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The effect of mass transfer on the catalytic combustion of benzene and methane over palladium catalysts supported on porous materials

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Abstract

Catalytic combustion of benzene and methane over palladium catalysts supported on FAU and MOR zeolites and MCM-41 and KIT-1 mesoporous materials were studied to illustrate the effect of pore size and shape of supports on their catalytic activities. The palladium catalysts supported on mesoporous materials showed high activity and a steep increase in the conversion of benzene with rising temperature. The low activity of palladium catalysts supported on FAU zeolite was ascribed to mass transfer limitation. However, conversion profiles of methane on palladium catalysts were similar, although their supports were different as zeolites and mesoporous materials. The catalytic behavior of palladium catalysts in the combustion of benzene and methane was explained by the diffusion properties of fuels in the pores of zeolites and mesoporous materials.

Keywords: Catalytic combustion; Benzene; Methane; Palladium; Zeolite; Mesoporous material; Diffusion

1. Introduction

The increase in the amount of chemicals used in industry and at home brings about frequent exposures of humans to harmful chemicals. Among various chemicals, volatile organic compounds (VOC) are considered to be the most harmful because of their high vapor pressure and toxicity [1]. Nevertheless, the regulation of VOC content in the air is not easy because they are discharged from a variety of sources. Because of this, the minimization of VOC discharge from industries which use a large amount of organic solvents including various aromatic compounds, is a necessary measure in order to maintain clean air.

VOC can be removed by using several methods: absorption, adsorption, incineration, photodecomposition, and catalytic combustion [2,3]. Practical applications of these removal methods are essentially dependent on the type of VOC, tolerance limits, and operating budgets. However, catalytic combustion is considered to be a preferable removal method of VOC composed of carbon and hydrogen because of its high feasibility based on no requirement of further treatment, high removal efficiency, and low operating costs. Active combustion catalysts lower burning temperatures and enhance combustion stability, further enhancing its feasibility.

Since noble metals are active for catalytic combustion of hydrocarbons even at low temperatures, they

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are employed as active phases for the catalytic combustion of aliphatic and aromatic hydrocarbons [4]. Supports with a high surface area are feasible to obtain a large amount of exposed noble metal atoms even with a small loading [5]. Since surface areas of porous supports are, however, essentially correlated to their pore sizes, a high surface area is obtained only on the support with an extremely large number of ultrafine micropores. This means that a support with a high surface area usually has small pores inevitably inducing mass transfer limitation, especially in the catalytic combustion of aromatic compounds of large molecular sizes.

Since combustion reactions are exothermic, the temperature increase at the catalyst surface due to the heat of combustion accelerates the rate, inducing a highly probable condition of mass transfer limitation. In addition, mass transfer rates of hydrocarbons in pores are strongly dependent on their sizes and shapes. Therefore, catalyst supports with considerably different pore sizes and shapes were employed in this study to verify the effect of pore size and shape on the catalytic combustion of methane and benzene. FAU and MOR zeolites with micropores of about 8 Å and MCM-41 and KIT-1 mesoporous materials with about 30 Å mesopores were selected as supports of palladium catalysts. MOR zeolite has ordered linear pores, and FAU zeolite has micropores with a three-dimensional structure. Mesopores of MCM-41 mesoporous material are linear and ordered, but those of KIT-1 mesoporous material are bent and disordered. The combustion profiles of methane and benzene with the reaction temperature on the palladium catalysts supported on these porous materials with different pore sizes and shapes, are then illustrated and discussed relating to their mass transfer limitation.

2. Experimental

2.1. Catalyst preparation

FAU and MOR zeolites, MCM-41 and KIT-1 mesoporous materials were used as supports for palladium catalysts. FAU zeolite with a SiO_2/Al_2O_3 ratio of 5.5 (JRC-Z-HY5.5) and H-form MOR zeolite with a SiO_2/Al_2O_3 ratio of 20 (JRC-Z-HM20) were provided by the Japan Catalysis Society. MCM-41 and KIT-1 mesoporous materials with a SiO_2/Al_2O_3 ratio of 40 were synthesized by following a procedure described elsewhere [5–7].

Palladium was supported on zeolites and mesoporous materials by the ion-exchange method. Three palladium catalysts with different loadings for each FAU zeolite and MCM-41 mesoporous material were prepared to illustrate the effect of palladium loading on catalytic activity. Palladium diamine nitrate (Wako Chemicals, min. Pd assay; 59%) solutions with different concentrations were equilibrated with zeolites and mesoporous materials for 12 h at an ambient temperature. After filtering and drying at 100 °C for 1 day, supported palladium catalysts were obtained by calcination at 550 °C for 4 h [5]. Filtrates were analyzed by ICP (Jobin Yvon JY 38plus: Korea Basic Science Institute/Gwangju Branch) to determine the ion-exchanged amount of palladium. Catalysts are denoted as Pd(χ)/support: χ meaning the palladium loading in wt.% with the names of supports being abbreviated as FAU, MOR, MCM, and KIT for FAU and MOR zeolites and for MCM-41 and KIT-1 mesoporous materials, respectively.

2.2. Characterization of prepared catalysts

Nitrogen adsorption isotherms of palladium catalysts were measured at the liquid nitrogen temperature by using a home-built volumetric adsorption measurement apparatus. Catalysts were evacuated at 300 °C for 2 h prior to nitrogen adsorption. Surface areas were calculated using BET equation and pore size distribution using a method described in elsewhere [8].

The dispersion of palladium was determined from hydrogen uptake measured using the volumetric adsorption measurement apparatus following the method proposed by Suh et al. [9]. Hydrogen was adsorbed on evacuated palladium catalysts at 100 °C to prevent its penetration to palladium bulk as a hydride form. Following this, the measurements of hydrogen uptake samples were cooled to ambient temperature and placed in the air for the monolayer adsorption of oxygen on the palladium surface. The reproducible adsorbed amounts of hydrogen on oxygen-adsorbed palladium catalysts were used for calculating palladium dispersion.

TEM photographs of supported palladium catalysts were obtained using a transmission electron

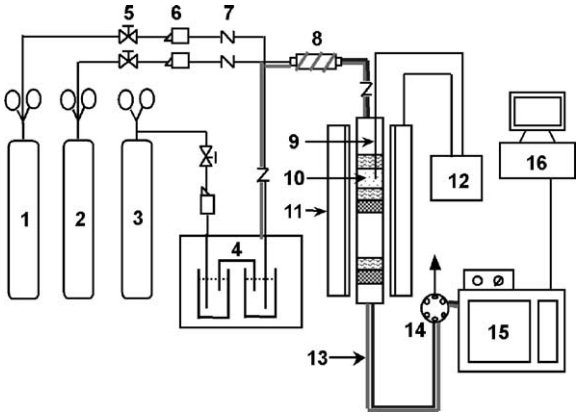

Fig. 1. Schematic diagram of the apparatus for catalytic combustion of benzene and methane: (1) air cylinder; (2) methane cylinder; (3) nitrogen cylinder; (4) benzene evaporator; (5) on/off valve; (6) mass flow controller; (7) check valve; (8) mixing chamber; (9) thermocouple; (10) catalyst bed; (11) heater; (12) PID controller; (13) heated line; (14) sampling port; (15) gas chromatograph; (16) data treatment system.

microscope (JEOL, JEM-2000FAXII) at an acceleration voltage of 200 kV.

2.3. Catalytic combustion of benzene

An atmospheric flow-type reactor such as the one shown in Fig. 1 was used to study benzene combustion on the palladium catalysts. A catalyst of 0.05 g was mixed with 1.3 g of quartz sand of 325–400 mesh (Wako Pure Chemical), minimizing temperature change in the catalyst bed and preventing thermal degradation of catalysts due to a large amount of combustion heat. Diluted catalysts were loaded at the center of a stainless steel tube reactor 1.27 cm. OD and 40 cm in length. The apparent volume of catalyst was about 1 cm^3. Catalysts were pre-treated at 150 °C for 30 min in nitrogen (Shinil Gas Co., 99.999%) before benzene feeding. Benzene (Yakuri Pure Chemicals, G.R.) concentration in a nitrogen flow was controlled at 1.0 vol.% by the evaporator temperature of bath and the flow rate of nitrogen gas. Since the molar ratio of oxygen to benzene was 18 at this composition, oxygen content was sufficient to achieve complete combustion. Space velocity of reactant was 60,000 h^{-1}.

Catalytic combustion was examined from 150 to 600 °C with an interval of 25 °C. Combustion products were sampled after maintaining the reactor temperature for 30 min with each every temperature increase. A gas chromatograph (Donam DS 6200) with a packed column of Porapak Q (4 mm × 5 m) was employed for product analysis. Conversion of benzene was defined as the percentage of benzene to be burned and determined from the decrease of benzene content in product streams. The content of carbon dioxide and water in product streams was also measured and used to confirm the accuracy of the conversion determination.

Combustion of methane was also studied in a manner as similar to that of benzene. Methane content in reactant flow was 2.0 vol.%. The molar ratio of oxygen to methane in the feed was 4.0. The space velocity was controlled at 60,000 h^{-1}.

3. Results and discussion

3.1. Characterization of prepared catalysts

Since only noble metals are highly active in the combustion of hydrocarbons at low temperatures, the activity of combustion catalysts is primarily dependent on their loading amount and dispersion. Therefore, the study of the mass transfer limitation of hydrocarbon combustion on palladium catalysts should be carried out on the premise that the number of exposed palladium atoms does not differ significantly.

Characteristics of the prepared palladium catalysts, such as palladium loading, hydrogen uptake, and palladium dispersion are listed in Table 1. BET surface areas of Pd/FAU and Pd/MCM catalysts did not vary with the loading amount of palladium, showing that loaded palladium was too small to block the pores of supports. On the other hand, hydrogen uptakes on palladium catalysts increased with palladium loading and varied with the supports. Palladium dispersions determined from hydrogen uptakes, however, were almost similar to 20–30%, regardless of palladium loading and support. Although the palladium dispersions of prepared catalysts are not high, their dispersion similarity may be helpful in discussing the effects of pore size and shape of supports on their combustion activity.

The dispersed state of palladium on porous supports was also investigated using TEM. As shown in Fig. 2, the distribution of palladium particles varies with supports. Most palladium particles observed from

Table 1
Characteristics of prepared palladium catalysts for benzene combustion

Support	Catalyst	Pd loading (wt.%)	BET surface area (m^2/g)	H_2 uptake (μmol/g)	Dispersion (%)
Zeolite					
FAU	Pd(0.8)/FAU	0.8	530	22	29
	Pd(1.6)/FAU	1.6	530	29	19
	Pd(2.3)/FAU	2.3	530	39	18
MOR	Pd(0.8)/MOR	0.8	340	24	32
Mesoporous material					
MCM-41	Pd(0.4)/MCM	0.4	1070	–	–
	Pd(0.7)/MCM	0.7	1070	17	26
	Pd(1.3)/MCM	1.3	1070	–	–
KIT-1	Pd(0.8)/KIT	0.8	800	22	29

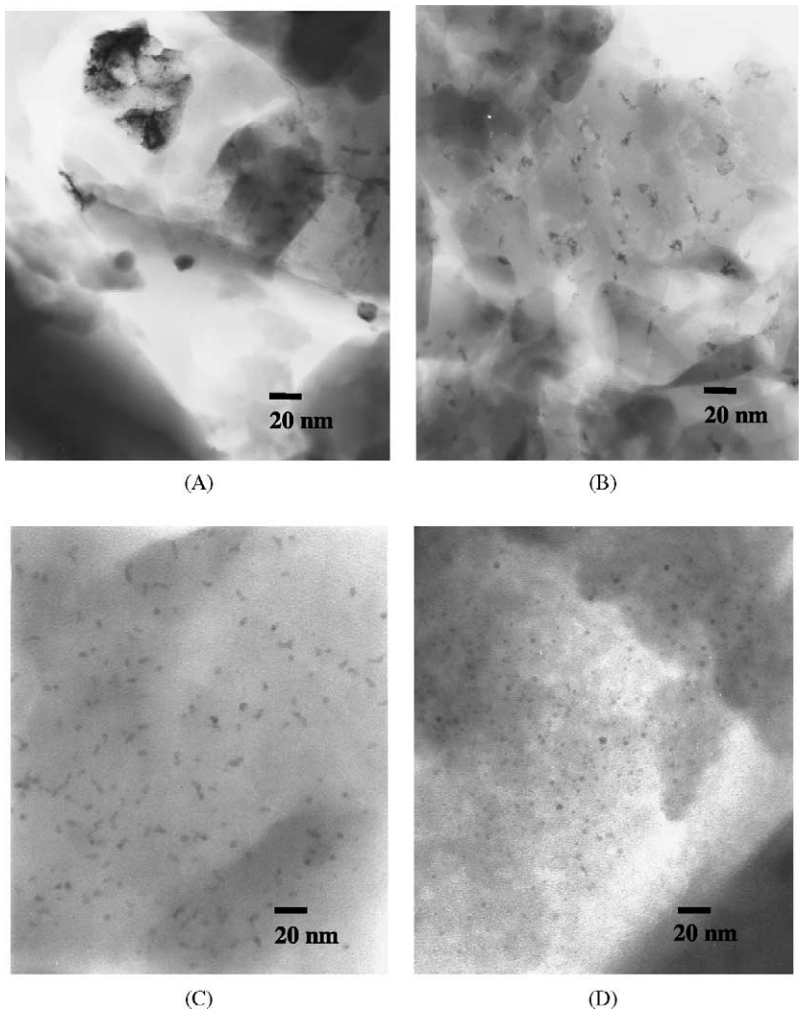

Fig. 2. TEM photographs of palladium catalysts: (A) Pd(0.8)/MOR; (B) Pd(0.8)/FAU; (C) Pd(0.7)/MCM; (D) Pd(0.8)/KIT.

the Pd(0.8)/FAU, Pd(0.7)/MCM, and Pd(0.8)/KIT catalysts are small, showing that palladium dispersions are high. The particle sizes of palladium observed from the photographs remove any ambiguity about the location of palladium particles in mesopores of the mesoporous materials, though it is not easy to deduce the location site of palladium in zeolite pores because of the resolution limit. On the contrary, a number of slightly large particles—which are not definitely allowed to be in zeolite pores—are observed on the Pd(0.8)/MOR catalyst. If all the loaded palladium is dispersed around these particle sizes, a relatively high dispersion of the Pd(0.8)/MOR catalyst 0.32 cannot be obtained. This means that most of the palladium must be dispersed as small particles in MOR zeolite pores, with only a small portion of palladium being aggregated into large particles on the external surface.

Although pore size and shape of zeolites are determined according to their types, the pore size distribution of mesoporous materials and alumina vary with their template materials. Fig. 3 shows nitrogen adsorption isotherms and pore size distributions of the palladium catalysts. The Pd(0.8)/FAU and Pd(0.8)/MOR catalysts exhibit perfect Langmuir type isotherms due to their micropores. The adsorption isotherms of the Pd(0.7)/MCM and Pd(0.8)/KIT catalysts, with a steep increase at about 0.35 of P/P_0, are a typical of mesoporous materials, revealing the existence of mesopores [7].

The differences in pore size distributions of the palladium catalysts supported on zeolites and mesoporous materials are obvious, as shown in Fig. 3(B). Since pore size of porous supports less than 10 Å cannot be calculated from nitrogen adsorption isotherms, the pore size of the Pd(0.8)/FAU and Pd(0.8)/MOR catalysts at 8 Å was cited from [10]. Average pore diameters of the Pd(0.7)/MCM and Pd(0.8)/KIT catalysts were determined to be 30 Å from their adsorption isotherms.

3.2. Catalytic combustion of benzene and methane

Although benzene burns on the supports without palladium loading at temperatures above 600 °C, benzene combustion starts at 250 °C on the supported palladium catalysts. The temperature conversion profiles, however, varied considerably with the palladium loading and catalyst supports. Fig. 4 shows the conversion profiles of benzene combustion on Pd/FAU catalysts. The conversion is low on the Pd(0.8)/FAU catalyst with the lowest palladium loading, achieving a full conversion at about 500 °C. The increase in the conversion with the temperature is also very slow. The increase in palladium loading of the Pd/FAU catalysts, however, brings about enhancements of both the conversion and increasing rate with rising temperature. The increase in active sites for catalytic combustion enhances benzene combustion.

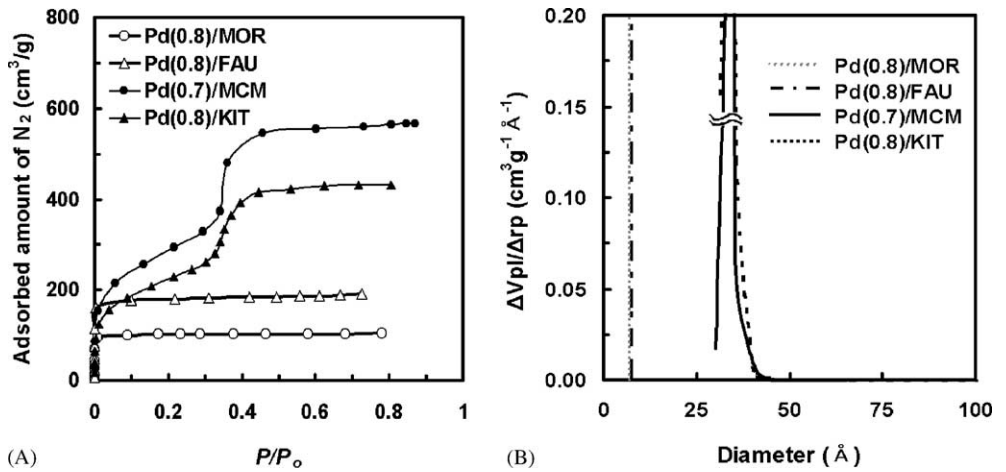

Fig. 3. Nitrogen adsorption isotherms (A) and pore size distributions (B) of palladium catalysts.

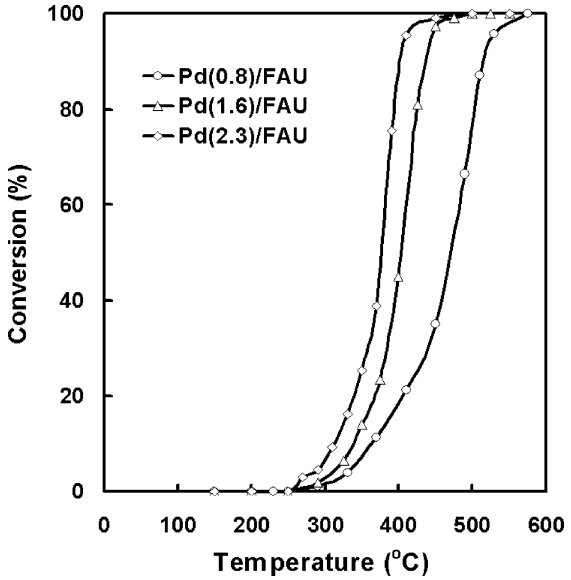

Fig. 4. Conversion profiles of benzene combustion on the Pd/FAU catalysts.

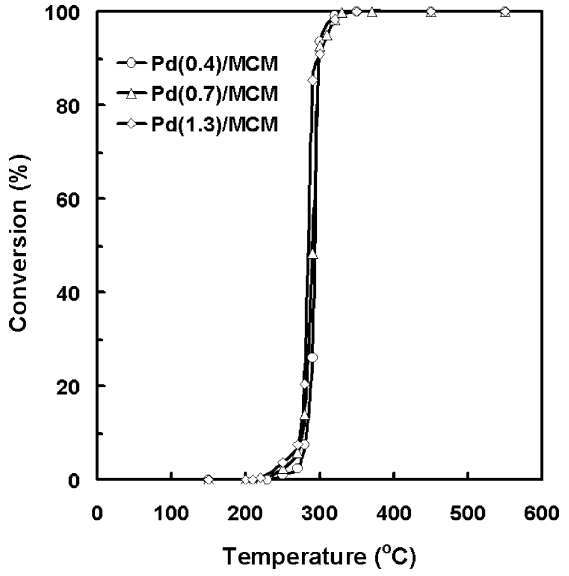

Fig. 5. Conversion profiles of benzene combustion on the Pd/MCM catalysts.

The increasing rate of conversion with rising temperature is strongly related to the activation energy of catalytic reactions. The high activation energy causes a steep increase in the conversion, while the increasing rates are slow when the reaction rates are limited by mass transfer. The slow increase in the conversion with rising temperature over Pd/FAU catalysts in the catalytic combustion of benzene indicate that the surface reactions may not be the rate-determining step. An incorporation of diffusion reduces activation energy, resulting in a slow increase in conversion with rising temperature.

On the contrary, the conversion profiles of benzene combustion on the Pd/MCM catalysts, as shown in Fig. 5, were remarkably different from those on the Pd/FAU catalysts. The temperature at which benzene combustion was started on the Pd/MCM catalysts, was similar to that on the Pd/FAU catalysts at nearly 250 °C, but the conversion increase with rising temperature was very steep, achieving complete conversion even at 300 °C. The conversion profiles of benzene combustion on the Pd/MCM catalysts were all the same, regardless of the palladium loading. The catalytic activities of Pd/MCM catalysts were sufficiently high to achieve 100% at 300 °C, even though the palladium loading was small at 0.4 wt.%.

Since the palladium dispersions were similar for all palladium catalysts regardless of support, the differences in combustion activity and the slope of conversion increase with rising temperature between the Pd/FAU and Pd/MCM catalysts were caused by the extent of diffusion limitation to surface reaction due to their differences in pore size. Relatively large pores of MCM-41 mesoporous material give rapid diffusion, resulting in a high reaction rate on Pd/MCM catalysts. A similar conversion profile of benzene combustion was also obtained on the Pd(0.8)/KIT catalyst as shown in Fig. 6. Large pores of KIT-1 mesoporous material minimize the restriction of mass transfer to surface reaction, showing high activity.

The Pd(0.8)/MOR catalyst also shows high activity as do palladium catalysts supported on mesoporous materials and alumina. The considerably different behavior of the Pd(0.8)/MOR catalyst from the Pd(0.8)/FAU catalyst may be due to the difference in the dispersed state of palladium as shown in Fig. 2. Large particles dispersed on the external surface do not suffer any mass transfer limitation and even a small amount of palladium—0.4% palladium loading of Pd/MCM catalysts—is enough for catalytic combustion of benzene, resulting in high activity for this diffusion-controlled catalytic reaction.

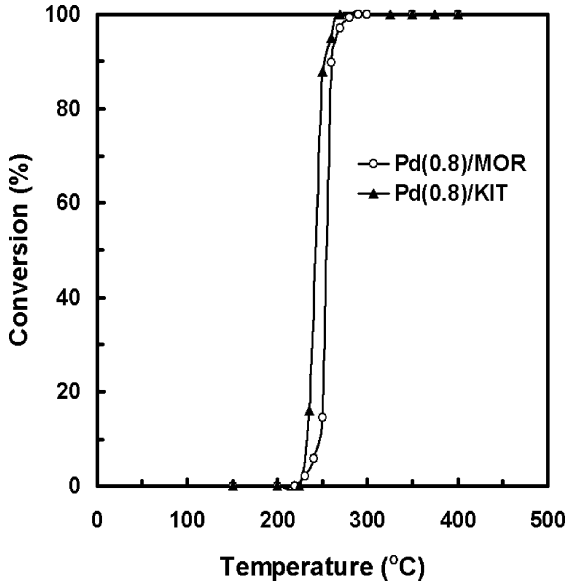

Fig. 6. Conversion profile of benzene combustion on the palladium catalysts supported on KIT-1 and MOR.

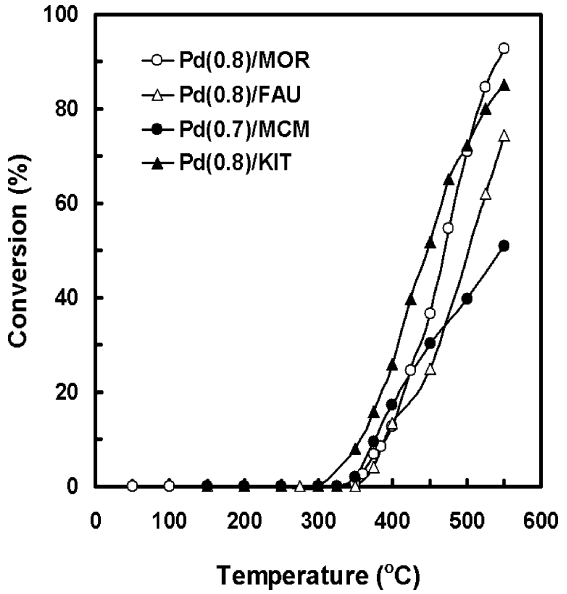

Fig. 7. Conversion profiles of methane combustion on the palladium catalysts with different supported materials.

Diffusion limitation on catalytic reaction is significant when the molecular size of the reactant is close to the pore size, or the mean free path of the reactant is considerably long compared to the pore diameter. Molecules with a large molecular size experience large amounts of high restriction due to hydrodynamic drag and steric hindrance [11]. In addition, the long mean free path of reactant molecules results in excessive collisions with the pore wall, reducing the diffusion rate significantly. Therefore, the combustion reaction of methane, whose molecular size and mean free path are considerably different from that of benzene, is helpful to understand the differences in combustion activity and the slopes of conversion increases between the Pd/FAU and Pd/MCM catalysts.

Fig. 7 illustrates conversion profiles of methane combustion on the palladium catalysts. The conversion profiles were similar to each other in that there was a slow increase in methane conversion with temperature, while the conversions were slightly high on the Pd(0.8)/KIT catalyst. If the slow increase in the benzene conversion with temperature on the Pd/FAU catalysts was attributed to the diffusion limitation to surface reaction due to their micropores, those in the conversion profiles of methane combustion on the palladium catalysts were similarly considered to be attributed to the diffusion limitation of methane. The long mean free path of methane at the reaction condition largely reduces its diffusion rate, exhibiting marked inhibition of mass transfer in methane combustion.

3.3. Discussion on the diffusion limitation to catalytic combustion

Diffusion limitation of reactants to catalytic reaction is negligible when the rate of the surface reaction is sufficiently slow. On the other hand, the diffusion limitation is predominant on metal catalysts supported on porous materials, when rates of collisions of reactant molecules with the pore wall are higher than those of intermolecular collisions. Too frequent collisions with the pore wall, the so-called Knudsen diffusion, induce the retardation of mass transfer, resulting in a low reaction rate. The inhibition due to the Knudsen diffusion of reactants on catalytic reaction is estimated by Knudsen number N_{kn}, defined as $N_{kn} = \lambda/2r$, where λ and r denote the mean free path and pore radius, respectively. A high reduction of the reaction rate by the diffusion limitation is expected when the Knudsen number is larger than 10 [12]. A small pore size and

Table 2
Deduced Knudsen numbers of benzene and methane in the pores of the zeolites and mesoporous materials at 1 bar and 300 °C

	Support	
	FAU, MOR ($d = 8.0$ Å)	MCM-41, KIT-1 ($d = 30$ Å)
Benzene		
λ (Å)	450	450
N_{kn}	56	15
Methane		
λ (Å)	1300	1300
N_{kn}	160	43

long mean free path of reactants increase the rate of collisions of molecules with the pore wall, delaying mass transfer and retarding catalytic reaction.

The Knudsen numbers of benzene and methane in the pores of zeolites and mesoporous materials can be determined from their mean free paths and average pore radii of supports. Viscosities of diffusants at 1 bar and 300 °C, required for the determination of the mean free path, were estimated from reported experimental data obtained at another temperature [13] as 1.43×10^{-9} and 1.85×10^{-9} Pa s for benzene and methane, respectively. Table 2 summarizes the deduced Knudsen number of benzene and methane in the FAU and MOR zeolites and MCM-41 and KIT-1 mesoporous materials. Estimated Knudsen numbers vary greatly according to molecular sizes of diffusant and pore radii of catalyst supports. The Knudsen number of benzene in the mesoporous materials was the smallest, indicating that the mass transfer restriction to surface reaction was relatively small compared to other reaction systems. Although the criteria of the Knudsen number suggested for the negligible diffusion limitation is 10, the Knudsen number 15 of benzene at the catalytic combustion on the Pd/MCM catalysts, shows a very small effect of mass transfer on overall reaction rate. The large Knudsen number of benzene in the FAU and MOR zeolites suggests a severe mass transfer limitation of the catalytic combustion of benzene on palladium catalysts supported on zeolite supports due to the fact that the molecular size of benzene is slightly less than pore diameter of the zeolites.

The molecular size of methane is considerably small compared to that of benzene, and thus the restriction of mass transfer to catalytic combustion of methane is expected to be negligible. However, high values of Knudsen numbers for methane were obtained both in the zeolites and mesoporous materials. Although the molecular size of methane is small, the high speed of methane molecules due to their small molecular weight brings about frequent collisions with the pore wall, resulting in slow mass transfer. Since the reaction rate is controlled by the mass transfer, the increasing rate of methane conversion with rising temperature must be slow.

Although the pore shapes of MCM-41 and KIT-1 mesoporous materials are different, there was no difference in catalytic activity in the combustion of methane and benzene on Pd/MCM and Pd/KIT catalysts, exhibiting the negligible contribution of pore shape to catalytic activity. On the other hand, Pd/FAU and Pd/MOR catalysts with different pore shapes showed considerable difference in the catalytic activity of benzene combustion, but this was due to the difference in palladium aggregation, not pore shape. Mass transfer limitation by pore size is predominant, and thus, the effect of pore shape on catalytic combustion is not significant in the catalytic combustion of methane and benzene. The fact that a simple structure of combustion intermediates also reduces the importance of pore shape of supports compared to that of pore size.

4. Conclusions

The activities of palladium catalysts in benzene combustion were considerably different according to their supports. The palladium catalysts supported on the MCM-41 and KIT-1 mesoporous materials showed high conversions and steep increases in the conversion with rising temperature. The activity of the palladium catalysts supported on the FAU zeolite, however, was considerably low and their conversions increased slowly with rising temperature. These differences are caused by the consequence of the difference in pore sizes of catalyst supports. On the other hand, palladium catalysts supported on zeolites and mesoporous materials showed similar conversion profiles in methane combustion due to severe mass transfer limitation. The slow diffusion of methane in the pores of the supports

reduced overall reaction rates and resulted in a slow increase of the conversion with rising temperature.

Acknowledgements

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