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Pd–Pt bimetallic catalyst supported on SAPO-5 for catalytic combustion of diluted methane in the presence of water vapor

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The examination of the combustion of a trace amount of methane over Pd-ion-exchanged silicoaluminophosphate-5 (Pd-SAPO-5) at low temperature in the presence of water vapor reveals that water vapor strongly depresses methane combustion and causes a significant decrease in catalytic activity with time. The newly prepared bimetallic catalyst Pd–Pt-SAPO-5, on the other hand, shows higher performance for methane combustion under similar conditions.

Keywords: methane, combustion, water vapor, ion-exchanged SAPO, Pd–Pt bimetal

1. Introduction

In the past decade, various systems using a lean-burn natural gas engine have attracted considerable attention because of their cleanness and economy. However, exhaust gas from a lean-burn natural gas engine contains a trace amount of unburned methane. From the view point of both environmental protection and energy efficiency, the unburned methane is desired to be completely oxidized by using catalysts. Pd/Al_2O_3 catalysts have been well known to exhibit high performance for catalytic combustion of methane [1], but they are not so effective at low temperature compared to Pd-zeolite catalysts [2].

Recently, Ishihara et al. reported that a Pd-SAPO-5 catalyst is superior for methane combustion at low temperature compared to Pd/Al_2O_3 and Pd-zeolite catalysts, and furthermore, it has an excellent thermal stability [3]. Thus, Pd-SAPO-5-based catalysts are expected to be applied to the oxidation of diluted methane under exhaust gas temperatures. However, it would be a serious problem that methane combustion over Pd catalysts is strongly inhibited by the presence of water vapor in exhaust gas, as reported in literature [2,4–6]. Cullis et al. suggested that the inhibitory effect of water vapor is due to the formation of $Pd(OH)_2$ on the surface [7]. Since SAPO is known to have a hydrophilic property, water vapor might easily cause a decrease in activity of Pd-SAPO-5-based catalysts. From a practical point of view, however, the development of effective catalysts for combustion of methane under exhaust gas conditions where water vapor coexists is awaited, and some modifications of Pd-SAPO-5-based catalysts might be required for.

In the present study, we examined diluted methane combustion over several ion-exchanged SAPO catalysts under nearly practical reaction conditions, i.e., in the presence of 10% water vapor together with carbon dioxide and carbon monoxide. Here, the carbon monoxide was oxidized completely under the examined temperatures, as we confirmed separately. The activity of the examined catalysts toward the methane combustion was compared on a per gram basis, and the durability was evaluated at 673 K, from a practical point of view.

2. Experimental

The catalysts examined in the present study are listed in table 1. SAPO-5 (Mizusawa Industrial Chemicals, Ltd., surface area is 321 m^2/g), -11 and -34 (UOP Inc.) were used after calcination at 873 K for 6 h. SAPO was ion-exchanged at 353 K for 12 h using an aqueous solution of corresponding metal salts, such as $M(NH_3)_4(OH)_2$ ($M = Pd$, Pt) and $M'(NH_3)_6(OH)_3$ ($M' = Rh$, Ir). Ion-exchanged SAPO was filtered, washed and then dried at 383 K for 12 h. In suc-

Table 1
List of catalysts.

Catalyst	Metal loading (wt%)				Metal dispersion (%)
	Pd	Pt	Rh	Ir	
Pd-SAPO-5	1.13	–	–	–	16.7
Pd-SAPO-11	1.10	–	–	–	–
Pd-SAPO-34	1.11	–	–	–	–
Pt-SAPO-5	–	1.26	–	–	4.9
Pd–Pt-SAPO-5	1.06	1.11	–	–	10.4
Pd–Rh-SAPO-5	0.98	–	0.54	–	–
Pd–Ir-SAPO-5	0.99	–	–	0.82	–
Pd/Al_2O_3	0.95	–	–	–	–

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cession, it was reduced at 573 K for 3 h in a hydrogen flow and calcined at 873 K for 6 h in an oxygen flow. Pd/Al_2O_3 was prepared by an impregnation method using an aqueous solution of $Pd(NH_3)_4(OH)_2$ and Al_2O_3 (JRC-ALO-1 obtained from the Committee on Reference Catalyst of the Catalyst Society of Japan [8,9], surface area is 160 m^2/g), followed by drying, reducing and calcining as mentioned above. The dispersion of metal was estimated by the standard CO-pulse method recommended by the Catalyst Society of Japan [10]. Metal loading was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The catalytic test was carried out using a conventional continuous-flow reactor at atmospheric pressure and a powdery catalyst which was pelleted and then crushed into 16–60 mesh granular form. The granular catalyst (0.1 g) was dispersed in 0.2 g of fused quartz grains to prevent scattering and packed in a quartz tube with an inside diameter of 10 mm, at the center of which a quartz tube with an outside diameter of 6 mm was installed to cover the thermocouple, so as to touch the catalyst layer. Before the test, the packed catalyst was calcined at 873 K for 2 h in an air flow. After cooling to the desired temperature, the model exhaust gas consisting of CH_4 (4000 ppm), CO (500 ppm), CO_2 (5%), O_2 (10%), H_2O (10%), and N_2 (balance) was supplied at a flow rate of 5000 ml/h.

3. Results and discussion

The methane conversion over the Pd-SAPO-5 and Pd/Al_2O_3 catalysts as a function of temperature is shown in figure 1. In the absence of water vapor, the Pd-SAPO-5 catalyst showed higher activity on a per gram basis than the Pd/Al_2O_3 catalyst, and the reaction was completed at near 673 K, 75 K lower than in the case of the Pd/Al_2O_3 catalyst. On the other hand, in the presence of water vapor, the conversion was significantly reduced and each curve was shifted to the higher-temperature side. In the case of the Pd-SAPO-5 catalyst, a reaction temperature of 660 K was required to complete the reaction, 55 K higher than in the absence of water vapor. A similar drop due to water vapor was observed in the case of the Pd/Al_2O_3 catalyst. It is obvious that the Pd-SAPO-5 catalyst shows higher activity on a per gram basis than the Pd/Al_2O_3 catalyst, even under the conditions where water vapor coexists. A few Pd-SAPOs other than Pd-SAPO-5, such as Pd-SAPO-11 and -34, were examined and eventually the activity was found to be in the order of Pd-SAPO-5 $>$ -11 $>$ -34, which is in accordance with other reports on the catalytic activity of SAPOs toward several reactions of hydrocarbons [3,11,12].

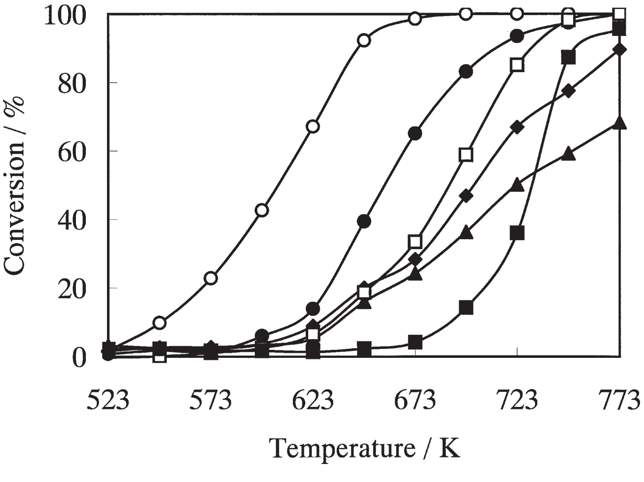

Figure 1. Methane conversion over Pd-SAPO-5 (●, ○), Pd-SAPO-11 (◆), Pd-SAPO-34 (▲) and Pd/Al_2O_3 (■, □) in the presence (closed symbols) and absence (open symbols) of water vapor as a function of temperature. The test was started after the temperature was lowered to 523 K.

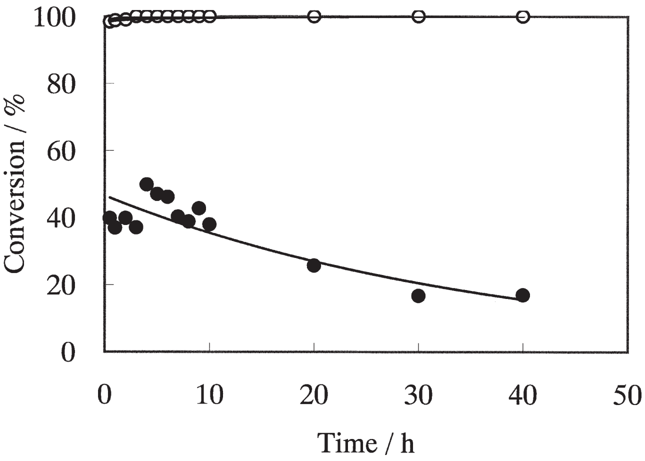

Figure 2. Time dependence in methane conversion over Pd-SAPO-5 at 673 K in the presence (●) and absence (○) of water vapor. The test was started after the temperature was lowered to 673 K.

In figure 2, the time dependence of methane conversion over the Pd-SAPO-5 catalyst at 673 K is shown. In the absence of water vapor, ca. 98% of the methane was oxidized at the initial stage of the test (1–2 h). After that, the conversion rose to 100% and was kept up even after 40 h. The phenomenon of activity rising with time has been observed in methane combustion over supported Pd catalysts [13–15]. On the other hand, in the presence of water vapor, the conversion was significantly decreased from ca. 40 to ca. 17%, and the final conversion relative to the initial one was almost half of it. The dispersion of Pd particles was 16.7% before the reaction, and fell to 7.0 and 6.1% after the test for 40 h in the absence and presence of water vapor, respectively. Thus, the decrease in activity with time is not due to the sintering of Pd particles, but possibly due to other morphological changes in Pd particles, such as the formation of $Pd(OH)_2$ [7].

To improve the durability in the presence of water vapor, the Pd–Pt-, Pd–Rh- and Pd–Ir-SAPO-5 catalysts were further examined. Similar noble metal addition has so far been employed for oxidation of hydrocarbons including methane over alumina-supported Pd catalysts [16–19]. Figure 3 shows the time dependence of methane conversion over these Pd-based bimetallic catalysts as well as Pt-SAPO-5 for comparison. In the case of the Pd–Pt-SAPO-5 catalyst, the conversion was ca. 55% at the initial stage, slightly

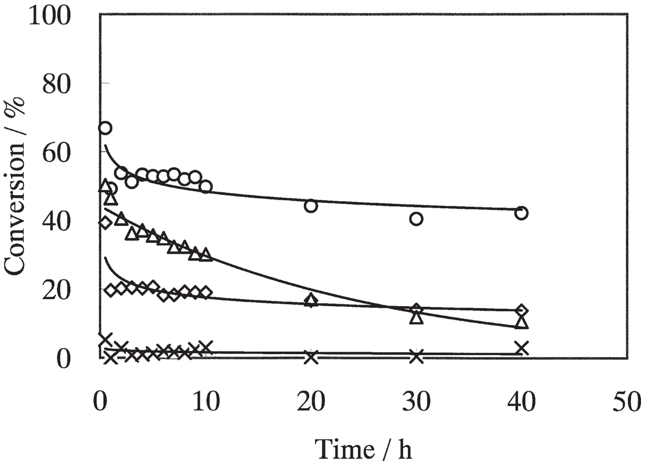

Figure 3. Time dependence in methane conversion over Pd–Pt-SAPO-5 (○), Pd–Rh-SAPO-5 (◊), Pd–Ir-SAPO-5 (△) and Pt-SAPO-5 (×) at 673 K in the presence of water vapor. The test was started after the temperature was lowered to 673 K.

higher than in the case of the Pd-SAPO-5 catalyst. At the final stage, the conversion was still above 40% and any further deactivation was not observed. Since the Pt-SAPO-5 catalyst hardly showed any activity for methane oxidation, the high durability of the Pd–Pt-SAPO-5 catalyst might be due to a synergistic effect of Pd and Pt. On the other hand, both at the initial and final stages of the test, the Pd–Rh-SAPO-5 catalyst showed less activity than the Pd-SAPO-5 catalyst, and the Pd–Ir-SAPO-5 catalyst showed almost the same activity as the Pd-SAPO-5 catalyst. Accordingly, the synergetic effect of noble metals lowering the decrease in activity due to water vapor with time is especially found in the combination of Pd and Pt. Burch et al. reported on the trend in activity of Pd and Pt catalysts in combustion of hydrocarbons from the viewpoint of the produced water vapor [20], in which they suggested that Pd catalysts are poisoned by water vapor more easily than Pt catalysts; thus, Pd and Pt catalysts show higher activity for oxidation of methane and higher hydrocarbons, respectively. In this aspect, although the details are not yet known, the synergetic effect of the newly prepared bimetallic catalyst Pd–Pt-SAPO-5 might be resulted from the high activity of Pd toward methane and the resistibility of Pt toward water vapor.

In conclusion, catalytic activity of Pd-SAPO-5 was significantly decreased with time under model exhaust gas conditions, where the temperature is lower and water vapor coexists; on the other hand, a Pd–Pt-SAPO-5 catalyst showed higher durability under similar conditions because of a synergistic effect of Pd and Pt. It was demonstrated that Pd–Pt-SAPO-5 would be a promising catalyst for combustion of diluted methane under real exhaust gas conditions.

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