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Redox properties of CeO_2 and Pt-Rh/CeO_2 studied by TAP method

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Redox properties of CeO_2 and Pt-Rh/CeO_2 were studied by temporal analysis of products (TAP) method using alternative pulses of CO and O_2. A portion of pulsed CO was oxidized to CO_2 and a portion of CO was adsorbed on the surface. Pulsing $^{18}O_2$ onto the catalyst which has surface species derived from CO, evolved CO_2 contained no ^{18}O suggesting that the surface species will be carbonate ions.

KEY WORDS: redox property; ceria; temporal-analysis-of-products; noble metal; promotion effect.

Ceria has been widely used as a catalyst support for three-way catalysts in order to enlarge the efficient operating air/fuel (A/F) window. Fast redox character of CeO_2 is expected to work as an oxygen reservoir [1,2] usually; TPR and TPD are used for evaluation of oxidation activity and oxygen storage capacity of catalysts. However, it takes several 10 min to obtain a spectrum and data contains surface and bulk information. The data is sometimes far from the actual situation of catalysis. Temporal analysis of products (TAP) reactor system, an important tool for investigating 'gas–solid' reactions, adopts shots of different gases with a very short interval. Therefore, TAP analysis would be helpful to analyze catalytic reaction on metal oxides.

CeO_2 was provided by (Anan Chem. Co., Japan). The loading of Pt and Rh for Pt-Rh/CeO_2 are 0.19 wt% and 0.56 wt%, respectively. The Pt-Rh/SiO_2 was also prepared with same loading amount of Pt and Rh (SiO_2, Degussa, Aerosil, OX-50). CeO_2 and Pt-Rh/CeO_2 are confirmed to be cubic fluorite-type structure. The BET surface specific areas (SSA) of CeO_2, Pt-Rh/CeO_2 and Pt-Rh/SiO_2 are 118, 116 and 50 m^2/g, respectively.

TAP reactor system was used for CO–O_2 pulse reaction. Four solenoid-operating gas-valves are arranged to supply a small amount of gas pulse. A quartz tube reactor with an internal diameter of 4 mm is used. Samples were pressed, crushed, and sieved with the size of 32–60 mesh. About 50 mg of a sample was packed in the reactor located in the center of an electrical furnace. The reactor was evacuated to $10^{-2} \sim 10^{-3}$ Pa by a rotary pump. A capillary tube, of which one end is located just after the catalyst bed, is used for introducing gaseous products into a mass spectrometer. The chamber of mass spectrometer was kept high vacuum ($\sim 10^{-6}$ Pa) by a turbo-molecular pump. Prior to measurements, the catalysts are evacuated at 500 °C for 3 h and then fully oxidized by O_2 pulses. The accurate amount of each pulse is determined by measuring the pressure of gases in a vessel with known volume after injecting $50 \sim 100$ pulses with a high accuracy pressure gauge. And the accurate amount of CO (and O_2) consumed and CO_2 formed upon each pulse are determined by mass spectrometer. Peaks of CO (m/e = 28), O_2 (m/e = 32), and CO_2 (m/e = 44) are monitored. The relative sensitivity of CO, O_2 and CO_2 are calibrated using each gas. Since CO_2 gave m/e = 28 peak as a fragment peak, which is 11% of the parent peak area of m/e = 44, the amount of CO was corrected by this amount.

Approaching to the actual operating condition of automotive exhaust, redox properties of samples were studied using alternative CO and O_2 pulses. The alternate pulse TAP experiments were carried out using the feed stream condition (O_2:0.12 MPa, ON 10 ms (10.6 μmol), OFF 15 s; CO:0.12 MPa, ON 10 ms (13.8 μmol), OFF 15 s, delay 4 s). Figure 1 shows the time course of the MS signals of the reactants and products. For CeO_2, when 266 μmol/g of CO pulse was introduced at 500 °C (Figure 1(b)), the CO uptake was 221 μmol/g, 137 μmol/g of CO_2 was evolved, then 84 μmol/g of CO was absorbed. After the first CO pulse, 204 μmol/g of O_2 pulse was introduced to the sample. 98 μmol/g of O_2 was consumed, 82 μmol/g of CO_2 and 3 μmol/g of CO were evolved. Therefore, all of absorbed CO was released. CO_2 was observed to produce upon each CO and O_2 pulse in the oscillating condition. The former CO_2 production is due to CO oxidation by reacting with oxygen atoms of CeO_2. The adsorbed CO was responsible for the appearance of CO_2 production upon O_2 pulses. The CeO_2 is completely recovered the

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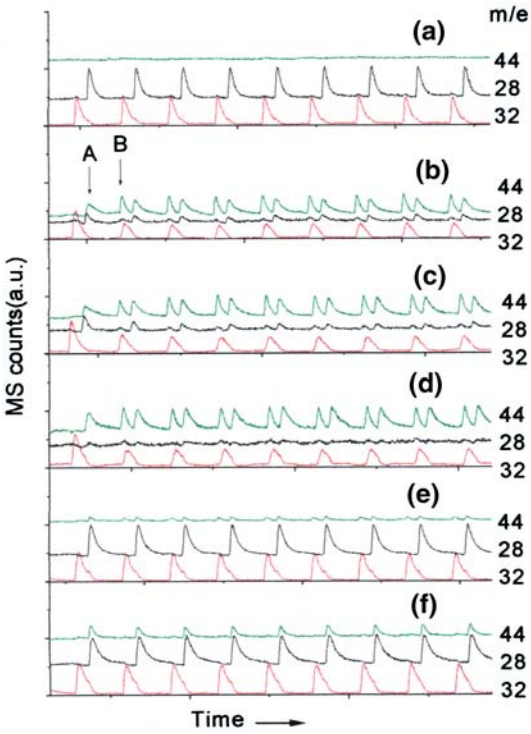

Figure 1. Mass spectral response of selected peaks in the alternative reaction by CO and O_2 pulses. (a) CeO2 at 200 °C; (b) CeO_2 at 500 °C; (c) Pt-Rh/CeO_2 at 200 °C; (d) Pt-Rh/CeO_2 at 500 °C; (e) Pt-Rh/SiO_2 at 200 °C; (f) Pt-Rh/SiO_2 at 500 °C; A: 1st CO pulse, B: 1st O_2 pulse.

initial state after the 2nd O_2 pulse. From 2nd to 10th CO pulses, the amount of CO uptake seems to take a steady value (204 μmol/g). The reduction and re-oxidation of the sample are reversible. A cyclic steady state is very quickly reached in the transient experiment. The steady state values (μmol/g) measured by alternate pulses of CO and O_2 are summarized in Table 1. The total of CO_2 production upon CO and O_2 pulses is consistent with that of CO uptake. And a consistence is also obtained between the CO and O uptake. The same experiment of Pt-Rh/CeO_2 at 500 °C (Figure 1(d)) gave that, in the cyclic steady state, CO uptake was increased to 250 μmol/g, 122% of the value for CeO_2, Selectivity for CO_2 evolution and CO absorption are similar to those for CeO_2. Redox reaction at 200 °C was also studied on CeO_2 and Pt-Rh/CeO_2, No CO consumption was observed over CeO_2 (Figure 1 (a)). However, Pt-Rh/CeO_2 showed high activity of CO oxidation (Figure 1(c)). The CO uptake upon CO pulses decreased to 85% of that at 500 °C. The presence of noble metals significantly lowered the reduction temperature of and increased the amount of CO (and/or O_2) uptake and CO_2 production. It is clear that supporting Pt-Rh improves the redox property of CeO_2. The following possibilities are considered: (1) adsorption of CO begins on noble metals; (2) adsorbed CO is oxidized to CO_2 at the interface of supported metals and CeO_2, and the reactive O on the CeO_2 surface is increased by supporting noble metals; (3) disproportionation of CO takes place over noble metals. The possibility of (1) could be ruled out when temperature is as high as 500 °C. It was known that the amounts of Pt and Rh on the sample were about 9.7 and 54.4 μmol/g, respectively, which much smaller than the amount of CO uptake. To clarify the role of supported noble metals, alternate pulse experiments were carried out on Pt-Rh supported SiO_2 (Figure 1(e), (f)) for comparison. At 500 °C, only 40 μmol/g of CO reacted with the sample and almost all CO was oxidized to release out as CO_2. Since residual C was very small, there is no possibility to proceed disproportionation of CO: $2CO \rightarrow C + CO_2$. So that CO_2 may be formed from the reaction of adsorbed CO and oxidized noble metal (PtO, Rh_2O_3). Similar enhancement of the reducibility of CeO_2 by supporting Pt was observed and the strong Pt—CeO_2 interactions was estimated [3]. The reason for increase in the reducibility of CeO_2 by supporting noble metals is not clear, however, we tentatively suppose that the supported noble metals would give partial negative charge to Ce^{4+} ions, and the slightly reduced CeO_2 ions may be more reducible than pure CeO_2.

Finished the introduction of CO pulses, significant amount of CO was retained on the CeO_2 and Pt-Rh/CeO_2, and could not be removed by He pulses. What is the adsorbed structure of CO ? The formation of carbon residuals was interpreted by carbonates species CO_3 [2,4–7] or/and carbon deposit [6–9]. It was reported that the CO disproportionation ($2CO \rightarrow C + 2CO_2$) only took place on strongly reduced Pt/ceria and CO_2 was continuously produced up to 100 pulses under successive pulses of CO [7]. Various structured species are proposed over various catalysts. However, it is important to collect the information on CeO_2 and Pt-Rh/CeO_2. It emerges three possibilities. The first is the formation of C by disproportionation of CO because the formed amount of CO_2 is about one half of the amount of consumed CO. The second is molecular type adsorbate as CO. However, adsorption of molecular type CO is

Table 1
Steady state values (μmol/g) measured by alternative pulses of CO and O_2

Sample	T	CO pulses			O_2 pulses		
	/°C	CO[a]	CO_2[b]	CO[c]	O_2[a]	CO_2[b]	CO[b]
CeO_2	200	0	0	0	0	0	0
	500	204	118	86	98	82	3
Pt-Rh/CeO_2	200	213	123	90	108	81	3
	500	250	162	88	119	88	0
Pt-Rh/SiO_2	200	28	12	16	11	10	0
	500	40	38	2	18	0	0

Each CO pulse = 13.8 μmol, each O_2 pulse = 10.6 μmol.[a] amount of CO and O_2 uptake, [b] amount of CO_2 and CO evolved, [c] amount of CO adsorbed.

Table 2
Oxidation of absorbed CO by $^{18}O_2$ over CeO_2

Pulse No.	CO pulse[a]			$^{18}O_2$ pulses[b]			
	CO[c]	CO_2[d]	CO[e]	$^{18}O_2$[c]	CO_2[d]	$CO^{18}O$[d]	$C^{18}O_2$[d]
CO 1	234	135	99				
$^{18}O_2$ 1				36	34	0	0
$^{18}O_2$ 2				35	32	0	0
$^{18}O_2$ 3				33	28	0	0
$^{18}O_2$ 4				13	5	0	0
$^{18}O_2$ 5				1	0	0	0.
Total	234	135	99	118	99	0	0

Sample: CeO_2, 50.4 mg, [a] CO pulse = 274 μmol/g, [b] $^{18}O_2$ pulse = 36 μmol/g. [c] amount of CO and $^{18}O_2$ uptake, [d] amount of CO_2, $CO^{18}O$ and $C^{18}O_2$ evolved,[e] amount of CO adsorbed.

unlikely at high temperature of 500 °C. The third is the carbonate type adsorbate, CO_3^{2-} To estimate the adsorbed structure, a tracer study using $^{18}O_2$ was carried out. When first CO pulse was introduced to CeO_2, significant amount of CO was adsorbed. After the CO pulse, gaseous $^{18}O_2$ that is 1/3 of the adsorbed amount of CO were pulsed into reactor for 5 times and the ^{18}O distribution was measured for the formed CO_2 molecules. The results are shown in Table 2. CO_2 was evolved upon the pulses of $^{18}O_2$, and no ^{18}O was observed in the formed CO_2. This result strongly suggested that the CO was adsorbed as CO_3^{2-} on the ceria surface. If CO was adsorbed as CO or carbon atom(s) on the ceria, when it was oxidized by gaseous $^{18}O_2$, it would choose the added ^{18}O atom rather than lattice oxygen ions. Thus the existence of adsorbed C species is unlikely. We concluded that CO was adsorbed on the ceria as CO_3^{2-} at 500 °C:

$$CO(g) + 20^2(1) \rightarrow CO_3^{2-}$$

$$CO_3^2 + 1/2^{18}O_2(g) \rightarrow CO_2(g) + {}^{18}O^{2-}(1) + O^{2-}(l)$$

where g: gas, 1: lattice.

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