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Effects of the addition of lanthana on the thermal stability of alumina-supported palladium

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Abstract

Promotional effects of lanthana on the catalytic property of Pd/Al_2O_3 toward methane combustion were examined. The results revealed that Pd/Al_2O_3 became active on raising the temperature above 767 K but its activity decayed considerably at high temperatures. Addition of La_2O_3 to the Pd/Al_2O_3 catalyst inhibited this activity decay. Hydrogen chemisorption and BET measurements revealed that the addition of La_2O_3 to Pd/Al_2O_3 not only enhanced the thermal stability of γ-Al_2O_3 but also retarded the supported Pd from sintering upon calcinations at $T > 923$ K. Temperature-programmed oxidation studies further demonstrated that the retardation in Pd sintering resulted from an increase in the bond strength of Pd–O. Therefore, the increase in the bond strength of Pd–O may account for the promotional effect of lanthana and the long lifetime of La-added Pd/Al_2O_3 catalyst in methane combustion.

1. Introduction

Catalytic combustion has a better efficiency towards very lean fuel–air mixture and produces less pollutant than conventional flame combustion [1]. Many studies have been focused on the development of material for combustion catalysts [2]. A good combustion catalyst should permit a high working temperature but it should have a low ignition temperature [3]. The superiority of Pd/Al_2O_3 catalysts for the catalytic combustion of methane has been well known for years [4,5]. However, they may lose their catalytic activity due to the desorption of oxygen from palladium at high combustion temperatures, and the oxygen desorbed catalyst cannot restore its catalytic activity toward CH_4 combustion until O_2 is readsorbed at low temperatures [6].

The sintering of alumina due to the transformation of γ-phase to α-phase is another source of activity decay of Pd/Al_2O_3 at high temperatures. Addition of La_2O_3 to Al_2O_3 is known [7–10] to raise the temperature required for the phase transformation. In this study, the effects of La_2O_3 on the property of Pd/Al_2O_3 catalyst were characterized by means of catalytic activity towards methane combustion, BET measurements, chemisorption of hydrogen, and temperature-programmed oxidation (TPO). We found that the addition of La_2O_3 to the Pd/Al_2O_3 catalyst not only enhanced the thermal stability of γ-Al_2O_3 but also inhibited the oxygen desorption from PdO and, therefore, retarded supported Pd from sintering at a high combustion temperature.

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2. Experimental

2.1. Sample preparation

Lanthana-modified Al_2O_3 was prepared via impregnating Al_2O_3 (Merck, 106 m^2/g) with an aqueous solution of lanthanum nitrate. The impregnated samples were subsequently dried overnight at 383 K, calcined at 723 K for 7.5 h and saved as carriers for preparing supported palladium catalysts. A portion of each sample was further calcined at temperatures higher than 723 K (for 4 h) to examine the effect of thermal treatment. Pd was introduced into various supports (Al_2O_3 and La_2O_3 modified Al_2O_3) via the incipient wetness technique with H_2PdCl_4. Impregnated catalysts were also dried overnight at 383 K and then calcined at 723 K for 7.5 h. These palladium catalysts are designated as fresh samples. 2Pd/6La–Al_2O_3, for example, indicates a catalyst containing 0.02 g of palladium and 0.06 g of La_2O_3 per 0.94 g of Al_2O_3. A portion of each fresh catalyst was further calcined at temperatures higher than 723 K for 4 h so as to examine the effects of thermal treatment on these palladium samples.

2.2. Adsorption measurements

BET surface areas were measured with physisorption of nitrogen at 78 K on samples pretreated with evacuation at 573 K. Dispersion of palladium was measured volumetrically via H_2 chemisorption on a vacuum system at 298 K utilizing a precision pressure gauge (Texas Instruments Model 145). Palladium catalysts were reduced in flowing H_2 at 573 K for 1 h and evacuated at 573 K for 1 h prior to chemisorption measurement.

2.3. TPO measurements

5% O_2 in He (7 ml/min) was employed as the carrier gas in the TPO experiments. The carrier gas flowed sequentially through the reference side of a thermal conductivity detector (TCD), the catalyst (in a quartz tube of 4 mm i.d.), a cell containing silica gel (to remove H_2O) and the sample side of the TCD. The temperature of the quartz tube was raised at a heating rate of 7 K/min from room temperature to 1173 K with an oven controlled by a temperature programmer. After reaching 1173 K, the temperature was cooled down to room temperature by turning off the power of the oven. Prior to the TPO measurement, each sample was pretreated with a flow of hydrogen/argon (10/90) at 1173 K to reduce the sample and to remove carbon dioxide absorbed in La_2O_3 [11].

2.4. Measurement of catalytic activity

The catalytic activity towards methane combustion was carried out in a reactor made of 4 mm i.d. quartz tubing in which a 0.06 g catalyst sample was mounted. The flow-rate of feed gas (comprising 1/120 v/v of CH_4/air) was regulated at 121 ml/min with mass flow controllers (Tylan, FC-280). The composition of outflow gas was monitored continuously by a flame ionization detector (FID) on raising the reactor temperature at a rate of 5 K min^{-1}.

The methane conversion($C/\%$) is defined as

$$C/\% = (1 - [I_t/I_r]) \times 100\% \qquad (1)$$

where I_t and I_r are the FID signal intensity measured at reaction temperature and room temperature, respectively.

3. Results and discussion

3.1. Catalytic activity

Fig. 1 compares the catalytic activities of a fresh 2Pd/Al_2O_3 sample with that of a fresh 2Pd/6La–Al_2O_3 sample on methane combustion. The reaction was carried out in a temperature-programmed system with a heating rate of 5 K min^{-1}. Apparently the 2Pd/6La–Al_2O_3 catalyst exhibits a lower initial catalytic activity than the 2Pd/Al_2O_3 catalyst mainly due to an increase in PdO bond strength at the presence of La_2O_3 (will be described later). A life test at 1133 K, however, found that the activity of the $2Pd/Al_2O_3$ catalyst decayed rapidly with time (showed in Fig. 2) while a high catalytic activity could be retained by addition of 6% La_2O_3 to the sample.

3.2. BET surface area measurements

Fig. 3 exhibits the surface area of supports (Al_2O_3 and $6La–Al_2O_3$) calcined at various temperatures. The surface area of both supports decreased with increasing the calcination temperature. For $T \leq 1173$ K, the addition of La_2O_3 decreased the surface area of the Al_2O_3 support, this may be due to the fact that a certain number of the pores of Al_2O_3 were plugged. While the surface area of the lanthana-modified Al_2O_3 became larger than that of pure Al_2O_3 upon severe calcination ($T \geq 1273$ K). Therefore, addition of

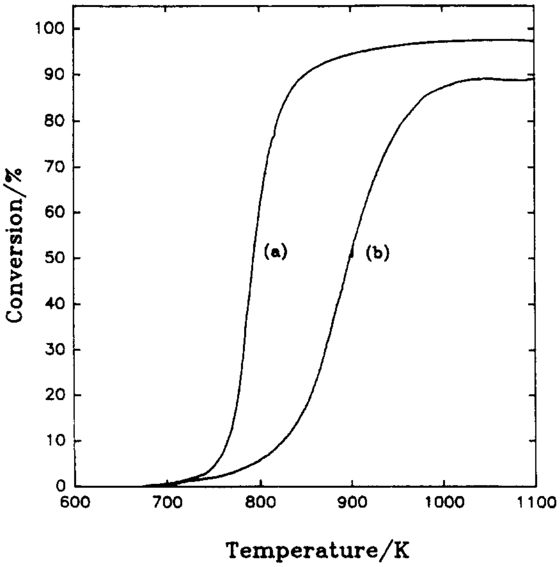

Fig. 1. The temperature dependence of CH_4 conversion on fresh catalysts: (a) $2Pd/Al_2O_3$, and (b) $2Pd/6La–Al_2O_3$.

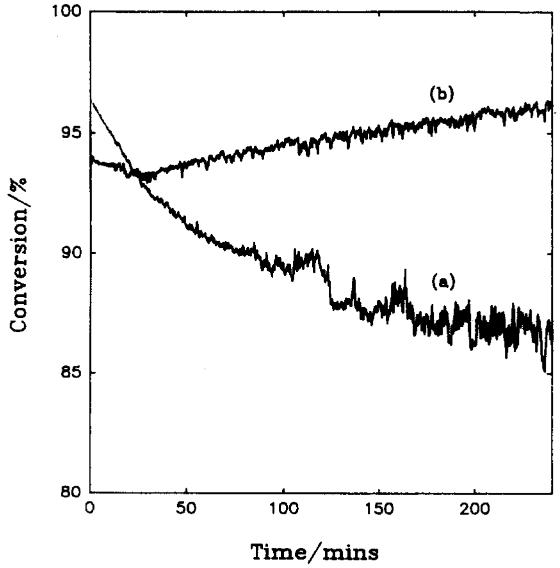

Fig. 2. A 4-h life test of fresh $2Pd/Al_2O_3$ (a), and $2Pd/6La–Al_2O_3$ (b) catalysts for catalytic combustion of CH_4 at 1133 K.

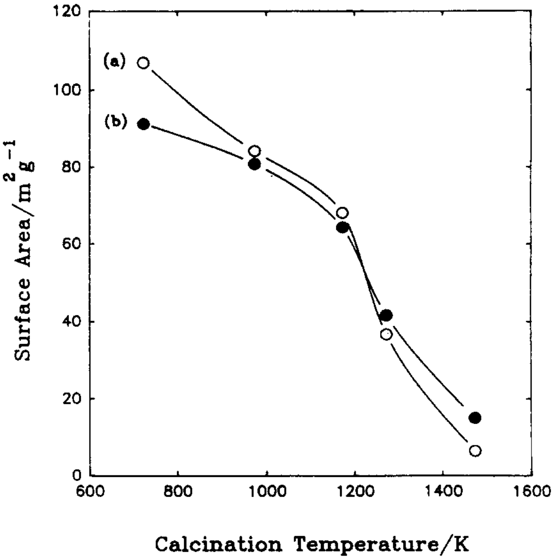

Fig. 3. Effect of calcination temperature on the BET surface area of (a) Al_2O_3, and (b) $6La–Al_2O_3$.

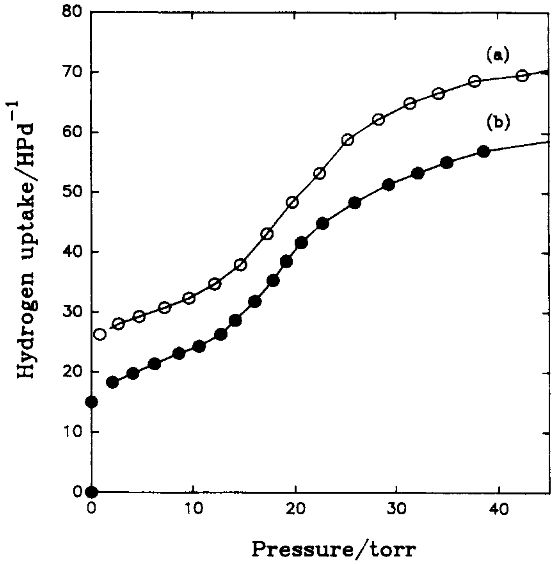

Fig. 4. Isotherms of hydrogen chemisorption on fresh samples: (a) $2Pd/Al_2O_3$, and (b) $2Pd/6La–Al_2O_3$.

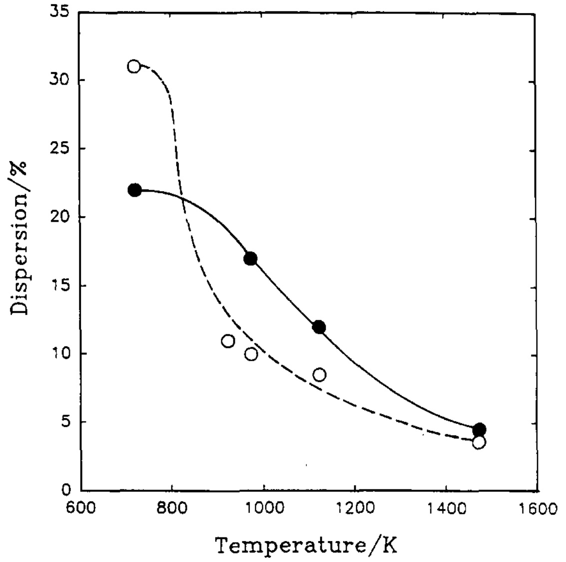

Fig. 5. Effect of 4 h calcination on Pd dispersion: (○) $2Pd/Al_2O_3$, and (●) $2Pd/6La\text{–}Al_2O_3$.

lanthana to Al_2O_3 tended to promote the thermal stability of Al_2O_3 on calcination at $T \geq 1273$ K.

3.3. Hydrogen chemisorption

Fig. 4 shows the isotherms of hydrogen chemisorption for the fresh $2Pd/Al_2O_3$ and the fresh $2Pd/6La\text{–}Al_2O_3$ catalysts. Each isotherm contains two distinct uptake stages. The first stage of the hydrogen uptake has been suggested in a previous study [12] to be due to the chemisorption on the surface Pd and the second stage was due to the absorption into the bulk of Pd crystallites, i.e.,

$$2Pd_s + H_2 \rightarrow 2Pd_s\text{–}H \quad (<10\ \text{Torr}) \qquad (2)$$

$$Pd_b + 0.3H_2 \rightarrow Pd_b\text{–}H_{0.6} \quad (>10\ \text{Torr}) \qquad (3)$$

where Pd_s denotes the surface palladium atom and Pd_b is the palladium atom in the bulk of the Pd metal crystallites. The dispersion of Pd could be estimated from the hydrogen uptake at $P_{H_2} = 10$ Torr in the obtained isotherms.

Fig. 5 summarizes the effects of the addition of La_2O_3 upon the metal dispersion of Pd catalysts calcined at different temperatures. Palladium on $2Pd/6La\text{–}Al_2O_3$ has a smaller initial (calcination at 700 K) dispersion than that on $2Pd/Al_2O_3$ because the $6La\text{–}Al_2O_3$ has a smaller surface area than the Al_2O_3 (Fig. 3). But the dispersion of palladium on the $2Pd/Al_2O_3$ abruptly decreased, from 31% to 11%, as the calcination temperature was raised to 923 K. This abrupt decrease in Pd dispersion may possibly have resulted from the decomposition of PdO around 923 K. This decomposition will be discussed in the TPO part of this report. Addition of 6% La_2O_3 to the $2Pd/Al_2O_3$ is observed in Fig. 5 to effectively inhibit the sintering of supported palladium in the temperature range of 800–1200 K.

3.4. TPO measurements

The TPO curves obtained from the fresh $2Pd/Al_2O_3$ sample (curve (a) of Fig. 6A) may be

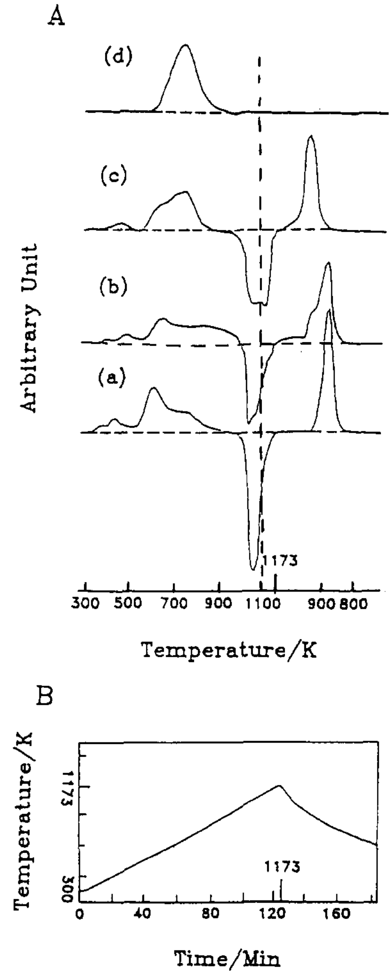

Fig. 6. (A) Effect of La_2O_3 on the TPO profiles of fresh samples: (a) $2Pd/Al_2O_3$, (b) $2Pd/6La\text{–}Al_2O_3$, (c) $2Pd/16La\text{–}Al_2O_3$, and (d) $2Pd/La_2O_3$. (B) Temperature profile of the TPO system.

roughly separated into three signals, i.e., a broad peak (S_1) of oxygen consumption on heating the sample from room temperature to around 930 K, a negative peak (S_2) of oxygen desorption during heating from around 930 K to 1173 K and a second peak (S_3) of oxygen consumption in the cooling phase. All of these three peaks can be explained with the following reversible reaction:

$$Pd + 1/2O_2 \Leftrightarrow PdO \qquad (4)$$

Pd supported on Al_2O_3 gradually becomes oxidized into PdO in the TPO system upon heating to around 930 K (S_1). However, the PdO formed became unstable at $T > 930$ K and was thermally decomposed to metallic Pd (S_2) according to the reverse of reaction (4). The decomposed Pd was reoxidized (S_3) by oxygen during the cooling phase with a peak of around 880 K. The temperature discrepancy between the S_2 and S_3 presents a hysteresis for the reversible reaction (4). This hysteresis has been recently investigated with TGA and has been suggested to affect the catalytic activity of Pd/Al_2O_3 towards CH_4 combustion [6].

Similar S_1, S_2 and S_3 signals were also observed in the $2Pd/Al_2O_3$ samples doped with La_2O_3 (curves (b) and (c) in Fig. 6A). A shift of S_2 and S_3 signals towards a higher temperature, however, was observed in the presence of lanthana. The degree of the shift obviously increased with the lanthana loading. In Pd/La_2O_3, where plain La_2O_3 was used as a support instead of Al_2O_3, the shift was so extensive that desorption of oxygen did not occur, as shown in the curve (d), where the highest temperature designed for our TPO experiments was 1173 K. These results imply that the Pd–O bond of PdO/La_2O_3 is stronger than that of Pd/Al_2O_3. Since oxygen-desorbed palladium crystallites tend to sinter at high temperatures [13], the observed shift of reaction (4) may also be used to explain why the $2Pd/6La–Al_2O_3$ exhibits (in Fig. 5) a higher Pd dispersion than the $2Pd/Al_2O_3$ after a calcination treatment at temperatures higher than 923 K.

Oxygen desorbed PdO/Al_2O_3 samples could not restore their catalytic activity toward CH_4 combustion until they re-adsorbed O_2 at low temperatures [6]. The increase in bond strength of Pd–O of PdO/Al_2O_3 via impregnating La_2O_3 consequently suggested that $Pd/La_2O_3–Al_2O_3$ can tolerate a severer combustion condition than Pd/Al_2O_3.

4. Conclusions

The effects of La_2O_3 upon the catalytic properties of Pd/Al_2O_3 in combustion reaction were investigated with BET measurement, H_2 chemisorption, and TPO techniques. Primary modifications observed included: (1) oxygen desorption from PdO and its transformation into Pd crystallites around 1050 K was retarded due to an increase in the bond strength of Pd–O; (2) the extent of Al_2O_3 sintering at $T > 1200$ K was also decreased and therefore, (3) the lifetime of $Pd/La–Al_2O_3$ catalysts toward catalytic combustion of CH_4 was significantly enhanced.

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