ELSEVIER

Catalysis Today 59 (2000) 87–93

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Promotion of methane combustion activity of Pd catalyst by titania loading

Tae-Gu Kang [a], Jong-Ho Kim [a], Sung Gyu Kang [b], Gon Seo [a,*]

[a] Department of Chemical Technology, The Institute for Catalysis Research, Chonnam National University, Kwangju 500-575, South Korea

[b] Korea Institute of Energy Research, Taeduk Science Town, Taejon 305-343, South Korea

Abstract

Methane combustion over Pd catalyst supported on KIT-1 mesoporous material was investigated. The catalytic activity of the Pd catalyst was considerably improved by titania loading. The stability of the Pd catalyst to the exposure at high temperature is also enhanced by titania loading. Titania which is chemically bonded with the skeletal of mesoporous material interacts with palladium co-loaded and suppresses the decomposition of palladium oxide; more active phase in the methane combustion compared to palladium metal, resulted in the improvement in the catalytic performance of the Pd catalyst. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Titania; Catalytic combustion; Methane; Mesoporous material

1. Introduction

Catalytic combustion of fuel is carried out with no flame at low temperature, so it is safer than a conventional burning system and more friendly to the environment due to reduction of NO_x and unburned hydrocarbon emissions [1,2]. As the burning temperature becomes lower, these advantages are more amplified. Therefore, highly active noble metals such as palladium and platinum are commonly used as active phases of combustion catalyst in order to achieve high activity even at low temperature [3,4]. Conventionally, alumina is used as a support due to its high thermal stability and strong interaction with metal, but in order to enhance activity and mass transfer, it is more efficient to use the support having a strong interaction with metal and large pores to achieve a high dispersion of metal and a negligible restriction to mass transfer.

Since the combustion of fuel generates heat, the stability of a combustion catalyst to high temperature is very important. The catalytic activity may be reduced due to sintering of metal, change in the chemical state of active species or fouling of support. The strong interaction between metal and support is helpful to retain the active phase of the combustion catalyst during its exposure to high temperature [5].

Mesoporous material synthesized using detergent as a template has uniform mesopore with a diameter ranging from 25 to 100 nm [5,6]. The volume of reactant per catalyst bed is usually large in the catalytic combustion, so the low restriction to mass transfer at the mesopore is helpful to treat combustion stream of high space velocity, resulting in a good catalytic performance. Furthermore, the fact that metal can be dispersed on mesoporous material with a high dispersion by ion-exchange method as well as zeolite promises a high catalytic activity with a small amount of precious

---

* Corresponding author. Tel.: +82-62-530-1876;
fax: +82-62-530-1899.
E-mail address: gseo@chonnam.chonnam.ac.kr (G. Seo)

0920-5861/00/$ – see front matter
PII: S0920-5861(00)00275-3

metal [7]. The low hydrothermal stability is considered to be a weak point for the application of mesoporous material as a catalyst support for the combustion, and the stability is considerably improved by inactivation of surface hydroxyl group by titania loading [8].

This paper is about the Pd catalyst supported on mesoporous material. The catalytic activity and stability of the Pd catalyst were considerably enhanced by titania loading as well as improvement of its hydrothermal stability. The impregnated state and promotion role of titania were discussed based on their characterization results and catalytic properties.

2. Experimental

Disordered mesoporous material (KIT-1) was synthesized from the gel of $6SiO_2$–1HTACl–$1.5Na_2O$–$4Na_4EDTA$–$0.15(NH_4)_2O$–$0.75Al_2O_3$–$350H_2O$ following Ryoo's procedure [9]. HTACl (25%, Aldrich) was used as templating material. Aluminum hydroxide (28%, Aldrich) was added to reactant gel to get KIT-1 mesoporous material having Si/Al ratio of 40. After synthesis at 98°C for 2 days, pH of synthesizing solution was adjusted to 10.2. The pH adjustment was carried out twice. Mesoporous material was obtained after 4 days of hydrothermal synthesis and calcined at 550°C for 4 h in air flow of 50 ml min^{-1}. Cation was ion exchanged to ammonium ion by ammonium nitrate solution. Calcination at 550°C produced proton-form mesoporous material.

Palladium was impregnated on KIT-1 mesoporous material by incipient wetness method with $Pd(NH_3)_4Cl_2$ (99%, Aldrich) solution. Pd catalyst was obtained after calcination at 550°C for 4 h following by the reduction at 320°C for 2 h in hydrogen flow of 30 ml min^{-1}. Titania was loaded on Pd catalyst through a liquid-phase reaction between dehydrated mesoporous material and titanium *tert*-butoxide (99%, DuPont) in anhydrous ethanol solvent (99.5%, Duksan). After washing with anhydrous ethanol to remove non-reacted titanium *tert*-butoxide, the sample was calcined at 550°C for 4 h in air to remove organic template and convert titanium alkoxide to titania.

The X-ray diffraction pattern of mesoporous material was recorded on a X-ray diffractometer (Rigaku, D/MAX-1200) with Cu Kα X-ray at 40 eV and 20 mA conditions. An SEM (JEOL, JSM-5400) with an EDX attachment (Noran, Series II) was used to determine the loading amount of titania. The position and chemical state of palladium and titania were investigated by X-ray photoelectron spectroscopy (XPS, Surface Science 2701 MX-Probe) with Al Kα X-ray at 10 kV and 8 mA conditions. Beam size was 300 μm and the surface was sputtered by an Ar^+ ion beam with the sputtering speed of 0.5 Å s^{-1} (as SiO_2). Nitrogen adsorption isotherm was recorded on a home-built volumetric adsorption apparatus at liquid nitrogen temperature. Pore size distribution was calculated following the suggested procedure [10]. Hydrogen uptakes of the Pd catalysts were measured by the volumetric adsorption apparatus at 100°C to determine the adsorbed hydrogen at surface only [11].

Temperature programmed desorption (TPD) profiles of oxygen from Pd catalyst and titania-loaded Pd catalyst were recorded on a TPD apparatus (Pulse ChemiSorb 2705) from room temperature to 600°C with a ramp rate of 10°C min^{-1}. The catalyst was reduced at 320°C for 1 h in hydrogen flow of 30 ml min^{-1}. Then, oxygen was adsorbed on the sample under a helium flow of 30 ml min^{-1} containing 3% of oxygen. The amount of oxygen desorbed from the sample was determined with a thermal conductivity detector (TCD).

The desorption behavior of carbon monoxide on Pd catalyst and titania-loaded Pd catalyst was examined by FT-IR (BIORAD, FTS 175S) with an in situ cell (GREASEBY, SPECAC) at a resolution of 4 cm^{-1}. A self-supporting wafer of a 10 mg sample was evacuated at 300°C for 1 h and exposed to 20 kPa of carbon monoxide at 30°C for 20 min. The sample was heated to 550°C with a ramp rate of 20°C min^{-1} after evacuation at 30°C.

Methane combustion reaction was carried out at an atmospheric flow microreactor system. A quartz tube reactor (OD $\frac{1}{2}$ in.) was charged with 0.26 g of the catalyst. A reactant comprising of methane and air with a volume ratio of 1:99 was supplied to the reactor and a WHSV was adjusted at 10 000 h^{-1}. Conversion was defined by the fraction of methane consumption. Combustion reaction was investigated from 200 to 800°C in 50°C intervals. A downward test to examine the thermal stability of the catalyst was followed by a reverse of the upward test. Reaction products were analyzed by using a gas chromatograph (HP 5890) equipped with a Porapak Q column.

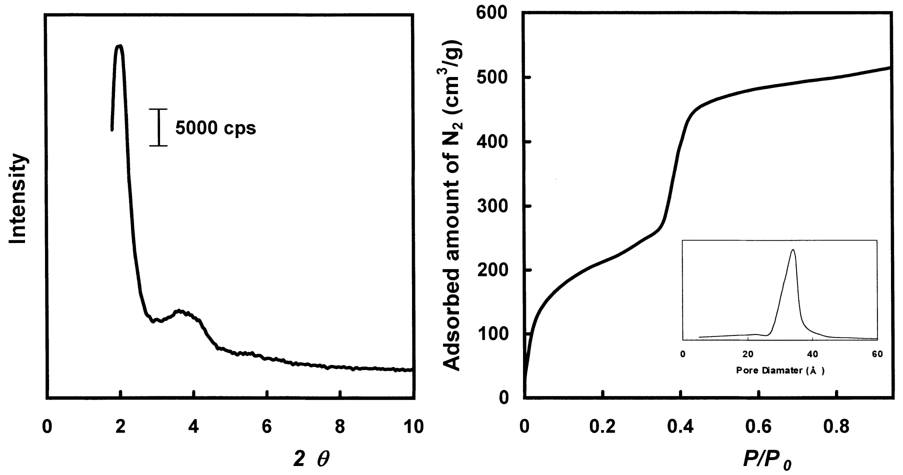

Fig. 1. XRD pattern and nitrogen adsorption isotherm of the prepared KIT-1 mesoporous material.

3. Results and discussion

Mesoporous material shows a sharp diffraction peak at low angle in X-ray diffraction pattern due to its mesopore. A sharp peak at 2° was observed from KIT-1 mesoporous material prepared in this study as shown in Fig. 1. The weak and not-resolved peak at 4° is a characteristic of disordered mesoporous materials [9]. The nitrogen adsorption isotherm also shows a capillary condensation at 0.4 of P/P_0, indicating the presence of mesopore. The average diameter of mesopores was estimated at 35 Å using BJH method [10]. The BET surface area was 1100 $m^2\,g^{-1}$, similar to the reported one [6], supposing a high purity of the prepared mesoporous material.

Impregnation of palladium on KIT-1 mesoporous material by 2 wt.% caused a partial collapse of pore as shown in Fig. 2. The adsorption amount of nitrogen on mesoporous material was reduced by palladium loading. On the contrary, the adsorption amount of nitrogen did not decrease by titania loading, and even the loading amount was high at 10 wt.%. Titanium alkoxide reacts with the hydroxyl group of pore wall and converts to titania in the calcination step. Since titania loading did not bring about the decrease in the adsorption amount of nitrogen, the considerable decrease in the adsorption amount with palladium loading might be related to the reduction treatment. The poor hydrothermal stability of mesoporous material causes a partial collapse of pore with the reduction treatment producing water vapor.

The fact that titania is chemically bonded on the pore surface with a tetrahedral coordination was reported previously in our paper [12]. Thus, any diffraction peaks relating to crystalline titania were not observed in X-ray diffraction patterns of titania-loaded Pd catalysts. The absorption band of 230 nm in UV–Vis spectra due to titania loading confirmed the tetrahedral coordination of titanium,

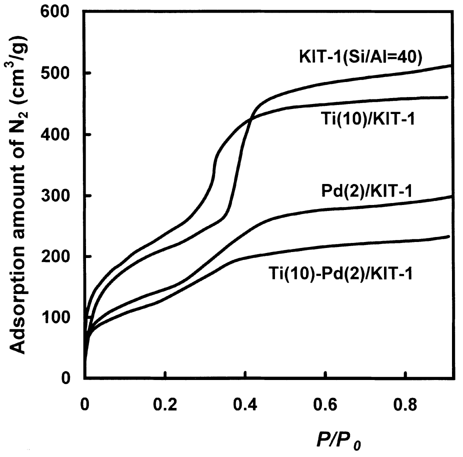

Fig. 2. Nitrogen adsorption isotherms of KIT-1, Pd(2)/KIT-1, Ti(10)/KIT-1 and Ti(10)–Pd(2)/KIT-1 catalysts.

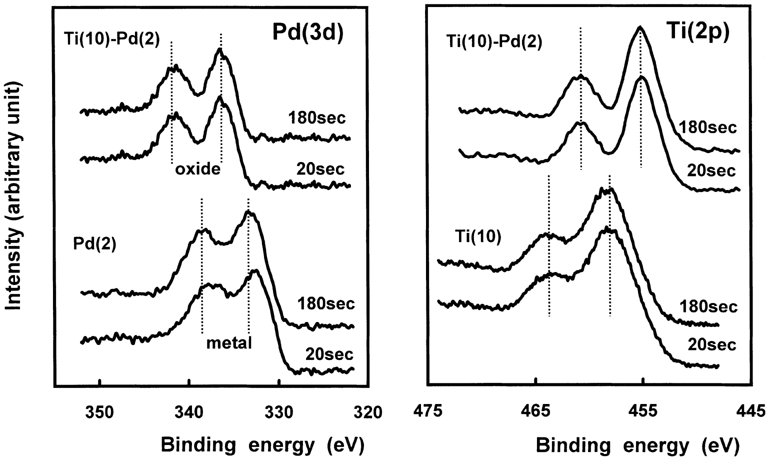

Fig. 3. XPS spectra of Pd(2)/KIT-1 and Ti(10)–Pd(2)/KIT-1 catalysts after sputtering for 20 and 180 s.

excluding the formation of bulk titania such as anatase or rutile [12,13]. XANES spectrum of titania-loaded Pd catalyst was the same with that of titania-loaded mesoporous material reported previously [12], indicating that the present palladium did not affect the coordination state of titania.

XPS spectra of palladium and titanium suggest the interaction between palladium and titania (Fig. 3). The Pd 3d peaks from the Ti(10)–Pd(2)/KIT-1 catalyst reveal that palladium is dispersed as palladium oxide, while metallic palladium is observed on the Pd(2)/KIT-1 catalyst. The reduction of palladium oxide was suppressed by the interaction between titania and palladium. The binding energy of titanium $2p_{3/2}$ peak was 458.4 eV on the Ti(10)/KIT-1 catalyst, while that shifted to 455.2 eV on the Ti(10)–Pd(2)/KIT-1 catalyst. The shift to low value in the binding energy indicates that titania prefers to reduce partially with palladium loading, supposing the electronic interaction between palladium and titania. The XPS peak intensity of titanium did not alter with sputtering from titania-loaded Pd catalyst as expected from our previous paper, indicating that titania was distributed in pore as well as the external surface [12].

The combustion activities of KIT-1 mesoporous material and titania-only loaded catalysts are very low as shown in Fig. 4. The temperature for 50% conversion in the methane combustion was above 600°C on the KIT-1 and Ti(10)/KIT-1 catalysts. Although titanium-loaded zeolite is known as an oxidation catalyst, the enhancement of the combustion activity by titania loading is negligible. However, the temperature for 50% conversion was lowered to about 500°C with palladium loading of 0.5%. The temperature was gradually lowered by increasing the loading amount of palladium to 400°C on the Pd(1.0)/KIT-1 catalyst. But further enhancement in the catalytic activity was not observed even by increasing the palladium loading to 2.0%. Although the increase in the activity with the loading amount of palladium is limited to

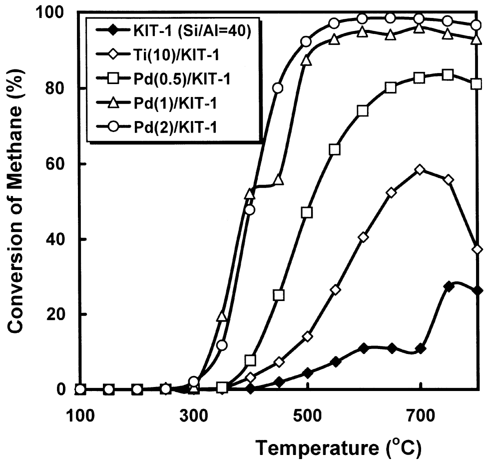

Fig. 4. Comparison of catalytic activity of KIT-1, Ti(10)/KIT-1, Pd(0.5)/KIT-1, Pd(1)/KIT-1 and Pd(2)/KIT-1 catalysts in the methane combustion.

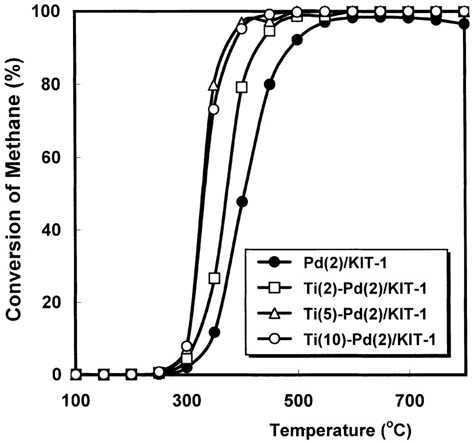

Fig. 5. Methane conversion on the Pd(2)/KIT-1 catalysts with different loadings of titania.

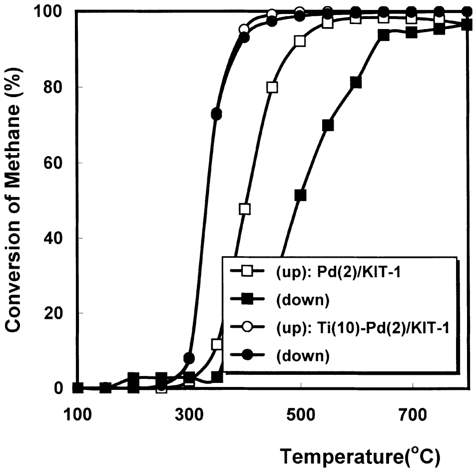

Fig. 6. Comparison of catalytic activity at the upward and downward test of Pd(2)/KIT-1 and Ti(10)–Pd(2)/KIT-1 catalysts in the methane combustion.

1.0%, it is certain that palladium is the active phase responsible for the catalytic combustion.

The combustion activity of Pd/KIT-1 catalyst was considerably improved by titania loading. The temperature for 50% methane combustion was lowered to 300°C on the Ti(5)–Pd(2)/KIT-1 catalyst as shown in Fig. 5. Since the intrinsic activity of titania on the combustion is negligible, the improvement in the combustion activity of the Pd catalyst by titania loading is caused by the interaction between palladium and titania, not by loaded titania itself. The combustion activity was gradually improved by titania loading within the loading amount of 5%, so the Ti(10)–Pd(2)/KIT-1 catalyst shows similar activity to the Ti(5)–Pd(2)/KIT-1 catalyst.

The other essentially required property of a combustion catalyst, besides the high catalytic activity, is the stability in the catalyst performance to the variance in the combustion condition. The stability is usually examined at the upward and downward tests. Downward test reflects the degradation of the catalytic activity with the exposure to high temperature. A large difference between conversion profiles of upward and downward tests indicates a poor stability with the change in the reaction condition. The conversion profiles of the upward and downward tests on the Pd(2)/KIT-1 catalyst are not coincident as shown in Fig. 6. The conversion profile of the downward test shifted to high temperature compared to that of the upward test, indicating loss of activity due to the exposure to high temperature. However, an irreversible deactivation of the catalyst by sintering or fouling is not considered, because the repeated run of the upward test was followed the first run with a good accord. The possible cause for low activity at the downward test is ascribed to the reduction of palladium oxide due to decomposition at high temperature. This deduction is based on the fact that palladium oxide is more active than palladium metal in the methane combustion and is decomposed to palladium metal at high temperature [2].

On the other hand, both conversion profiles at the upward and downward tests on the Pd catalyst with titania loading [Ti(10)–Pd(2)/KIT-1] are nicely coincident. There is no decrease in the activity at downward test, indicating that thermal stability of the Pd catalyst is significantly improved by titania loading. The decomposition of palladium oxide is suppressed with the interaction between titania and palladium.

The hydrogen uptake on Pd catalyst varies with the oxidation state of palladium. Additional hydrogen is required to remove surface oxygen of palladium oxide compared to palladium metal. The amount of hydrogen uptake of the Pd catalysts with titania loading and the dispersion of palladium obtained from hydrogen uptake are summarized in Table 1. The dispersion of palladium on the Pd catalyst increases with titania loading, indicating the retention of palladium oxide on the titania-loaded Pd catalyst. Titania inhibits the

Table 1
The amount of hydrogen uptake and the palladium dispersion of Pd(2)/KIT-1 catalysts with different loadings of titania

Catalyst Catalyst	Amount of hydrogen uptake ($cm^3\,g^{-1}$)	Dispersion of palladium
Pd(2)/KIT-1	1.74	0.14
Ti(2)–Pd(2)/KIT-1	2.56	0.25
Ti(5)–Pd(2)/KIT-1	2.68	0.26
Ti(10)–Pd(2)/KIT-1	3.05	0.29

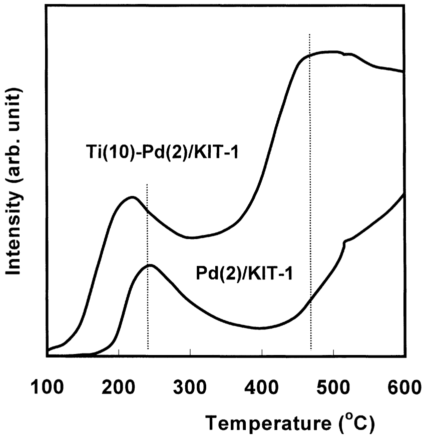

Fig. 8. Oxygen TPD profiles from Pd(2)/KIT-1 and Ti(10)–Pd(2)/KIT-1 catalysts.

reduction of palladium, resulting in the improvement in the stability of palladium oxide.

Fig. 7 shows the adsorption behavior of carbon monoxide over Pd(2)/KIT-1 and Ti(10)–Pd(2)/KIT-1 catalysts. Three absorption bands are observed at 1690, 1710 and 1628 cm^{-1} on Pd(2)/KIT-1 catalyst after the evacuation of 30°C. The intensities of these absorption bands decrease by increasing the evacuation temperature. On the other hand, on Ti(10)–Pd(2)/KIT-1 catalyst, only one absorption band at 1628 cm^{-1} is observed. The intensity of this band is high on Ti(10)–Pd(2)/KIT-1 catalyst, indicating the increase of available surface oxygen as adsorption sites for carbon monoxide by titania loading. Although it is difficult to deduce the adsorbed form of carbon monoxide from this finding, it is clear that the adsorbed state of oxygen on palladium changes with the loading of titania.

The TPD profiles of oxygen are distinct from the loading of titania as shown in Fig. 8. On the Pd(2)/KIT-1 and Ti(10)–Pd(2)/KIT-1 catalysts, two desorption peaks, one at 210–230°C (*l*-peak) and the other at above 450°C (*h*-peak) are observed. The peak area of the *h*-peak increases with the loading of titania, indicating the increase in the amount of oxygen adsorbed on the catalyst surfaces. Furthermore, the *l*-peak position shifts to lower temperature by the loading of titania. It can be understood that the amount of oxygen adsorbed on Ti(10)–Pd(2)/KIT-1 catalyst is large and this oxygen reacts easily with methane compared to that of Pd(2)/KIT-1 catalyst.

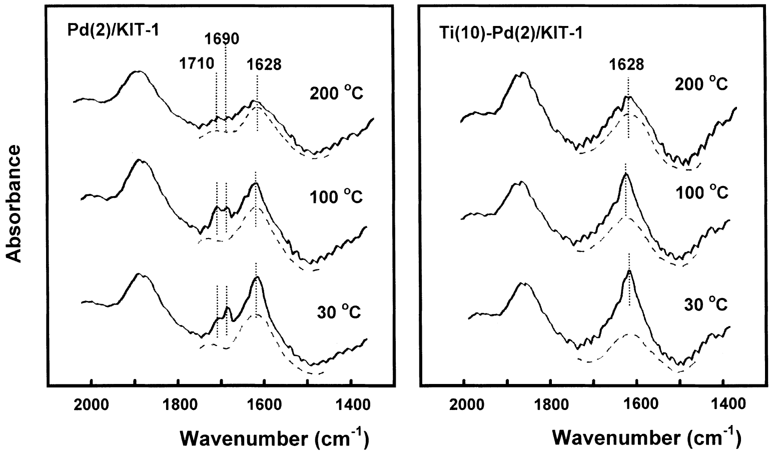

Fig. 7. IR spectra of Pd(2)/KIT-1 and Ti(10)–Pd(2)/KIT-1 catalysts evacuated at various temperatures after exposure to carbon monoxide. Dotted lines denote evacuated catalysts at 300°C.

Titania loaded on mesoporous material by liquid-phase reaction of titanium alkoxide is dispersed on pore wall amorphously, but has a tetrahedral coordination like silicon atoms which are composing the framework [12]. The improvement in the combustion activity and stability of the Pd catalyst by titania loading is ascribed by the interaction between palladium and titanium through oxygen. Highly stable titania suppresses the reduction of palladium oxide to metallic palladium. Since palladium oxide is more active than palladium metal in the methane combustion, maintenance of palladium oxide enhances the combustion activity. The interaction between palladium and titania suppresses the decomposition of palladium oxide even at high temperature, improving the stability of Pd catalyst with titania loading.

Application of mesoporous material as a support for a combustion catalyst is a good example emphasizing the availability of its regular mesopore. Furthermore, promotion of combustion activity and stability of the Pd catalyst by titania loading increases its applicability to combustor operating at medium temperature.

4. Conclusion

The catalytic activity and stability of Pd catalyst supported on KIT-1 mesoporous material were considerably enhanced by titania loading. This improvement is ascribed to the interaction between palladium and titania, suppressing the decomposition of palladium oxide at high temperature.

Acknowledgements

This work was financially supported by the Korea Institute of Energy Research.

References

[1] J.J. Chen, E. Ruckenstein, J. Phys. Chem. 85 (1981) 1606.
[2] T.R. Baldwin, R. Burch, Catal. Lett. 6 (1990) 131.
[3] A.K. Neyestanaki, N. Kumar, L.-E. Linfors, Fuel 74 (1995) 690.
[4] R. Burch, P.K. Loader, Appl. Catal. B 5 (1994) 149.
[5] J.S. Beck, R.F. Socha, D.S. Shihabi, J.C. Vartuli, US Patent 5 143 707 (1992).
[6] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[7] J.-H. Lee, D.L. Trimm, Fuel Process. Technol. 42 (1995) 339.
[8] T.-G. Kang, J.-H. Kim, G. Seo, H.-C. Park, Hwahak Konghak 36 (1998) 364.
[9] J.M. Kim, J.H. Kwak, S. Jun, R. Ryoo, J. Phys. Chem. 99 (1995) 16742.
[10] J.M. Thomas, W.J. Thomas, Principles and Practice of Heterogeneous Catalysis, VCH, Weinheim, 1997, p. 267.
[11] D.J. Suh, T.-J. Park, S.-K. Iim, J. Catal. 149 (1994) 486.
[12] W.S. Ahn, D.H. Lee, T.J. Kim, J.-H. Kim, G. Seo, R. Ryoo, Appl Catal. A 181 (1999) 39.
[13] C.B. Dart, C.B. Khouw, H.-X. Li, M.E. Davis, Microporous Mater. 2 (1994) 425.