The CO_2–CeO_2 interaction and its role in the CeO_2 reactivity

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The interaction between CO_2 and CeO_2 and its role in the surface reactivity of alumina-supported cerium oxide has been studied by programmed thermodesorption (TPD) of CO_2 and FTIR spectroscopy. The performance of Ce/Al_2O_3 systems was then analyzed for the propane oxidation in presence of CO_2. The results have shown that the catalytic activity decreased when carbonate species are formed at the surface of CeO_2. This behavior was attributed to the presence of CO_2 from three different sources: contamination before use, during the handling of the samples, contamination proceeding from the reactants and from CO_2 produced by the reaction itself.

Keywords: cerium, gas carbonic, propane, oxidation

1. Introduction

Cerium oxide presents acid–basic and oxidation–reduction behavior, which are potentially able to perform many catalytic reactions [1,2]. In general the presence of cerium oxide in automotive catalysts is related to oxygen storage, which occurs according to a Mars and van Krevelen [3] mechanism, as presented by Jim et al. [4]. It is known that CeO_2 is able to oxidize CO [5,6] and hydrocarbons [7]. However, very little has been reported concerning the contribution of cerium oxide on the elimination of these pollutants in automotive catalysis.

The basic strength of CeO_2 promotes a strong interaction with CO_2 [8–10]. This molecule is present in exhaust gas and is one of the products of combustion reactions. Laachir [11] using TGA observed that the CO_2 generated by CO oxidation reaction is partially adsorbed at the CeO_2 surface, and consequently inhibits the reaction. Their results showed that the dynamic behavior of carbonaceous species at the surface of the automotive catalyst plays an important role in the behavior of these catalytic systems. However, in spite of its potential importance, there are very few published works dealing with this subject.

The aim of this work is to study the influence of CO_2 on the catalytic behavior and adsorption capability of alumina-supported cerium oxide, using propane oxidation as a model reaction. Infrared spectroscopy analysis and programmed thermodesorption experiments are helpful for understanding the interaction of CO_2 with CeO_2 at the surface.

2. Experimental

The catalysts were prepared as reported in [12] by dry impregnation, using aqueous solution of $Ce(NO_3)_3$ on γ-alumina (Engelhard, 156 m^2/g), dried at 75 °C for 20 h and then calcined under air flow at 600 °C, for 4 h, varying the Ce concentration (1.7, 5, 14 wt%). Catalysts containing 1.7 and 14 wt% Ce were pretreated first by reduction at 440 °C for 3 h and then by reoxidation at 25 °C for 2 h.

The catalytic tests were performed in conventional equipment using a continuous fixed-bed reactor and analyzed on-line with chromatography. Synthetic and purified air containing CO_2 (0.3 Torr) from the compressor, were used as oxidant agents. The reaction was performed under isoconversion (10%) at 420 °C, by flowing propane and air at 33.4 μmol/min and 1.59 mmol/min, respectively. The catalyst weight varied between 200 and 300 mg. The reactor was heated at 5 °C/min, under air flow. The data were obtained under steady-state conditions.

Infrared spectroscopy analyses were performed using a Magna 750-Nicolet (FTIR) apparatus. The sample, approximately 30 mg, was pressed into a thin wafer, treated at 400 °C for 1 h by pulsing O_2, under primary vacuum, then evacuated at 10^{-8} Torr at 400 °C for 2 h and cooled to room temperature. The wafers were then exposed to CO_2 at 11 Torr for 1 h, evacuated for 1 h before analysis. Then, the sample was heated up to 100 °C for 1 h under high vacuum (10^{-6} Torr), cooled to room temperature and reanalyzed. Such a procedure was repeated at 350 °C for 0.5 h, in the case of Ce/Al_2O_3 samples.

The TPD analyses were performed in a Micromeritics TPD/TPR 2900 system. The catalysts were pretreated with 5% O_2/He mixture, raising the temperature at a heating rate

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of 10 °C/min up to 600 °C, held at 600 °C for 4 h, under air flow and then cooled to room temperature or 400 °C. The CO_2 was introduced by flowing 30 cm^3/min at RT and at 400 °C for 30 min, followed by He flux under similar conditions and cooled to room temperature before thermodesorption, raising the temperature up to 1000 °C at a heating rate of 2 °C/min.

3. Results and discussion

Figure 1 shows the FTIR spectra of CO_2 on Al_2O_3. Figure 1(a) displays two bands at 1565 and 1477 cm^{-1} on the treated alumina, which correspond to the intrinsic absorption bands of γ-alumina (Parkins [13]), while figure 1(b) displays the adsorption bands after desorption at room temperature, denoting bands at 1647, 1445 and 1230 cm^{-1}. According to Parkins [13] and Frety et al. [14], the absorption bands at 1647, 1489, 1230 cm^{-1} can be associated to hydrogenocarbonate ions. This suggests that the intrinsic band around 1477 cm^{-1} contains the band at 1489 cm^{-1} and that the band 1445 cm^{-1} should be related to another kind of carbonate. Figure 1(c) shows the spectrum after desorption at 100 °C, indicating that almost all CO_2 species were desorbed, being similar to that obtained on pure alumina (figure 1(a)). Therefore, the interaction between alumina support and carbon dioxide is relatively weak.

Figure 2 shows the infrared spectra recorded between 1100 and 1800 cm^{-1}, after CO_2 adsorption on the Ce/Al_2O_3 system. Figure 2(b) shows the CO_2 adsorption after desorption at room temperature. It displays absorption bands at 1654, 1437, 1328 and 1230 cm^{-1}. These bands should be associated to the species resulting from the interaction of CO_2 with ceria as well as with alumina. After desorption at 100 °C (figure 2(c)), these bands decrease drastically, probably due to the desorption from the alumina support. However, one large band around 1600 cm^{-1} still remains besides the band at 1433 and 1340 cm^{-1}, together with a small band at 1230 cm^{-1}. However, definite species cannot be attributed to these bands except as suggestions, since the available data were obtained for bulk CeO_2 under different conditions. In addition a strong absorption band for alumina appeared below 1200 cm^{-1} which implies less reliable interpretation. In spite of this, we may suggest that the absorption bands around 1600 and 1230 cm^{-1} are concerned to the remaining carbonaceous species linked to alumina. The other bands might be associated to monodentate carbonates (Li et al. [8,9]).

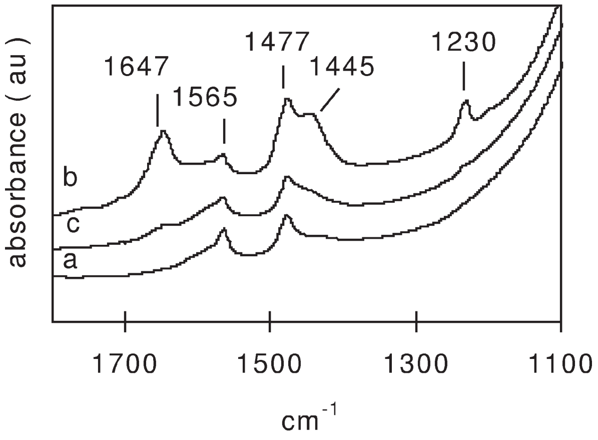


Figure 1. Infrared spectra for CO_2 adsorption on Al_2O_3. Curve (a) was obtained after cleaning the alumina surface, (b) after adsorption of CO_2 at room temperature, and (c) after 100 °C desorption procedure.

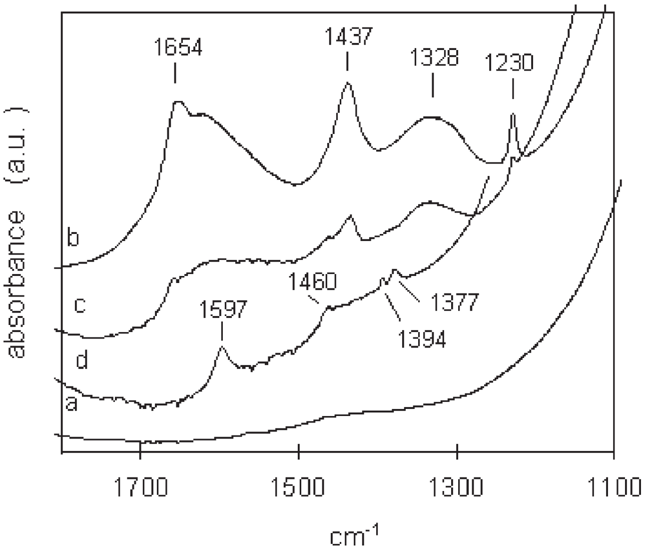
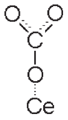
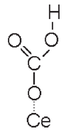


Figure 2. Infrared spectra of CO_2 adsorption on 14% Ce/Al_2O_3. Curve (a) was obtained after cleaning the surface, curve (b) after CO_2 adsorption and desorption at room temperature, (c) and (d) after desorption at 100 °C for 1 h and 350 °C for 0.5 h, respectively.

Figure 2(d) exhibits the spectra after desorption at 350 °C, indicating absorption bands at 1597, 1461, 1394 and 1377 cm^{-1}. These bands can tentatively be assigned to internal polydentate carbonaceous species (1360–1460 cm^{-1}, Binet et al. [10]), hydrogenocarbonate (1608–1393 cm^{-1}, Binet et al. [10]) and inorganic carboxylate ions (1560–1410 cm^{-1}, Jim et al. [4]). However, hydrogenocarbonate ions at this temperature range (350 °C) should be taken with caution, since, according to the literature [10], for bulk CeO_2, these species are not stable. Probably after desorption at 350 °C, only the carboxylate ions and the internal polydentate carbonate species remain linked at the surface. In conclusion, these results show that CO_2 adsorption on CeO_2 at low temperatures generates species that are stable at high temperatures. A schematic description of these species is depicted in table 1.

The TPD results after adsorption at room temperature and at 400 °C on the 14% Ce sample are shown in figure 3. The desorption profile at room temperature (figure 3(b)) exhibits different peaks at 96, 389 and 771 °C, which indicate the presence of, at least, three species generated after CO_2 adsorption on Ce/Al_2O_3. The infrared results suggest that the first peak could be associated to hydrogenocarbonate ions linked to alumina and to monodentate carbonates. Probably, the second peak could be ascribed to carboxylate ions, and the third one to internal polydentate carbon-

Table 1
Schematic description of carbonate species.

Species	Frequency (cm^{-1})	Species
Monodentate carbonates [8,9]	856 1045 1354 1454	
Inorganic carboxylate [4]	1410 1560	
Hydrogenocarbonate [10]	1042 1393 1608	
Internal polydentate carbonate [10]	1070 1360 1460	

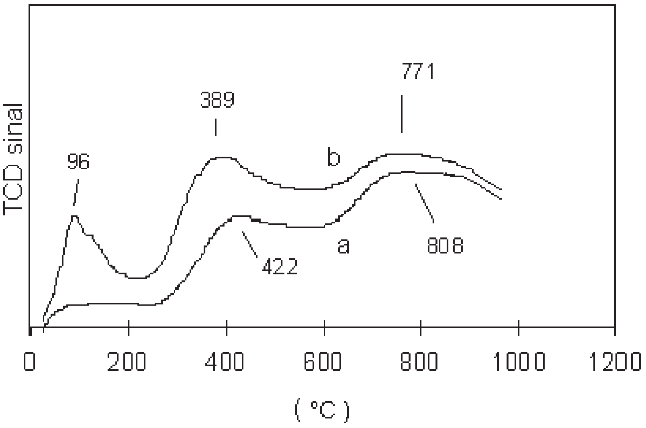


Figure 3. TPD curves of 14% Ce/Al_2O_3 after CO_2 adsorption at 400 °C (a) and at room temperature (b).

ates. After adsorption at 400 °C (figure 3(a)), it exhibits two peaks at 422 and 808 °C, which correspond to the assigned species suggested before.

The total amount of CO_2 adsorbed at room temperature and at 400 °C was estimated to 335 and 209 mmol/g of CO_2, respectively. The CO_2 volume adsorbed at room temperature is higher than at 400 °C.

TPD results agree with FTIR data, suggesting that the CO_2 adsorption at room temperature generates stable carbonate species on CeO_2 even at the high temperature. It shows that CO_2 can also be adsorbed on CeO_2 at the same temperature where oxidation of propene occurs and remains on the sample even at higher temperatures.

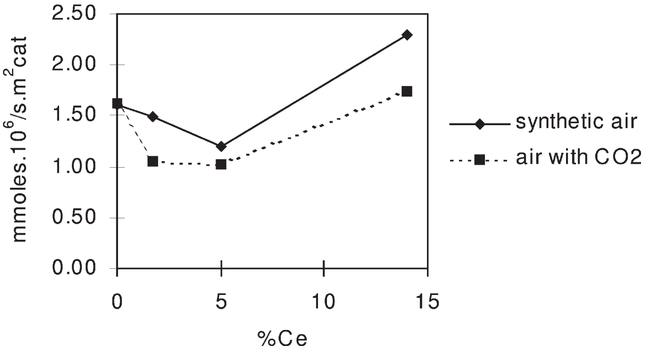


Figure 4. Reaction rate (consumption of propane per s and per m^2 of Ce/Al_2O_3) as function of cerium concentration. The (■) and (♦) symbols represent the experiments with air with CO_2 and of synthetic air, respectively.

Table 2
Rate of consumption of propane on catalysts reduced *in situ* and reoxidized compared to non-pretreated samples (temperature 420 °C and synthetic air as oxidant agent).

Catalyst	Pretreated samples rates (mmol propane/s m^2-cat.)	Non-pretreated samples rate (mmol propane/s m^2-cat.)
1.7% Ce-A	2.6×10^{-6}	1.5×10^{-6}
14% Ce-A	3.7×10^{-6}	2.3×10^{-6}

The main products of propane oxidation on Ce/Al_2O_3 and Al_2O_3 were CO_2, H_2O and propene. Pure alumina displayed also low selectivity for CO. The selectivities for CO_2 and propene were roughly 82 and 8%, respectively, and did not change significantly with increasing cerium concentrations under these reaction conditions. However, the remaining 10% selectivity needed for mass balance should be attributed to oxygenated compounds not detected, such as: propanal, acetic acid, ethanal and acrylaldehyde according to Sam et al. [15].

Figure 4 displays the reaction rates (mole propane reacted per unit of time and specific area) as a function of the cerium concentration with both synthetic air and compressed air. It shows that alumina presents low activity for this reaction (1.63 mmol propane/s m^2-cat.). For low cerium concentration (1.7 and 5% Ce) the reaction rate is also very low, smaller than on alumina. However, increasing the Ce concentration (14%) increases the reaction rate. With synthetic air it was higher than with air contaminated with CO_2. This effect was not observed on pure γ-alumina.

Table 2 shows the reaction rates of propane oxidation for 1.7 and 14% Ce contents after pretreatment *in situ*, such as reduction and reoxidation. It shows that after pretreatment the activity increases, which suggests that, during the reduction the blocking compounds are eliminated.

TPD and FTIR results indicate that the CO_2 adsorption at low temperatures generates stable carbonate species on CeO_2, even at the reaction temperature. This suggests that during handling the catalyst surface carbonaceous species could be formed. Therefore, the reduction–oxidation procedures probably facilitate the elimination of contaminants improving the reaction rate.

The reaction rates decrease by increasing the cerium content from 0 to 1.7 wt% Ce (figure 4). These rates are smaller than on alumina. It then suggests that CeO_2 can poison the alumina sites which are active for this reaction, replacing these sites by ceria with the formation of carbonate adsorbed species, almost inactive. Increasing the Ce content from 1.7 to 5% the rate is smaller, which suggests that a large amount of sites on alumina are covered by inactive species. However, around 14% Ce the reaction rate increases, due to the greater Ce surface, exhibiting also Ce which are free from carbonates and suitable for the reaction. This suggestion agrees with the fact that the pretreated samples present higher rates than the alumina itself, even at low concentration, indicating that the carbonate species turns Ce/Al_2O_3 almost inactive.

The TPD results indicate that CO_2 is also adsorbed on CeO_2 at reaction temperature. Thus, it decreases the number of active sites and inhibits the reaction. These results agree with those of Laachir [11] showing that CO_2 remains adsorbed on the catalyst, which is a product of the CO oxidation.

The reaction rates obtained by using purified air are lower (figure 4) than with synthetic air. According to the FTIR and TPD results CO_2 present in purified air can be adsorbed during the reaction and the heating time period, decreasing the reaction rates. These are additional effects beside the already cited above.

Oxidation conditions favor formation of carbonate species at the surface of CeO_2, affecting strongly the reactivity. This behavior is a limiting factor for CeO_2 as an oxidation catalyst. However, for a real automotive catalyst working in reduction and oxidation cycles, the CeO_2 surface should have a dynamic behavior of formation and elimination of carbonate species.

4. Conclusions

The catalytic performance of the CeO_2/Al_2O_3 system in propane oxidation is strongly affected by the presence of carbonate species at the surface. These species should be attributed to the contamination of CeO_2 by CO_2 during handling before use, or contamination from the reactants, as, for example, in the exhaust gases of automotive catalysts, or by CO_2 generated by the reaction itself. These results suggest the formation of carbonate compounds over the CeO_2 sublayer affecting the adsorption of reactants, and the oxygen supply from the lattice of the crystalline structure.

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