ESI (electronic supplementary information)

Title:

Effects of metal cation doping in CeO_2 support on catalytic methane steam reforming at low temperature in an electric field

Authors:

Ayako Takahashi[a], Reona Inagaki[a], Maki Torimoto[a], Yudai Hisai[a], Taku Matsuda[a], Quanbao Ma[b], Jeong Gil Seo[c], Takuma Higo[a], Hideaki Tsuneki[a], Shuhei Ogo[a], Truls Norby[b], Yasushi Sekine[a,*]

Affiliation:

[a] Department of Applied Chemistry, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo, 169-8555, Japan

[b] Department of Chemistry, University of Oslo, FERMiO, Gaustadalléen 21, NO-0349, Oslo, Norway

[c] Department of Energy Science and Technology, Myongji University, Nam-dong, Cheoin-gu, Yongin-si, Gyeonggi-do 449-728, South Korea

Corresponding Author:

E-mail: ysekine@waseda.jp (Y. Sekine)

Selection of support

For EIS measurements, CeO_2 and Al-CeO_2 pellets were prepared in the following steps. First, CeO_2 and Al-CeO_2 powders were synthesized following the same procedure of *2.1*. The both of dried-up powders were pre-calcined at 673 K for 2 h, then calcined at 1123 K for 10 h. CeO_2 powder was pressed at 60 kN for 4 min and sintered at 1273 K for 2 h with the heating ramp rate 5 K min^{-1} in ambient air. Al-CeO_2 powder was pressed at 60 kN for 2 min and sintered at 1323 K for 3 h with the heating ramp rate 5 K min^{-1} in ambient air. The diameter and the thickness of calcined CeO_2 pellet were 17.8 mm and 0.85 mm, while these of Al-CeO_2 pellet were 17.4 mm and 1.00 mm, respectively. The relative density of pellet was calculated as 62.0% for CeO_2 and 59.6% for Al-CeO_2 from each sample's weight and geometry. At last, circular Pt electrodes were painted on both sides using Pt ink (Pt ink number 356010; Nilaco Corp.) and annealed at 1173 K for 1 h with the heating ramp rate 4 K min^{-1} in ambient air.

The difference in adsorbed H_2O amount between Pd/CeO_2 and Pd/Al-CeO_2 may attribute to the difference in the physical property of catalyst support. To clarify that, lattice strain and crystalline phase of samples were investigated using XRD measurement and Raman spectroscopy. Figure. S6 represents the XRD patterns of (A) catalyst supports and (B) 1.0wt%Pd loaded catalysts. Comparing the XRD patterns of CeO_2 and Al-CeO_2, it was confirmed that the crystal structure was maintained as fluorite type even though Al was doped to CeO_2. Raman spectra of CeO_2 and Al-CeO_2 are shown in Fig. S7. As a result, both samples showed a peak around 460 cm^{-1}, which is assignable to F_{2g} mode of CeO_2.[S1] Both Raman and XRD results indicated that the crystallinity decreased by Al doping to CeO_2, since the peaks of Al-CeO_2 got broader and its intensity diminished. Therefore, the crystal structure was suggested to be distorted by Al doping to CeO_2, and this detorsion may have a role for obtaining larger adsorbed H_2O amount. Additionally, from the ICP-OES measurements, the actual

molar ratio of Al/Ce was 0.1238. This ratio was roughly in agreement with the theoretical amount. The crystal structure of Pd/Al-CeO_2 is distorted even with such a small amount of doping Al, which caused a significant increase in the amount of H_2O adsorption.

S1 Z.D. Dohčević-Mitrović, M.J. Šćepanović, M.U. Grujić-Brojčin, Z.V. Popović, S.B. Bosˇković, B.M. Matović, M.V. Zinkevich and F. Aldinger, *Solid State Commun.*, 2006, **137**, 387–390.

S2 Bin Wang, Duan Weng, Xiaodong Wu, Rui Ran, *Appl. Surface Science*, 2011, **257**, 3878–3883.

S3 Xiu-Ge Zhao, Qian Lin, Wen-De Xiao, *Appl. Catal. A: General*, 2005, **284**, 253–257.

Table S1. Catalytic activity without EF; catalyst, 1.0 wt% Pd/M-CeO_2 (M=Ca, Ba, La, Y or Al); flow, CH_4 : H_2O : Ar = 1 : 2 : 7; total flow rate, 120 SCCM; furnace temperature, 523 – 723 K; current, 0 mA.

Dopant	$T_{thermocouple}$ / K	$r_{(CO+CO2)}$ / mmol min^{-1}	Conv. / %	E_a / kJ mol^{-1}
-	573	0.00565	1.10	63.3
	668	0.0398	7.24	
	715	0.0777	14.4	
Ca	569	0.00469	0.925	68.5
	671	0.0382	6.86	
	724	0.110	16.8	
Ba	570	0.00387	0.781	65.0
	669	0.0329	5.79	
	723	0.0677	11.8	
La	577	0.00608	1.21	61.3
	673	0.0432	8.07	
	720	0.0738	14.0	
Y	570	0.00596	1.17	63.3
	673	0.0499	8.77	
	720	0.0932	16.7	
Al	576	0.00577	1.20	63.1
	675	0.0477	8.64	
	723	0.0802	14.4	

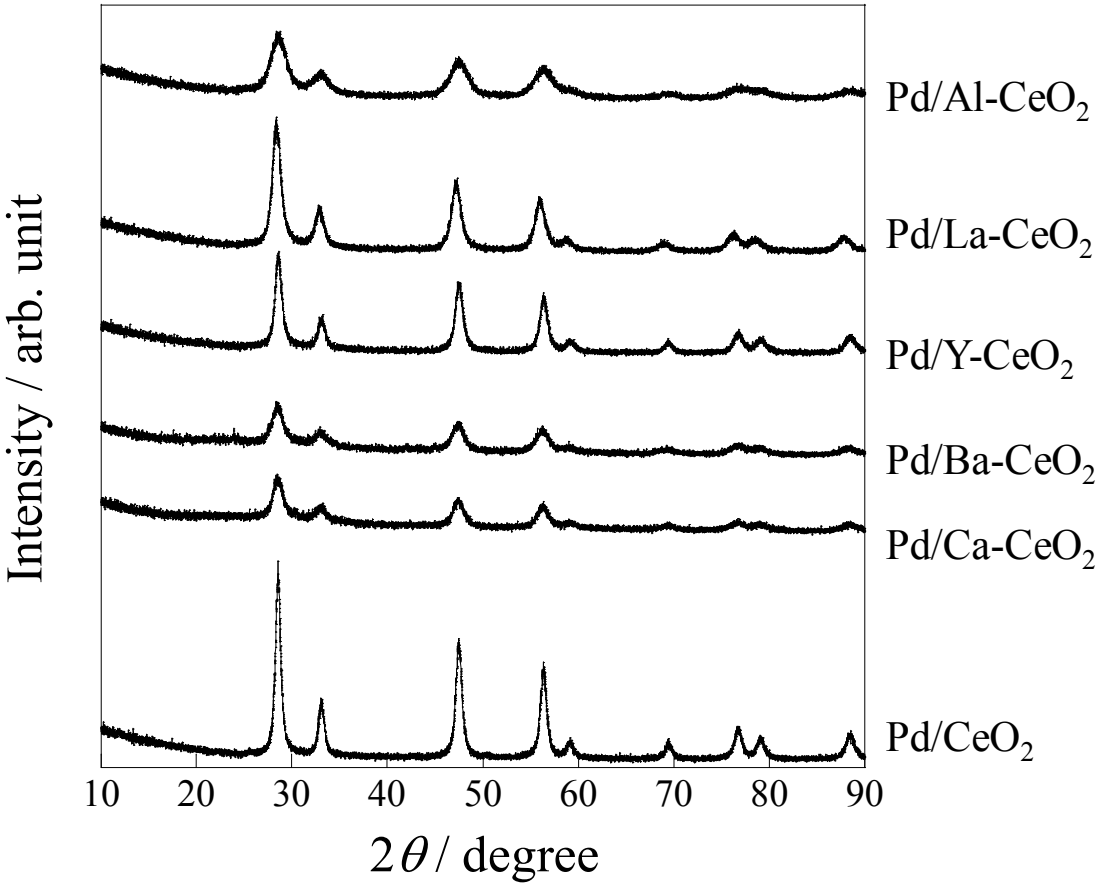

Fig. S1. XRD patterns of 1.0 wt% Pd supported M-CeO_2 (M = None, Ca, Ba, Y, La or Al).

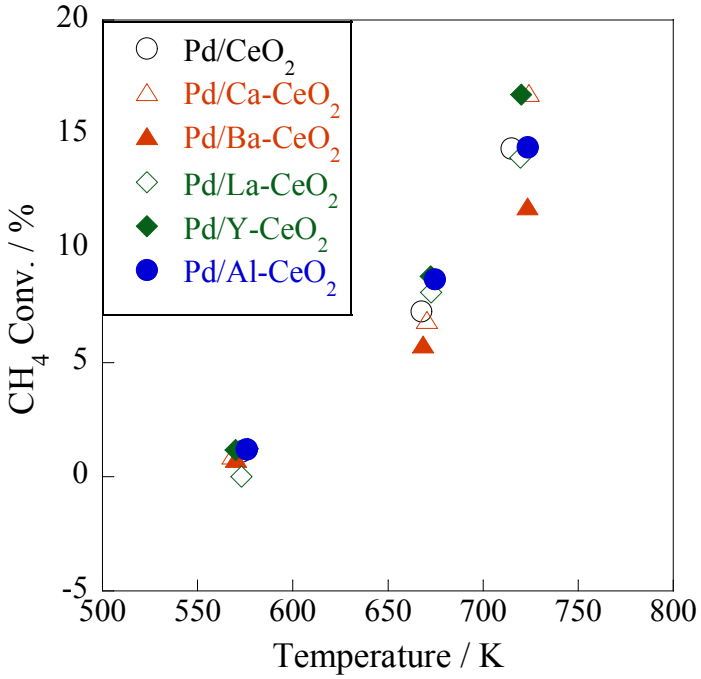

Fig. S2. Catalytic activity without the electric field at 523–723 K.

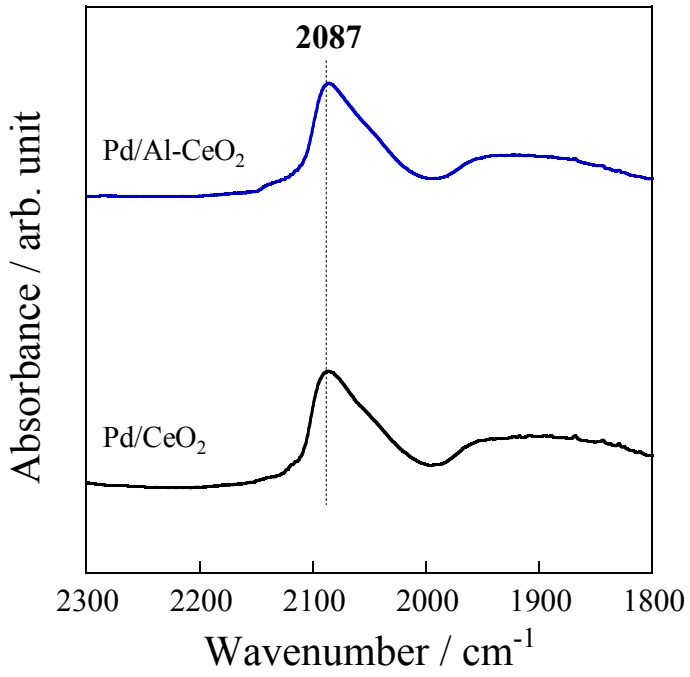

Fig. S3. FT-IR spectra of CO adsorption on 1.0wt%Pd/CeO_2 or 1.0wt%Pd/Al-CeO_2; flow, CO : Ar = x : 65-x (x=0, 5); total flow rate, 65 SCCM, temperature, 373 K.

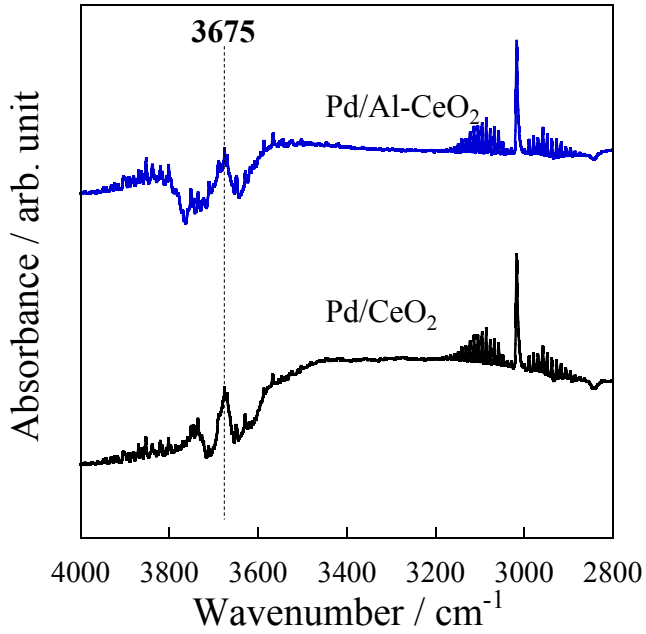

Fig. S4. *In-situ* DRIFTS spectra of adsorbed H_2O on Pd/CeO_2 and $Pd/Al\text{-}CeO_2$ at 473 K.

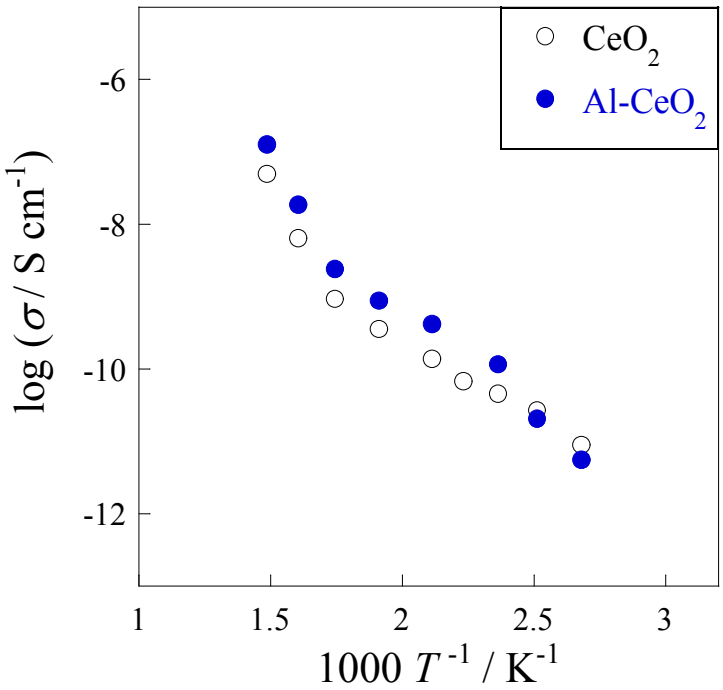

Fig. S5. Temperature dependence of electrical conductivity of CeO_2 and $Al\text{-}CeO_2$ under dry condition (Ar).

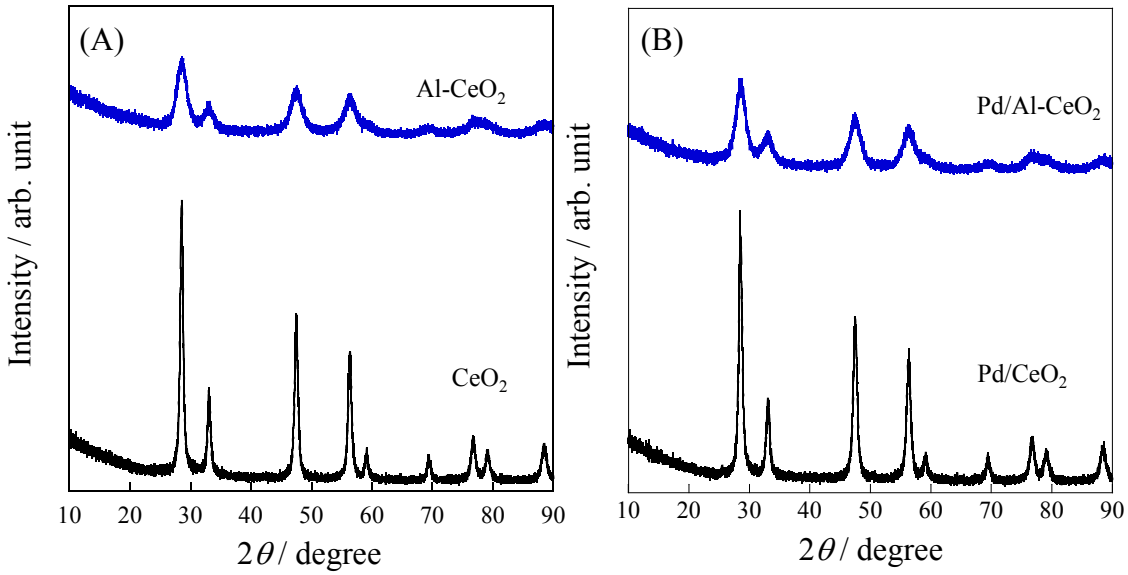

Fig. S6. XRD patterns of (A) bare and (B) 1.0 wt% Pd supported CeO_2 and Al-CeO_2.

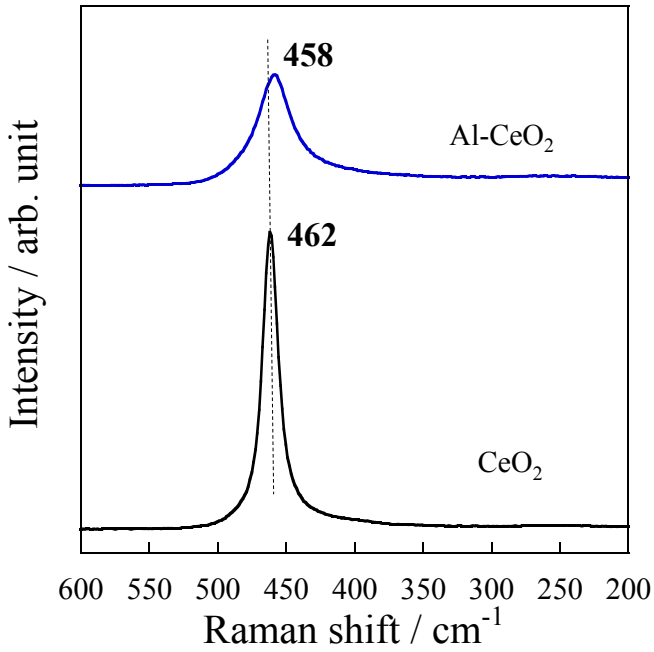

Fig. S7. Raman spectra of CeO_2 and Al-CeO_2