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Effect of Additives on the Stability of Pd/Al_2O_3 for Carbon Dioxide Reforming of Methane

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The effect of additives such as alkaline earth metal (Ca and Ba) and rare earth metal (La and Ce) oxides to Pd/Al_2O_3 catalyst for the CH_4/CO_2 reforming was investigated at 1023 K under 0.1 MPa in terms of catalytic stability and coke deposition. Catalytic stability of Pd/Al_2O_3 was improved by all additives; the rare earth metal oxides were more effective than the alkaline earth metal oxides. Temperature programmed hydrogenation (TPH) for those catalysts after exposure to CH_4/CO_2 showed that rate of coke deposition (deactivating catalysts), probably due to CH_4 decomposition, was in the order: $Pd/Al_2O_3 > Ba/Pd/Al_2O_3 \gg La/Pd/Al_2O_3$, being in accordance with the catalytic stability. Temperature programmed oxidation (TPO) showed that rate of CH_4 decomposition was in the order: $Pd/Al_2O_3 > Ba/Pd/Al_2O_3 > La/Pd/Al_2O_3$. Further, the peak on $La/Pd/Al_2O_3$ was observed at lower temperature than on the others during the TPO, implying that the reaction between CH_x and CO_2 on $La/Pd/Al_2O_3$ occurs more easily than on the others. Therefore, the (slow) decomposition of CH_4 and the (fast) removal of the CH_x would be balanced on Pd/Al_2O_3 with the rare earth metal oxides. Thus the catalysts do not show significant coke deposition and keep stable activity for a long time during the CH_4/CO_2 reforming.

CH_4/CO_2 reforming is attractive to generate synthesis gas with a H_2/CO ratio of one. This ratio can be adjusted by combining CO_2 reforming with steam reforming from 1 to 3. Note that gas fields sometimes contain CO_2 ($\geqq$ 25 vol%), which may be an incentive to apply CO_2 reforming rather than separating methane and CO_2. Typically, supported Ni or noble metals are reported as potential catalysts for the reaction.[1–11]

Catalyst deactivation is a serious drawback for the CH_4/CO_2 reforming and must be overcome by effective catalysts. Two potential causes of deactivation exist, i.e., coke deposition[1–11] and sintering of the metal particles.[1,2,6,8]. Most authors agree, however, that coke deposition is the main cause of the deactivation. Coke originates mainly from two reactions, i.e., methane decomposition ($CH_4 \rightarrow C + 2H_2$) and carbon monoxide disproportionation ($2CO \rightarrow C + CO_2$). The former is endothermic and favored at high temperatures, while the latter is exothermic and favored at low temperatures.

Addition of basic metal oxides (alkaline, alkaline earth, and rare earth) to Ni-based catalysts and the use of those oxides as a support for Ni catalysts has been known to be an efficient way for decreasing coke deposition[10,12–14] and preventing sintering of Ni.[15] Further, Stagg–Williams et al.[16–18] have reported that the addition of La_2O_3 and CeO_2 stabilizes catalytic activity of Pt/ZrO_2 catalysts. However, it is still unclear what kind of oxide is most effective to stabilize the activity of noble metal catalysts.

In this contribution, palladium is selected as an active element due to its high amount in the noble metals in the crust, and the effect of additives such as alkaline earth metal (Ca, and Ba) and rare earth metal (La and Ce) oxides is studied in terms of catalytic stability and coke deposition. For that purpose, the CH_4/CO_2 reforming is performed at 1023 K for 50 h. Then, temperature programmed hydrogenation (TPH) is carried out to compare the amount of coke deposition on the catalysts during the reaction. The TPH is also performed after CH_4/He, CO/He, and CO_2/He flow, in order to investigate the source of coke deposition. Further, temperature programmed oxidation (TPO) is also carried out to compare the rate of CH_4 decomposition on these catalysts. From those results, the factors preventing coke deposition are discussed.

Methods

Catalyst Preparation. Pd/Al_2O_3 was prepared by impregnating Al_2O_3 (JRC-ALO-4; reference catalyst of the Catalysis Society of Japan) with $Pd(NO_3)_2$ (Wako chemicals) in water. The palladium loading was set to 2 wt% against the catalysts. The catalyst was dried overnight at 395 K in static air and subsequently reduced with H_2 at 723 K for 2 h. Further, it was impregnated with $Ba(NO_3)_2$, $Ca(NO_3)_2\cdot4H_2O$, $Ce(NO_3)_3\cdot6H_2O$, or $La(NO_3)_3\cdot6H_2O$ (Wako chemicals) for preparing 3-component catalysts. Such catalysts are hereafter denoted as xM/Pd/Al_2O_3. The mole ratio of additives to Pd is x (= 1 or 5), and M is the element of additives. The catalysts which were in powder form were pressed into pellets at 200 bar for 5 min. The pellets were crushed and sieved to obtain grains with diameters between 0.3 and 0.6 mm.

Activity and Stability Tests. The catalyst (0.2 g) was loaded into a tubular quartz reactor. This catalyst was reduced with H_2 (20 mL min^{-1}) at 1073 K for 3 h, and the temperature was lowered in Ar to 1023 K. The reactant gas (CH_4/CO_2 = 1 vol/vol with a total flow rate of 50 mL min^{-1}) was subsequently fed to the reactor. The products were analyzed by TCD gas

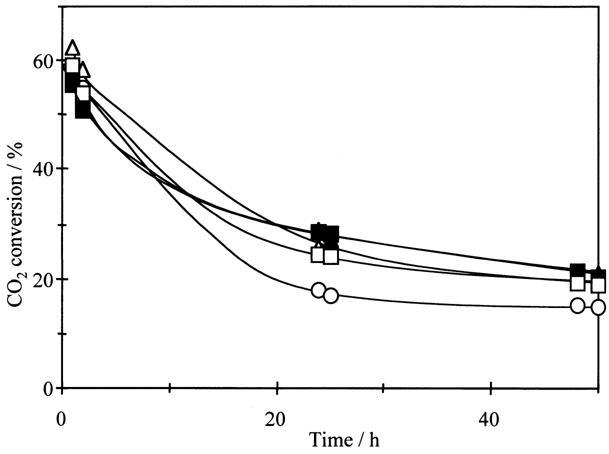

Fig. 1. Stability tests for *x*M/Pd/Al_2O_3 (M; alkaline earth metal) catalysts at 1023 K with CH_4/CO_2 = 25/25 mL min^{-1} under 0.1 MPa. 0.2 g catalysts. ○; non, △; 1Ca, ▲; 5Ca, □; 1Ba, ■; 5Ba.

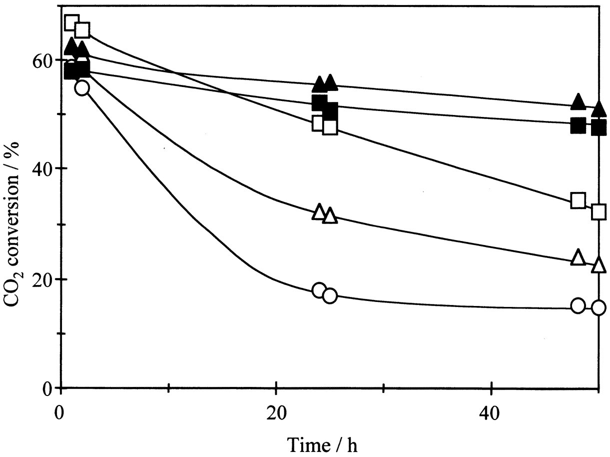

Fig. 2. Stability tests for *x*M/Pd/Al_2O_3 (M; rare earth metal) catalysts at 1023 K with CH_4/CO_2 = 25/25 mL min^{-1} under 0.1 MPa. 0.2 g catalysts. ○; non, △; 1La, ▲; 5La, □; 1Ce, ■; 5Ce.

chromatographs with Porapak Q and MS-13x columns. Carbon balance was assumed to be kept during the reaction, and conversions and yields were calculated.

Temperature Programmed Hydrogenation (TPH) and Temperature Programmed Oxidation (TPO). The catalyst (0.1 g) was loaded into a tubular quartz reactor and a thermocouple was placed at the top of the catalyst layer. The catalyst was reduced with H_2 at 1073 K for 3 h. After the reduction, the temperature was lowered to 1023 K in flowing He and some feed gas mixture (CH_4/CO_2 = 1/1, CH_4/He = 1/1, CO/He = 1/1, or CO_2/He = 1/1 (vol/vol) with a total flow rate of 25 mL min^{-1}) was fed to the reactor for the required time. Then the catalyst was kept in He for 30 min at the previous temperature and next cooled to 323 K.

For the TPH experiments, the sample was subsequently exposed to a flow of H_2 (40 mL min^{-1}) at 323 K and heated up to 1273 K (heating rate was 10 K min^{-1}). CH_4 originating from the carbon species on the catalyst was measured with a gas chromatograph (Shimadzu GC-8A) with a FID.

For the TPO experiments, O_2/He (5/95) with a total flow rate of 30 mL min^{-1} was fed instead of H_2 in the TPH. CO and CO_2 were analyzed by a mass spectrometer.

Transmission Electron Microscopy (TEM). TEM images were observed for the catalysts by using JEOL 200CX with an accelerated voltage at 200 kV, after reduction with H_2 or the CH_4/CO_2 reforming for 1 h.

Results and Discussion

Effect of Additives on Catalytic Stability for Pd/Al_2O_3. Stability of Pd/Al_2O_3 with alkaline earth metal and rare earth metal oxides was measured; the results are shown in Figs. 1 and 2, respectively. As a comparison, the stability of Pd/Al_2O_3 is also shown in those figures. Further, the results of stability tests including deactivation ratio are summarized in Table 1. Since equilibrium CO_2 conversion at 1023 K under 0.1 MPa was 90% and the highest value of CO_2 conversion in the current work was much lower than this value, the contribution of reverse reactions to activity and catalytic stability would be minimized. A small amount of addition increased initial activities for most additives, while a large amount of addition had the reverse effect. The additives would play a role as a poison due to coverage on the catalytic active sites. Pd/Al_2O_3 lost most of its activity (conversions and yields) during the initial 24 h, but the activity loss was decreased by additives (see the deactivation ratio in Table 1). Both of the alkaline earth metal (Ca and Ba) oxides improved the catalytic activity of Pd/Al_2O_3 a little. On the other hand, both of the rare earth metal (La and Ce) oxides improved it very much. Thus the rare earth metal oxides were much more effective than alkaline earth metal oxides. Further, the effect of additives to the catalytic stability was increased with the loading, indicating that the amount of additives was too small to prevent coking in the case of $x = 1$. In order to elucidate the effect of additives on coke deposition, BaO from alkaline earths metal oxides and La_2O_3 from rare earth metal oxides were chosen and the TPH experiments were performed after various treatments. The results are shown with those of Pd/Al_2O_3 hereafter.

Effect of Additives on Coke Deposition for Pd/Al_2O_3 during the CH_4/CO_2 Reforming. In order to study the effect of additives on coke deposition during the CH_4/CO_2 reforming, the TPH was carried out for Pd/Al_2O_3, 5Ba/Pd/Al_2O_3, and 5La/Pd/Al_2O_3 after the reaction for 15 min and 1 h; the results are shown in Fig. 3. A single peak was observed about 1073 K for Pd/Al_2O_3, and this increased with time of exposure. Three peaks appeared about 623, 923, and 1073 K for 5Ba/Pd/Al_2O_3, and a peak with a top about 1073 K was increased with time of exposure. A sole peak was visible about 623 K for 5La/Pd/Al_2O_3 after exposure for 15 min, and the size of this peak did not change much as time passed. A small peak also appeared about 1123 K after exposure for 1 h. The peaks with a top above 1073 K for all catalysts increased with time of exposure and the order of the increasing rate of the peak intensity was Pd/Al_2O_3 > 5Ba/Pd/Al_2O_3 ≫ 5La/Pd/Al_2O_3. The results would provide explanations about the high stability of 5La/Pd/Al_2O_3 (low coke deposition) and the low stability of Pd/Al_2O_3 and 5Ba/Pd/Al_2O_3 (high coke deposition). From such considerations, the peaks with a top above 1073 K were attributed to coke deactivating the catalysts.

Table 1. The Results of Stability Tests[a)] for Pd Catalysts

Catalyst	Time/h	Conversion/%		Yield/%		Deactivation ratio[b)]
		CO_2	CH_4	CO	H_2	
Pd/Al_2O_3	1	59	52	55	50	
	50	15	12	13	11	0.75
$1Ca/Pd/Al_2O_3$	1	62	55	59	51	
	50	21	16	19	15	0.67
$5Ca/Pd/Al_2O_3$	1	56	48	52	45	
	50	19	15	17	14	0.65
$1Ba/Pd/Al_2O_3$	1	59	52	55	49	
	50	19	15	17	15	0.68
$5Ba/Pd/Al_2O_3$	1	56	48	52	46	
	50	20	16	18	15	0.64
$1La/Pd/Al_2O_3$	1	62	56	59	51	
	50	23	18	20	16	0.64
$5La/Pd/Al_2O_3$	1	63	54	58	49	
	50	51	45	48	40	0.18
$1Ce/Pd/Al_2O_3$	1	67	59	63	53	
	50	32	26	29	22	0.52
$5Ce/Pd/Al_2O_3$	1	58	48	53	43	
	50	48	38	43	35	0.18

a) Reaction condition: $CH_4/CO_2 = 25/25$ mL min^{-1}, 1023 K, 0.1 MPa, 0.2 g catalysts.

b) Deactivation ratio is calculated as $1 - $ (CO_2 conversion at 50 h)/(CO_2 conversion at 1 h).

Source of Coke Deactivating Catalysts. The TPH was also performed for Pd/Al_2O_3, $5Ba/Pd/Al_2O_3$, and $5La/Pd/Al_2O_3$ after exposure to CH_4/He, CO/He, and CO_2/He for 5 min, in order to investigate the source of coke deposition. The results are shown in Figs. 4, 5, and 6, respectively. The peaks appeared above 1123 K for all catalysts after exposure to CH_4/He (Fig. 4), and the peak intensities at 1273 K were higher than background level. Some of coke seems not to be removed from catalysts by reaction with H_2 below 1273 K at the coking condition. Peaks appeared in three regions for all catalysts after exposure to CO/He (Fig. 5). As CO disproportionation would occur on those catalysts under CO/He, the form of adsorbed carbon species might be adsorbed CO, CO_2, and/or coke deposition. As the reactivity of coke toward H_2 is lowest in those species, the peaks which appeared at the highest temperatures were attributed to those of coke. The peak intensities of the coke were almost identical for all catalysts, indicating that the contribution of CO to coke deposition is the same for all catalysts. Peaks were observed about 573 K after exposure to CO_2/He (Fig. 6) for all catalysts, and the temperature was much lower than that of coke deactivating catalysts. These peaks may be assigned to carbonate species on the catalysts.

The peak intensities of coke deactivating catalysts (above 973 K) were highest after exposure to CH_4/He for all catalysts, indicating that the main cause of the coke would be CH_4 decomposition. On the other hand, the peaks appearing around 623 K ($5Ba/Pd/Al_2O_3$ and $5La/Pd/Al_2O_3$) and 923 K ($5Ba/Pd/Al_2O_3$) in Fig. 3 may be assigned to adsorbed CO and/or coke (more reactive than coke appearing above 973 K) from CO.

High Stability of Pd/Al_2O_3 with Rare Earth Metal Oxides. The size of Pd particle was measured by TEM after the H_2 reduction; the results are shown together with specific surface areas in Table 2. The size of Pd particle was almost the same for all catalysts, indicating that the additives did not affect the initial Pd particle size that may change catalyst performance for coke deposition. Further, no sintering was observed for Pd/Al_2O_3, $5Ba/Pd/Al_2O_3$, and $5La/Pd/Al_2O_3$ after the CH_4/CO_2 reforming for 1 h.

During the CH_4/CO_2 reforming, CH_4 is dissociated on the catalysts, generating CH_x ($x = 0$–3) species on the catalysts and H_2 in gas phase. The CH_x species would be removed from catalysts by reaction with (directly from gas phase and/or activated) CO_2. As we revealed that the source of coke was CH_4, the imbalance in the rate of CH_4 decomposition (generation of CH_x on the catalysts) and removal of the CH_x would give the coke deposition and subsequent deactivation of the catalysts.[19]

In order to compare the rate of CH_4 decomposition, temperature programmed oxidation (TPO) was performed for Pd/Al_2O_3, $5Ba/Pd/Al_2O_3$, and $5La/Pd/Al_2O_3$ after exposure to CH_4/He. The results are shown in Fig. 7 (note that some of the coke was not removed from catalysts during the TPH at the same coking condition). The intensity for CO ($m/e = 28$) was 11% of that for CO_2 ($m/e = 44$) for all TPO experiments, corresponding to fragmentation of CO_2 (not shown). Thus, all coke was converted to CO_2 during the TPO. The rate of coke deposition (total area of the peak) after exposure to CH_4/He was in the order: $Pd/Al_2O_3 > 5Ba/Pd/Al_2O_3 > 5La/Pd/Al_2O_3$; such order was in agreement with the order of coke deposition after exposure to CH_4/CO_2. Momterio and Noronha[20] have demonstrated that the addition of CeO_2 to Pd/Al_2O_3 decreases H_2 uptake for the reduced catalyst and diminishes the H/Pd ratio, by so-called SMSI (strong metal support interaction). Some Pd particles may be covered by oxides in the current work and the number of sites of CH_4 dissociation would be decreased. However, difference of the coke amount (Fig. 7) among the catalysts was less remarkable than that after exposure to CH_4/“CO_2” reforming gas (Fig. 3). Hence, not only CH_4 decomposition but also the removal of CH_x species by “CO_2” would also affect the coke deposition during the CH_4/CO_2 reforming. As the reactants are CH_x and CO_2 in this step,

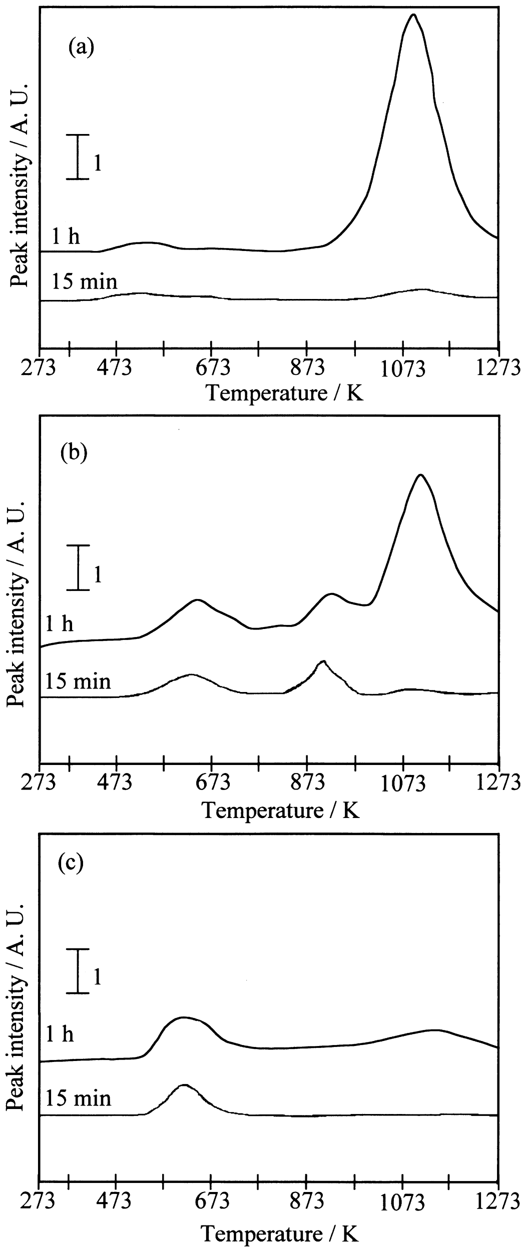

Fig. 3. Temperature programmed hydrogenation (TPH) profiles for Pd catalysts after exposure to CH_4/CO_2 for 15 min and 1 h at 1023 K. (a); Pd/Al_2O_3, (b); $5Ba/Pd/Al_2O_3$, (c); $5La/Pd/Al_2O_3$.

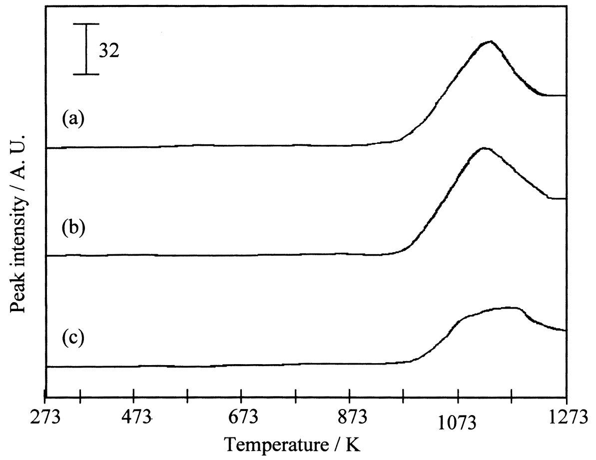

Fig. 4. Temperature programmed hydrogenation (TPH) profiles for Pd catalysts after exposure to CH_4/He for 5 min at 1023 K. (a); Pd/Al_2O_3, (b); $5Ba/Pd/Al_2O_3$, (c); $5La/Pd/Al_2O_3$.

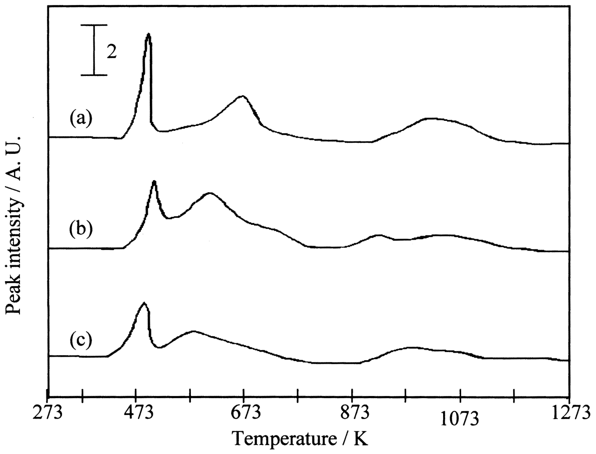

Fig. 5. Temperature programmed hydrogenation (TPH) profiles for Pd catalysts after exposure to CO/He for 5 min at 1023 K. (a); Pd/Al_2O_3, (b); $5Ba/Pd/Al_2O_3$, (c); $5La/Pd/Al_2O_3$.

the difference of reactivity of each (by doping additives) would bring about the difference in the reactivity of CH_x toward CO_2.

In this context, the TPH has been used to investigate the nature and reactivity of the coke on catalyst and the peak appearance temperature is related to the composition of the carbon.[21–23,24] Erdöhelyi et al.[23] distinguished three forms of carbon on Rh supported catalysts: (i) the highly reactive carbidic form, which can be hydrogenated even below 350–400 K, (ii) a less reactive amorphous layer, T_p = 235–495 K, and (iii) the relatively inactive graphitic form, which reacts with hydrogen only above 650 K. The peak for coke deactivating catalysts was observed at the higher temperature on $5La/Pd/Al_2O_3$ than on the others, after the catalysts were exposed to CH_4/CO_2 (Fig. 3) and CH_4/He (source of coke) (Fig. 4) in the current work. The results imply that the reactivity of coke itself is lower on $5La/Pd/Al_2O_3$ than on $5Ba/Pd/Al_2O_3$ and Pd/Al_2O_3. Therefore, the reactivity of coke toward CO_2 is not correlated to the reactivity of coke itself, but to the reactivity of CO_2.

During the TPO (Fig. 7), a sole peak appeared about 933 K with shoulders about 913 K and 983 K for Pd/Al_2O_3. A single peak was observed about 913 K for $5Ba/Pd/Al_2O_3$, and the temperature was identical with that of the shoulder for Pd/Al_2O_3. The only peak with a shoulder about 913 K was visible about 833 K for $5La/Pd/Al_2O_3$, and the temperature of the peak (833 K) was almost 80 K lower than the temperatures of peaks and shoulders for the other catalysts. These results indicate that the coke reactivity toward O_2 is higher on $5La/Pd/Al_2O_3$ than on the others. As the reactivity of coke itself was lower on $5La/Pd/Al_2O_3$ than on the others (Figs. 3 and 4), the difference of O_2 reactivity would bring about the distinction of coke reactivity toward O_2. The results may also predict the high re-

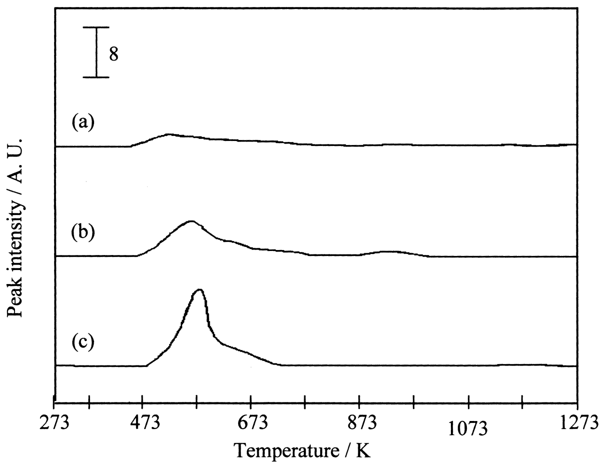

Fig. 6. Temperature programmed hydrogenation (TPH) profiles for Pd catalysts after exposure to CO_2/He for 5 min at 1023 K. (a); Pd/Al_2O_3, (b); 5Ba/Pd/Al_2O_3, (c); 5La/Pd/Al_2O_3.

Table 2. Pysico-Chemical Properties[a)] of Pd Catalysts

Catalyst	Specific surface area /m^2 g^{-1}	Pd particle size /nm
Pd/Al_2O_3	147	20
5Ba/Pd/Al_2O_3	144	23
5La/Pd/Al_2O_3	117	18

a) Measured after reduction with H_2.

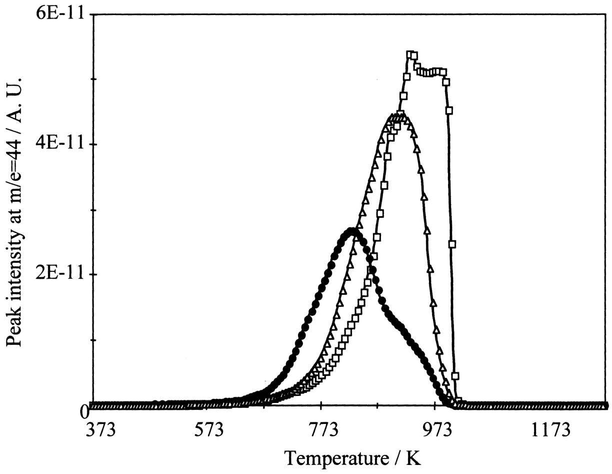

Fig. 7. Temperature programmed oxidation (TPO) profiles for Pd catalysts after exposure to CH_4/He for 5 min at 1023 K. □; Pd/Al_2O_3, △; 5Ba/Pd/Al_2O_3, ●; 5La/Pd/Al_2O_3.

activity of CO_2 on 5La/Pd/Al_2O_3. The enhancement of CO_2 activation would be due to the formation of new surface structure, i.e., $La_2O_2(CO_3)$.[10] In the case of Pd/Al_2O_3 with CeO_2, CO_2 activation may be enhanced by the reducibility of Ce^{4+}, i.e., $Ce_2O_3 + CO_2 \rightarrow 2CeO_2 + CO$.[25] Therefore, the (slow) decomposition of CH_4 and the (fast) removal of CH_x would be balanced on Pd/Al_2O_3 with rare earth metal oxides. Thus, the catalysts do not show any significant coke deposition during the CH_4/CO_2 reforming.

Conclusions

The addition of alkaline earth metal (Ca and Ba) and rare earth metal (La and Ce) oxides to Pd/Al_2O_3 catalyst for CH_4/CO_2 reforming improved catalytic stability of Pd/Al_2O_3, and the rare earth metal oxides were much more effective than the alkaline earth metal oxides. The amount of coke (causing deactivation, mainly from CH_4) on the catalysts during the CH_4/CO_2 reforming was in the order: Pd/Al_2O_3 $>$ Ba/Pd/Al_2O_3 $\gg$ La/Pd/Al_2O_3; such order was in agreement with the catalytic behavior of those catalysts. The decomposition of CH_4 and the removal of CH_x would be balanced on Pd/Al_2O_3 with rare earth metal oxides, due perhaps to the partial coverage of Pd particles by the reduced oxides of rare earth metal (SMSI) and the formation of new phases.

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