Adsorption of CO and NO on Ceria- and Pt-Supported TiO₂: In Situ FTIR Study

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Received June 19, 2013; revised August 8, 2013; accepted September 2, 2013

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ABSTRACT

Pt/TiO₂, Ce/TiO₂ and binary system PtCe/TiO₂ catalysts were prepared by impregnation method and the structural properties of these catalysts were investigated by means of XRD, CO-TPD and UV-vis diffuse reflectance spectroscopy. As investigated by XRD, the composition of the prepared samples anatase and rutile phases with higher amount of anatase phase and its particle size was in the range of 19 - 22 nm. The band gap also decreased from 3.1 to 2.85 after addition of metal to TiO₂. The adsorption and interaction properties of NO and/or CO gases were monitored using an in situ FTIR technique. The intensity and position of the infrared peaks were strongly dependent on the composition of the catalyst. In presence of Pt, the main oxidative reductive products of (NO + CO) are CO₂ and NCO complex. The formation of NCO depends on not only the presence of platinum in the catalyst but also the presence of Lewis acid sites which is Ti⁴⁺ in this study. However, the interaction between NO and CO gases increased in presence of CeO₂. The optimum Ce content in PtCe/TiO₂ was 0.1% (Ce/TiO₂) at which the maximum peak intensity was observed for NCO and CO₂.

Keywords: In Situ FTIR; NO Reduction; CO Oxidation; TPD-CO; Platinum-Cerium

1. Introduction

The importance of environmental gas monitoring and controlling is now recognized as an important area to diminish the hazardous chemical vapors present beyond specified levels. CO and NO are known to be extremely harmful to the human body and also a main cause of air pollution since they are two of the most hazardous products released in car exhausts [1]. The best employed methods for eliminating NO and CO are the catalytic reductive and oxidative mechanisms, respectively. Both CO and NO are used as common probe molecules in surface science to obtain fundamental information about the gas-surface interactions, adsorption sites, and reactive dynamics on variety of metals [2]. One of the most important reactions in automobile exhaust catalysis is the reaction between NO and CO over metal oxide surfaces:

\[
\text{NO}_\text{(g)} + \text{CO}_\text{(g)} \rightarrow \text{CO}_2\text{(g)} + \frac{1}{2}\text{N}_2\text{(g)}
\]

(1)

Rhodium, platinum and palladium are mostly used to catalyze the reaction in Equation (1) [3]. A Pt/TiO₂ sample has been studied by adsorption and co-adsorption of CO + NO [4]. The activity of Rh supported on the ceria doped titania was investigated and it was found that the presence of ceria favors the Rh dispersion [5]. González et al. [6] reported that Pt supported on Ce-modified TiO₂ support exhibited better activity for water gas shift reaction than those corresponding to individual CeO₂ and TiO₂-supported catalysts. These catalysts were prepared by using metal/Ti ratios of 0.5 for Pt/Ti and 0.005 - 0.07 for Ce/Ti. It will be important to prepare Ce-promoted Pt/TiO₂ catalyst and test it for NO + CO adsorption and interaction as an oxidative/reductive catalytic method for harmful gas removal.

In situ IR spectroscopy study of adsorbed probe molecules, especially of CO, is very useful for the characterization of solid surfaces and gives a unique possibility to characterize the coordination state and electrophilic properties of accessible sites [7]. Activity measurements, when coupled with the physicochemical characterization of catalysts suggest that the modifications in the surface reducibility of the support play an essential role in the enhancement of activity and stability observed when Pt-modified TiO₂ was promoted with CeO₂. Hence, testing the gas interaction over the reduced catalyst should be informative.

The purpose of the present work is to investigate the
effect of cerium oxide addition on the structure and adsorption properties of titania-supported platinum catalyst. CO and/or NO were admitted to the prepared catalysts and the interaction of admitted gases over the catalysts surface was monitored by in situ FTIR spectroscopy technique. X-ray diffraction (XRD), Temperature Programmed Desorption (TPD) of CO and Diffuse reflection spectra (UV) were used for solid characterization.

2. Experimental

2.1. Catalyst Preparation

Analytical grade reagents, Pt(NH3)2Cl2·H2O, Ce(NO3)3·6H2O and TiO2 (Degussa P25, known as a commonly used photocatalyst), were employed as starting materials in this study. The metal supported TiO2 nanoparticles were prepared by the incipient wetness impregnation method. TiO2 (4 g) was placed and stirred in water to form a homogenous suspension. A proper amount of an aqueous solution of Pt2+, Ce3+ and (Pt2+ + Ce3+) was added to TiO2 suspension to form the required Pt, Ce, and (Pt + Ce)/TiO2 ratios, respectively. The molar ratio Pt/Ti was fixed at 1% and Ce/Ti was changed in the range of 0.05% - 1%. The Pt, Ce and (Pt + Ce) supported TiO2 precursors slurry were refluxed at 80°C with continuous stirring for 3 h. After impregnation the sample was allowed to evaporate using rotary evaporator and the residues were dried at 110°C over night. The obtained solids were then calcined at 500°C in air for 3 h with ramp rate of 2°C/min. The samples were referred to as Pt/TiO2, Ce/TiO2 and PtCe/TiO2 for Pt, Ce and PtCe-supported titania, where x denotes to the Ce/Ti ratio.

2.2. Catalysts Characterizations

X-ray diffraction (XRD) technique was used to determine the bulk crystalline structures of the prepared catalysts. The XRD patterns were obtained with an x-ray diffractometer, D8 Advance (Bruker axs), with a Cu Kα radiation source (30 kV and 20 mA) in the 2θ range of 0.05°- 1°. The average crystallize size (D) of the obtained powders was calculated by Hall-equation-Scherrer’s formula: $D = \frac{0.9\lambda}{\beta\cos\theta}$ [8], where λ represents the x-ray wavelength (1.54 Å), θ is the Bragg’s angle and β (in radians) is the pure full width of the fraction line at half of the maximum capacity.

Temperature Programmed Desorption (TPD) experiments were carried out using CO gas in a fixed-bed reactor system. Before TPD measurements, the catalyst (30 mg) was treated at 500°C for 1 h in air. Then the heated sample was evacuated for 1 h at the same temperature under vacuum (10−4 torr). The sample was then cooled under the same pressure until room temperature and then an amount of CO gas with partial pressure of 7 torr was added and left to equilibrate for 30 min. The sample was then degassed for 1 h at room temperature. The degassed CO molecules (n/z = 28) were monitored by a gas desorption analyzer (ANELVA, M-QA100TS) equipped with a quadruple mass analyzer in a high-vacuum chamber of 7.5 × 10−9 torr range. TPD profiles were recorded by linear heating of the samples from 25°C to 750°C at constant ramp rate of 5°C/min.

The UV-vis diffuse reflectance spectra of various samples in the 700 - 200 nm range were obtained using a Jasco V-570 (serial number, C29635) spectrophotometer equipped with a diffuse reflectance attachment, using BaSO4 as a reference.

2.3. Gas Adsorption and Catalytic Activity Measurements

In situ FTIR spectra of CO and/or NO adsorption (7 torr of each) were recorded using JASCO FTIR-660 Plus. Briefly, 15 - 20 mg/cm2 self-supporting pellets of the catalyst powder were prepared and treated directly in the purpose-made IR quartz cell equipped with CaCl2 windows. The IR cell was connected to a static vacuum-adsorption system with a residual pressure below 10−4 torr. The samples were heated at 500°C for 2 h in air followed by 1 h evacuation at same temperature. Then the catalysts were cooled at room temperature (RT) and at this point, background spectrum was recorded. CO and/or NO gas mixtures were then admitted. The gases were used in equal partial pressure of 7 torr of each (CO:NO; 1:1). After gas admission, the cell was left to equilibrate for 20 min at RT after which the spectrum was recorded again. The former spectrum (before gas admission) was subtracted from the latter one (after gas admission) and will be discussed below. To test the adsorption at higher temperature, the temperature of the IR cell, including the sample wafer and the gas mixture, was raised to the desired temperature. It was kept at such temperature for 20 min after which the IR cell was cooled to RT and then the spectrum was recorded, and kept to test the effect of the addition of trace amount of water vapor, it was added in the gas mixture with a ratio of (CO + NO + H2O; 7:7:1).

3. Results and Discussions

3.1. Catalyst Characterization

3.1.1. X-Ray Diffraction

XRD was usually used for identification of the crystal phase and estimation of the ratio of the anatase to rutile as well as crystallite size of each phase. Figure 1 shows the XRD patterns of titania and metal supported TiO2 catalysts. The patterns proved the presence of both anatase and rutile phases in all samples. The peaks at 2θ = 26.1 (101), 38.6 (112), 48.8 (200) and 55° (211) in the spectrum of all samples are easily identified as the crystal
of anatase form [PDF# 84 - 1286], whereas the XRD peaks at 2θ = 28.2 (110), 36.9 (101), 42 (111) and 55.9° (211) are easily taken as the crystal of rutile form [PDF# 88 - 1175]. In addition, small peak at 2θ = 37.9° due to titanate (H₂Ti₄O₉·1.9H₂O) [PDF# 39 - 0040] was observed and increased in samples containing Pt. The patterns did not show any peaks for loaded metal oxides, indicating that these metal oxides were well dispersed in all cases. The XRD intensities of the anatase peak at 2θ = 26.1° and the rutile peak 2θ = 28.2° were also analyzed to determine the percentage of anatase in the samples from the respective integrated XRD peak intensities using the following equation [9]:

\[ X(\%) = 100 \left( 1 + 1.265 \frac{I_R}{I_A} \right) \]

where \( I_A \) represents the intensity of the anatase peak at 2θ = 28.2° and \( I_R \) is that of the rutile peak at 2θ = 28.2°. The patterns in Figure 1 and the data listed in Table 1 show that most of the structure of the prepared samples is anatase form. It could be seen that the presence of other metal oxides such as Pt or Ce oxides increased the anatase ratio. These data demonstrated that the employed metal oxides could inhibit the transformation from anatase to rutile. These observations are in good agreement with previous reports [10].

Table 1. Crystallite size of parent TiO₂ and Ce- and Pt-supported TiO₂ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Phase % by XRD</th>
<th>Crystallite size, nm</th>
<th>Band gap, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anatase/Rutile</td>
<td>Anatase, Rutile</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>72.6/27.4</td>
<td>19.9/25.1</td>
<td>3.1</td>
</tr>
<tr>
<td>PtTiO₂</td>
<td>80.0/20.0</td>
<td>21.5/27.2</td>
<td>2.95</td>
</tr>
<tr>
<td>Ce₀.1/TiO₂</td>
<td>72.3/27.7</td>
<td>20.6/25.7</td>
<td>2.85</td>
</tr>
<tr>
<td>PtCe₀.05/TiO₂</td>
<td>76.0/24.0</td>
<td>17.8/24.9</td>
<td>-</td>
</tr>
<tr>
<td>PtCe₀.1/TiO₂</td>
<td>82.3/17.7</td>
<td>22.6/34.9</td>
<td>2.9</td>
</tr>
<tr>
<td>PtCe₀.2/TiO₂</td>
<td>74.6/25.4</td>
<td>19.4/26.7</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. X-ray powder diffraction patterns of parent TiO₂ and Pt and Ce-supported TiO₂ catalysts.

3.1.2. Temperature Programmed Desorption (TPD)

The TPD spectra after CO adsorption of pure TiO₂ and the prepared catalysts are shown in Figure 2. The magnitude of the desorption maxima differs somewhat between the metal-free and supported TiO₂ samples. The CO peak maximum for pure TiO₂ is observed at approximately ~540°C. This profile changed after loading of Pt and Ce to TiO₂ surface. In case of Pt/TiO₂, three CO desorption peaks can be distinguished at ~175°C, 560°C and ~695°C. However, Ce₀.1/TiO₂ showed one CO desorption peak at ~615°C. This indicates that CeO₂ does not show any CO adsorption which in accordance with other reports [11], though it caused the shift of CO desorption peak to higher temperature compared to that of Ce-free TiO₂. Bimetallic PtCe₀.1/TiO₂ sample showed two desorption peaks at ~125°C and another one at ~560°C. The CO desorption temperatures of Ce₀.1/TiO₂ and Pt/TiO₂ are anomalously high comparing to the desorption values of TiO₂ i.e. these samples have higher molecular CO desorption energy due to the creation of strong basic sites. The strong basic sites of Pt/TiO₂ attenuated in presence of Ce in Pt/Ce₀.1/TiO₂. Such attenuation may be due to site-blocking effect of the other metal ion (Ce) which occupies adsorption sites for CO and suppresses CO chemisorptions [12]. The data showed that the apparent area under peaks for Pt/TiO₂ is larger than that for PtCe₀.1/TiO₂ indicating that the dispersion of Pt in the former is higher than that in the later [11].

3.1.3. UV-vis Diffuse Reflectance

Diffuse reflection spectra of pure TiO₂ and metal sup-

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ported catalysts are shown in Figure 3. Generally, anatase-type TiO2 crystalline has a strong absorption edge below 380 nm [13]. From the presented profiles, the prepared samples showed mainly anatase structure which is consistent with XRD patterns. In addition, after mounting metal ions to the surface of TiO2, the slopes of the absorption edges slightly changed compared with pure TiO2. The band gap energy was estimated with the Kubelka-Munk method using diffuse reflectance spectra [14]. After calculations, unpromoted titania has a typical band gap of 3.1 ev, whereas the band gap magnitude of the metal supported titania decreased slightly; that is 2.95, 2.9 and 2.85 ev for Pt/TiO2, PtCe0.1/TiO2 and Ce0.1/TiO2, respectively, as listed in Table 1. These results disclose one crucial fact that the employed metals interact with TiO2 and hence the band gap changed.

3.2. Adsorption of CO on the Prepared Samples

The results of CO adoption (7 torr) over the pure TiO2 and metal loaded TiO2 at RT in the range of 2400 - 1100 cm\(^{-1}\) are presented in Figure 4. Since the absorptions regions of Pt\(^{n+}\)-CO and Ti\(^{4+}\)-CO carbonyls may overlap, it was important to study the adsorption of CO over metal free TiO2. Adsorption of CO on TiO2 sample, Figure 4(a), leads to the appearance of two bands, at 2205 and 2189 cm\(^{-1}\) which are produced by carbonyl complexes of two types of coordinatively unsaturated sites (c.u.s.) Ti\(^{4+}\) cations (\(\alpha\)- and \(\beta\)-Ti\(^{4+}\), respectively) [15]. The \(\beta\)-Ti\(^{4+}\) sites are the highly unsaturated sites due to kinks and corners [5]. It was reported that the IR bands in the 1600 - 1200 cm\(^{-1}\) is mainly due to the formation of large number of different adsorbed carbonate species. In addition, formate (HCOO\(^{-}\)) species can be excluded because they are formed at relatively high temperatures (227˚C) [16]. Consequently, the existence of different bands in the region of 1600 - 1220 cm\(^{-1}\) (1356, 1435 and 1533 cm\(^{-1}\)) under the present adsorption conditions may be taken with a higher degree of confidence to \(\nu\)\(_{\text{as}}\)(COO\(^{-}\)) and \(\nu\)\(_{\text{as}}\)(COO\(^{-}\)) with a geometry change of these species [16]. This indicates that CO can be converted to carbonate species over TiO2 even at RT. Indeed, the formation of carbonate has been previously confirmed spectroscopically on surfaces of various oxides as a result of the adsorption of CO on coordinatively unsaturated Lewis acid-base pair sites (M\(^{n+}\)-O\(^{2-}\)), similar to the results reported for CO adsorption over ZrO2 [17], PrO2 [16] or PtY [18].

To reveal the effect of Ce and Pt loading on TiO2 surface, the in-situ FTIR of CO adsorption on the samples Ce0.1/TiO2, Pt/TiO2 and PtCe0.1/TiO2 was performed and the results are presented in Figures 4(b)-(d) as well. In case of Pt/TiO2, the peaks characteristic of Ti\(^{4+}\) at 2189 and 2205 cm\(^{-1}\) were observed besides three peaks at 2082, 2096 and 2128 cm\(^{-1}\) which are attributed to linearly adsorbed Pt\(^{6+}\)-CO, Pt\(^{6+}\)-CO and Pt\(^{4+}\)-CO, respectively [18,19]. The adsorption peaks at 1276, 1362 and 1467, 1690 cm\(^{-1}\) are also related to the presence of carbonate species which are formed on Pt\(^{n+}\)-O\(^{2-}\) or Ti\(^{4+}\)-O\(^{2-}\) sites. A peak at 1737 cm\(^{-1}\) was observed which is due to carboxylate (COO\(^{-}\)) species [20].

For Ce0.1/TiO2 catalyst, there were only two peaks at 2187 and 2205 cm\(^{-1}\). It was reported in literature that, two weak peaks at 2177 and 2156 cm\(^{-1}\) were found for CO adsorbed on ceria after evacuation at liquid nitrogen temperature [21]. However, our adsorption temperature is much higher than −196˚C, so it is expected to not observe any of CO adsorption peaks on ceria. Consequently, the peaks at 2187 and 2205 cm\(^{-1}\) are characteristic of CO adsorption on \(\beta\)- and \(\alpha\)-Ti\(^{4+}\) sites, respectively. This is also in agreement with the work of Chen et al. [22]. This spectrum also shows peaks characteristic of CO oxidation products such as (-COO\(^{-}\)) at 1735 cm\(^{-1}\) and carbonate species at 1700, 1694, 1467, 1384 and 1273 cm\(^{-1}\).
Finally, with respect to PtCe0.1/ TiO2 spectrum, only one peak due to CO adsorption on β-Ti4+ was observed at 2192 cm\(^{-1}\), however, the CO adsorption peak at 2205 cm\(^{-1}\) characteristic of α-Ti4+ was not observed. Additionally, the sample presented small peaks at 2101 and 2140 cm\(^{-1}\) which are due to Pt\(^{-}\)-CO and Pt\(^{2+}\)-CO, respectively. It is noticed that, these peaks are located at higher frequencies than those in Pt/TiO2. This shift may be due to the presence of Ce\(^{3+}\) which decreases the electron density on Pt\(^{2+}\) species. It is noteworthy to mention that, bridged Pt\(_{2}\)(CO) species were not observed in all the samples in CO adsorption experiments. This phenomenon means that Pt particles are mostly isolated with high dispersion over the surface and this is in good accordance with XRD data. The spectrum of CO adsorption on PtCe0.1/ TiO2 showed mostly the same carbonate like species in the frequency range of 1800 - 1100 cm\(^{-1}\).

### 3.3. Adsorption of NO + CO on the Prepared Samples

The spectra (not shown) collected after exposure of the prepared catalysts to NO gas (7 torr) did not lead to the formation of any nitrosyls complexes adsorbed on the metal loaded TiO2. This was not consistent with the previous literature [23] and it may be due to the low concentration of admitted NO gas and the relatively high adsorption temperatures.

#### 3.3.1. In Situ FTIR Results of NO and CO Co-Adsorption on TiO2 Catalyst

Figure 5 shows the spectra of TiO2 (2400 - 1100 cm\(^{-1}\)) after admission of gas mixture of CO + NO (7:7) at different temperatures in the range of RT to 200°C. At RT, it was observed in the spectrum that, two peaks at 2187 and 2350 cm\(^{-1}\) were detected after 20 min of gas exposure. Based on previous literature reports, the former band is assigned to CO adsorbed on β-Ti4+ cations and the latter one is attributed to CO2 [4-6]. These results indicate that some fraction of the adsorbed CO molecules undergo oxidation to CO2 upon the contact with gas phase NO through TiO2 surface even at room temperature.

Additionally, a peak characteristic of carboxylate species (COO\(^{-}\)) was noticed at 1736 cm\(^{-1}\) [20]. Carbonate species were detected at several positions such as 1700 cm\(^{-1}\), however, the corresponding asymmetric \(\nu_{as}\)(COO\(^{-}\)) peaks for these species are detected at 1470 and 1442 cm\(^{-1}\). Different types of carbonates species exhibited peaks at 1700, 1531, 1385 and 1271 cm\(^{-1}\) [24]. The peak at 1695 and 1470 cm\(^{-1}\) may be due to carbonate species [24] or \(\nu_{as}\) and \(\nu_{as}\) of NH\(_{4}\)\(^{+}\) [25,26]. However, we could not notice any vibrations in the range of 2600 - 3000 cm\(^{-1}\) due to adsorbed NH\(_{3}\). Therefore, the absorption peaks at 1695 and 1470 cm\(^{-1}\) are due to carbonate species. When the temperature of the infrared cell containing wafer was increased to 100 and 200°C while keeping the same gas mixture CO + NO, the same group of bands was noticed with an increase in the intensity of the peaks characteristic of CO oxidation products. This indicates the increase of the possibility of CO oxidation and NO reduction with increasing the wafer temperature. It is noticed that, after admission of NO gas together with CO, the peak at 2205 cm\(^{-1}\) which is due to α-Ti4+-CO was not observed. This may be due to the increase in the coverage of strongly adsorbed carbonate species resulting from CO oxidation. The peak at 1653 cm\(^{-1}\) is due to \(\delta(HOH)\) mode of adsorbed molecular water [27].

#### 3.3.2. In Situ FTIR Results of NO and CO Co-Adsorption with Pt/TiO2 Catalyst

After recording the spectrum of the sample prior admission of gas mixture, the IR spectra of CO + NO (7:7) adsorption over platinum supported TiO2 in the range of 2400 - 1100 cm\(^{-1}\) at different temperatures (RT - 200°C) are shown in Figure 6. After 20 min of admission of gas mixture at RT, the spectrum presented peaks due to α-Ti4+-CO at 2205 cm\(^{-1}\), β-Ti4+-CO at 2187 cm\(^{-1}\) and the peak at 2077 cm\(^{-1}\) assigned to singleton frequency of CO molecules linearly adsorbed on-top metallic Pt atoms (Pt\(^{0}\)-CO) [28]. These results indicate that some fraction of the Pt\(^{2+}\) species, which are initially present in the sample, underwent reduction to metallic Pt at RT in presence of CO gas.

Other peaks characteristic of the CO oxidation products such as physisorbed CO\(_{2}\) at 2350 cm\(^{-1}\) and a group of peaks characteristic of (-COO\(^{-}\)) species at 1737 cm\(^{-1}\) and the peaks at 1693, 1582, 1461, 1386 and 1276 cm\(^{-1}\) were recorded and attributed to carbonate species adsorbed on different sites or in different geometry [16].

![Figure 5. FTIR spectra after admission of gas mixture (NO + CO; 7:7) on TiO2 at different temperatures.](image)
The intensity of these peaks increases with increasing temperature from RT to 200°C.

In addition to the oxidation products of CO, the appearance of a new small peak at 2236 cm$^{-1}$ was noticed in the collected spectra (at RT) in this case. Figure 6. It should be mentioned that, the peak at 2236 cm$^{-1}$ was not observed when only one reactant, either CO or NO, was admitted to the catalyst surface. It was only observed when CO + NO were present simultaneously. Also, it was not observed when CO + NO were admitted to Pt-free catalysts. Based on previous literature reports [29], this band can be assigned to the asymmetric vibration of a surface NCO species as presented in Equation (3). Although, the mechanism of NCO formation is not clear until now, the assumption in Equation (3) is supported by the presence of physisorbed CO$_2$ gas [3]:

$$\text{NO} + 2\text{CO} \rightarrow \text{NCO} + \text{CO}_2$$ \hspace{1cm} (3)

$$2\text{NCO} + 2\text{O-S} \rightarrow \text{N}_2 + 2\text{CO}_2 \text{-S}$$ \hspace{1cm} (4)

$$\text{NCO} + \text{NO} \rightarrow \text{N}_2 + \text{CO}_2$$ \hspace{1cm} (5)

According to previously published data, the formation of isocyanate requires the presence of platinum group metals in the catalyst [30-32]. In addition, the process of NCO formation is typically followed by the migration of these species from the metal sites to the support which means that NCO may be adsorbed on Ti$^{4+}$ sites. The formation of NCO may lead to the formation of CO$_2$ via the reaction with the oxygen of oxide species (Equation (4)) or with the reaction with NO molecules (Equation (5)) [29].

Elevating the temperature of the FTIR cell to 100°C and 200°C leads to the increase of CO$_2$ peak at 2350 cm$^{-1}$, Figure 6. An increase of the intensity of the peak at 2080 cm$^{-1}$ was detected besides a development of a new peak at 2028 cm$^{-1}$. These two peaks can be most probably assigned to symmetric and asymmetric stretching, respectively, of gymbicarbonyl species (CO-Pt$^4$-CO). At 200°C, the peak at 2236 cm$^{-1}$ became very intense and centered at 2215 cm$^{-1}$. Besides the possibility of the presence of absorption peak characteristic of α-Ti$^{4+}$-CO (2205 cm$^{-1}$), the shape of this peak suggests that at least three overlapping components are present which indicates that several types of adsorbed species on Pt/TiO$_2$ catalyst surface are located in this wide peak. The first component can be distinguished at 2187 cm$^{-1}$ which was attributed to CO adsorption on β-Ti$^{4+}$. The second component is centered at 2215 cm$^{-1}$ which is attributed to isocyanate species (NCO) [30]. The last component is located at ~2235 cm$^{-1}$ and can be assigned NCO adsorbed on different sites or to nitrous oxide (N$_2$O) [33]. N$_2$O may be formed either by reduction of NO by CO Equations (6) and (7) or by disproportionation process as Equation (8). It was reported that, N$_2$O is easily formed on Ti$^{3+}$ and Ce$^{3+}$ sites formed after reduction of the catalyst by H$_2$ gas [5]. In this work, this band was not observed after admitting NO + CO to the reduced catalyst as will be shown later on. This indicates that the peak at 2235 cm$^{-1}$ is most probably assigned to NCO. Close inspection of Figure 6, it can be inferred that, the peak assigned to physisorbed CO$_2$ gas (2350 cm$^{-1}$) increases in parallel with NCO (2216 cm$^{-1}$) species. This may point to the formation of NCO through reduction (Equations (3)-(5)) rather than disproportionation (Equation (8)). The presence of other NO-derived species at Pt/TiO$_2$ can be inferred from the small peaks at 1226 and 1197 cm$^{-1}$. For example, the peak at 1200 cm$^{-1}$ could be associated with a chelating nitrite species (NO$_2^-$) [15].

$$\text{NO} + \text{CO} \rightarrow \text{CO}_2 + 1/2\text{N}_2$$ \hspace{1cm} (6)

$$\text{NO} + 1/2\text{N}_2 \rightarrow \text{N}_2\text{O}$$ \hspace{1cm} (7)

$$\text{NO} + 2\text{NO} \rightarrow \text{N}_2\text{O} + \text{N}_2\text{O}_2$$ \hspace{1cm} (8)

It is well known that, isocyanate, nitrous oxide or nitrogen dioxide are proposed to be connected to the reaction mechanism of NO-CO reaction [34]. This result was also noticed by Keiski et al. [3] since they detected an increase of isocyanate complex peak after heating at 300°C. They reported that, the formation of NCO surface complexes over CeO$_2$ catalyst required that the surface of the catalyst was first occupied by NO. In our case, the formation of NCO species did not require NO admission prior to CO. However it was formed just after NO + CO gases are admitted together at relatively low temperature (RT).

### 3.3.3. In Situ FTIR Results of NO and CO Co-Adsorption with Ce$_{0.1}$/TiO$_2$ Catalyst

In situ FT-IR spectra (2400 - 1100 cm$^{-1}$) of the co-adsorption of NO and CO over Ce$_{0.1}$/TiO$_2$ catalyst at RT...
was shown in Figure 7. After exposure of NO + CO mixtures to the catalyst surface and equilibrate for 20 min, the peaks at 2189 cm\(^{-1}\) which are due to CO adsorption over \(\beta\)-Ti\(^{4+}\) was observed. Other peaks characteristic of CO oxidation products were detected at 1740, 1700, 1465, 1362 and 1276 cm\(^{-1}\). The peak at 1740 cm\(^{-1}\) is attributed to carboxylate (COO\(^{-}\)) species. The other peaks are due to carbonate species adsorbed at different sites or adsorbed in different geometry [16]. With the stepwise increasing temperature from RT to 200 °C, the intensity of these peaks slightly increases with a parallel slight increase of the peak at 2350 cm\(^{-1}\) which is due to physically adsorbed CO\(_2\). Since NCO was not observed at all, it can be concluded that CO\(_2\) was formed due to the oxidation of CO with lattice oxygen. Moreover, NO oxidation product was detected at 1622 cm\(^{-1}\) due to bridged nitrate species [27]. A peak at 1653 cm\(^{-1}\) was detected and assigned to \(\delta\)(HOH).

By careful examination of the spectra in Figure 7, it can be noticed that, there were some differences between the spectra obtained after admission of NO + CO gas mixture to Pt-containing and Ce-containing catalysts as follows:

- The \(\alpha\)-Ti\(^{4+}\)-CO adsorption peak disappeared.
- The Pt\(^{n+}\)-CO adsorption peaks disappeared.
- An oxidation product of NO was observed at 1617 cm\(^{-1}\) which is assigned to NO\(_2\) [3] and a peak at 1360 cm\(^{-1}\) due to nitrate species [15,35].
- Due to the absence of platinum group metals, the spectra did not show any peaks characteristic of NCO species [29].

3.3.4. In Situ FTIR Results of NO + CO Co-Adsorption with PtCe\(_{0.1}\)/TiO\(_2\) Catalyst

Figure 8 reports the evolution of the adsorbed gaseous species under the reaction conditions from RT to 300°C over the bimetallic Ce- and Pt-supported on TiO\(_2\) (PtCe\(_{0.1}\)/TiO\(_2\)) catalyst. At RT, the spectrum shows peaks at 2189 and 2205 cm\(^{-1}\) which are characteristic of CO adsorbed over Ti\(^{4+}\) sites as previously mentioned. Other bands at 2134 and 2100 cm\(^{-1}\) are due to carbonyl complexes formed with the participation of platinum cations Pt\(^{2+}\)-CO and Pt\(^{+}\)-CO, respectively [36-38]. The spectrum shows also a small peak at 2234 cm\(^{-1}\) due to NCO species.

The spectrum showed also peaks due to CO and NO interaction over the PtCe\(_{0.1}\)/TiO\(_2\) catalyst surface. CO Oxidation products were observed as strong peak at 2350 cm\(^{-1}\) due to physically adsorbed CO\(_2\). Other peaks at 1737 cm\(^{-1}\) due to (COO\(^{-}\)) species and 1700, 1465 and 1273 cm\(^{-1}\) due to carbonate species adsorbed on different sites were observed. Some NO oxidation derivatives were detected as well at 1581 cm\(^{-1}\) due to bidentate NO\(_{2}\)^– and at 1206 cm\(^{-1}\) due to NO\(_{3}\)^– [15].

It is clear that there are drastic changes in the spectra with elevation of the temperature of sample wafer and IR cell including adsorbed CO on Pt\(^{n+}\) sites and CO + NO oxidation reduction derivatives. These changes can be summarized as:

- The peaks characteristic of Pt\(^0\)-CO increased indicating further reduction of Pt\(^{n+}\) sited with CO at high temperature.
- A new peak at 2028 cm\(^{-1}\) appeared. This peak was detected (small intensity) in case of Pt/TiO\(_2\) catalyst. Hence it can be assigned to CO adsorbed on Pt\(^0\) sites. This also ensures the possibility of Pt\(^{n+}\) reduction in presence of CO at high temperature.
- Increase of CO\(_2\) peak on the expense of other CO oxidation products which means that CO\(_2\) is the predominant CO oxidation product at high temperature.
Moreover, this data points to the fact that, carbonate species are the intermediates in CO oxidation to CO₂.

- The peak centered at 2220 cm⁻¹ may be composed of three components at 2187 cm⁻¹ (due to α-Ti⁴⁺-CO), a peak at 2220 and 2235 cm⁻¹ (due to NCO species). CO absorption peak at α-Ti⁴⁺ may be one of these components too.
- Increase of the peak characteristic of NCO with a simultaneous decrease of each of the peaks at 1360 cm⁻¹ (NO₂⁻), 1737 cm⁻¹ (COO⁻) and 1700, 1465 and 1273 cm⁻¹ may point to the reaction of these species to form NCO and CO₂. However the exact mechanism of these reactions is not exactly known. It was reported in literature that, the addition of cerium to Rh/TiO₂ [5] and Rh/Al₂O₃ [39,40] enhances the NO dissociation rate at quite low temperatures and suppresses the N₂O formation. Consequently, isocyanate is the dominant product that arises after the co-adsorption of NO + CO gas to the PtCe/TiO₂.

Examining the results of NO + CO adsorption over Pt/TiO₂ and Ce₀.₁/TiO₂, Figure 8, points to the fact that, NCO can be formed only on the surface of Pt/TiO₂ but not on Ce₀.₁/TiO₂ surface. This is in good agreement with the previously reported data [3]. In general, it is believed that NCO formation occurs on Lewis acid sites via the reaction of CO and nitrogen atoms that is formed by 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 are more stable [28]. Additionally, investigating Figures 6 and 8, it is observed that, the intensity of the peaks characteristic of CO₂, NCO are higher in Figure 8 (PtCe₀.₁/TiO₂). It can be concluded that, Ce enhanced the formation of NCO and CO₂. This may be due to the availability of more Lewis acid sites which is necessary to form NCO [28]. It will be interesting to eliminate the Lewis acid sites by reducing one of the employed catalysts and check the possibility of the formation of isocyanate species.

### 3.3.5. In Situ FTIR Results of NO + CO Co-Adsorption with Reduced PtCe₀.₁/TiO₂ Catalyst

It is well known that, the capability of the oxidized and the reduced forms of platinum are different towards the CO or NO adsorption and interaction on its surface. Therefore, PtCe₀.₁/TiO₂ was reduced by H₂ gas at 400°C for 30 min in static vacuum system in presence of liquid nitrogen trap. The reduced catalyst PtCe₀.₁/TiO₂ was exposed to NO + CO gas mixture at RT and left for 20 min before spectrum measurements. The changes in the spectra (2400 - 1100 cm⁻¹) as a function of wafer temperature were recorded and shown in Figure 9. Notably, no peak absorptions belonging to Ti⁴⁺-CO were noticed even after raising the IR cell temperature to 100°C, however, two components were observed at 2199 and 2215 cm⁻¹ due to CO adsorption on Ti⁴⁺ sites and NCO, respectively, at 200°C. Similar to NO + CO adsorption over reduced Rh/Al₂O₃ [3], gyn-dicarbonyl species were observed at 2084 and 2030 cm⁻¹ after admission of gases at RT. These peaks are characteristic of symmetric and asymmetric stretching of C-O bond, respectively, of adsorbed CO on Pt sites. The absorption peak related to asymmetric C-O bond (2030 cm⁻¹) decreases while the intensity of symmetric C-O bond (2084 cm⁻¹) increases with blue shift to lower wavelength (2079 cm⁻¹) indicating the decrease of CO concentration. Increasing the wafer temperature to 200°C leads to an increase of the absorption peak at 2345 cm⁻¹ which is characteristic of physisorbed CO₂. The appearance of CO₂ was accompanied by a decrease of gyn-dicarbonyl species which points out to the transformation of CO to CO₂.

In the low wavelength region (1800 - 1100 cm⁻¹), different peaks were attributed to CO oxidation species were observed at 1738 cm⁻¹ due to carboxylate species (COO⁻) and the peaks at 1700, 1582, 1472, 1383 and 1276 cm⁻¹ were recorded and attributed to carbonate species adsorbed on different sites. Additionally, the peak at 1655 cm⁻¹ may be due to H₂O vibration or HCO⁻. The progress of both 1655 and 1224 cm⁻¹ confirms the assumption that these peaks are related to the presence of asymmetric bicarbonate species (HCO⁻) [41] and their intensity increase by increasing the wafer temperature.

Besides the CO oxidation products, NO reduction derivatives were also observed. The small broad peak centered at 2657 cm⁻¹ (not shown) is attributed to physisorbed ammonia (NH₃). This peak did not change even with increasing the IR cell temperature. The peaks at
1696 and 1472 cm$^{-1}$ were also observed and they are assigned to the $v_{1}$ and $v_{as}$ vibrations, respectively, of NH$_4^+$ ions [25,26]. A new peak at 1178 cm$^{-1}$ was noticed after admission of the gas mixture at RT to the reduced catalyst surface. According to Liu et al. [35], the peak at 1178 cm$^{-1}$ is due to anionic nitrosyle (NO$^-$) species. With increasing temperature to 100°C and 200°C, the intensity of this peak increased with a red shift to higher wavelength (1183 cm$^{-1}$). It is noteworthy to mention that, NH$_3$ and NO$^-$ were detected only after admission of the gas mixture (NO + CO) over reduced PtCe$_{0.1}$/TiO$_2$ catalyst but not over Pt/TiO$_2$, Ce$_{0.1}$/TiO$_2$ or as-prepared PtCe$_{0.1}$/TiO$_2$. These data confirms that, at RT, the formation of NCO (as reductive derivative) is preferable over as-prepared Pt-containing catalysts while NH$_3$ or NO$^-$ is preferable over reduced catalysts.

It is clear that, all the absorption peaks characteristic of C containing species are shifted to lower wavelength with raising temperature. However, the peak at 1692 cm$^{-1}$, which was detected at 100°C and 200°C, can be assigned to (CO$_2^-$) rather than (NH$_4^+$) species.

It is noteworthy to mention that, the absorption peak related to Pt$^6$-CO increased with increasing temperature to 100 and 200°C. Also, two peaks at 2345 and $\approx$ 2200 cm$^{-1}$ were observed at 200°C. These peaks are attributed to physisorbed CO$_2$ and NCO species, respectively. The increase of the absorption peak characteristic of Pt$^6$-CO and the increase of the peak characteristic of CO$_2$ may indicate that carbonate species formed at RT may be reduced once again to CO and forms Pt$^6$-CO or they may be oxidized further to CO$_2$ which is detected at 200°C. These results confirm the assumption that CO$_2^-$ anion is an intermediate in the oxidation of CO to CO$_2$. Furthermore, reduction of NO with CO (NO$^+$ + CO$^+$ → NCO$^{-}$ + O$^-$) on the reduced catalysts surface occurs only at relatively high temperature (200°C) on the reduced surface. Though, this reaction takes place at RT in the Pt-containing as-prepared catalysts.

It was mentioned earlier that the presence of Pt sites are essential to the formation of NCO. The absence of both the absorption peaks characteristic of Ti$^{4+}$-CO and NCO in the temperature range of RT - 100°C provides clear evidence that Lewis acid sites (most probably Ti$^{4+}$) is essential for the stabilization of isocyantane species. Nevertheless, NCO species formed at Pt sites can spill onto the support surface where they are accumulated and stabilized [29,30].

The rational increase of the peak characteristic of HCO$_3^-$ with the decrease of NH$_4^+$ may indicate that bicarbonate species are formed by the interaction between NH$_4^+$ species and CO$_2^-$.

$$\text{NH}_4^+ + \text{CO}_2^- \rightarrow \text{NH}_3^- + \text{HCO}_3^- \quad (9)$$

### 3.3.6. In Situ FTIR Results of NO + CO

**Co-Adsorption with PtCe$_{0.1}$/TiO$_2$ Catalyst in Presence of Water Vapor**

Addition of trace amount of water vapor increased the activity towards the CO oxidation in presence of Pt and decreased the oxidation temperature as well [18,42-44]. Moreover, the gas exhaust usually contains water vapor and then it will be valuable to add trace amount of H$_2$O vapor to the gas mixture to detect its effect on the NO + CO interaction. Figure 10 shows the spectra taken after 20 min of admission of the gas mixture (NO + CO + H$_2$O; 7:7:1) over PtCe$_{0.1}$/TiO$_2$ to shade light on the effect of introducing water vapor during NO reduction by CO (more realistic conditions). After adsorption of the gas mixture at RT, several peaks were observed due to CO adsorption over Pt$^6$-CO and Pt$^6$-CO at 2094 and 2072 cm$^{-1}$, respectively. A new peak at 1840 cm$^{-1}$ due to bridged Pt$^6$-CO-Pt$^6$ was observed [4]. This indicates that the presence of water vapor leads to the decrease of Pt particles dispersion.

With increasing temperature, the intensity of the peak at 2092 cm$^{-1}$ decreases and the peak at 2072 cm$^{-1}$ slightly shifted to lower frequency and even gained some intensity. This phenomenon is, however, most probably due to some reduction of cationic platinum to metal during the CO desorption. Also, at 200°C, small intensity peaks were observed at $\approx$ 2350 cm$^{-1}$ indicating the formation of physically adsorbed CO$_2$. Inspecting of Figure 10, isocyanate species NCO (2240 - 2200 cm$^{-1}$) could not be observed in presence of water which means that the interaction of gas mixture (NO + CO) do not proceed in the pathway to form NCO even at high temperature. The small intensity peaks characteristic of CO$_2$ may be formed by direct CO oxidation with lattice oxygen. It is clear that the Ti$^{4+}$ sites were not observed except very
weak peak at 2180 cm\(^{-1}\) after raising IR cell temperature to 200°C. This may be due to the competitive adsorption of H$_2$O and CO over Ti\(^{4+}\) sites. The unavailability of Ti\(^{4+}\) and the absence of isocyanate species confirm the assumption that, Ti\(^{4+}\) sites (Lewis acid) are necessary as hosts for NCO species after their formation over Pt sites.

The spectra were also studied in the frequency range of 1800 - 1100 cm\(^{-1}\). Different peaks characteristic of CO oxidation products were observed at 1738 cm\(^{-1}\) for carboxylate (COO\(^{-}\)), 1554 and 1225 cm\(^{-1}\) for bicarbonate (HCO\(_3^-\)) and (1700, 1611 and 1383 cm\(^{-1}\)) for CO\(_2\)\(^{-}\). Finally, some NO reduction products were also observed at 1696 and 1465 cm\(^{-1}\) for NH\(_3\) and 1183 cm\(^{-1}\) for NO\(^-\). It can be seen that, by increasing the wafer temperature, the peak characteristic of NO\(^-\) is red shifted to low wavenumber and the intensity of the peaks characteristic to CO + NO oxidative reductive products increased.

3.3.7. Effect of Ce Ratio on the in Situ FTIR Results of NO + CO Co-Adsorption with PtCex/TiO\(_2\) Catalysts

The influence of the amount of Ce in PtCe\(_x\)/TiO\(_2\) on the NO + CO adsorption and interaction on the catalyst surface was studied using the same above-mentioned experimental conditions, except that the ratio of Ce/TiO\(_2\) was changed in the range of 0.05% - 1%. For the sake of simplicity, Figure 11 shows the spectra recorded after admission of the gas mixture and heating the wafer at 200°C in the range of 2400 - 2000 cm\(^{-1}\) since the spectra did not show significant difference below 2000 cm\(^{-1}\) (now shown) in the CO oxidation products region. The spectra recorded after admission of gases to Pt/TiO\(_2\) was added for comparison. This spectrum Figure 11(a) shows different peaks characteristic of linear Pt\(^{4+}\)-CO (2077 cm\(^{-1}\)), CO absorption peak on \(\beta\)-Ti\(^{4+}\) (2187 cm\(^{-1}\)), NCO species adsorbed on different sites (2217 and 2236 cm\(^{-1}\)) and finally physisorbed CO\(_2\) (2350 cm\(^{-1}\)). Addition of Ce with 0.05 and 0.1% did not change the peak positions however it caused drastic changes in the intensity of all the peaks since the peaks intensity was maximum in PtCeo.1/TiO\(_2\) sample. Increasing Ce content to 0.5% leads to the decrease of the peak intensity and all the peaks (except CO absorption peak on \(\beta\)-Ti\(^{4+}\)) disappeared after raising the Ce content to 1%. As previously discussed, according to Di Monte et al. [33], the formation of isocyanate requires the presence of platinum group metals in the catalyst. The decrease of NCO and CO\(_2\) with increasing Ce and the vanish of the adsorption peaks of Pt\(^{n+}\)-CO indicate that Ce atoms may block Pt sites at Ce/TiO\(_2\) ratio more than 0.1% and it totally mask Pt sites when Ce/TiO\(_2\) ratio is 1%. Consequently, neither NCO nor CO\(_2\) could be formed. As a result, the optimum ratio of Ce in Pt/TiO\(_2\) to reduce NO and oxidize CO is being 0.1%.

It is noticed that, NCO was not detected after admission of NO + CO over (PtCe\(_1\)/TiO\(_2\), Ce0.1/TiO\(_2\) and TiO\(_2\)) and also after admission of (NO + CO + H\(_2\)O) over PtCe0.1/TiO\(_2\). In the former case, we could not observe any peak due to Pt\(^{n+}\)-CO and in the later case we could not observe any peak due to Ti\(^{4+}\)-CO. However, we observed NCO after admission of (NO + CO) over Pt/TiO\(_2\) and PtCe0.1/TiO\(_2\). In these cases, we observed both of Pt\(^{n+}\)-CO and Ti\(^{4+}\)-CO as well. From forgoing results, it is concluded that the presence of the mutual sites Pt\(^{n+}\) and Ti\(^{4+}\) is crucial for the formation of NCO as a result of NO reduction. Additionally, the activity of PtCe0.1/TiO\(_2\) was higher than Pt/TiO\(_2\), indicating that Ce enhances the reaction towards NO reduction and forms NCO.

4. Conclusion

Platinum and cerium supported TiO\(_2\) catalysts were successfully prepared by incipient wetness impregnation method in the particle size range of 19 - 22 nm. Different reductive/oxidative species were observed after adsorption of NO and/or CO gasses. The presented results instantly allowed us to estimate the chemisorbed species after the admission of NO + CO gas mixture and their interactions on Pt and Ce-containing catalysts supported on TiO\(_2\). The formation of both NCO and CO\(_2\) was parallel indicating that their formation belongs to the same mechanism which is not certain until now. It was found that, the presence of both Pt sites and Ti\(^{4+}\) is important for NO reduction and NCO formation. Addition of Ce increased the formation of both NCO and CO\(_2\) and it was optimum Ce/TiO\(_2\) ratio of 0.1%.
REFERENCES


