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Improvement of Pt/ZrO_2 by CeO_2 for high pressure CH_4/CO_2 reforming

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CH_4/CO_2 reforming over Pt/ZrO_2, Pt/CeO_2 and Pt/ZrO_2 with CeO_2 was investigated at 2 MPa. Pt/ZrO_2, which shows stable activity under 0.1 MPa, and Pt/CeO_2 showed gradual deactivation with time at the high pressure. The deactivation was suppressed drastically on Pt/ZrO_2 with CeO_2 prepared by different impregnation order (co-impregnation of Pt and CeO_2 on ZrO_2, and consecutive impregnation of Pt and CeO_2 on ZrO_2). The amount of coke deposition was found insignificant and similar among all the catalysts (including Pt/ZrO_2 and Pt/CeO_2). Catalytic activity after the reaction for 24 h was in agreement with Pt particle size after the reaction for same period, indicating that the difference of the catalytic stability is mainly dependent on the extent of Pt aggregation through catalyst preparation, H_2 reduction, and the CH_4/CO_2 reforming. Pt aggregation and the amount of coke deposition were least pronounced on $(Pt\text{–}Ce)/ZrO_2$ prepared by impregnation of CeO_2 on Pt/ZrO_2 and the catalyst showed highest stability.

KEY WORDS: CH_4/CO_2 reforming; Pt/ZrO_2, effect of CeO_2; stability; coke deposition; Pt aggregation.

1. Introduction

Methane is preserved at high pressure in natural gas fields and most of Fischer–Tropsch synthesis and the methanol synthesis from synthesis gas are performed at high pressures. Hence, the CH_4/CO_2 reforming producing synthesis gas should also be carried out at high pressure (more than 1 MPa) in such process, from an economical point of view. Catalytic deactivation is a serious drawback for CH_4 reforming and must be overcome by an effective catalyst [recent review in Ref. [1]]. Three potential causes of deactivation exist, i.e., coke deposition, sintering of the metal particles, and metal oxidation. However, most authors agree that coke deposition is the main cause of deactivation. Coke deposition 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 thermodynamically favored at higher temperatures and lower pressures, while the latter is exothermic and thermodynamically favored at lower temperatures and higher pressures. Moreover, higher pressures favor both reactions kinetically. Since it is well known that higher pressure favors coking, the real effectiveness of the catalysts can only be discussed from the results under high pressure. [2–4].

Pt/ZrO_2 has been reported to be stable for a wide range of temperatures under 0.1 MPa [5–10]. Nevertheless, in the current research we have found that Pt/ZrO_2 deactivates gradually with time in the CH_4/CO_2 reforming at 2 MPa. Therefore, we attempted to improve catalytic stability by the addition of CeO_2, since the addition of CeO_2 has been reported to enhance the catalytic stability of supported Ni catalysts [11,12], Pd/Al_2O_3 [13] and Pt/ZrO_2 [14,15] for the CH_4/CO_2 reforming at 0.1 MPa. Note that the effect of CeO_2 addition to the catalysts in the high pressure CH_4/CO_2 reforming is, nevertheless, not reported and preparation method of Pt/ZrO_2 with CeO_2 is not argued.

Current research aims at developing a stable Pt catalyst for the CH_4/CO_2 reforming at 2 MP. CeO_2 is used as an additive to Pt/ZrO_2 and the impregnation order of Pt and CeO_2 on ZrO_2 was studied. Stability of those catalysts is compared with Pt/ZrO_2 and Pt/CeO_2. In order to understand factors preventing catalytic deactivation, amounts of deposited coke are quantified by temperature-programmed oxidation (TPO) and average Pt particle sizes are measured by transmission electron microscopy (TEM).

2. Methods

2.1. Catalyst preparation

Pt/ZrO_2 and Pt/CeO_2 were prepared by the wet impregnation technique. A solution of $H_2PtCl_6 \cdot 6H_2O$ in water (0.01 g Pt per ml) and powders of ZrO_2 (RC-100, Gimex, Japan, monoclinic phase) and CeO_2 were used for preparing Pt/ZrO_2 and Pt/CeO_2. $Ce(NO_3)_2 \cdot 6H_2O$ (Wako chemicals) in aqueous solution

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was mixed with a 5% aqueous ammonia solution having a pH of approximately 9 to prepare CeO_2. Deposited hydrate was filtered and then calcined in air at 873 K for 4 h. The supports were calcined at 1125 K (heating rate 3 K min^{-1}) for 15 h in flowing air (30 ml min^{-1}) prior to the impregnation with Pt (0.5 wt%). The catalysts were dried at 365 K for 2 h in a rotating evaporator and dried overnight at 395 K in static air. Pt/ZrO_2 with CeO_2 were prepared by following three kinds of methods.

1. Consecutive impregnation of $H_2PtCl_6 \cdot 6H_2O$ prior to $Ce(NO_3)_3 \cdot 6H_2O$ on ZrO_2. The first procedure was carried out by impregnation of solution, evaporation, drying and reduction at 673 K (to remove chlorine from Pt precursor). The same procedure, except for reduction was repeated for CeO_2 impregnation.
2. Consecutive impregnation of $Ce(NO_3)_3 \cdot 6H_2O$ prior to $H_2PtCl_6 \cdot 6H_2O$ on ZrO_2. The first procedure was carried out by impregnation of solution, evaporation, drying and calcination at 1073 K (to remove nitrate from CeO_2 precursor). The same procedure, except for calcination, was repeated for Pt impregnation.
3. Co-impregnation of $H_2PtCl_6 \cdot 6H_2O$ with $Ce(NO_3)_3 \cdot 6H_2O$ on ZrO_2.

Pt loading was set to 0.5 wt% against the catalyst, and the molar ratio of CeO_2 to Pt was fixed to five. The notations of catalysts with preparation methods are listed in table 1. The catalysts which were in powder form were pressed into pellets at 200 bar for 5 min. The pellets were crushed and sieved to grains with diameters between 0.3 and 0.6 mm.

2.2. *Kinetic measurements*

0.2 g of the catalyst was loaded into a tubular aluminum reactor with inconel outside tube passivated by aluminum diffusion coating. After the catalysts were reduced *in situ* in H_2 (20 ml min^{-1}) at 1123 K for 1 h at 0.1 MPa followed by Ar purge at 1023 K and the pressure was increased up to 2 MPa in Ar, a reactant gas ($CH_4/CO_2 = 1$ vol/vol with a total flow rate of 50 ml min^{-1}) was passed over the catalyst. The reaction products were analyzed by a gas chromatograph (Hitachi, G-3000) with an active carbon column and a thermal conductivity detector (TCD). CH_4 conversion and H_2 yield was calculated with carbon balance, as the amount of coke deposited was very small to negligible.

Table 1
Methods of catalyst preparation

Catalyst	Method
Pt/ZrO_2	Impregnation of Pt
Pt/CeO_2	Impregnation of Pt
(Pt–Ce)/ZrO_2	Impregnation of Pt prior to CeO_2
(Ce–Pt)/ZrO_2	Impregnation of CeO_2 prior to Pt
(PtCe)/ZrO_2	Co-impregnation of Pt and CeO_2

2.3. *Catalyst characterization*

The amount of coke deposited on the catalyst was quantified by TPO. After the reaction, the reactant gas was replaced with Ar and the catalyst was cooled to room temperature. All of the catalyst was taken out of the reactor and transferred to a tubular quartz reactor with a thermocouple at the top of the catalysts layer. The sample was heated up to 973 K in He and subsequently cooled to the room temperature. O_2/He (5/95 vol/vol with a total flow rate of 30 ml min^{-1}) was switched to the reactor at the temperature and the catalyst was heated up to 1273 K (heating rate 10 K min^{-1}). During the experiment, CO and CO_2 originating from coke deposited were converted to CH_4 (through a methanizer), and quantified by a gas chromatograph with a FID.

TEM images were observed by using (JEOL) JEM-2010F (A Multidisciplinary Center for Chemical and Environmental Research at Tokyo Institute of Technology) with an accelerated voltage at 200 kV, after the catalysts were reduced in H_2 or exposed to the reactant gas for 24 h.

The specific surface area of the catalysts after H_2 reduction was determined by BET method.

3. Results and discussion

3.1. *Kinetic measurements*

Activities of Pt/ZrO_2 and Pt/CeO_2 in the CH_4/CO_2 reforming are shown in figure 1. Initial activity of Pt/CeO_2 was lower than that of Pt/ZrO_2 and both of the catalysts showed deactivation with time. As it has been reported that Pt/ZrO_2 shows stable activity under 0.1 MPa in wide temperatures (855–1125 K) [5–10], our results indicate that coke deposition and/or sintering

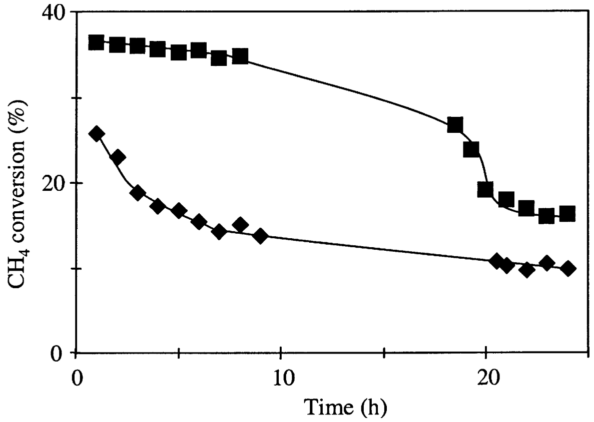

Figure 1. CH_4 conversion over (■) Pt/ZrO_2, (◆) Pt/CeO_2 (reaction condition: $CH_4/CO_2 = 25/25$ ml min^{-1}; 1023 K; 2 MPa; 0.2 g catalysts).

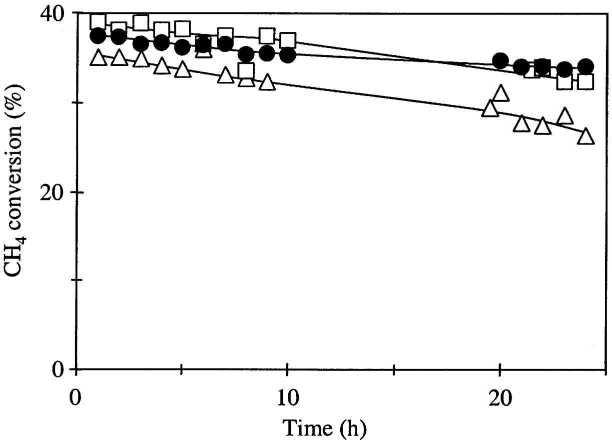

Figure 2. CH_4 conversion over Pt/ZrO_2 with CeO_2 prepared by different methods (reaction condition:$CH_4/CO_2 = 25/25$ ml min^{-1}; 1023 K; 2 MPa; 0.2 g catalysts). (●) $(Pt–Ce)/ZrO_2$; (□) $(Ce–Pt)/ZrO_2$; (△) $(PtCe)/ZrO_2$.

Table 2
Results fo activity tests[a] and amounts of coke deposited over Pt catalysts

Catalyst	Time (h)	CH_4 converstion (%)	H_2 Yield (%)	Coke[b] (%)
Pt/ZrO_2	1	36	27	
	24	16	8	1.07
Pt/CeO_2	1	26	15	
	24	10	3	1.42
$(Pt–Ce)/ZrO_2$	1	37	27	
	24	34	24	0.86
$(Ce–Pt)/ZrO_2$	1	39	28	
	24	32	22	1.47
$(PtCe)/ZrO_2$	1	35	25	
	24	26	17	1.19

[a] Reaction condition:$CH_4/CO_2 = 25/25$ ml min^{-1}; 1023 K; 2 MPa; 0.2 g catalysts.

[b] Measured after the reaction for 24 h.

of Pt particle occurs more easily at the high pressure than atmospheric pressure.

Activities of Pt/ZrO_2 with CeO_2 prepared by different impregnation order are shown in figure 2 and the results are summarized in table 2. Initial activities were almost identical for all catalysts probably due to high CH_4 conversion limited by equilibrium (34.6% of CH_4 conversion). Slightly higher CH_4 conversion compared to equilibrium value would be due to experimental error. All of Pt/ZrO_2 with CeO_2 showed improved stability, higher CH_4 conversion at 24 h, compared with Pt/ZrO_2 and Pt/CeO_2, and $(Pt–Ce)/ZrO_2$ had highest stability among the catalysts.

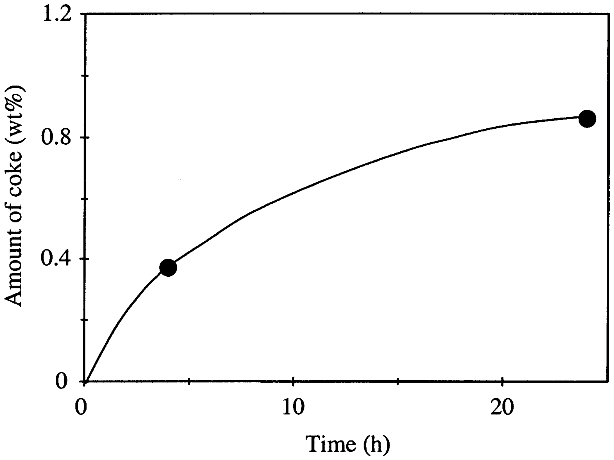

Figure 3. Time on stream of amount of coke deposition for $(Pt–CeO_2)/ZrO_2$ during the CH_4/CO_2 reforming at 1023 K under 2 MPa.

3.2. *Influence of deposited coke and Pt aggregation on the difference of the catalytic stability*

To elucidate nature of catalysts determining catalytic stability, the amounts of coke and average Pt particles were compared among the catalysts. The amounts of deposited coke in the CH_4/CO_2 reforming for 24 h were listed in table 2. Approximately 1 wt% of coke was accumulated on all catalysts and decreased in the order:$(Ce–Pt)ZrO_2$, Pt/CeO_2, $(PtCe)/ZrO_2$, Pt/ZrO_2, $(Pt–Ce)/ZrO_2$; however, the difference among the catalysts was not remarkable and was not in accordance with the order of the catalytic stability. The amount of coke deposited on $(Pt–Ce)/ZrO_2$ having highest stability was measured after the reaction with different period and its relation with reaction time is plotted in figure 3. Increasing rate of the amount seemed to decrease with time of exposure, implying that the amount of coke deposition may be saturated at a certain value after some time.

Average Pt particle sizes were estimated by TEM observation before and after the CH_4/CO_2 reforming for 24 h and are summarized in table 3. Pt particle size before the reaction was decreased in the order:$(PtCe)/ZrO_2$, Pt/CeO_2, Pt/ZrO_2, $(Pt–Ce)/ZrO_2$. On the other hand, it was decreased in the order after the reaction:Pt/CeO_2, Pt/ZrO_2, $(PtCe)/ZrO_2$, $(Pt–Ce)/ZrO_2$. Pt particles on the catalysts, except for $(PtCe)/ZrO_2$, were found to be sintered during the CH_4/CO_2 reforming, and the sintering of the Pt particles was less extensive on $(PtCe)/ZrO_2$ and $(Pt–Ce)/ZrO_2$ than

Table 3
Physio-chemical properties of Pt catalysts before[a] and after the CH_4/CO_2 reforming[b]

Catalyst	BET surface area[a] (m^2 g^{-1})	Pt particle size (nm)	
		Before reaction[a]	After reaction[b]
$(Pt–Ce)/ZrO_2$	22	2.4	3.0
$(PtCe)/ZrO_2$	20	4.9	4.7
Pt/ZrO_2	32	2.9	6.0
Pt/CeO_2	12	3.1	59.5

[a] Measured after H_2 reduction at 1123 K.

[b] Measured after the reaction for 24 h.

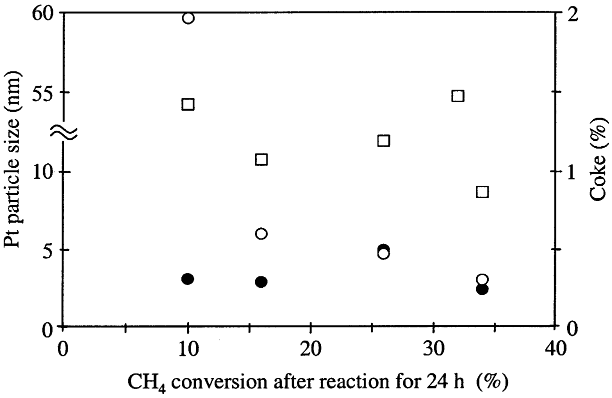

Figure 4. Pt particle sizes (•) before and (○) after CH_4/CO_2 reforming and amounts of coke over Pt catalysts versus (□) CH_4 conversion after the reaction for 24 h (reaction condition; $CH_4/CO_2 = 25/25$ ml min^{-1}; 1023 K; 2 MPa; 0.2 g catalysts).

those on the others. The order of the Pt particle size after the reaction appears to be in agreement with the order of the catalytic stability.

The amounts of coke deposited and Pt particle sizes are shown as a function of CH_4 conversion at 24 h in figure 4. The figure illustrates good correlations between the CH_4 conversion and Pt particle size after the reaction for 24 h. Therefore, we conclude that the difference of catalytic stability among the catalysts in the current work would be mainly ascribed to the difference of degree of Pt aggregation through catalyst preparation, reduction with H_2, and CH_4/CO_2 reforming. Note that (PtCe)/ZrO_2 deactivated slowly with time, although the catalyst did not show Pt aggregation during the reaction. The result indicates that catalytic deactivation is at least associated with coke deposition.

It has been clarified that the addition of CeO_2 to Pt/ZrO_2 (in different preparation methods) leads to suppression of Pt aggregation, and, consequently, the catalysts show stable activity at 2 MPa. In particular, the extent of Pt aggregation and the amount of coke deposition were least pronounced on the catalyst prepared by consecutive impregnation of Pt prior to CeO_2 on ZrO_2 ((Pt–Ce)/ZrO_2), which showed highest stability among the catalysts. Resasco and co-workers [14,15] reported that CeO_2 inhibited the aggregation of Pt supported on ZrO_2, prepared by Pt impregnation on CeO_2–ZrO_2. They mentioned that this resulted from high metal-support interfacial area, which is crucial for proceeding CH_4/CO_2 reforming [9,14,15]. In addition, CeO_2 is known to have a very high oxygen exchange capacity with redox mechanism between Ce^{4+} and Ce^{3+} [16] and, thus, precursor of the deposited coke can be removed efficiently by the mobile oxygen species activated on CeO_2. Another possible effect of CeO_2 can be destruction of large ensembles of Pt necessary for carbon deposition, which was described for Pt/TiO_2 [1,17]. Such positive influences would be maximized on (Pt–Ce)/ZrO_2, which was prepared with impregnation of CeO_2 on Pt/ZrO_2. We speculate that CeO_2 suppress Pt aggregation by anchoring Pt particle to ZrO_2 and resulted in high efficiency for preventing coke accumulation on the catalyst.

4. Conclusions

Pt/ZrO_2 with CeO_2 prepared by several methods (co-impregnation of Pt and CeO_2 on ZrO_2, and consecutive impregnation of Pt and CeO_2 on ZrO_2) had higher stability than that of Pt/ZrO_2 and Pt/CeO_2 in the CH_4/CO_2 reforming at 2 MPa. CeO_2 addition to Pt/ZrO_2 drastically increased the catalytic stability. The difference of the catalytic stability among the catalysts was mainly attributed to the difference of Pt aggregation through catalyst preparation, reduction with H_2, and CH_4/CO_2 reforming. In particular, (Pt–Ce)/ZrO_2 prepared by impregnation of CeO_2 on Pt/ZrO_2 showed the highest stability among the catalysts. This correlates with the facts that the extent of Pt aggregation and coking on the catalyst were minimized the most. It was proposed that CeO_2 suppress Pt aggregation by anchoring Pt particle to ZrO_2 on the catalyst and resulted in high efficiency for preventing coke accumulation on the catalyst.

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