Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 127 (2007) 189–198

CATALYSIS TODAY

www.elsevier.com/locate/cattod

In situ FTIR characterization of the adsorption of CO and its reaction with NO on Pd-based FCC low NO_x combustion promoters

Oleg S. Alexeev [a], Sundaram Krishnamoorthy [b], Cody Jensen [a], Michael S. Ziebarth [b], George Yaluris [b], Terry G. Roberie [b], Michael D. Amiridis [a,*]

[a] *Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, United States*
[b] *GRACE Davison Refining Technologies, Columbia, MD 21044, United States*

Abstract

The adsorption of CO and its reaction with NO in the 400–600 °C temperature range on $Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ and $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ type materials used commercially as FCC additives were monitored by FTIR spectroscopy. Exposure of both types of samples to CO leads to the formation of carboxylates and carbonates. The concentration of these species was higher in samples containing Pd, indicating that palladium catalyzes their formation. The Pd^{n+} cations initially present in these samples undergo partial reduction to form metallic Pd in the presence of CO even at room temperature. More complete reduction of Pd, along with some aggregation, was observed after exposure to CO at elevated temperatures. Exposure of both types of samples to NO/CO mixtures in the 400–600 °C temperature range leads to the formation of surface isocyanate species. Both Na^{+} and Ce^{n+} promote the formation of such NCO species. However, surface isocyanate species were formed with substantially higher rates in the presence of palladium. The formation of the isocyanate species strongly correlates with changes observed in the ν_{OH} region, indicating that hydroxyls actively participate in the surface chemistry involved and are capable of protonating the NCO species. The isocyanates are also reactive towards O_2 and NO yielding CO_2 and N_2. These results suggest that isocyanates are possibly involved as intermediates in the CO–NO reaction over the materials examined.

Keywords: FTIR; FCC additive; Palladium; Carbon monoxide adsorption; Isocyanates; NO_x reduction

---

1. Introduction

Fluid Catalytic Cracking (FCC) is currently the primary process used to convert crude oil into a variety of higher-value light products in most petroleum refineries [1,2]. Even though FCC is a mature process, commercially deployed for over 60 years, this technology continues to advance in order to meet new challenges [3]. The reduction of CO and NO_x emissions, formed in the FCC process during the regeneration of the catalyst, to levels satisfying current environmental demands is one of these challenges. The addition to the circulating FCC catalyst inventory of small amounts of materials capable of catalyzing the reduction of CO and NO_x emissions *in situ*, is considered a very efficient and cost-effective solution [2,4,5]. However, Pt-based combustion promoters that are commonly used as additives to reduce CO emissions from the regenerator have also been observed to convert N-containing coke species to NO_x [2]. A successful reduction of both the CO and NO_x emissions can be achieved either by the use of a mixture of additives operating independently from each other, or with a single promoter capable of providing the simultaneous reduction of NO and CO emissions. The development of such additives requires complete understanding of the chemistry taking place under FCC regenerator conditions. However, there is only a limited number of available literature reports focusing on such chemistry [6–11].

As a part of an ongoing investigation of Pd-based FCC additives [12], we report in this paper the results of *in situ* FTIR experiments characterizing the interactions of CO and CO/NO mixtures with the surface of such additives at elevated temperatures under conditions approaching those existing in FCC units.

2. Experimental methods

2.1. Reagents and materials

Aluminum oxide with a BET surface area of 200 m^2/g was used as the support. The palladium nitrate solution used was

---

* Corresponding author. Tel.: +1 803 777 7356.
E-mail address: amiridis@engr.sc.edu (M.D. Amiridis).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.05.003

obtained from Alfa Aesar (99.95% purity). He (UHP grade, National Welders) was additionally purified prior to use by passage through an oxygen/moisture trap (Model OT3-2, Agilent) capable of removing traces of O_2 and water to 15 and 25 ppb, respectively. The NO/He and CO/He mixtures (National Welders) were purified prior to their use by passage through a moisture trap (Model GMT-2GCHP, Agilent) capable of removing water to 25 ppb.

2.2. Sample preparation

$Ce^{n+}/Na^+/Al_2O_3$ was prepared as a slurry containing proprietary quantities of each component and then spray dried in a Bowen Spray dryer. Milling of the slurry was carried out in a 4 L Drais mill. The spray-dried material was calcined for 2 h at 538 °C.

The palladium containing samples were prepared by incipient wetness impregnation of the respective support with an aqueous solution of palladium nitrate. The amount of the palladium precursor was chosen to yield samples containing approximately 0.11 wt% of Pd. The samples were then dried in air at 110 °C for 24 h and calcined for 2 h at 538 °C.

2.3. FTIR spectroscopy

FTIR spectra were collected with a Nicolet Nexus 470 spectrometer equipped with a MCT-B detector cooled by liquid nitrogen. Powder samples (25 mg) were pressed into self-supported wafers under 5000 psi of pressure. These wafers were subsequently mounted in the IR cell, which was connected to a gas distribution manifold. The design of the IR cell was similar to that described elsewhere [13]. Samples were pretreated in a 10% O_2/He flow at 400 °C for 2 h and then purged with He at the same temperature prior to each measurement. Spectra were recorded in the 400–600 °C temperature range at a spectral resolution of 2 cm^{-1} accumulating 64 scans per spectrum. The comparison of infrared spectra for different samples was performed assuming that the extinction coefficient for a given adsorbed species remains unchanged from sample to sample.

3. Results and discussion

3.1. Interaction of CO with $Ce^{n+}/Na^+/\gamma$-Al_2O_3

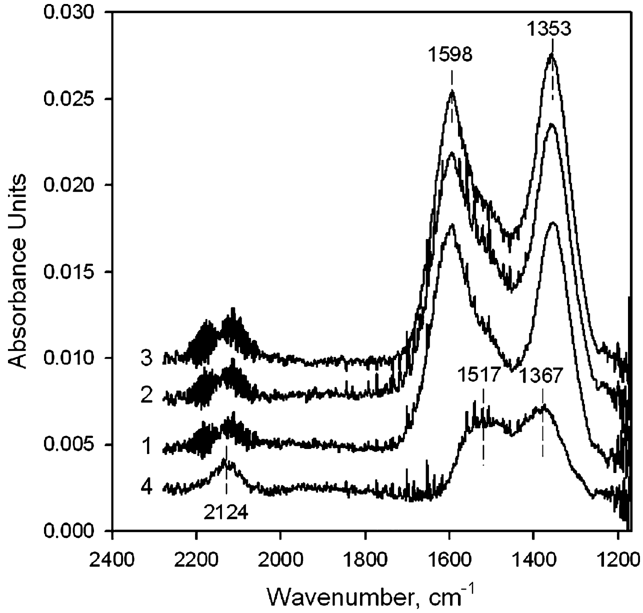


Fig. 1. FTIR spectra of $Ce^{n+}/Na^+/\gamma$-Al_2O_3 collected at 400 °C during exposure to a 0.25% CO/He mixture for (1) 2 min; (2) 30 min; (3) 60 min; (4) subsequent purging with He for 20 min at 400 °C.

When a $Ce^{n+}/Na^+/\gamma$-Al_2O_3 sample was exposed to a 0.25% CO in He mixture at 400 °C, two bands were observed in the spectra at 1598 and 1353 cm^{-1} (Fig. 1, spectra 1–3). The presence of bands in the 1700–1000 cm^{-1} region usually indicates the formation of surface carboxylate or carbonate species. Both monodentate and bidentate carbonates exhibit three infrared active bands, one of which is located below 1080 cm^{-1} and cannot be observed in our experiments due to the strong absorbance of alumina in this region. Two known types of bidentate carbonates on alumina exhibit ν_{CO} bands in the 1670–1530 cm^{-1} region [14]. However, the corresponding asymmetric $\nu_{as(COO)}$ bands for these species are located in the 1220–1270 cm^{-1} region. Similarly, the $\nu_{as(COO)}$ bands for monodentate carbonates are typically observed at higher frequencies (1530–1470 cm^{-1}) with the symmetric $\nu_{s(COO)}$ vibrations at approximately 1370–1300 cm^{-1} [14]. Therefore, if the two bands observed in our experiments at 1598 and 1353 cm^{-1} represent the same type of surface species, these bands cannot be assigned to either mono- or bidentate carbonates with a high degree of confidence. At the same time, surface carboxylate species exhibit two distinct bands corresponding to the asymmetric and symmetric ($\nu_{as(COO^-)}$ and $\nu_{s(COO^-)}$) vibrations in the 1630–1560 and 1420–1350 cm^{-1} regions, respectively [14]. Consequently, the bands at 1598 and 1353 cm^{-1} can be assigned with a higher degree of confidence to the asymmetric and symmetric vibrations of carboxylate (COO^-) species, respectively. Indeed, the formation of carboxylates has been previously confirmed spectroscopically on surfaces of various oxides including ceria upon exposure to CO [14–16]. The intensities of these bands did not change substantially with time on stream, indicating that nearly the maximum concentration of carboxylates was reached on the $Ce^{n+}/Na^+/\gamma$-Al_2O_3 surface during initial exposure to CO under our experimental conditions. Furthermore, these carboxylate species appeared to be weakly bonded to the $Ce^{n+}/Na^+/\gamma$-Al_2O_3 surface and could be easily removed by purging the sample with He at 400 °C (Fig. 1, spectrum 4). Two broad bands that remained in the spectrum at 1517 and 1367 cm^{-1} following this step could be assigned to a monodentate carbonate species [14], which appears to be more stable than the carboxylates under these conditions (Fig. 1, spectrum 4).

Following the removal of CO from the gas phase, the spectrum of the $Ce^{n+}/Na^+/\gamma$-Al_2O_3 material suggests that some additional species other than carbonates and carboxylates were also formed on the surface, as indicated by the characteristic

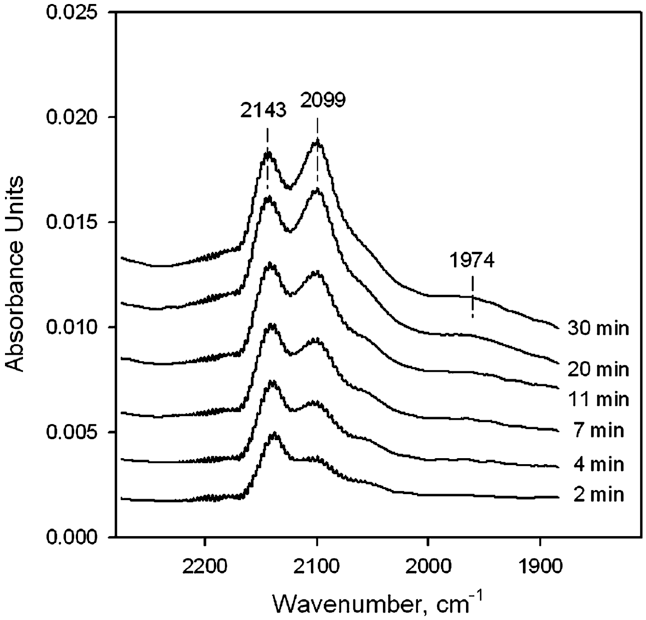


Fig. 2. FTIR spectra collected at different times during exposure of a fresh $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma$-$Al_2O_3$ sample to a 0.25% CO/He mixture at 25 °C.

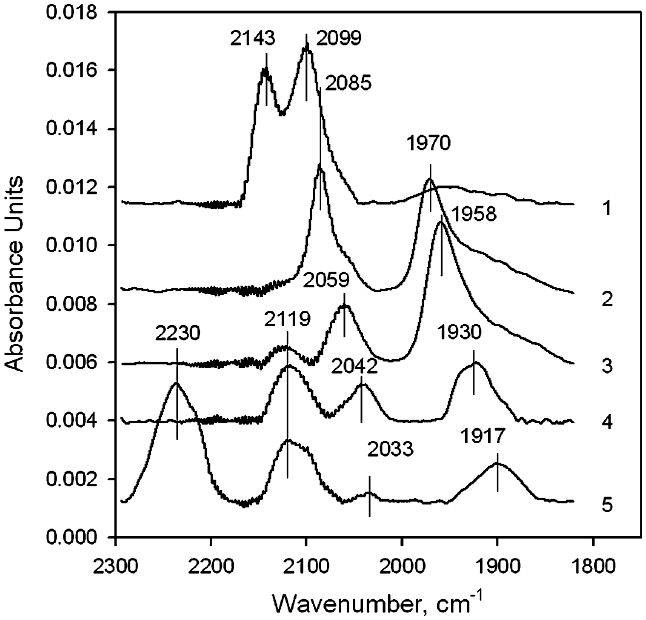


Fig. 3. FTIR spectra collected following a 30 min exposure of a fresh $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma$-$Al_2O_3$ to a 0.25% CO/He mixture at: (1) 25 °C; (2) 100 °C; (3) 200 °C; (4) 300 °C; (5) 400 °C.

band at 2124 cm^{-1} (Fig. 1, spectrum 4). The intensity of this band is low, but was somewhat increased when Pd was added to the material. The origin and behavior of the 2124 cm^{-1} band is discussed in more detail in the following section.

3.2. Interaction of CO with $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma$-$Al_2O_3$

EXAFS data reported elsewhere [12] show that in a freshly prepared $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma$-$Al_2O_3$ sample palladium is present in the form of highly dispersed PdO species. When such a sample was exposed to a mixture of 0.25% CO in He at 25 °C, two low intensity bands were observed immediately in the spectrum at 2143 and 2099 cm^{-1} (Fig. 2). Based on previous literature reports, the band at 2143 cm^{-1} can be assigned to CO adsorbed on Pd^{2+} cations [17–19], while the band at 2099 cm^{-1} can be assigned to terminal CO species adsorbed on reduced metallic Pd sites [17–19]. These results indicate that some fraction of the PdO species, which are initially present in the sample, undergo reduction to metallic Pd even at room temperature upon initial contact with gas phase CO. These metallic Pd sites initially formed on the surface appear to be mostly isolated, since only a very small fraction of bridging CO species could be observed in the spectrum. The intensity of the band at 2099 cm^{-1} increased with time on stream, and after 10–30 min a new well defined band characteristic of bridging CO species also appeared in the spectrum at approximately 1974 cm^{-1} (Fig. 2), indicating a more complete reduction of the PdO species and the formation of larger metallic Pd surfaces at that point.

When the temperature of the infrared cell was increased to approximately 100 °C under the CO/He flow, the band at 2143 cm^{-1} disappeared from the spectrum, indicating the complete reduction of Pd^{2+} to Pd^0 under these conditions (Fig. 3). Both the terminal and the bridging CO bands associated with Pd^0 decreased in intensity, and shifted to lower frequencies as the temperature was progressively increased to 400 °C (Fig. 3), suggesting a gradual decrease of the surface CO concentration.

To verify the assignment of these bands, we also performed similar FTIR measurements with a $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma$-$Al_2O_3$ sample that was reduced with H_2 at 500 °C prior to exposure to CO. The EXAFS data [12] in this case indicate that such treatment leads to the formation of highly dispersed Pd particles, characterized by an average first-shell Pd–Pd coordination number of approximately 5. When this reduced sample was exposed to the 0.25% CO/He mixture at room temperature, the two bands characteristic of terminal and bridging CO adsorbed on fully reduced Pd were immediately observed in the spectrum with high intensities at 2085 and 1965 cm^{-1}, respectively (Fig. 4). These bands shifted to lower frequencies and decreased in intensity as the temperature was increased to approximately 300 °C, indicating the gradual desorption of the corresponding species. Thus, the infrared data collected with the reduced sample suggest a similar behavior and provide further confirmation for the assignments of these two bands.

The observed shifts in the position of the terminal and bridging CO species adsorbed on reduced Pd with increasing temperature can be explained by a decrease of the dipole–dipole coupling between CO molecules, which in turn is a function of the surface coverage [20]. Alternatively, the observed behavior could also be attributed to an increase in the strength of interaction between Pd and the other components present in the sample (i.e. ceria) with increasing temperature, so that the Pd electronic and chemisorptive properties become altered, similar to what has been reported in the case of strong metal-support interactions (SMSI) [21]. It should also be mentioned that in the case of both the fresh and reduced

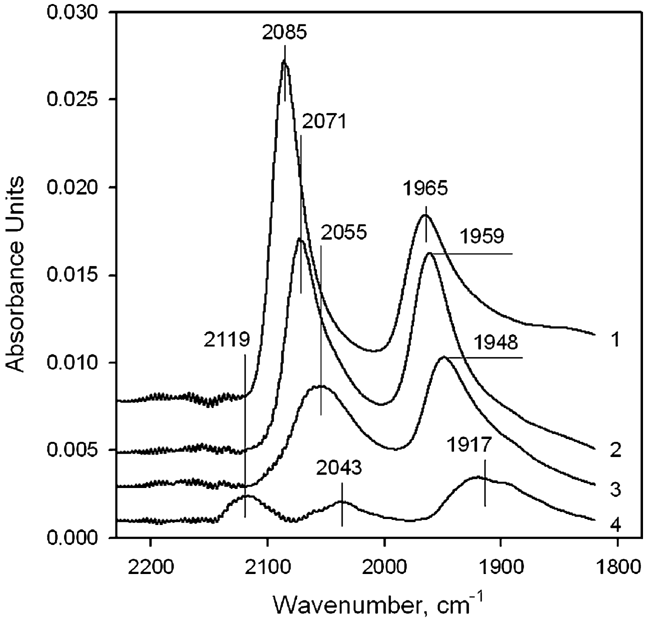


Fig. 4. FTIR spectra collected during exposure of a $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample reduced with H_2 at 500 °C to a 0.25% CO/He mixture at: (1) 25 °C; (2) 100 °C; (3) 190 °C; (4) 290 °C.

samples an increase in the ratio of bridging to terminal CO species was observed with temperature (Figs. 3 and 4). This behavior suggests that at elevated temperatures the adsorbed CO molecules may also trigger the nucleation of palladium to a certain degree.

When the temperature of the exposure to the CO/He mixture was raised above 200 °C, a new low intensity band was observed in the spectra at 2119 cm^{-1} regardless of the conditions used to pretreat the $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample (Figs. 3 and 4). It is possible, that at such high temperatures CO can induce the reconstruction of the Pd surface, leading for example, to the formation of highly dispersed Pd clusters, in which the Pd atoms could bear some positive charge due to strong interactions with either oxygen or hydroxyl groups from the support. Therefore, one could assign the band at 2119 cm^{-1} to CO adsorbed on $Pd^{\delta+}$ species formed under these conditions [17]. However, such an assignment is fairly problematic in our case, because our earlier experiments with the $Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample conducted under identical conditions, also revealed a very similar band at 2124 cm^{-1} which appeared in the spectrum at high temperatures (Fig. 1). Therefore, since the origin of these bands is most likely not related to the Pd species, we should consider some other possibilities. Alkali-exchanged zeolites for example, are known to adsorb CO [22,23]. More specifically, after the adsorption of CO on Na-ferrierite, FTIR bands were observed at 2175, 2159 and 2111 cm^{-1} and were assigned to various Na^{+}–CO and Na^{+}–OC species [24]. Similar data were also reported for CO adsorbed on NaY zeolite [25]. However, most of these infrared experiments were conducted at temperatures as low as 100 K, indicating that CO is only weakly polarized by Na^{+} cations. Therefore, the stability of such Na^{+}–CO complexes at elevated temperatures is very questionable. It is also possible to assign these bands to CO adsorbed on Ce^{3+} cations, which presumably can be formed on the $Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ surface in the reducing environment induced by the presence of CO in the gas phase at elevated temperatures. For example, literature reports provide evidence for the formation of Ce^{3+}–CO species in Ce-exchanged SAPO-18 catalysts at room temperature with a characteristic band observed at 2117 cm^{-1} [26]. Once again, in most cases, such species were found to be weakly adsorbed, and were observed only when CO was present in the gas phase. In contrast, our data indicate that the species responsible for the characteristic bands at 2119–2124 cm^{-1} were stable enough to be observed in the infrared spectrum for at least 20 min at 400 °C in the complete absence of CO in the gas phase (Fig. 1, spectrum 4).

Based on the above, one other possible explanation is that the bands at 2124–2119 cm^{-1} are not related to a surface species formed under our experimental conditions following the adsorption and/or reaction of CO. Consistent with such a notion, Binet et al. [27] observed a band at approximately 2120 cm^{-1} after the reduction of pure ceria in H_2 or CO at temperatures higher than 350 °C. This band could not be assigned to carbonyl species produced from the thermal decomposition of carbonate impurities in ceria due to the absence of any $^{12}C \rightarrow {}^{13}C$ exchange [27]. Moreover, it was found that this band is not perturbed by the adsorption of methanol, suggesting that its origin is not related to a surface defect but rather to a subsurface one, originating from oxygen migration to the reduced surface. Therefore, the band at approximately 2120 cm^{-1} was tentatively assigned to the forbidden $^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ electronic transitions of Ce^{3+} located at subsurface defect sites, which was allowed in this case due to a crystal field effect [27]. Such interpretation could be extended to the $Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ and $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ samples in our case, since both materials incorporate ceria in the oxide form. The presence of Pd in the sample is expected to promote the reduction of ceria, leading to an increase in the number of defects at both the surface and subsurface layers, and therefore, an increase in the intensity of the 2124 cm^{-1} band, consistent with our observations.

When the temperature of the exposure of $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ to the CO/He mixture was further increased to 400 °C, an additional broad band was observed at 2230 cm^{-1} (Fig. 3, spectrum 5). The same band was also observed immediately in the spectrum when a fresh $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample was brought in contact with a CO/He mixture at 400 °C and the intensity of this band increased with time on stream (Fig. 5). It is likely that this band can be attributed to CO adsorbed on coordinatively unsaturated Al^{3+} cations of the support. Such an assignment is consistent with similar assignments in the 2225–2235 cm^{-1} range reported previously in the literature for Al^{3+}–CO complexes on Al_2O_3, Na/Al_2O_3, HNaY and Pd/NaY surfaces [14], although, such ν_{CO} values for Al^{3+}–CO complexes are somewhat lower than those predicted for such species based on theoretical calculations [28]. It is interesting to note, that the formation of this band (2230 cm^{-1}) was observed in the case of $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$, but not for $Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$, implying that the presence of Pd in the sample is an important factor for the formation of the corresponding species.

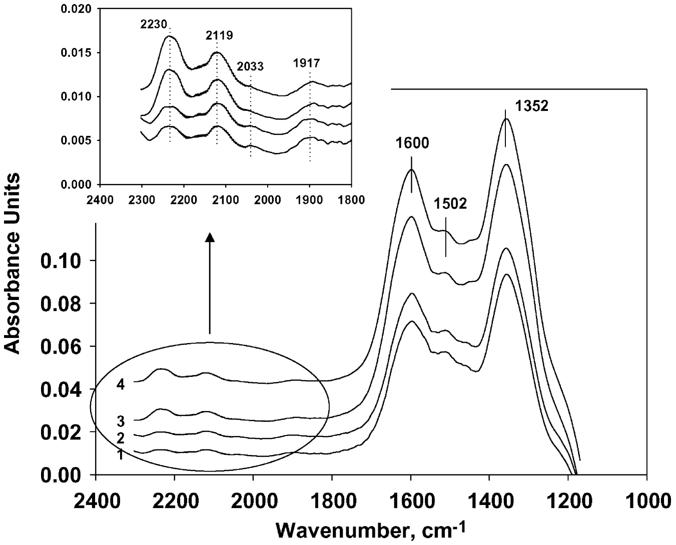


Fig. 5. FTIR spectra collected during exposure of a fresh $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample to a 0.25% CO/He mixture at 400 °C for: (1) 4 min; (2) 8 min; (3) 50 min; (4) 66 min.

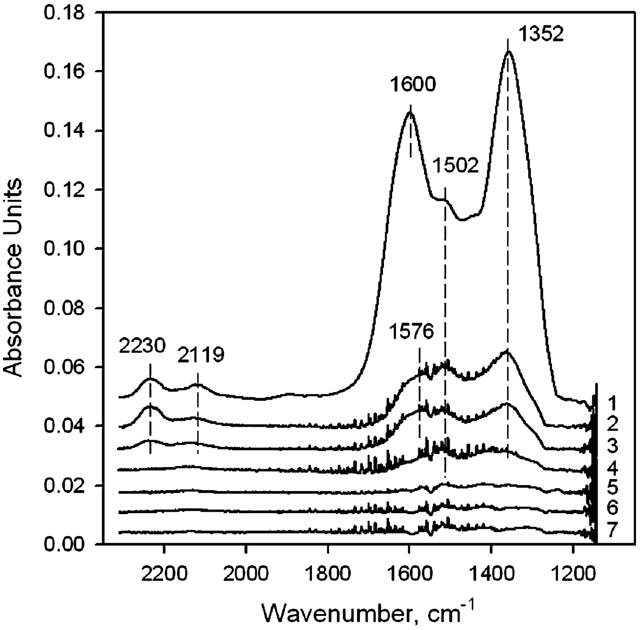


Fig. 6. FTIR spectra of a fresh $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample exposed to (1) 0.25% CO/He flow at 400 °C for 60 min, and subsequently treated at 400 °C with (2) He for 20 min and 0.05% NO/He for (3) 2 min; (4) 12 min; (5) 26 min; (6) 46 min; (7) 60 min.

Finally, all other features observed at lower frequencies in the spectra of $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ (Fig. 5) were very similar to those described in the previous section for the $Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample (Fig. 1). The bands at 1600, 1502 and 1356 cm^{-1} indicate the formation of carbonate/carboxylate species on the $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ surface, as well. However, the concentration of these species was substantially higher in the presence of Pd^{n+} (Figs. 1 and 5), indicating that Pd promotes their formation. Pd most likely provides CO to the metal-support interface, where the transformation of CO molecules to carbonates and/or carboxylates takes place. Similar to what was observed for the $Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample (Fig. 1), some of these carboxylate/carbonate species appear to be weakly bonded to the $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ surface, as indicated by the strong decrease in the intensity of these bands after the removal of the gas phase CO (Fig. 6). The remaining broad bands in the spectrum likely represent more stable carbonate species. These species can also be removed from the surface by treatment of the $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample with 0.05% NO/He at 400 °C. Since no new bands were observed during this treatment (Fig. 6), the exact mechanism of the carbonate removal by NO remains unclear. However, the NO treatment at 400 °C completely cleans the surface of the $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample not only from carboxylates and carbonates, but also from other carbonyl species such as those with the characteristic bands at 2230 and 2119 cm^{-1}. This result indicates that all these species have the ability to actively interact with NO molecules at elevated temperatures.

3.3. Interaction of NO/CO mixture with $Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$

When samples are exposed to mixtures containing both NO and CO, it is difficult to unambiguously assign all features in the 1700–1200 cm^{-1} region, due to the significant overlapping of bands associated with various nitrite/nitrate and carboxylate/carbonate species, that are formed on their surfaces. However, based on the results obtained from individual NO and CO adsorption experiments described in detail above and elsewhere [12], it follows that the carboxylate/carbonate bands typically exhibit stronger intensities than the nitrite/nitrate bands. Therefore, when the $Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample was exposed to a 0.25% CO/0.05% NO/He mixture at 400 °C, the bands at 1600 and 1350 cm^{-1} observed in the spectrum (Fig. 7) can be tentatively assigned to the carboxylate/carbonate species that dominate the surface during CO adsorption under similar conditions. Similar to what was observed during the adsorption of CO on this sample, the concentration of these species did not change with time on stream, indicating that a maximum concentration was reached at the very early stages of the experiment.

In addition, the appearance of a new band centered at 2229 cm^{-1} is apparent in the spectra collected in this case (Fig. 7). Based on previous literature reports [29,30], this band can be assigned to the asymmetric ν_{NCO} vibrations of a surface isocyanate (NCO) species. Such species are also known to exhibit a symmetric component of ν_{NCO} observed as a lower intensity band at approximately 1340 cm^{-1} [31]. However, this band could not be clearly identified in our spectra due to the overlap with the corresponding bands of the carboxylate/carbonate species.

Previously published FTIR data indicate that the formation of isocyanates requires the presence of platinum group metals in the catalyst [32–34]. In general, it is believed that such formation takes place on metal sites via the reaction between adsorbed CO and nitrogen atoms that are formed as a result of NO dissociation. It has also been suggested that the process of NCO formation is typically followed by the migration of these species from the metal sites to the support, where such species

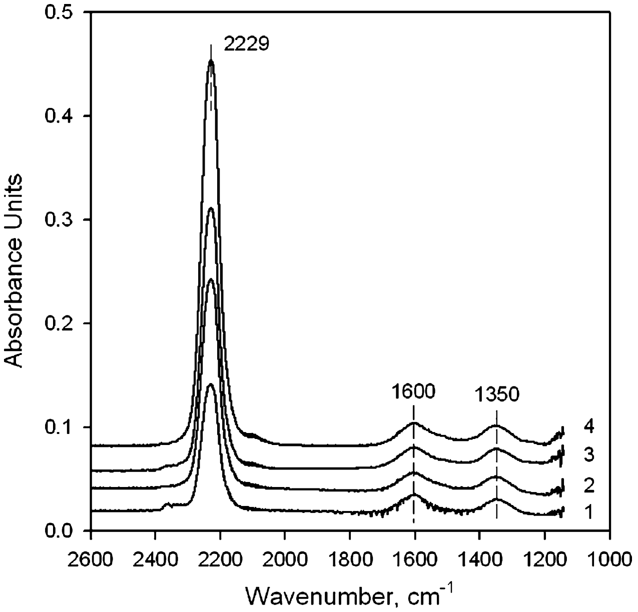


Fig. 7. FTIR spectra collected during exposure of $Ce^{n+}/Na^+/\gamma$-Al_2O_3 to 0.05% NO/0.25% CO/He at 400 °C for (1) 5 min; (2) 18 min; (3) 26 min; (4) 60 min.

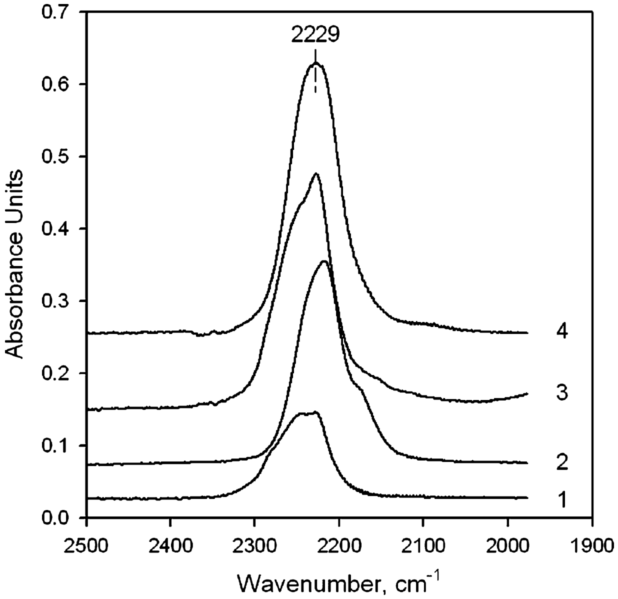


Fig. 8. FTIR spectra collected during exposure of (1) γ-Al_2O_3; (2) Na^+/γ-Al_2O_3; (3) Ce^{n+}/γ-Al_2O_3; (4) $Ce^{n+}/Na^+/\gamma$-Al_2O_3 to a 0.25% CO/0.05% NO/He mixture at 400 °C.

are more stable [35–37]. In this perspective, the formation of the NCO species on the metal-free $Ce^{n+}/Na^+/\gamma$-Al_2O_3 surface is certainly puzzling. The results of additional experiments conducted at 400 °C with the different components of the $Ce^{n+}/Na^+/\gamma$-Al_2O_3 material indicate that the formation of the NCO species is promoted to some extent by the presence of Na^+ or Ce^{n+} cations, since the intensity of the characteristic band at 2229 cm^{-1} was found to be higher in the case of Na^+/Al_2O_3 and Ce^{n+}/Al_2O_3 than on bare γ-Al_2O_3 (Fig. 8). Nevertheless, the formation of the NCO species directly from NO and CO even on bare γ-Al_2O_3 was observed, as indicated by the appearance of the two characteristic bands [38,39] at 2253 and 2229 cm^{-1} (Fig. 8, spectrum 1). Since we have obtained similar results for two different types of γ-Al_2O_3 (i.e. Grace-alumina and Alumina C) that were provided by Grace-Davison and Degussa, respectively, the potential role of contaminants in the formation of such isocyanate species can be excluded. In contrast, we did not observe the formation of any NCO species under similar experimental conditions when SiO_2 was used, suggesting that the presence of Lewis acid sites (such as Al^{3+} in this case) is required for the NCO formation reaction to proceed. The data in Fig. 7 further indicate that the concentration of the NCO species on the $Ce^{n+}/Na^+/\gamma$-Al_2O_3 surface (i.e. intensity of the band at 2229 cm^{-1}) increases with time on stream, suggesting a relatively low rate of their formation under our experimental conditions.

The concentration of isocyanate species on the surface of γ-Al_2O_3 is apparently small. Nevertheless, the mechanism leading to the formation of such species remains unclear at this time. Assuming that the formation of NCO species directly from CO and NO requires the dissociation of NO, it is also unclear how Ce^{n+} cations can promote the formation of isocyanates, especially when literature reports indicate that NO adsorbs in a molecular form on the surface of cerium oxide [40]. The formation of the isocyanates in the case of Na^+/γ-Al_2O_3 is also somewhat surprising, since it has been reported that sodium only in its metallic form strengthens the adsorption of NO on noble metals and promotes its dissociation [41]. Our infrared results further indicate that the isocyanate species formed on the $Ce^{n+}/Na^+/\gamma$-Al_2O_3 surface are reactive towards oxygen. For example, when following their formation during exposure of the sample to a 0.25% CO/0.05% NO/He mixture at 400 °C 0.2% O_2 was added to the reaction mixture, the isocyanate species were completely removed from the surface and more carbonates/carboxylates were formed, as indicated by the appearance of stronger bands in the 1600–1130 cm^{-1} region (Fig. 9). This process was also accompanied by the formation of CO_2, as evidenced by the appearance of the characteristic bands in the 2380–2300 cm^{-1} region (Fig. 9). When the flow of O_2 was stopped while the flow of NO and CO continued, the intensity of the band at 2229 cm^{-1} once again increased with time. Thus, the results indicate that once O_2 is removed, the surface concentration of NCO species can be replenished.

3.4. Interaction of NO/CO mixture with $Pd^{n+}/Ce^{n+}/Na^+/\gamma$-$Al_2O_3$

When a freshly prepared $Pd^{n+}/Ce^{n+}/Na^+/\gamma$-$Al_2O_3$ sample was exposed to a 0.25% CO/0.05% NO/He mixture at 400 °C, the changes observed in the 1600–1200 cm^{-1} region were similar to those described above for the $Ce^{n+}/Na^+/\gamma$-Al_2O_3 sample, and are consistent with the formation of surface carbonate and nitrate species. Furthermore, a strong isocyanate band appeared in the spectrum at 2236 cm^{-1}, the intensity of which increased with time on stream (Fig. 10A). The intensity of this band was substantially higher than the intensity of the corresponding band observed on the $Ce^{n+}/Na^+/\gamma$-Al_2O_3 sample

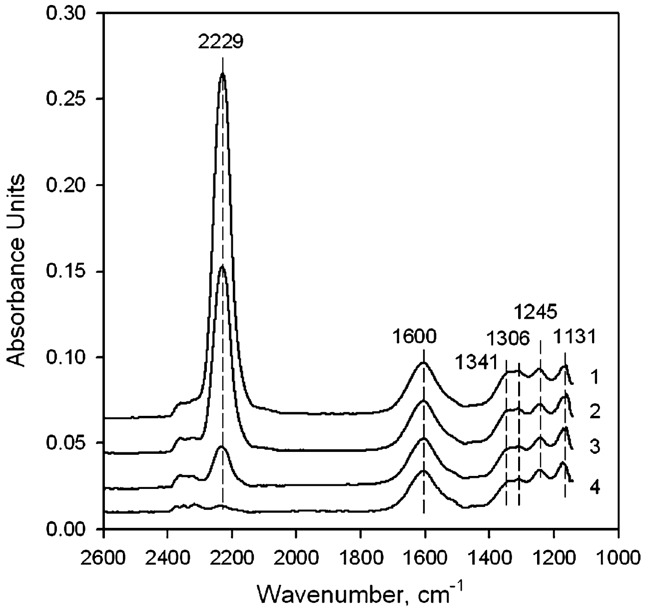


Fig. 9. FTIR spectra collected after exposure of Ce^{n+}/Na^{+}/γ-Al$_2$O$_3$ to 0.25% CO/0.05% NO/He at 400 °C for 2 h and subsequent addition of 0.2% O$_2$ to the 0.25% CO/0.05% NO/He mixture at 400 °C for (1) 2 min; (2) 10 min; (3) 20 min; (4) 30 min.

(Fig. 9), providing clear evidence that Pd significantly promotes the formation of the isocyanate species. As mentioned above, the formation of NCO on metal surfaces occurs via the interaction between adsorbed CO and N atoms [32–34]. The formation of the later species through the dissociation of NO is believed to be the rate-limiting step at high CO surface coverages [42]. In fact, NCO species were detected by FTIR on metal surfaces only at low temperatures (i.e. below 25 °C) due to their instability at elevated temperatures [32,43–45]. Nevertheless, isocyanates formed on metal sites can spill onto the support surface where they are accumulated and stabilized [32,43–45]. The shape of the band centered at 2236 cm^{-1} in our spectra (Fig. 10A) suggests that at least two overlapping bands are present, indicating that several adsorption sites on the Pd^{n+}/Ce^{n+}/Na^{+}/γ-Al$_2$O$_3$ surface are capable of accommodating isocyanate species. This result agrees with literature reports indicating that Al^{3+} sites of different coordination on the surface of γ-Al$_2$O$_3$ can adsorb isocyanic acid (HNCO) and the corresponding infrared bands of the resulting isocyanate species are not well resolved and overlapping with each other [38,39].

When similar experiments were performed at 600 °C, the isocyanate species were once again accumulated on the catalyst surface, as indicated by the strong band at 2221 cm^{-1} (Fig. 10B). This confirms that at temperatures close to FCC conditions isocyanate species can be formed on the surface, and therefore, could be regarded as potential intermediates leading to the reduction of NO$_x$ as suggested below. Furthermore, in this case, the isocyanate band was narrow and symmetric, indicating that at this temperature only a single isocyanate adsorption site remains active. The observed changes can be attributed to differences in stability of the various isocyanate species formed at 400 °C. This suggestion is consistent with an observed substantial decrease in the overall intensity of the band assigned to the isocyanate species when the temperature was increased from 400 to 600 °C, indicating the dependence of the concentration of these species on temperature, consistent with previous literature reports [46]. Furthermore, previous literature reports also indicate that the nature of the support strongly influences both the frequency of the characteristic isocyanate bands and their stability [47]. For example, it has been shown that such bands appear at 2210 cm^{-1} on Pt/TiO$_2$, while under similar experimental conditions on Pt/MgO and Pt/γ-Al$_2$O$_3$ they were typically observed at 2241 and 2272 cm^{-1}, respectively [47]. Therefore, it is also possible that exposure of

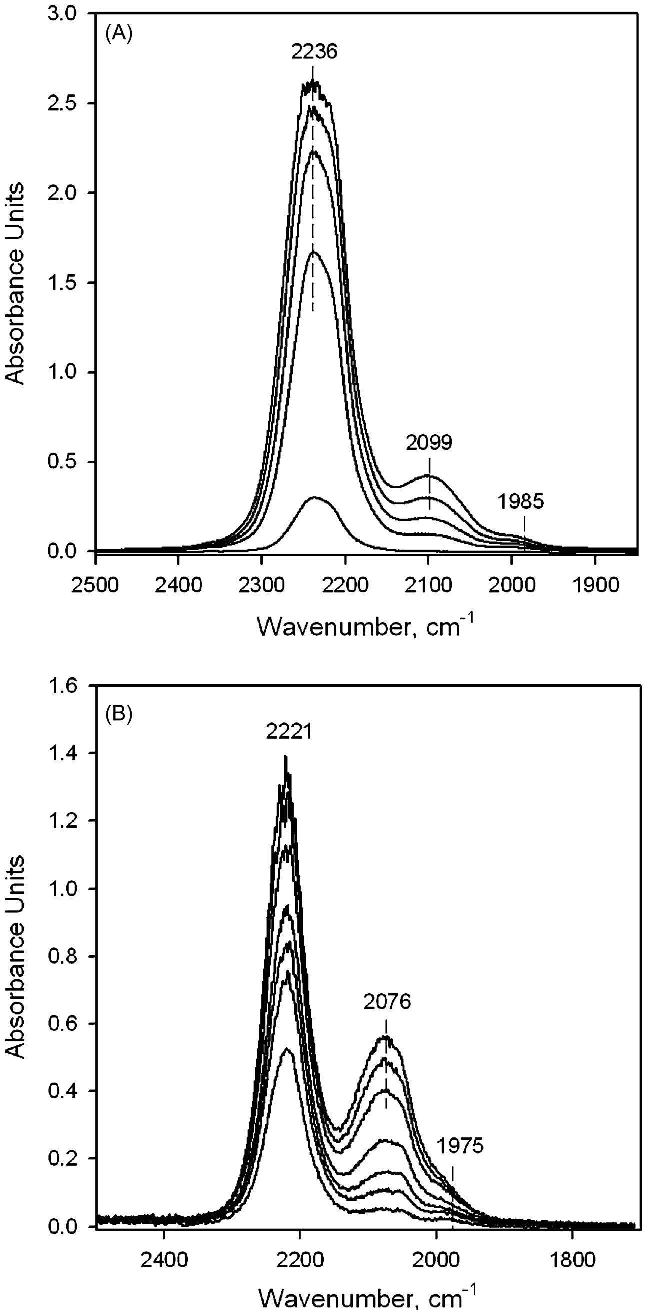


Fig. 10. FTIR spectra collected during exposure of Pd^{n+}/Ce^{n+}/Na^{+}/γ-Al$_2$O$_3$ to a 0.25% CO/0.05% NO/He mixture for a period of 60 min at (A) 400 °C and (B) 600 °C.

the sample in our case to the NO/CO mixture at temperatures as high as 600 °C may have caused the partial reduction of the cerium oxide component by CO, leading to stronger interactions between this component and the surface of γ-Al_2O_3. It is further possible that in such an event, some adsorption sites on the γ-Al_2O_3 surface become unavailable for the adsorption of the isocyanate species, and the band at 2221 cm^{-1} corresponds to isocyanate species accumulated on the remaining sites of γ-Al_2O_3 or, alternatively, on the Ce oxide.

The increase in the concentration of the isocyanate species with a time on stream in the 400–600 °C temperature range clearly correlates with the development of two other bands. For example, when experiments were performed at 400 °C, two additional bands at 2099 and 1985 cm^{-1} were also observed in the spectra, and their intensities were also increased with time on stream (Fig. 10A). These bands correspond to terminal and bridging CO species adsorbed on metallic palladium particles, respectively [17–19]. The appearance of these bands can be related to the reduction of the palladium oxide phase, which is initially present in the sample, to metallic palladium by CO, which is present in excess in the CO/NO mixture used. However, the positions of these bands are blue-shifted compared to what was observed during adsorption of CO on this sample at 400 °C (Fig. 3), indicating incomplete reduction of palladium in the presence of NO under these conditions. When similar experiments were performed at 600 °C, the reduction of palladium by CO was apparently more complete, as indicated by the appearance of characteristic bands for the terminal and bridging CO species at 2076 and 1975 cm^{-1}, respectively (Fig. 10B). The presence of a relatively small fraction of bridging CO species suggests that the metallic palladium particles formed under these conditions are highly dispersed. This result is consistent with our EXAFS data reported elsewhere [12], which indicate that the more severe reduction of the $Pd^{n+}/Ce^{n+}/Na^{+}$/γ-Al_2O_3 material with H_2 at 500 °C leads only to the formation of small Pd clusters incorporating on average approximately 6–8 metal atoms. These results also suggest that when the CO/NO mixture is used, the reduction of PdO species by CO is followed by subsequent oxidation of the reduced metal by NO. When the concentration of NO in the mixture is low, the reduction process apparently prevails over the oxidation and the majority of the metal is in a reduced state. Nevertheless, even the partial oxidation of some reduced Pd sites by NO appears to help maintain palladium in a highly dispersed form as well as prevent its aggregation.

3.5. Thermal stability and reactivity of isocyanates

The isocyanate species formed on the surfaces of supported metal catalysts are often regarded as spectators, due to previous reports indicating that such species are unreactive, for example, towards NO/O_2 mixtures [46]. In contrast, it has also been reported that surface isocyanate species can show reactivity towards hydrolysis, leading to the formation of ammonia and CO_2 [33]. Our infrared data indicate that the isocyanate species formed on the surface of the $Pd^{n+}/Ce^{n+}/Na^{+}$/γ-Al_2O_3 sample after exposure to the NO/CO mixture can be desorbed during purging of the sample with He at 400 °C. To distinguish between the thermal stability of the isocyanates and their reactivity towards O_2 and NO, we have formed these species at 400 °C, decreased the reaction temperature to 250 °C with the NO/CO mixture still flowing over the sample, and only then replaced the CO/NO mixture with a 0.2% O_2/He or 0.05% NO/He one. The results thus obtained are shown in Fig. 11. These data clearly indicate that the isocyanate species were removed at a significantly higher rates from the surface in the presence of O_2 or NO than in He, demonstrating that these species react with both O_2 and NO. The data of Fig. 11 further show that isocyanates are more reactive towards NO than O_2. Therefore, the formation of isocyanates followed by the reaction with O_2 and/or NO according to the scheme shown below, could be possible pathways leading to the reduction of NO under FCC regeneration conditions:

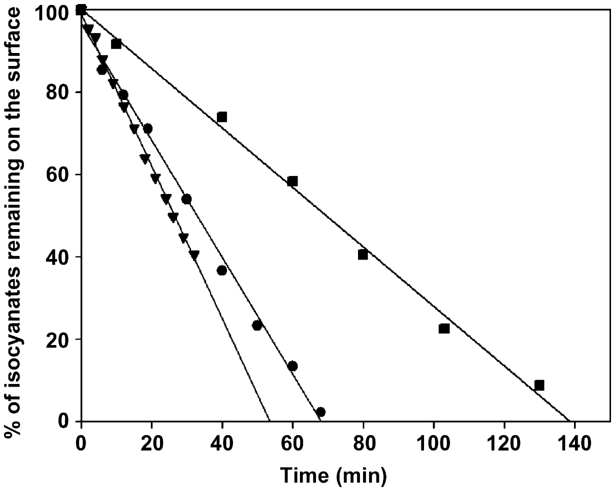


Fig. 11. Percent removal of isocyanate species from the surface of $Pd^{n+}/Ce^{n+}/Na^{+}$/γ-Al_2O_3 with time on stream at 250 °C in (■) He, (●) a 0.2% O_2/He mixture and (▼) a 0.05% NO/He mixture.

$$NO + 2CO \rightarrow NCO + CO_2 \tag{1}$$

$$2NCO + O_2 \rightarrow N_2 + 2CO_2 \tag{2}$$

$$NCO + NO \rightarrow N_2 + CO_2 \tag{3}$$

3.6. Role of the support

As it was mentioned above, it is generally assumed that isocyanate species formed on the surfaces of metals migrate onto the support where they are stabilized on Al^{3+} sites of different coordination [38,39]. It is further believed that isocyanates can be also stabilized on the support surface in a form of isocyanic acid (HNCO) [33,48,49]. Therefore, in general terms, the formation and stabilization of surface isocyanates can be represented as follows:

$$NO + 2CO + [H] \rightarrow HNCO + CO_2 \tag{4}$$

The origin of the proton included in this reaction is uncertain. For example, it has been suggested that hydrogen

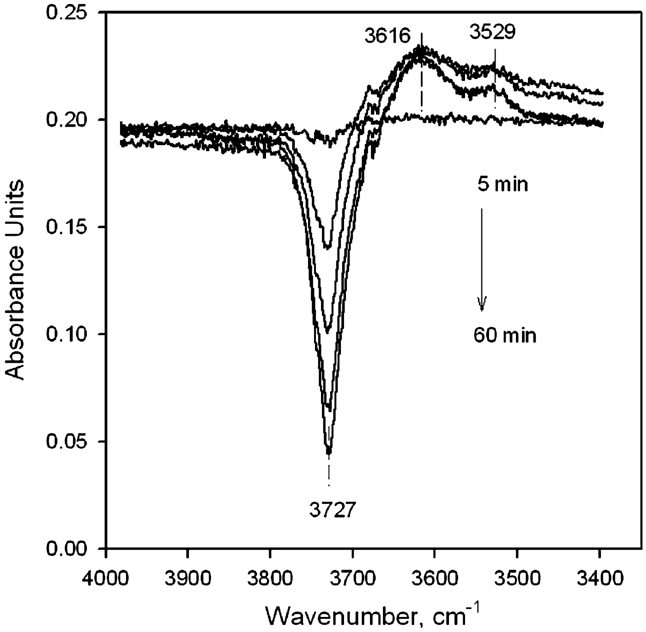
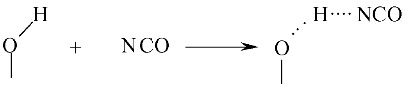


Fig. 12. FTIR difference spectra illustrating changes in the ν_{OH} region during exposure of $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ to a 0.25% CO/0.05% NO/He mixture at 400 °C.

formed through a water–gas shift scheme can account for one of possible ways to fulfill this need [50]. Our infrared data summarized in Figs. 12 and 13 allow us to suggest an alternative possibility for the potential source of protons. For example, during exposure of the $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample to the NO/CO mixture and formation of the surface isocyanate species (Fig. 10A), substantial changes were also observed in the ν_{OH} region (Fig. 12). More specifically, the intensity of the band at 3727 cm^{-1} assigned to isolated hydroxyls clearly decreased with time on stream, while two new bands appeared at 3616 and 3529 cm^{-1} (Fig. 12). All these changes directly correlate with the development of the isocyanate band at 2236 cm^{-1} (Fig. 10A). Furthermore, when the NO/CO/He mixture was subsequently replaced with the O_2/He one, the isocyanate species were gradually removed from the surface. During this process the intensity of the band at 3727 cm^{-1} gradually increased with time on stream, while the bands at 3616 and 3529 cm^{-1} disappeared from the spectrum (Fig. 13). The strong correlation observed between the appearance of the bands at 3616 and 3529 cm^{-1}, the decrease in intensity of the band at 3727 cm^{-1} and the growth of the isocyanate band at 2236 cm^{-1}, suggest that the observed changes in the ν_{OH} region are directly related to the formation of the isocyanate species. We therefore propose that isocyanate species initially formed on palladium migrate onto the support where they are directly interacting with acidic hydroxyls having sufficiently mobile protons capable of protonating the NCO species as follows:



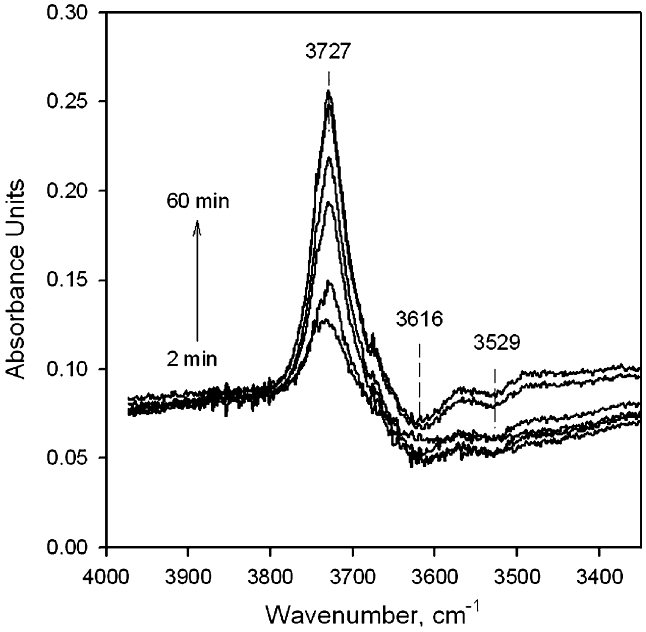


Fig. 13. FTIR difference spectra illustrating changes in the ν_{OH} region during treatment of a $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ sample exposed to a 0.25% CO/0.05% NO/He mixture with a 0.2% O_2/He mixture at 400 °C.

This scheme is similar to one described elsewhere [14] for the interaction of ammonia with Brønsted acid sites on oxide supports. In such an event, the low intensity band observed in our spectra at 3529 cm^{-1} can be assigned to the NH stretching vibrations of the protonated NCO species [31,51].

It is further expected that upon such coordination, the proton becomes multi-centered between the oxygen atom of the hydroxyl and the nitrogen atom of the NCO species. Such delocalization of the proton is expected to lead to broadening of the ν_{OH} band of free hydroxyls and a shift towards lower frequencies [14]. Therefore, the gradual disappearance of the characteristic band of free hydroxyls at 3727 cm^{-1} and the appearance of the broad band at 3616 cm^{-1} are consistent with the process described above. As we pointed out in the previous section, subsequent treatment of the sample in oxygen leads to the decomposition of the isocyanate species formed. Under such conditions, the ν_{NH} (i.e. 3529 cm^{-1}) band disappears from the spectra, and the initial intensity of the free hydroxyls band at 3727 cm^{-1} is restored (Fig. 13). Therefore, our infrared data provide solid evidence that hydroxyls on the surface of the $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ catalyst actively participate in the surface chemistry taking place between CO and NO molecules through the stabilization of NCO intermediates.

4. Conclusions

The adsorption of CO and the reaction between CO and NO in the 400–600 °C temperature range were monitored by FTIR over $Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ and $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma\text{-}Al_2O_3$ samples. Exposure of both samples to CO leads to the formation of surface carboxylates weakly bonded to the support and more stable surface carbonates. The concentration of carboxylates/carbonates was found to be higher in the samples incorporating palladium, indicating that Pd promotes the formation of these species. Furthermore, Pd oxide species initially present in the $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma$-$Al_2O_3$ sample undergo reduction to metallic Pd in the presence of CO even at room temperature. This reduction is more complete at elevated temperatures. Under these conditions, CO also triggers limited sintering of Pd.

Exposure of both samples to NO/CO mixtures in the 400–600 °C temperature range leads to the formation of surface isocyanate species. The FTIR results provide clear evidence that such species in small concentrations can be also formed on the surface of bare γ-Al_2O_3 at 400 °C. The exact mechanism of formation in this case remains unclear. However, since no such species were formed on the surface of SiO_2 under identical conditions, we suggest that the presence of Lewis acid sites is essential for the formation of such species. The FTIR results further show that the presence of both Na^{+} and Ce^{n+} promote the formation of NCO species to a small degree. However, substantially higher rates of isocyanate formation were observed when palladium was present in the sample. The formation of such isocyanate species strongly correlates with changes observed in the ν_{OH} region, indicating that surface hydroxyls actively participate in the surface chemistry during NCO stabilization and are capable of protonating the NCO species. The isocyanate species formed on the surfaces of $Ce^{n+}/Na^{+}/\gamma$-Al_2O_3 and $Pd^{n+}/Ce^{n+}/Na^{+}/\gamma$-$Al_2O_3$ are reactive towards O_2 and NO, suggesting that these species may be involved in NO reduction schemes.

Acknowledgements

The authors gratefully acknowledge W.R. Grace and Co.-Conn. for financial support and permission to publish this work.

References

[1] G.H. Unzelman, AM 88-25, Natl. Pet. Refiners Assoc. Annual Meeting, San Antonio, 1988.
[2] W.-C. Cheng, G. Kim, A.W. Peters, X. Zhao, K. Rajagopalan, M.S. Ziebarth, Catal. Rev. Sci. Eng. 40 (1998) 39.
[3] Y.-M. Chen, Powder Tech. 163 (2006) 2.
[4] G. Yaluris, T.J. Dougan, AM 05-21, National Petroleum Refiners Association Annual Meeting, San Antonio, 2005.
[5] A. Corma, A.E. Palomares, F. Rey, F. Marquez, J. Catal. 170 (1997) 140.
[6] G. Yaluris, A.W. Peters, in: J.G. Reynolds, M.R. Khan (Eds.), Designing Transportation Fuels for a Cleaner Environment, Taylor & Francis, Philadelphia, 1999, pp. 151–164.
[7] J.-O. Barth, A. Jentys, J.A. Lercher, Ind. Eng. Chem. Res. 43 (2004) 3097.
[8] J.-O. Barth, A. Jentys, J.A. Lercher, Ind. Eng. Chem. Res. 43 (2004) 2368.
[9] I.V. Babich, K. Seshan, L. Lefferts, Appl. Catal. B 59 (2005) 205.
[10] E.F. Iliopoulou, E.A. Efthimiadis, L. Nalbandian, I.A. Vasalos, J.-O. Barth, J.A. Lercher, Appl. Catal. B: Environ. 60 (2005) 277.
[11] E.F. Iliopoulou, E.A. Efthimiadis, L. Nalbandian, I.A. Vasalos, J.-O. Barth, J.A. Lercher, Appl. Catal. B: Environ. 47 (2004) 165.
[12] O.S. Alexeev, S. Krishnamoorthy, M.S. Ziebarth, G. Yaluris, T.G. Roberie, M.D. Amiridis, Catal. Today, (in press).
[13] T. Chafik, O. Dulaurent, J.L. Gass, D. Bianchi, J. Catal. 179 (1998) 503.
[14] A.A. Davidov, Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides, Wiley, Chichester, 1990.
[15] C. Binet, A. Jadi, J.C. Lavalley, J. de Chemie Physique et de Physico-Chemie Biologique 89 (1992) 1779.
[16] A. Badri, C. Binet, J.C. Lavalley, J. Phys. Chem. 100 (1996) 8363.
[17] H. Tiznado, S. Fuentes, F. Zaera, Langmuir 20 (2004) 10490.
[18] A. Palazov, C.C. Chang, R.J. Kokes, J. Catal. 36 (1975) 338.
[19] A. Holmgren, B. Andersson, D. Duprez, Appl. Catal. B: Environ. 22 (1999) 215.
[20] O. Dulaurent, K. Chandes, C. Bouly, D. Bianchi, J. Catal. 192 (2000) 273.
[21] R.T.K. Baker, S.J. Tauster, J.A. Dumesic (Eds.), Strong Metal Support Interactions, ACS, Washington, DC, 1986.
[22] S. Bordiga, C. Lamberti, F. Geobaldo, A. Zecchina, G. Turnes Palomino, C. Otero Areán, Langmuir 11 (1995) 527.
[23] A. Zecchina, S. Bordiga, C. Lamberti, G. Spoto, L. Carnelli, C. Otero Areán, J. Phys. Chem. 98 (1994) 9577.
[24] S. Bordiga, G. Turnes Palomino, C. Pazè, A. Zecchina, Micro. Meso. Mater. 34 (2000) 67.
[25] K. Hadjiivanov, H. Knözinger, Chem. Phys. Lett. 303 (1999) 513.
[26] C. Kladis, S.K. Bhargava, K. Foger, D.B. Akolekar, J. Mol. Catal. A: Chem. 175 (2001) 241.
[27] C. Binet, A. Badri, J.C. Lavalley, J. Phys. Chem. 98 (1994) 6392.
[28] S. Bites, J. Dwyer, J. Phys. Chem. 97 (1993) 5897.
[29] R.A. Dalla Betta, M. Shelef, J. Mol. Catal. 1 (1976) 431.
[30] T. Chafic, S. Kameoka, Y. Ukisu, T. Miyadera, J. Mol. Catal. A 136 (1998) 203.
[31] S. Raunier, T. Chiavassa, F. Marinelli, A. Allouche, J.-P. Aycard, J. Phys. Chem. A 107 (2003) 9335.
[32] F. Solymosi, T. Bánsági, J. Catal. 156 (1995) 75.
[33] R. Dümpelmann, N.W. Cant, D.L. Trimm, Appl. Catal. B: Environ. 6 (1995) L291.
[34] A.M. Sica, C.E. Giola, Appl. Catal. A: Gen. 239 (2003) 121.
[35] F. Solymosi, J. Raskó, J. Catal. 63 (1980) 217.
[36] M. Macleod, R.M. Lambert, Chem. Commun. (2003) 1300.
[37] K. Almusaiteer, S.C. Chuang, J. Catal. 184 (1999) 189.
[38] R. Dictor, J. Catal. 109 (1988) 89.
[39] F. Solymosi, L. Völgyesi, J. Raskó, Z. Phys. Chem. 120 (1980) 79.
[40] G. Li, K. Kaneko, S. Ozeki, Langmuir 13 (1997) 5894.
[41] I.R. Harkness, R.M. Lambert, J. Chem. Soc., Faraday Trans. 93 (1997) 1425.
[42] J.H. Miners, A.M. Bradshaw, P. Gardner, Phys. Chem. Chem. Phys. 1 (1999) 4909.
[43] W.C. Hacker, A.T. Bell, J. Catal. 85 (1984) 389.
[44] F. Solymosi, J. Raskó, Appl. Catal. 10 (1984) 19.
[45] J. Kiss, F. Solymosi, J. Catal. 179 (1998) 277.
[46] A. Martínez-Arias, A.B. Hungría, M. Fernández-García, A. Iglesias-Juez, J.A. Anderson, J.C. Conesa, J. Catal. 221 (2004) 85.
[47] F. Solymosi, L. Völgyesi, J. Sárkáni, J. Catal. 54 (1978) 336.
[48] R. Dumpelmann, N.W. Cant, A.D. Cowan, Stud. Surf. Sci. Catal. 101 (1996) 1175.
[49] N.W. Cant, D.C. Chambers, I.O.Y. Liu, Catal. Today 93–95 (2004) 761.
[50] N.W. Cant, D.C. Chambers, I.O.Y. Liu, Appl. Catal. 46 (2003) 551.
[51] J.H. Teles, G. Maier, B.A. Hess, L.J. Schaad, M. Winnewisser, B.P. Winnewisser, Chem. Ber. 122 (1989) 753.