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Activation of an Ir-in-CeO_2 catalyst by pulses of CO: The role of oxygen vacancy and carbonates in CO oxidation

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ABSTRACT

An Ir-in-CeO_2 catalyst was activated by pulses of CO, and the effects of the formed oxygen vacancy and carbonates on CO oxidation were studied by a pulse calorimetry. A volcano-like relationship between the amount of oxygen vacancy and the catalyst activity is established. The presence of oxygen vacancy is favorable for CO oxidation, with the best activity when 1.5% amount of oxygen vacancy is obtained. However, the activity decreases with further increase of oxygen vacancy. A quantitative analysis of the reaction process suggests that the increase of oxygen vacancy promotes the buildup of strongly adsorbed carbonates, leading to the prohibition of the adsorption and activation of CO but not O_2. The reduced supply of adsorbed CO to react with oxygen species may result in the decreasing activity with more oxygen vacancy.

1. Introduction

CO oxidation on ceria-based catalysts has been extensively studied during the past decades, due to the high capacity of ceria to store and release oxygen as a reducible support [1–4]. Recently, a debate about the role of ceria in CO oxidation is ongoing. The reversible formation of oxygen vacancy (Ov) on the activated ceria was thought to operate in its catalytic cycle. The catalysts with noble metal (NM) encapsulated by ceria can still behave a high activity even without the direct participation of the NM [5–9]. It has been proposed that the addition of NM weakened the surface Ce–O bond strength and promoted the formation of Ov, which became the active sites.

Reactive oxygen removal from ceria with formation of Ov is a well known step during CO oxidation, concomitant with the transient CO_2 formation [10–12]. The presence of Ov was generally helpful for the activation of O_2 [13,14]. It was suggested that CO can react with these active oxygen species to produce carbonates, which would affect CO oxidation, either as a reaction-intermediate or as a spectator staying steady in the presence of Ov [15–18]. However, there were few studies to quantify the amount of Ov of ceria-based catalysts and further correlate it with the activity of CO oxidation [19]. That is, little attention was paid to find the optimum Ov content of the catalyst in its active state.

Our previous work has suggested that CO oxidation progressed on the activated ceria of an Ir-in-CeO_2 sample (most of iridium encapsulated by ceria) and reductive pretreatment increased its activity, indicating the important role of Ov [9,20]. In this study, we investigated the influence of CO pretreatment on this Ir-in-CeO_2 sample. With pretreatment by pulses of CO, different amounts of Ov and carbonates were obtained and their effects on CO oxidation were in turn studied. A volcano-like relationship between Ov and the activity of CO oxidation was established, the reasons of which were then investigated by analysis of the transient process during CO oxidation.

2. Experimental

2.1. Catalyst preparation

The Ir-in-CeO_2 catalyst was prepared by a redox co-precipitation method, as described previously [9]. An aqueous solution of H_2IrCl_6 and $Ce(NO_3)_3$ was added to a heated NaOH solution (353 K) to form a black precipitate. After aging for 2 h, the suspension was suction filtered and washed with deionized water several times until no Cl^- was detected by $AgNO_3$. Thereafter, the solid material was dried at 333 K overnight and finally calcined at 673 K for 2 h. The powder sample was pressed, crushed, sieved with a size of 20–40 mesh for characterization. The calculated metal content

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was around 1.6 wt% by ICP analysis. Brunauer–Emmett–Teller (BET) surface area detected by nitrogen adsorption at 77 K was about 120 m^2 g^{-1}. As a comparison, the pure CeO_2 was prepared under the similar conditions.

2.2. Catalyst characterization

Temperature programmed reduction of CO (CO-TPR) was performed in a quartz microreactor, and about 100 mg of a sample was used in each measurement. The calcined sample was pretreated under He flow at 393 K for 2 h and then cooled down to 313 K. The flow of 5% CO in He (50 mL min^{-1}) was then switched into the system and the sample was heated up to 1023 K at a rate of 3 K min^{-1}. CO, CO_2, and H_2 in the outlet gas were measured by a mass spectrometer (MS) OminiStar equipped with the software quadstar 32-bit. CO and H_2 signals were calibrated by using 5% CO/He and 10% H_2/Ar, respectively. CO_2 signal was calibrated by a pulse of pure CO_2 with a ten-port pulsing valve. The signals of CO, H_2, and CO_2 evolved during the measurement were determined from the MS and the flow rate of reducing agent.

Temperature programmed oxidation of O_2 (TPO) was done in the similar type. The calcined sample was pretreated by pulses of CO at 673 K and then cooled down to 313 K. The 2% O_2 in He (50 mL min^{-1}) was then switched into the system and the sample was heated up to 1073 K at a rate of 10 K min^{-1}. The signals were also detected by a MS OminiStar just as described in CO-TPR characterization.

The pulse calorimetric technique is composed of a calorimeter (HT-1000 calorimeter, Seteram, France) coupled with a pulse reactor system, which has been described in detail in our previous work [21]. The calorimeter response was calibrated using a standard joule calibrator. In a typical experiment, 100 mg of a sample ($m_{cat.}$) was placed in the sample vessel while the reference vessel was empty. The stainless steel plumbing system attached to the equipment enables an identical flow of gas through them. The effluents were analyzed by a gas chromatography (GC Agilent 6890N). The percentage of reactants adsorbed or reacted (x_a) was determined quantitatively from the change in the peak areas of reactants injected and eluted. In the pretreatment, a limited number of CO pulses were injected at 673 K and the pretreated sample was denoted as Ir-in-CeO_2-xp with x as the number of CO pulses. The amount of Ov concentration was calculated as:

$$\frac{N_A \times n^{out}_{CO_2}}{m_{cat.} \times O_s \times S_{BET}} \times 10^{-5}(\%) \tag{1}$$

N_A is Avogadro constant; $n^{out}_{CO_2}$ is the released amount of CO_2 during CO pretreatment; $m_{cat.}$ is the amount of a sample (100 mg); O_s denotes the density of surface O atoms, using a density of O atoms of 1.3×10^{15} atom cm^{-2} reported in [22]; S_{BET} denotes the BET surface areas of the catalyst.

The accumulation of carbonates (MLs: monolayers) was calculated as:

$$\frac{[(n^{in}_{CO} - n^{out}_{CO}) - n^{out}_{CO_2}] \times N_A}{m_{cat.} \times O_s \times S_{BET}} \times 10^{-7} \tag{2}$$

n^{in}_{CO} is the amount of CO injected (μmol); n^{out}_{CO} is the amount of CO eluted (μmol).

Then the pretreated sample was put into the calorimeter, and a fixed quantity (around 10.2 μmol) of O_2, CO, or CO_2 was dosed successively into the sample cell every 40 min at 393 K until the saturation adsorption of these probe gases. Through these, we detected the saturation adsorption amount of O_2, CO, or CO_2 and the evolution of heat evolved with the pulse number of these probe gases. In another experiment, pulses of CO + O_2 (2:1) were dosed successively into the pretreated sample at 393 K until the steady state, where a stoichiometric consumption of CO and O_2 with the corresponding amount of CO_2 formation was obtained. The remained quantity of Ov and carbonates under steady state was calculated from the equilibrium of C and O species. During coadsorption of CO + O_2 (2:1), we detected the quantity of O_2, CO adsorbed or reacted (n) and CO_2 produced per pulse of reactants, correspondingly the evolution of differential heat (Q).

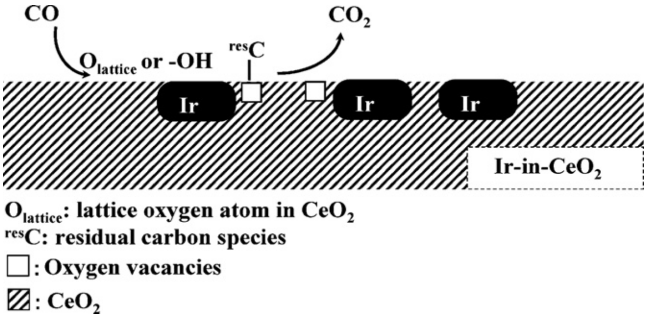

Fig. 1. A schematic picture of CO pulses on Ir-in-CeO_2.

$$n = n_t \lambda x_a \tag{3}$$

n_t is the amount of an adsorbate pulse (around 40.6 μmol); λ is the ratio of the velocity of adsorbate flow in sample vessel to the total velocity in sample and reference vessels (around 1/2); x_a is the percentage of reactants adsorbed or reacted.

Enthalpy change q (mJ) denotes the heat generated during the interaction of adsorbate with the catalyst. The relationship between differential heat Q (kJ mol^{-1}) and q is depicted as follows:

$$Q = \frac{q}{n} \tag{4}$$

n is the amount of an adsorbate pulse adsorbed or reacted (μmol).

3. Results and discussion

3.1. Surface behavior during CO pretreatment

As depicted in Fig. 1, CO_2 is released with repeated pulses of CO on Ir-in-CeO_2, correspondingly with the accumulation of residual carbon species, might as graphite-like ones or carbonates. There are several possible explanations for the surface behavior during CO pretreatment.

1. CO reaction with OH groups on the surface.
2. Disproportionation reaction of CO.
3. CO reaction with the lattice oxygen provided by the CeO_2 and the remaining as a form of carbonates.

As shown in Fig. 2, the temperature of CO_2 released is in accord with that of CO consumed during CO-TPR of CeO_2 and Ir-in-CeO_2, and only negligible amounts of H_2O and H_2 were detected correspondingly. If CO reacts with the OH groups to produce CO_2, according to hypothesis 1, there would be a reasonable amount of H_2O or H_2 released [23,24]. This is not the case, however. This observation implies that the concentration of OH group is not high enough or the OH group is not easy to react with CO on Ir-in-CeO_2.

The production of CO_2 might also come from the CO disproportionation reaction according to hypothesis 2. This can complicate the quantification of Ov by calculating the amount of released CO_2. We pretreated the Ir-in-CeO_2 by pulses of CO at 673 K until few CO_2 was released. The remained carbon species in this pretreatment were ascertained by checking the temperature for CO_2 production in the process of TPO. As shown in Fig. 3, upon increasing the oxidation temperature from 298 K to 1073 K, a significant amount of CO_2

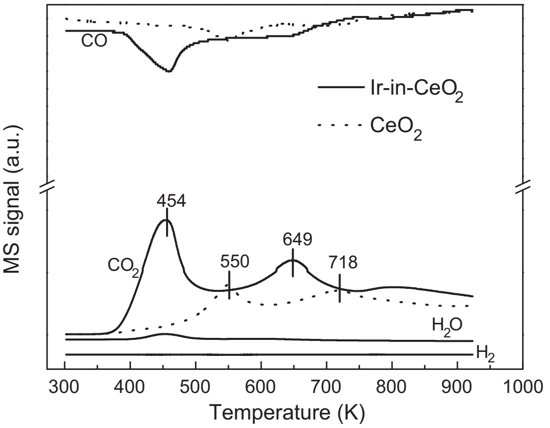

Fig. 2. CO-TPR profiles of the freshly calcined Ir-in-CeO_2 and CeO_2 samples.

is eluted, with one main peak centered at 386 K. If CO disproportionation reaction took place, the removal of the residual carbon species (mainly as graphite-like ones) required a temperature higher than 950 K [10,25]. However, such a weak intensity of CO_2 produced at around 900 K in the TPO experiment led us to conclude that the CO disproportionation made neglectable contributions to CO_2 formation. Therefore, most of the remaining carbon species stayed in a form of carbonates.

The conclusion reached from above observations was that the formation of Ov and carbonates predominated during CO pretreatment as depicted from the hypothesis 3. This is convenient for us to quantify the formation of Ov by the released amount of CO_2 and correspondingly the accumulation of carbonates with pretreatment by pulses of CO.

3.2. Relationship between pulses of CO pretreatment and the activity for CO oxidation

The formation of Ov and carbonates was one-step achieved by pulses of CO pretreatment. Table 1 lists the quantities of Ov and carbonates formed in this pretreatment at 673 K and remained under the steady state for CO oxidation at 393 K. The produced amounts of Ov by CO pretreatment are higher than those remained under the steady state for CO oxidation on these Ir-in-CeO_2-xp samples. On the other hand, more carbonates are accumulated with CO oxidation on the samples pretreated by less than 2 pulses of CO, while some carbonates are decomposed on the ones pretreated by more than 2 pulses of CO. For example, the coverage of carbonates decreases from 0.15 MLs initially to 0.12 MLs finally on Ir-in-CeO_2-8p. Under the steady state, the amount of carbonates grows as the quantity of Ov increases, indicating that the existence of Ov is favorable for the accumulation of carbonates.

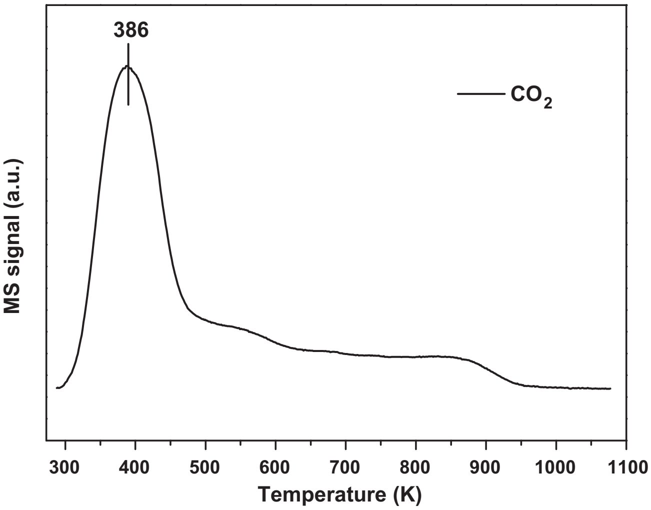

Fig. 3. TPO profile of Ir-in-CeO_2 catalyst pretreated by pulses of CO at 673 K.

Table 1

The quantities of Ov and carbonates formed on Ir-in-CeO_2 samples during CO pretreatment at 673 K and the corresponding amounts under steady state for CO oxidation on these pretreated samples at 393 K.

Pulse number[a]	O_v[b]/%	Carbonates[b]/MLs	O_v[c]/%	Carbonates[c]/MLs
0	–	–	0.4	0.02
1	3.0	0.03	1.0	0.07
2	6.3	0.06	1.5	0.08
4	10.6	0.10	1.8	0.09
8	14.0	0.15	3.9	0.12

[a] The total pretreated number of CO pulses at 673 K.

[b] Quantities of Ov and carbonates in the pretreatment at 673 K.

[c] Quantities of Ov and carbonates remained under the steady state for CO oxidation on these pretreated samples at 393 K, where a stoichiometric consumption of CO and O_2 with the corresponding amount of CO_2 formation was obtained.

By injecting successive pulses of CO + O_2, the yield of CO_2 under steady state was related with the pretreated number of CO pulses. As shown in Fig. 4, the released amount of CO_2 per pulse of CO + O_2 increases with the pretreated number from 0 to 2. However, this amount decreases with further increasing pretreated pulse number of CO, although the amount of Ov under steady state increases correspondingly. The catalytic performance is best on the Ir-in-CeO_2-2p sample with about 1.5% Ov remained under steady state.

3.3. Revealing the reasons for the activity loss with more pretreated number of CO pulses

The presence of Ov is favorable for CO oxidation on ceria-based catalysts. However, the volcano-like relationship between the amount of Ov and the yield of CO_2 reminds us that the formation of Ov might not be the sole factor for the change of its activity. Thus it is indispensable to further study the effects of these pretreatments on CO oxidation. The Ir-in-CeO_2-2p and Ir-in-CeO_2-8p samples were selected and compared in order to find out the reasons for the decreasing activity of CO oxidation with more pretreated number of CO pulses.

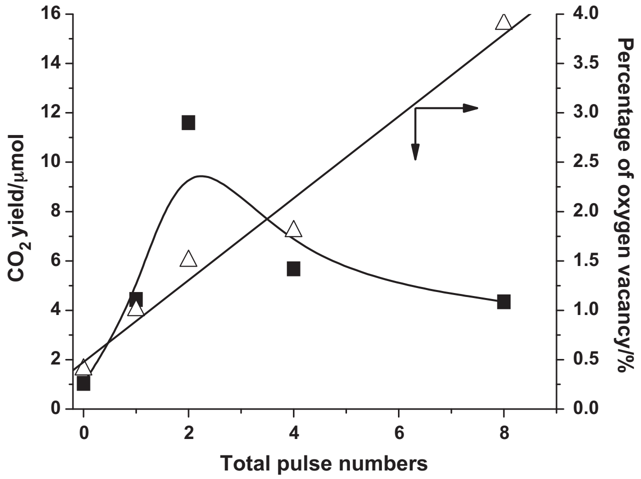

Fig. 4. The amount of CO_2 (■) released per pulse of CO + O_2 and percentage of Ov (△) remained under steady state for CO oxidation at 393 K vs. the pretreated number of CO pulses over Ir-in-CeO_2. The solid line was depicted for the easy guidance of the eyes.

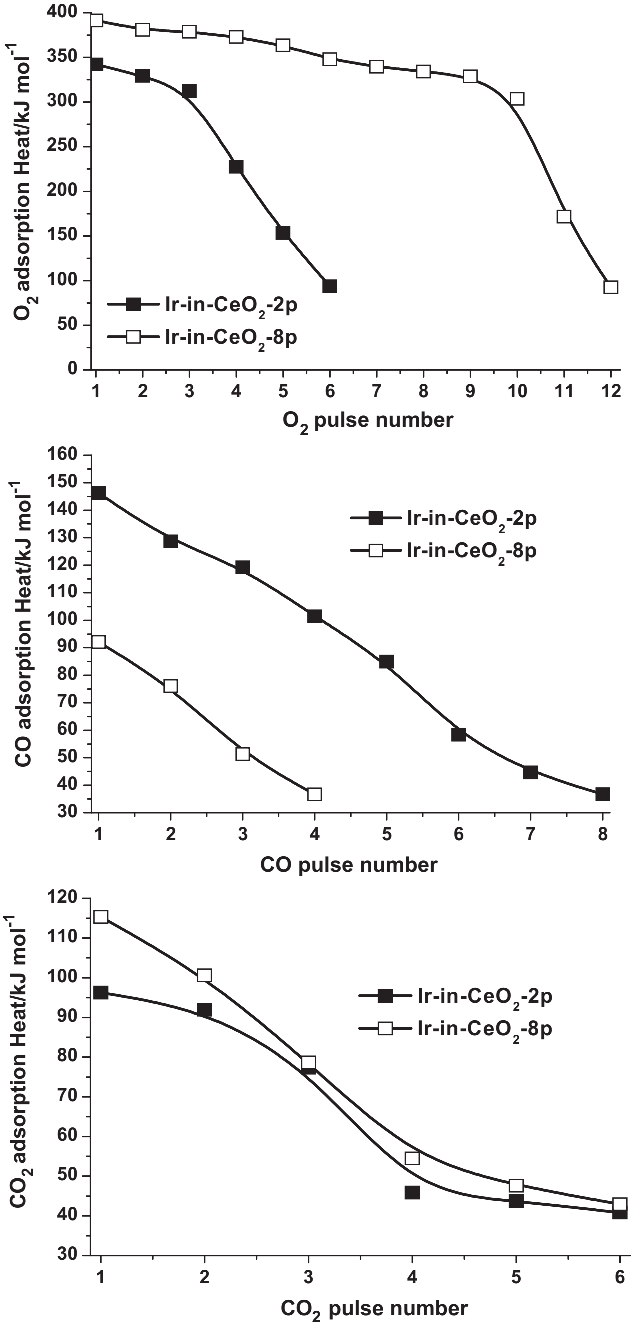

Fig. 5. Calorimetric adsorption of O_2, CO, and CO_2 over the Ir-in-CeO_2-2p and Ir-in-CeO_2-8p samples.

3.3.1. O_2, CO, and CO_2 adsorption on Ir-in-CeO_2-2p and Ir-in-CeO_2-8p

To address the effects of Ov and carbonates on the catalytic activity, we first studied the adsorption behaviors of O_2, CO, and CO_2 with the pulse number on the Ir-in-CeO_2-8p and Ir-in-CeO_2-2p samples at 393 K by the pulse calorimetry. The results are shown in Fig. 5 and Table 2. With the pulses of O_2, a little CO_2 is released, attributed to the behavior of oxygen-assisted decomposition of carbonates. The initial adsorption heat and the saturation uptake of O_2 are 391 kJ mol^{-1} and 42.5 μmol on Ir-in-CeO_2-8p while 342 kJ mol^{-1} and 15.0 μmol on Ir-in-CeO_2-2p, indicating that the presence of more Ov is favorable for O_2 adsorption and activation. Unexpectedly, the adsorption of CO is largely prohibited, with the adsorption heat and saturation uptake of only 92 kJ mol^{-1} and 1.0 μmol on Ir-in-CeO_2-8p relative to that of 146 kJ mol^{-1} and 3.4 μmol on Ir-in-CeO_2-2p. The CO_2 adsorption heat on Ir-in-CeO_2-8p (115 kJ mol^{-1}) is higher than that on Ir-in-CeO_2-2p (96 kJ mol^{-1}), although the saturation uptakes of CO_2 are similar. The CO_2 was usually adsorbed in a form of carbonates over ceria-based catalysts [12,26]. Thus, it suggests that on Ir-in-CeO_2-8p, there appeared more Ov, the existence of which leads to the strong adsorption of the carbonates.

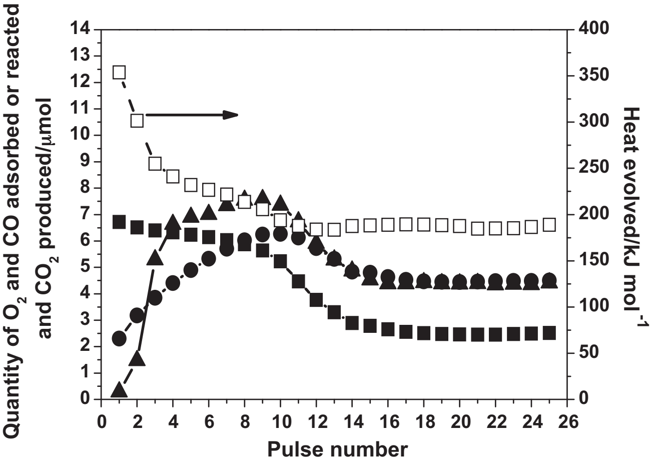

Fig. 6. Amount of O_2 (■), CO (●) adsorbed or reacted and CO_2 (▲) released and correspondingly the heat evolved Q (□) with the dose number of CO + O_2 (2:1) pulse at 393 K on Ir-in-CeO_2-8p.

3.3.2. Successive pulses of CO + O_2 at 393 K

The formation of more Ov was favorable for the adsorption of O_2 but led to the prohibition of CO adsorption and activation. On the other hand, it improved the adsorption strength of carbonates. The Ov and carbonates were both involved in the process of CO oxidation [15,16]. We then described the process of CO oxidation before the steady state by exposing the freshly pretreated catalysts to successive pulses of CO + O_2 (2:1). The CO-, O_2-, and CO_2-related quantities were shown as well as the heat evolved from the initial state to the steady state.

Fig. 6 displays the reaction process when the Ir-in-CeO_2-8p was subjected to pulses of CO + O_2 at 393 K. In the 1st or 2nd pulse of reactants, few CO_2 is released. The pronounced high amount of O_2 is consumed, indicating the overreduction of ceria compared with that under steady state, and the additional oxygen supply to decrease Ov content. Meanwhile, the lower consumption of CO is found. Nevertheless, the consumption amount of CO (2.3 μmol for the first pulse) is higher than the saturation adsorption amount of CO (1.0 μmol as shown in Table 2), indicative of the reaction of CO with adsorbed O_2. The difference between CO_2 formation and CO consumption can be ascribed to the formation of carbonates [27]. The initial heat of 354 kJ mol^{-1} is a little lower than that of O_2 adsorption (391 kJ mol^{-1}), indicating the preferential activation of O_2 rather than CO. In the subsequent 3rd to 10th pulse, both the amounts of released CO_2 and adsorbed/reacted CO increase significantly. It should be noted that the amount of released CO_2 is even higher than that of consumed CO. This indicates that part of CO_2 is produced by the decomposition of the pre-adsorbed carbonates. Correspondingly, the decreasing evolved heat with pulses of reactants could result from the endothermic step of carbonates decomposition other than the direct reaction of adsorbed CO with oxygen species. However, it is unexpected that the consumption amounts of CO and O_2 simultaneously decrease after 10th pulse of CO + O_2. Generally, the temperature (K) for desorption of adsorbed species nearly equates four times of adsorption heat

Table 2
Initial adsorption heat and saturation uptake of O_2, CO, and CO_2 on Ir-in-CeO_2-2p and Ir-in-CeO_2-8p samples at 393 K.

Absorbate	O_2		CO		CO_2	
	Ir-in-CeO_2-2p	Ir-in-CeO_2-8p	Ir-in-CeO_2-2p	Ir-in-CeO_2-8p	Ir-in-CeO_2-2p	Ir-in-CeO_2-8p
Heat evolved (kJ mol^{-1})	342	391	146	92	96	115
Uptake (μmol)	15.0	42.5	3.4	1.0	20.9	22.6

value (kJ mol^{-1}) [28,29]. The corresponding temperature for desorption of carbonates calculated from the initial adsorption heat of CO_2 on Ir-in-CeO_2-8p is around 460 K, which is higher than the reaction temperature (393 K) of CO oxidation. This indicates some carbonates irreversibly adsorb on this sample. Therefore, some of the reactive sites may be covered by these carbonates, resulting in the decreased yield of CO_2. After 16th pulse of CO + O_2, the quantity intensities show a stoichiometric and steady consumption of the reactants and a corresponding amount of CO_2 formation. The evolved heat keeps a constant of around 185 kJ mol^{-1}, consistent with the enthalpy of direct reaction between CO and O_2 [21,30].

Comparatively, the situation is different on Ir-in-CeO_2-2p. As shown in Fig. 7, the consumption amount of O_2 remains 6.5 μmol per pulse of reactant. The adsorbed/reacted amount of CO is higher than that on Ir-in-CeO_2-8p. In spite of the initial prohibition on CO adsorption and activation by pre-accumulation of carbonates, more and more CO is activated and transformed to CO_2 with pulses of reactants before the steady state for CO oxidation. The initial heat is about 250 kJ mol^{-1} for the 1st pulse, and then slowly decreases to around 180 kJ mol^{-1} until the 6th pulse. Compared with that on Ir-in-CeO_2-8p, the corresponding temperature for desorption of carbonates on Ir-in-CeO_2-2p calculated from the initial adsorption heat of CO_2 was only 384 K, lower than the reaction temperature. Thus, the carbonates can reversibly adsorb and do not prohibit the reaction of CO with O_2 under steady state on Ir-in-CeO_2-2p. Correlating with the results in Table 1, the amount of Ov 1.5% and carbonates 0.08 MLs coverage might be proper to promote CO oxidation.

For CO oxidation on ceria-based catalysts, Ov sites are chemically active and play an important role. A junction effect, arising from the contact between ceria and a metal with high work function, has been suggested to explain the high activity of NM-in-CeO_2 catalysts, on which the easily formed Ov becomes the active sites [31,32]. Although not absolutely excluding the possibility of the contribution of few exposed metal Ir sites, our results in Fig. 4 show a clear relationship between the amount of Ov and the catalytic activity on Ir-in-CeO_2. Not a linear increase of catalyst activity with the Ov but the best performance of CO oxidation with 1.5% Ov is found. The pulse calorimetric studies show that the adsorption and activation of CO but not O_2 is prohibited with more Ov. The analysis of transient step of CO oxidation suggests that the prohibition of CO adsorption and activation is probably caused by the buildup of carbonates. Moreover, the strongly adsorbed carbonates, accompanied with more Ov, would decrease the catalyst activity under steady state. This might be explained by a reaction scheme in which the supply of adsorbed CO (CO_{ad}) to react with oxygen species is reduced due to these strongly adsorbed carbonates, as the temperature needed for carbonates desorption is higher than the reaction temperature on Ir-in-CeO_2-8p. This process closely resembles the reasons leading to the deactivation of Au/TiO_2 sample, on which the accumulation of carbonates decreased the local density of CO_{ad} and correspondingly the amount of CO_2 by an in situ DRIFTS study [33]. In order to further demonstrate the effects of carbonates on CO oxidation, we also studied the surface behavior of Au-in-CeO_2, which has been extensively studied for CO oxidation. Unlike Ir-in-CeO_2, the pretreated number of CO pulses does not affect the final activity on Au-in-CeO_2 under steady state. This is in accord with the recent data from a temporal analysis of products reactor, showing that the final activity under steady state does not depend on the method of oxygen removal for Au/CeO_2 catalyst [19]. The initial adsorption heat of carbonates on Au-in-CeO_2 pretreated by 8 pulses of CO was only 90 kJ mol^{-1}, thus the carbonates could easily desorb at 393 K. Then the supply of CO_{ad} is not prohibited, and the catalyst activity does not decrease with more pretreated number of CO pulses. Therefore, the adsorption strength of carbonates remains a decisive factor to affect the catalyst performance under steady state. The buildup of strongly adsorbed carbonates prohibits the adsorption and activation of CO, leading to the deactivation of the Ir-in-CeO_2 catalyst.

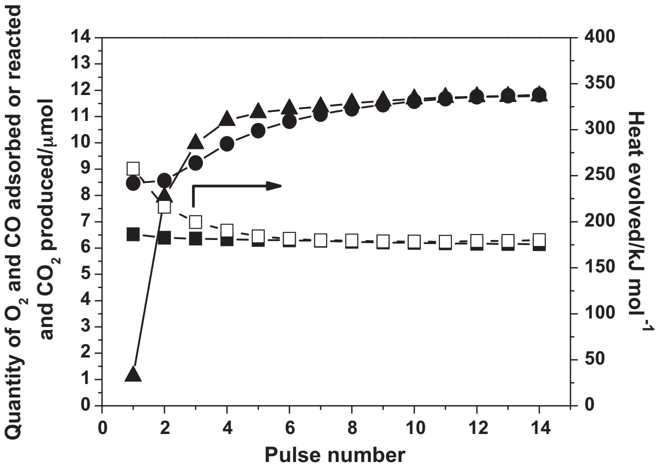

Fig. 7. Amount of O_2 (■), CO (●) adsorbed or reacted and CO_2 (▲) released and correspondingly the heat evolved Q (□) with the dose number of CO + O_2 (2:1) pulse at 393 K on Ir-in-CeO_2-2p.

4. Conclusions

The activation of Ir-in-CeO_2 by pulses of CO pretreatment for CO oxidation was studied. The formation of Ov and carbonates is one-step achieved during this pretreatment. By injecting pulses of reactants onto these pretreated samples, we observed a volcano-like relationship between Ov and catalyst activity under steady state. The presence of 1.5% Ov is best but more amount of Ov leads to the decreasing activity. The adsorption strength of carbonates plays a crucial role on the change of this activity. The prohibition of CO oxidation with more Ov may result from the decreased supply of adsorbed CO to react with oxygen species due to the buildup of strongly adsorbed carbonates.

Acknowledgements

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