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An in situ UV–vis and FTIR spectroscopy study of the effect of H_2 and CO during the selective catalytic reduction of nitrogen oxides over a silver alumina catalyst

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Abstract

The effect of hydrogen and carbon monoxide on the selective catalytic reduction of NO_x with decane over a 2 wt% Ag/Al_2O_3 catalyst was investigated. Hydrogen promoted NO_x conversion during the SCR reaction, in contrast to carbon monoxide, which had a slightly detrimental effect on catalyst activity. However, in situ UV–vis spectroscopy showed that both carbon monoxide and hydrogen promoted the formation of Ag clusters during the reaction. This, coupled with previous EXAFS experiments and UV–vis data on the rate of change of cluster formation, demonstrate that the enhanced activity from the addition of hydrogen to the NO_x-SCR mix cannot be attributed exclusively to the formation of Ag clusters. It is proposed that hydrogen itself participates directly in the reaction mechanism.

Keywords: SCR-NO_x; Ag/alumina; Ag clusters; H_2 effect in SCR-NO_x

1. Introduction

Since the pioneering work of Iwamoto et al. [1] and Held et al. [2], considerable effort has been expended in searching for active catalysts for the selective catalytic reduction of NO_x and also in studying the mechanism of reaction over these catalysts. It is well established that Ag/Al_2O_3 catalysts are among the most active and selective for the selective catalytic reduction of NO_x to N_2 [3]. However, until recently, one of the drawbacks preventing commercialization of these catalysts was very poor activity at temperatures below ca. 350 °C. This problem has been overcome by the recent discovery that adding hydrogen to the feed stream can result in a remarkable improvement in the level of NO_x reduction and the range of temperature over which NO_x can be reduced [4,5]. Several authors have investigated this “hydrogen effect” using different catalyst formulations and different gas mixes [6–17]. Several conclusions can be drawn from these investigations; first, it is evident that hydrogen promotes NO_x reduction over $Ag/\gamma\text{-}Al_2O_3$ catalysts when using a range of lower alkanes and alkenes [6] and higher alkanes [13,16] as reductants. The hydrogen effect is limited to Ag-based catalysts but is very dependent on the support used. The activity of Ag supported on $\alpha\text{-}Al_2O_3$, TiO_2, ZrO_2, SiO_2, or Ga_2O_3 is not enhanced by the addition of hydrogen [6]; however, $Ag/\gamma\text{-}Al_2O_3$ and Ag/MFI catalysts show markedly improved performance when hydrogen is added to the feed [7,8].

Hydrogen has a significant promotional effect on the partial oxidation of the hydrocarbon and the oxidation of NO to NO_2 [6,13]. Shibata et al. [9] claimed that the rate of NO_x reduction in the SCR reaction is directly dependent on the rate of partial oxidation of the hydrocarbon to surface acetate, and that hydrogen has a remarkable effect in promoting this oxidation reaction, thus having a positive effect on the proposed rate-determining step of the NO_x SCR reaction. There is no disagreement as to the effect of hydrogen on the SCR reaction; however, there is some debate as to the mechanism by which the hydrocarbon and NO are activated.

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Satokawa and co-workers [5–9] support an Ag cluster model. They used UV–vis spectroscopy to show that during the SCR reaction (in the absence of H_2), the silver in a low-loading Ag catalyst is predominantly in the form of isolated Ag^+ ions. However, they noticed that adding small concentrations of hydrogen (<1%) promoted the formation of small clusters of $Ag_n^{\delta+}$ (with estimated $2 \leqslant n \geqslant 4$). They suggested that at higher hydrogen concentrations (>1%), metallic Ag_m ($3 \leqslant m \geqslant 5$) clusters were formed, promoting unselective oxidation of the hydrocarbon. They argued that it is the $Ag_n^{\delta+}$ clusters that are responsible for the high activity of the Ag-based catalysts (Ag/MFI and $Ag/\gamma\text{-}Al_2O_3$), although they did not give any details of the mechanism by which these clusters promote the reaction, other than to comment that they promote the formation of surface acetates and oxidation of NO to NO_2.

Richter et al. [11] invoked the importance of Ag_2O/Ag^0 nanoclusters in their interpretation of the reaction mechanism during the hydrogen-promoted SCR reaction. They proposed that hydrogen rapidly reduces the nano-sized clusters of Ag_2O to Ag^0, and that these smaller silver clusters promote dissociation of NO and O_2. Although the authors found no direct evidence for the formation of adsorbed O ions on the surface of the Ag, they suggested that such a species is likely to form and to be active in the conversion of NO to nitrite species and of propane to O-functionalized intermediates or to surface acetate.

Brosius et al. [12] recently investigated the effect of adding hydrogen to a NO_x-containing stream (in the absence of hydrocarbons) over Ag/Al_2O_3. They provided evidence that the promotional effect of hydrogen is related to its role in reducing Ag(I) to Ag^0. Extrapolating this to the SCR of NO_x reaction, they suggested that the hydrogen reacts with stable Ag nitrate to form Ag^0, which can activate the hydrocarbon. This is consistent with the model proposed earlier by Burch [14].

In earlier publications [13,16], we proposed that the enhancing effect of hydrogen was not related to Ag cluster formation, but that the hydrogen reacts directly to either promote the formation and storage of a reactive species that can then readily reduce NO_x or, alternatively, to remove a species that is strongly bound at low temperatures. We found that hydrogen promoted the conversion of Ag^+CN to $Al^{3+}NCO$ at temperatures >520 K. We suggested that at temperatures <520 K, hydrogen could remove strongly bound nitrates, which can be a potential poison to the reaction in the absence of hydrogen. This direct mechanism does not require the formation of Ag clusters; however, it does not rule out the possibility that clusters may form as a consequence of the introduction of hydrogen. More recent in situ EXAFS experiments demonstrated that small clusters of Ag, containing an average of 3 atoms, were formed under SCR reaction conditions, but that adding hydrogen or carbon monoxide did not lead to any further cluster formation [15]. In another study [16], we provided evidence that hydrogen directly helps enhance the SCR-NO_x reaction and all of the related reaction steps. By recording in situ UV–vis spectra during the decane-SCR-NO_x reaction, we showed that small metallic $Ag_n^{\delta+}$ clusters ($n \leqslant 8$) are formed even in the absence of hydrogen. Experiments involving adding/removing hydrogen from the reactant feed and simultaneous time-scale monitoring of NO_x conversion and the UV–vis bands of $Ag_n^{\delta+}$ clusters revealed that the sharp decrease in NO_x conversion after the removal of hydrogen from the feed was not accompanied by a similar decrease in the number of Ag clusters, this number declined only gradually. Thus the high SCR-NO_x activity of Ag/alumina in the presence of hydrogen cannot be exclusively ascribed to the presence of Ag clusters. Hydrogen itself dramatically enhances the SCR-NO_x reaction by initiating most likely radical-type reactions and increasing the rate of all of the reaction steps.

The aim of the present study was to use in situ UV–vis and FTIR techniques to probe the effects of hydrogen and carbon monoxide on the state of silver in the catalyst and on the surface reaction intermediates formed during the reaction. We found that although both of these co-reductants significantly increased the number of small metallic silver clusters, only hydrogen increased NO_x reduction to nitrogen by increasing the rates of all reaction steps, manifested in the detected surface intermediate species.

2. Experimental

The catalyst used in this work was prepared by impregnating Al_2O_3 with a silver nitrate solution, followed by drying and calcination as described previously [18]. Catalyst testing was performed in a 5-mm-i.d. quartz tubular downflow reactor. The sample was held in place between plugs of quartz wool, and a thermocouple was placed in the center of the catalyst bed. The reactant gases (NO, NO_2, and O_2) and the carrier gas (He) were fed from independent mass flow controllers, whereas n-decane and H_2O were fed using a Razel syringe pump. All reactor lines were heated to prevent condensation. The NO and total NO_x were determined by a Signal 4000 series chemiluminescence detector. In these studies NO_x conversion is defined as the reduction of NO and NO_2 to N_2 and N_2O. The experimental conditions for the SCR reaction were as follows: total gas flow: GHSV, 62,256 $cm^3\,g^{-1}\,h^{-1}$; NO, 720 ppm; O_2, 4.3%; $n\text{-}C_{10}H_{22}$, 4350 ppm (as C_1); H_2O, 7.2%; CO_2, 7.2%; CO or H_2: 7200 ppm; balance He.

2.1. In situ UV–vis spectroscopy measurements

In situ UV–Vis diffuse reflectance spectra of the silver alumina catalysts were collected under the reaction mixture at the reaction temperature. The spectra were recorded using a Perkin Elmer Lambda 19 UV–vis-NIR spectrophotometer with a diffuse reflectance attachment equipped with a $BaSO_4$-coated integration sphere and a heated “homemade” flow-through quartz optical cell. The spectra were monitored in the range 4000–50,000 cm^{-1}. The absorption intensity was calculated using the Schuster–Kubelka–Munk equation,

$$F(R\propto) = (1 - R_\infty)^2/2R_\infty.$$

2.2. In situ FTIR spectroscopy measurements

FTIR spectra were collected under reaction conditions using a FTIR spectrometer (Thermo Nicolet) equipped with a

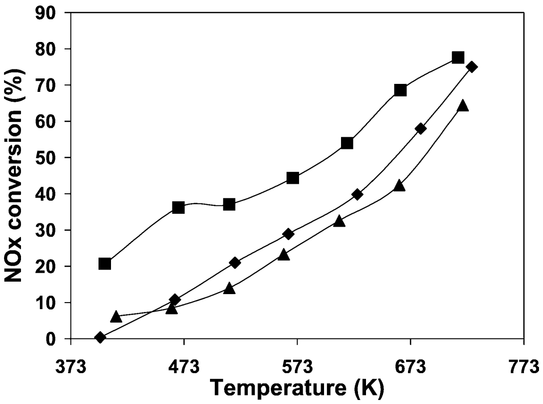


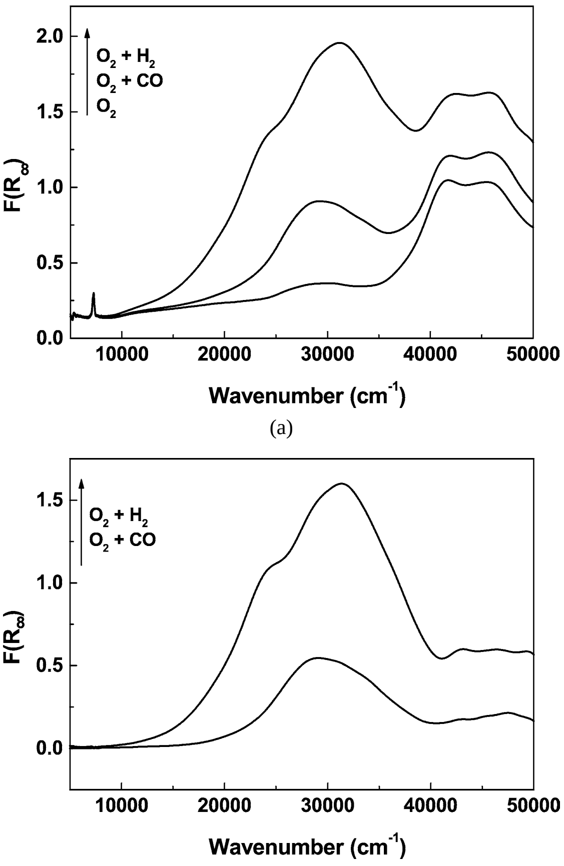
Fig. 1. NO_x conversion as a function of temperature for the SCR of NO_x with decane (◆); with 0.72% CO added (▲) and with 0.72% H_2 added (■) using conditions given in the text.

stainless steel flow-through IR cell reactor (in situ Research Instruments) with CaF_2 windows. A DTGS KBr detector was used, and FTIR spectra were measured with resolution of 2 cm^{-1}. The catalyst, in the form of a thin self-supporting wafer (ca. 10 mg cm^{-2}), was calcined at 723 K in an oxygen + helium stream for 1 h before all experiments and then cooled to the reaction temperature. The spectrum of the calcined sample (monitored in a helium stream with 4.3% water vapor) before the introduction of reactants was subtracted from the spectra collected under in situ conditions during reaction.

3. Results

The effects of adding CO and H_2 to the feed of the SCR-NO_x with n-decane are depicted in Fig. 1. The addition of hydrogen results in markedly improved catalyst activity over the temperature range of the tests. These results are similar to those obtained for the SCR reaction using n-octane as the primary reductant, although the effect of hydrogen was more dramatic in that case [13]. In contrast, the addition of CO has no (or a small negative) effect on catalyst activity.

Fig. 2a shows in situ UV–vis spectra of the silver alumina catalyst under flows of O_2, $H_2 + O_2$, and $CO + O_2$ at 473 K at similar conditions to that of the SCR-NO_x reaction. With Ag/alumina exposed to a stream of oxygen, bands at 41,600 and 46,600 cm^{-1}, corresponding to the electronic transitions of isolated Ag^+ ions, were observed (the spectra of Ag^+ ion and small metallic $Ag_n^{\delta+}$ clusters were interpreted previously [16]), along with very low-intensity absorption around 28,000–30,000 cm^{-1}, attributed to a small number of silver clusters. The spectrum obtained during catalyst exposure to O_2 was subtracted from those obtained during the $H_2 + O_2$ and $CO + O_2$ reactions (Fig. 2b). For the $H_2 + O_2$ reaction, the absorption maxima observed at ca. 24,000, 29,000, 31,000, and 34,000 cm^{-1} (obtained from the second derivative mode, not shown) were attributed to $Ag_n^{\delta+}$ clusters, for $n \leqslant 8$ [16]. The tail below 24,000 cm^{-1} indicates the presence of some larger metallic Ag particles. For the $CO + O_2$ reaction, the maxima of absorbance due to $Ag_n^{\delta+}$ clusters were located at ca. 29,000, 31,000, and 34,000 cm^{-1}. The intensities of the bands due to $Ag_n^{\delta+}$ clusters for the $CO + O_2$ reaction were substantially lower that those obtained during the $H_2 + O_2$ reaction. The difference spectra for both reactions clearly indicate that the intensity of the bands of the Ag^+ ions did not change significantly when $Ag_n^{\delta+}$ clusters were formed. This finding is in agreement with the very high absorbance of Ag clusters compared with Ag^+ ions and the fact that not all Ag^+ ion species are detected by UV–vis spectra [16]. Apparently, only a very small amount of the Ag^+ ions (<3%) were reduced to Ag clusters. The apparent increased intensity of the bands of Ag^+ ions in mixtures of $H_2 + O_2$ and $CO + O_2$ compared with those in O_2 may be caused by an overlap of the absorbance of Ag clusters to the region above 40,000 cm^{-1}.

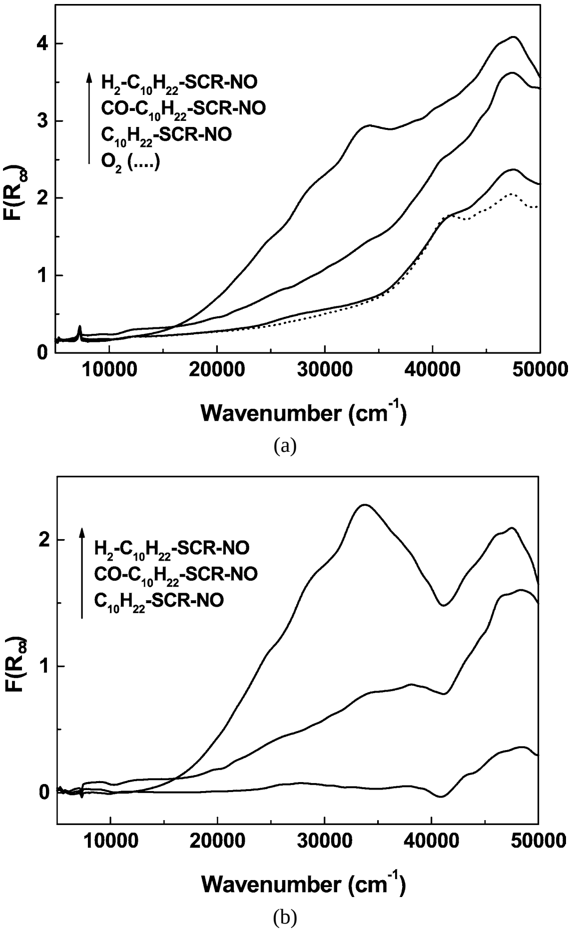


(a)

(b)

Fig. 2. (a) In situ diffuse reflectance UV–vis-NIR spectra of Ag/Al_2O_3 during hydrogen or CO oxidation over Ag/Al_2O_3 at 473 K. Feed: 7200 ppm H_2 or 7200 ppm CO, 4.3% O_2, rest He. (b) Difference spectra to that of Ag/Al_2O_3 in flow of O_2.

Figs. 3a and 3b show the in situ UV–vis spectra of Ag/alumina collected during the decane-SCR-NO_x reactions under similar conditions as in the catalytic tests. The spectra revealed that even at 473 K, where low conversion of NO to N_2 (<10%) occurs, traces of $Ag_n^{\delta+}$ clusters are formed (low absorption intensity around 28,000 and 38,000 cm^{-1}). The presence of adsorbed nitrates is reflected in increased absorbance intensity, with a maximum at 47,000 cm^{-1}. Adding CO to the reaction mixture produced increased absorption intensities, with maxima at ca. 25,000, 34,000, and 38,000 cm^{-1} (obtained from the second derivative mode). These bands can be attributed to the



(a)

(b)

Fig. 3. (a) In situ diffuse reflectance UV–vis-NIR spectra of Ag/Al_2O_3 during exposure to different reactant gas mixes at 473 K. SCR feed: 720 ppm NO; 435 ppm n-$C_{10}H_{22}$; 4.3% O_2; 4.3% H_2O; (7200 ppm CO or H_2). (b) Difference spectra to that of Ag/Al_2O_3 in flow of O_2.

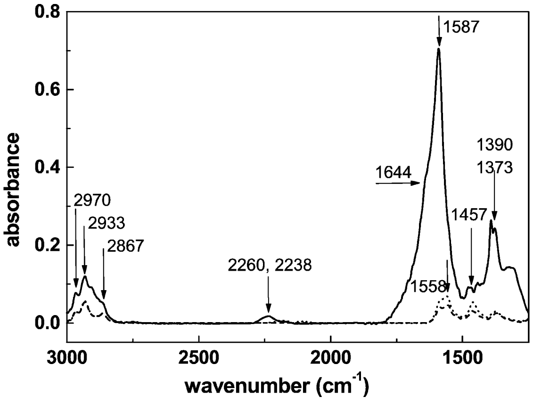


Fig. 4. In situ FTIR spectra of adsorbed species during $C_{10}H_{22}$-SCR NO (- - -), with CO added (···) and with H_2 added (—) at 473 K. Feed: 720 ppm NO; 435 ppm n-$C_{10}H_{22}$; 4.3% O_2; 4.3% H_2O; (7200 ppm CO). Subtracted spectrum was taken from sample treated in helium/water mixture.

Table 1

Bands observed on Ag/Al_2O_3 catalyst during in situ FTIR experiments and the corresponding surface species and vibrations to which they are assigned

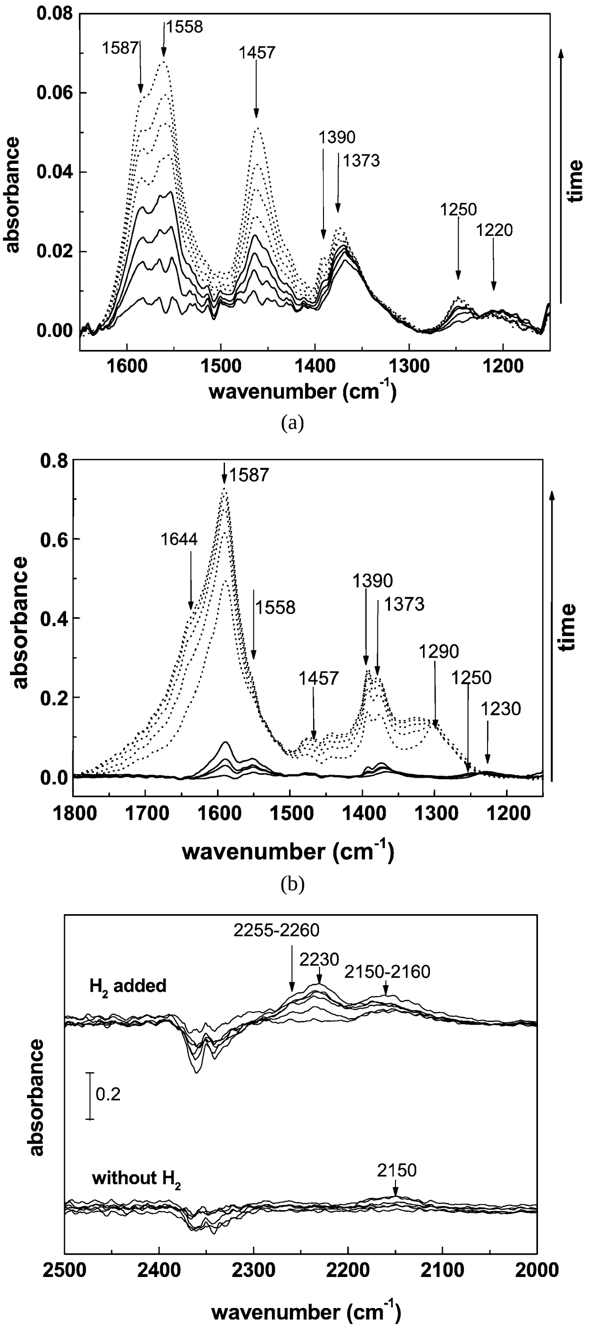
Wavenumber (cm^{-1})	Surface species	Vibration	References
1580	Carboxylate COO^-	ν^a_{OCO}	[19,20]
1457		ν^s_{OCO}	
1595	Formate $HCOO^-$	ν^a_{OCO}	[19–21]
1390		δ_{CH}	
1373		ν^s_{OCO}	
1550	Monodentate	$\nu_{N=O}$	[22–24]
1245	nitrate $NO_3{}^-$	ν^a_{ONO}	
1590	Bidentate	$\nu_{N=O}$	[22–24]
1295	nitrate $NO_3{}^-$	ν^a_{ONO}	
1220	Nitrite $NO_2{}^-$	ν^a_{ONO}	[19]
1560	Ad-NO_x		[25]
1300	Bulk-like $NO_2{}^-$		
1645	Acrylate	$\nu_{C=C}$	[9]
2230	Isocyanate—($Al_{IV}NCO$)		[26]
2260	Isocyanate—($Al_{VI}NCO$)		[26]
2146	Cyanide—AgCN		[21]

formation of small $Ag_n{}^{\delta+}$ clusters. Adding H_2 to the feed instead of CO substantially increased the intensity of the broad band ranging from 20,000 to 40,000. This band showed similar features (intensity maxima at 24,000, 28,000, 34,000, and 38,000 cm^{-1}) to those obtained under a CO-containing feed, indicating that similar types of silver clusters are formed in each case. The increase in spectrum intensity around 47,000 cm^{-1} after hydrogen or CO addition can be accounted for by the presence of some adsorbed species on Ag or Al ions (e.g., nitrates).

Fig. 4 compares the FTIR spectra measured at 473 K under the decane-SCR-NO reaction mix and under the same mix with the addition of CO or H_2. This figure clearly shows that hydrogen addition, unlike CO addition, produces a large increase in the quantity of surface species on the catalyst. The quantity of surface species slowly increases during the first 60 min of SCR-NO_x reaction; however, admission of H_2 into the feed stream produces a sudden, dramatic increase in the integrated peak areas. This is in marked contrast to the negligible effect on peak areas from adding CO. Clearly, H_2 promotes the formation of various surface species, whereas CO does not.

Once we found that adding both H_2 and CO to the SCR-NO_x feed promotes the formation of Ag clusters but only the presence of hydrogen enhances NO_x–N_2 conversion, it was important to identify the surface species formed during the addition of H_2 and CO. Figs. 5a–5c zoom in on specific regions of the IR spectrum and show the changes resulting from adding CO and H_2. Table 1 summarizes the attribution of peaks to various surface species.

Fig. 5a shows the evolution of several bands over time in the SCR mix (the first four spectra) and then after introduction of CO to the feed (the last four spectra). The peaks centered at 1457 and 1587 cm^{-1} can be attributed to a carboxylate species, and that at 1558 cm^{-1} can be attributed to an ad-NO_x species. The peaks at 1373 and 1390 cm^{-1} are most likely due to formate species. The broad band at 1230 cm^{-1} reflects nitrite species. All bands increase with time on stream except the broad peak at 1230 cm^{-1}, which decreases slowly. This demonstrates that nitrite species, which are formed very quickly after introduction of the feed, are gradually oxidized to nitrate species with increasing time on stream.



(a)

(b)

(c)

Fig. 5. (a) In situ FTIR spectra of adsorbed species during $C_{10}H_{22}$-SCR NO (—) and with CO added (···) as a function of time (10 min intervals) at 473 K. Feed: 720 ppm NO; 435 ppm n-$C_{10}H_{22}$; 4.3% O_2; 4.3% H_2O; (7200 ppm CO). (b) In situ FTIR spectra of adsorbed species (—) and with H_2 added (···) as a function of time (10 min intervals) at 473 K. SCR feed: 720 ppm NO; 435 ppm n-$C_{10}H_{22}$; 4.3% O_2; 4.3% H_2O; (7200 ppm H_2). (c) In situ FTIR spectra of adsorbed species during $C_{10}H_{22}$-SCR NO at the CN– and NCO– spectral regions before and after H_2 addition measured at 10 min intervals at 473 K. Feed: 720 ppm NO; 435 ppm n-$C_{10}H_{22}$; 4.3% O_2; (7200 ppm H_2). After addition of CO to the reaction mix the spectrum was identical to that without CO.

The addition of CO (Fig. 5a) does not result in the formation of additional bands; neither does it appear to increase the intensity of the bands above what would be expected had the switch to CO not occurred. A low concentration of –CN species (2130–2160 cm^{-1}) was detected, but no –NCO (2230–2250 cm^{-1}) species were observed, probably due to the low NO_x conversion ($<10\%$). The spectrum intensity of the –CN species was the same with and without CO; this is not shown in Fig. 5a but is similar to that shown in Fig. 5c without hydrogen. The addition of hydrogen resulted in a dramatic increase in the composition and number of adsorbed species. Fig. 5b shows a substantial increase in the number of oxidized carbon-containing species, such as carboxylates (1457 and 1587 cm^{-1}) and formates (1373 and 1390 cm^{-1}). The nitrites are immediately transformed to nitrates (1295, 1245, 1550, and 1590 cm^{-1}), of which bidentate nitrates (1295 and 1590 cm^{-1}) increased more than monodentate species (1245 and 1550 cm^{-1}), with the latter consumed faster during propagation of the SCR process. The peak at 1558 cm^{-1} due to an ad-NO_x species also increased. In the absence of hydrogen at 473 K, only –CN groups are detected (Fig. 5c; note that NO_x conversion was $<10\%$). The addition of hydrogen results in the appearance of isocyanate species formed on different Al sites, $Al_{IV}NCO$ at 2230 cm^{-1} and $Al_{VI}NCO$ at 2260 cm^{-1}, and the simultaneous slow increase of –CN species (2150 cm^{-1}). Such changes were not observed under CO addition, and in this case the spectra resemble those of the SCR mix without any added reductant When higher conversion of NO_x was achieved by increasing the contact time ($\sim 20\%$), similar development of the spectra was observed with formation of the –NCO bands at 2230 and 2260 cm^{-1}. At higher temperatures (>523 K), a similar trend was observed for the SCR of NO_x with octane and hydrogen over the same catalyst. But in this case the appearance of the –NCO species was accompanied by a disappearance of the –CN species [13]. A new species appeared as a shoulder peak at 1644 cm^{-1} on addition of H_2, this peak occurred at a position similar to that observed during addition of H_2 to an octane SCR-NO_x feed [13]. This was tentatively assigned to an organic species containing a C=N double bond, but could also be attributed to the C=C stretch of an acrylate species [9].

4. Discussion

Hydrogen has a significant promotional effect on the conversion of NO_x for the decane SCR reaction over Ag/Al_2O_3, although the extent of the promotional effect is not as great as that observed with other alkanes and alkenes [6,13]. CO was added to the reactant mix to investigate whether another reductant could have a similar effect to hydrogen. CO is readily oxidized to CO_2 over supported Ag catalysts; in fact, Ag^+ ions will preferentially oxidize CO in the presence of excess H_2 at low temperatures ($<100\,°C$) [27]. This may be an indication that in the absence of a hydrocarbon, CO is a stronger reductant of oxidized Ag than H_2. Clearly, CO does not promote the SCR reaction, and in fact it has a slightly detrimental effect on the reduction of NO_x. Although CO has no direct effect on the rate of NO_x conversion, in situ diffuse reflectance UV–vis spectroscopy results show that, similar to hydrogen, it does promote the formation of small Ag clusters during the CO oxidation and CO/decane-SCR-NO_x reactions. The extent of Ag cluster formation from the addition of CO is less than that observed from hydrogen addition but is nevertheless significant. Moreover, similar types of Ag clusters are formed.

The results of the in situ FTIR measurements are revealing. They show (in agreement with Eränen et al. [17] and Shibata et al. [9]) that the addition of H_2 to the reactant feed resulted in a huge increase in the number and variety of surface species formed during the reaction. This is in marked contrast to the results obtained from adding CO to the feed, which showed little or no change in the number of adsorbed species. This demonstrated that although CO can cause the formation of Ag clusters on the catalyst surface, it has no impact on the rate of reaction or on the nature and quantity of surface species formed during the reaction.

The effect of hydrogen on promoting surface species formation is complex and remains to be elucidated. Development of FTIR spectra after hydrogen addition clearly indicates enhancement of all reaction steps. At low temperatures (470–570 K) and under the reaction conditions of this study, hydrogen enhances the transformation of nitrites to nitrates and their further transformation, and also promotes the conversion of cyanides to isocyanates [13,16]. Isocyanate (–NCO) species are formed on Al sites, and the concentrations of cyanide species also increase slowly after the addition of hydrogen. Bion et al. [28] proposed that the slow step in the SCR reaction was the transformation of Ag^+CN species to $Al^{3+}_{tetra}NCO$ species.

Alternatively, we speculated in an earlier paper on the SCR of NO_x with octane [13] that at low temperatures (<520 K) the Ag/Al_2O_3 catalyst might be poisoned by strongly bound nitrates, and that hydrogen could promote the reaction by removing these species. Recently, Brosius et al. [12] showed that in the absence of a hydrocarbon, hydrogen can promote the removal of nitrates from Ag and promote the formation of nitrates on the Al_2O_3 support. These authors speculated that the reduced Ag may then promote partial oxidation of the hydrocarbon. The large number of species in the 1250–1700 cm^{-1} region of our spectra makes it impossible to determine whether reduction of Ag nitrate species and formation of Al nitrate species occur after the introduction of hydrogen. Therefore, this proposed mechanism of promotion cannot be ruled in or out.

The key point of this paper is to show that the highly positive “hydrogen effect” cannot be attributed to formation of Ag clusters due to hydrogen as a co-reductant, but is associated with a chemical function of hydrogen itself. We propose that the role of hydrogen is to accelerate the critical SCR-NO_x reaction steps, particularly the slow steps in the reaction. The critical rate-determining step may itself be a function of temperature and reaction conditions. However, the formation of silver clusters is not a sufficient condition for a catalyst that is active at low temperatures.

5. Conclusions

The formation of small metallic Ag clusters does not explain the dramatic increase in HC-SCR-NO_x activity in the presence of hydrogen. Ag clusters are also formed during the decane-SCR-NO_x reaction without hydrogen, and adding CO into the feed increases the number of Ag clusters but has no significant effect on NO_x conversion. These findings support our hypothesis that hydrogen has a direct chemical function in the reaction mechanism, as evidenced by the dramatic, steeply increased concentration of adsorbed species and NO_x conversion after the addition of hydrogen to the SCR reaction. It is this direct action of hydrogen, rather than Ag cluster formation, which is responsible for the enhanced activity.

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