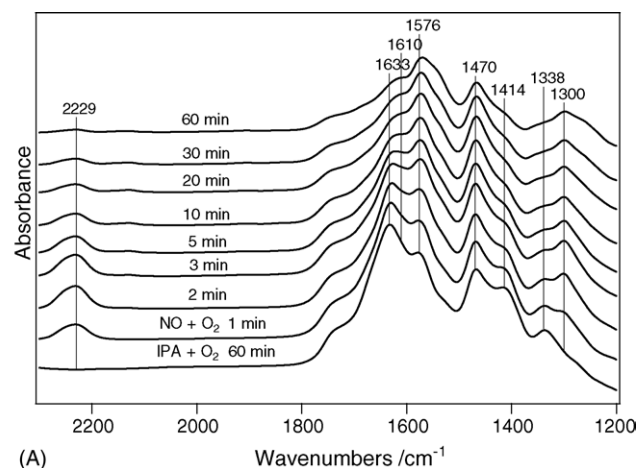
(A)



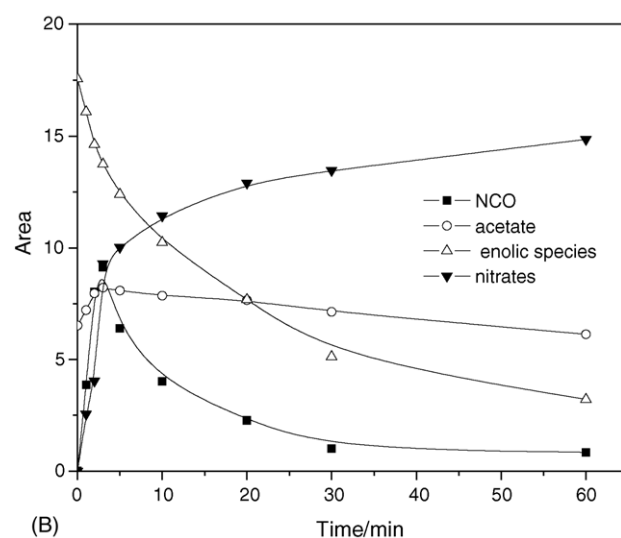
(B)

Fig. 9. (A) Dynamic changes of in situ DRIFTS spectra of adsorbed species on Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in a flow of NO + O<sub>2</sub> at 673 K. Before measurement, the catalyst was pre-exposed to a flow of C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> for 60 min at 673 K. Conditions: NO 800 ppm; C<sub>2</sub>H<sub>5</sub>OH 1565 ppm; O<sub>2</sub> 10%. (B) Time dependence of the integrated areas of the peaks for different adsorbed species in (A): (■) –NCO, 2160–2308 cm<sup>-1</sup>; (○) acetate, 1440–1505 cm<sup>-1</sup>; (▼) nitrates, 1210–1322 cm<sup>-1</sup>; (△) enolic species 1612–1710 cm<sup>-1</sup>.

1338 cm<sup>-1</sup> and acetate peaks were also observed at 1579 and 1466 cm<sup>-1</sup>. Switching the feed gas to a flow of NO + O<sub>2</sub> resulted in a sharp decrease of the enolic species. Meanwhile, a new –NCO peak appeared at 2229 cm<sup>-1</sup>, with its intensity increased initially and then decreased after it reached a maximum. The linkage between the formation of the –NCO species and the consumption of the enolic species strongly suggests the participation of the enolic species in the formation of –NCO species. When the enolic species was completely consumed, a large amount of nitrates and acetate became dominant surface species on Ag/Al<sub>2</sub>O<sub>3</sub>, while the surface concentration of –NCO was very low. This result indicates that the enolic species effectively reacts toward NO + O<sub>2</sub> to form –NCO species than acetate species does. As a result, it is the enolic species rather than the acetate



(A)



(B)

Fig. 10. (A) Dynamic changes of in situ DRIFTS spectra of adsorbed species on Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in a flow of NO + O<sub>2</sub> at 673 K. Before measurement, the catalyst was pre-exposed to a flow of IPA + O<sub>2</sub> for 60 min at 673 K. Conditions: NO 800 ppm; IPA 1200 ppm; O<sub>2</sub> 10%. (B) Time dependence of the integrated areas of the peaks for different adsorbed species in (A): (■) –NCO, 2160–2308 cm<sup>-1</sup>; (○) acetate, 1440–1505 cm<sup>-1</sup>; (▼) nitrates, 1210–1322 cm<sup>-1</sup>; (△) enolic species, 1612–1710 cm<sup>-1</sup>.

species, that plays a crucial role in the –NCO formation by reaction with NO + O<sub>2</sub>.

The same experiment was performed after exposing the catalyst to a flow of IPA + O<sub>2</sub> and we derived the same conclusion. As shown in Fig. 10A and B, after switching the feed gas to NO + O<sub>2</sub> within 30 min, the intensity of the enolic species decreased, accompanied by a clear increase in the intensity of –NCO species. This result strongly confirms that the enolic species is the key intermediate in the formation of –NCO.

Fig. 11A shows the dynamic changes of in situ DRIFTS spectra of the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst firstly exposed to CH<sub>3</sub>OH + O<sub>2</sub> for 60 min at 673 K and then switched to a flow of NO + O<sub>2</sub>. Compared with C<sub>2</sub>H<sub>5</sub>OH and IPA, it should be noted that the peak due to the enolic species

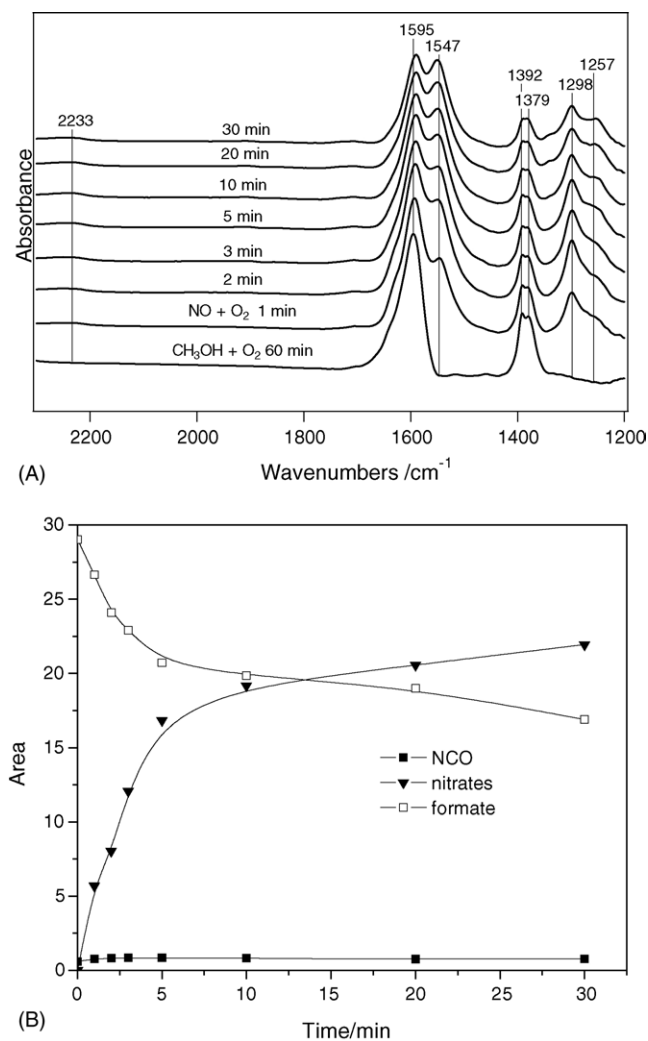


Fig. 11. (A) Dynamic changes of in situ DRIFTS spectra of adsorbed species on Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in a flow of NO + O<sub>2</sub> at 673 K. Before measurement, the catalyst was pre-exposed to a flow of CH<sub>3</sub>OH + O<sub>2</sub> for 60 min at 673 K. Conditions: NO 800 ppm; CH<sub>3</sub>OH 2250 ppm; O<sub>2</sub> 10%. (B) Time dependence of the integrated areas of the peaks for different adsorbed species in (A): (■) –NCO, 2160–2308 cm<sup>-1</sup>; (▼) nitrates, 1210–1322 cm<sup>-1</sup>; (□) formate, 1533–1720 cm<sup>-1</sup>.

(around 1633 cm<sup>-1</sup>) was not observed, whereas the peaks of the formate species (1595 and 1379 cm<sup>-1</sup>) were very strong. On the other hand, very weak band due to the –NCO species (2233 cm<sup>-1</sup>) was observed, as can be seen from Fig. 11A and B. This result strongly suggests again that the enolic species plays a crucial role in the –NCO formation during the SCR of NO<sub>x</sub> by alcohols.

#### 4. Conclusions

Based on the DRIFTS studies, the enolic species has been proved to be the main surface species during the partial oxidation of C<sub>2</sub>H<sub>5</sub>OH or IPA over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst. The

high reactivity of the enolic species with NO + O<sub>2</sub> results in high surface concentration of –NCO species and high efficiency of NO<sub>x</sub> reduction when using C<sub>2</sub>H<sub>5</sub>OH or IPA as reductants in the SCR of NO<sub>x</sub>. The linkage between the formation of the –NCO species and the consumption of the enolic species has been found. We have confirmed the similar mechanisms of the SCR of NO<sub>x</sub> by C<sub>2</sub>H<sub>5</sub>OH and IPA over Ag/Al<sub>2</sub>O<sub>3</sub>. However, CH<sub>3</sub>OH has not been found to follow the similar mechanism. CH<sub>3</sub>OH is much less reactive for the formation of –NCO species. The order of the facility for the formation of enolic species and –NCO species is in good agreement with the order of the activities (C<sub>2</sub>H<sub>5</sub>OH > IPA > CH<sub>3</sub>OH) in the moderate temperature range of 523–623 K during the SCR of NO<sub>x</sub>.

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#### References

- [1] T. Miyadera, Appl. Catal. B 2 (1993) 199.
- [2] K.A. Bethke, H.H. Kung, J. Catal. 172 (1997) 93.
- [3] S. Sumiya, H. He, A. Abe, N. Takezaka, K. Yoshida, J. Chem. Soc. Faraday Trans. 94 (1998) 2217.
- [4] S. Sumiya, M. Saito, H. He, Q.-C. Feng, N. Takezawa, Catal. Lett. 50 (1998) 87.
- [5] A. Abe, N. Aoyama, S. Sumiya, N. Kakuta, K. Yoshida, Catal. Lett. 51 (1998) 5.
- [6] F.C. Meunier, V. Zuzaniuk, J.P. Breen, M. Olsson, J.R.H. Ross, Catal. Today 59 (2000) 287.
- [7] K. Shimizu, J. Shibata, H. Yoshida, A. Satsuma, T. Hattori, Appl. Catal. B 30 (2001) 151.
- [8] F.C. Meunier, R. Ukropec, C. Stapleton, J.P. Breen, Appl. Catal. B 30 (2001) 163.
- [9] R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal. B 39 (2002) 283.
- [10] E.F. Iliopoulou, A.P. Evdou, A.A. Lemonidou, I.A. Vasalos, Appl. Catal. A 274 (2004) 179.
- [11] Y. Ukisu, S. Sato, A. Abe, K. Yoshida, Appl. Catal. B 2 (1993) 147.
- [12] Y. Ukisu, T. Miyadera, A. Abe, K. Yoshida, Catal. Lett. 39 (1996) 265.
- [13] T. Chafik, S. Kameoka, Y. Ukisu, T. Miyadera, J. Mol. Catal. A 136 (1998) 203.
- [14] F.C. Meunier, J.P. Breen, V. Zuzaniuk, M. Olsson, J.R.H. Ross, J. Catal. 187 (1999) 493.
- [15] S. Kameoka, Y. Ukisu, T. Miyadera, Phys. Chem. Chem. Phys. 2 (2000) 367.
- [16] N. Bogdanichkova, F.C. Meunier, M. Avalos-Borja, J.P. Breen, A. Pestryakov, Appl. Catal. B 36 (2002) 287.
- [17] N. Bion, J. Saussey, M. Haneda, M. Daturi, J. Catal. 217 (2003) 47.
- [18] A. Satsuma, K. Shimizu, Prog. Energy Combust. Sci. 29 (2003) 71.
- [19] Y. Yu, H. He, Q. Feng, H. Gao, X. Yang, Appl. Catal. B 49 (2004) 159.
- [20] S.G. Masters, D. Chadwick, Catal. Today 42 (1998) 137.
- [21] S.G. Masters, D. Chadwick, Appl. Catal. B 23 (1999) 235.
- [22] Standard IR Spectra, Sadler Research Labs.