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METHANOL DECOMPOSITION OVER SUPPORTED PALLADIUM AND PLATINUM

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Abstract – Methanol decomposition over supported Pt and Pd catalysts was investigated in the temperature range from 453 to 573 K with the partial pressure of methanol up to 0.8 atm. The specific activity of Pd was higher than that of Pt, and alumina-supported Pd was more active than silica-supported Pd, although alumina-supported catalysts produced dimethyl ether as a by-product. A silica-supported Pd catalyst prepared from a tetraamine salt solution with a proper pH exhibited higher activity than the other silica-supported Pd catalysts. Dependence of the decomposition rate on the partial pressure of methanol was similar regardless of the metal, the support or the preparation method. The apparent reaction orders were near 0.3 at low pressures below about 0.4 atm and became near zero or slightly negative at higher pressures. The apparent activation energies were about the same for most of the catalysts and were in the range from 66 to 77 kJ/g-mol.

Key words : Methanol Decomposition, Palladium, Platinum, Supported, Kinetics

INTRODUCTION

Decomposition of methanol to hydrogen and carbon monoxide, an endothermic reaction, can be utilized in a chemical heat pump system which absorbs low-temperature waste heat and then releases heat at a higher temperature by the reverse reaction. It has also been proposed that the methanol decomposition on board may be applied to automobiles since injection of the gaseous products into the engine provides higher thermal efficiency and less corrosion and pollution problems when compared with direct injection of liquid methanol [Takishita et al., 1985; Cheng and Kung, 1994]. Some other applications of dissociated methanol are considered for supplying hydrogen for fuel cells, supplemental gas turbine fuel at peak demand of electricity, fuel and cooling systems for hypersonic jets, and source of carbon monoxide and hydrogen for chemical processes [Cheng and Kung, 1994]. The catalysts for these applications are required to have high activity and selectivity especially at low temperatures.

Copper, nickel and noble metals are known to be effective for methanol decomposition. Below 573 K, copper and copper-based catalysts exhibit relatively low activity and produce significant amounts of formaldehyde and methyl formate along with hydrogen and carbon monoxide [Miyazaki and Yasumori, 1967; Cant et al., 1985; Madhusudhan Rao and Shankar, 1988; Idem and Bakhshi, 1994; Lee and Bell, 1996]. Nickel and noble metals are more active than copper and do not produce formaldeyde or methyl formate, but over these metals a small amount of methane is produced as a by-product by the methanation reaction [Yasumori et al., 1967; Bare et al., 1985; Takishita et al., 1985; Hahm et al., 1989; Shimizu and Takeoka, 1989; Park et al., 1992; Lee et al., 1993; Yoon et al., 1993; Kim and Yoon, 1996]. Among these metals Pd and Pt seem to be more active and produce smaller amounts of methane than the others [Joo et al., 1991]. However, kinetic parameters such as reaction orders and activation energies over Pd and Pt have rarely been reported. In particular, studies on the dependence of methanol partial pressure above 0.15 atm are scarce [Yoon et al, 1993; Kim and Yoon 1996].

In this work, the activities and selectivities of an alumina-supported Pt catalyst and alumina- and silica-supported Pd catalysts were compared for the decomposition of methanol. The activation energies and reaction orders were determined in the temperature range from 453 to 573 K and in the methanol partial pressure range from about 0.05 to 0.8 atm.

EXPERIMENTAL

1. Chemicals and Catalyst Preparation

Silica (Oriental Chemical Industries, Type B granules, pore volume 0.65 cm^3/g) and γ-alumina (Strem Chemicals 13-2,550, cylindrical pellet, pore volume 0.365 cm^3/g) were used as the supports. The silica granules were crushed and particles of −18/+40 mesh size were selected and then heat-treated at 1,073 K for 3 h to increase the strength and thermal stability. The alumina pellets were crushed and particles of -18/+80 mesh size were selected and then dried at 673 K for 1 h before use.

The precursor of Pt was chloroplatinic acid (Aldrich, assay 40 % Pt). The precursors of Pd were palladium chloride (Inuisho Precious Metals, assay 60 % Pd) and tetraamine palladium chloride hydrate (Aldrich, assay 39.5 % Pd). The catalysts were prepared by employing the incipient wetness method (dry impregnation). The chloroplatinic acid was dissolved in distilled

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water and the palladium chloride was dissolved in 1 N HCl solution. The tetraamine palladium chloride was dissolved in aqueous ammonia solutions whose pH's were adjusted to 8.1, 10.0, 11.4 and 12.2, respectively. The pH adjustment was done in order to see if it would affect the percentage exposed or the catalytic activity [Benesi et al., 1968]. After the impregnation, the catalysts were calcined in air at 773 K for 4 h. The metal contents were all 2 wt% nominal. The catalysts were designated as Pt/Al_2O_3, Pd/Al_2O_3 and Pd/SiO_2(a) for the catalysts prepared from the chloride salts, and as Pd/SiO_2(b) for the catalysts prepared from the amine salt, where b indicates the pH of the solution.

2. Reaction and Chemisorption Experiments

The reaction was carried out under ambient pressure in a conventional tubular microreactor made of 1/4 inch stainless steel tubing. Liquid methanol (Matsunoen Chemicals, 99.6+%) was fed by a syringe pump (Keun-A Mechatronics, KASP 005/150 MT) to an evaporator which was filled with glass beads and heated by a heating band and then to the reactor. Hydrogen for the activation of the catalyst and nitrogen for the adjustment of the partial pressure of methanol were fed through the mass flow controllers. The lines were heated to around 333 K by a heating wire to prevent condensation of methanol.

The reactor was normally loaded with about 200 mg of the catalyst. In some cases when the activity was very high, the loaded catalyst was reduced to 40 mg and mixed with 160 mg of the support. The catalyst was activated with flowing hydrogen at 473 K for 1 h and then the reaction experiments were done with a total gas flow rate of 50-100 cm^3/min (GHSV =15000-30000 cm^3/g·h). The partial pressure of methanol in the feed ranged from 0.05 to 0.8 atm. The effluent gas was analyzed with two gas chromatographs, one equipped with a Chromosorb 102 column (Alltech) using He as the carrier gas for the analysis of methane, carbon dioxide, methanol and dimethyl ether and the other with a Carbosieve S-II column using Ar as the carrier gas for the analysis of hydrogen, carbon monoxide, methane and carbon dioxide.

The hydrogen chemisorption experiments were carried out in a conventional glass adsorption apparatus by following the conventional procedure. The catalyst activation procedure was the same as described above. For the Pt catalyst, the adsorption experiment was carried out at room temperature. For the Pd catalysts, the adsorption experiment was carried out at 373 K to avoid the formation of β hydride of palladium [Benson et al., 1973].

RESULTS AND DISCUSSION

1. Hydrogen Chemisorption

The results of hydrogen chemisorption are shown in Table 1. The percentage exposed of Pt on alumina was about 100%. The percentage exposed of Pd on alumina was much higher than that on silica, which is a usually observed phenomenon due to different interactions between the metal ions and the two supports. Benesi et al. [1968] have reported that platinum amine ions can be highly dispersed on silica under high pH, but this was not found to be the case in our work for the palladium amine ions. The reason for this is not clear, but one might speculate that the poor dispersion of Pd is due to a different property of Pd itself from Pt or due to the different interaction of the silica with platinum amine ions and palladium amine ions. Rather, the percentage exposed of Pd obtained from the tetraamine salt was somewhat smaller than that obtained from the chloride salt and was shown to be little affected by the pH employed.

2. Activity and Selectivity

In Fig. 1, activities of the catalysts prepared from the chloride precursors (Pd/Al_2O_3, Pd/SiO_2(a) and Pt/Al_2O_3) for metha-

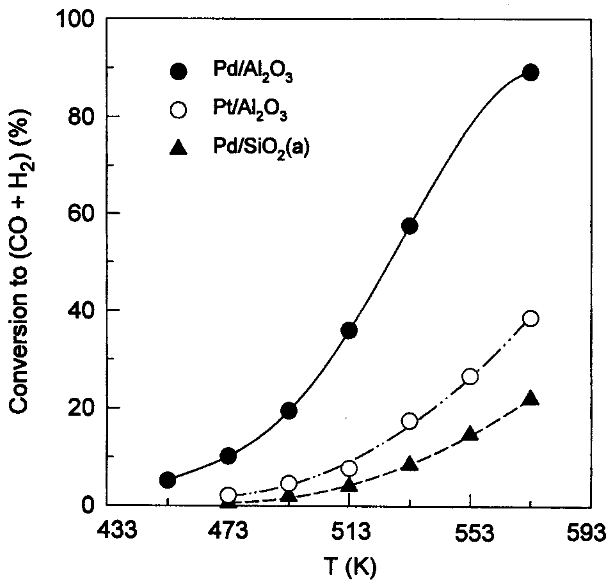

Fig. 1. Conversion for methanol decomposition to CO and H_2 with temperature over supported Pd and Pt catalysts (W=200 mg, $P_{A,in}$=0.2 atm, total flow rate=100 cm^3/min).

Table 1. Results of hydrogen chemisorption

Catalyst	Metal precursor	H_2 Chem. (μmol/g-cat.)	Active surface area (m^2/g-cat.)	% exposed
Pt/Al_2O_3	H_2PtCl6	54.4	5.24	100
Pd/Al_2O_3	$PdCl_2$	35.8	3.39	38.1
Pd/SiO_2(a)	$PdCl_2$	14.6	1.38	15.5
Pd/SiO_2(8.1)$^{a)}$	$(NH_3)_4PdCl_2$	10.9	1.04	11.6
Pd/SiO_2(10.0)$^{a)}$	$(NH_3)_4PdCl_2$	10.4	0.99	11.0
Pd/SiO_2(11.4)$^{a)}$	$(NH_3)_4PdCl_2$	10.4	0.99	11.1
Pd/SiO_2(12.2)$^{a)}$	$(NH_3)_4PdCl_2$	12.2	1.15	12.9

$^{a)}$The number in parentheses denotes the pH of the metal precursor solution.

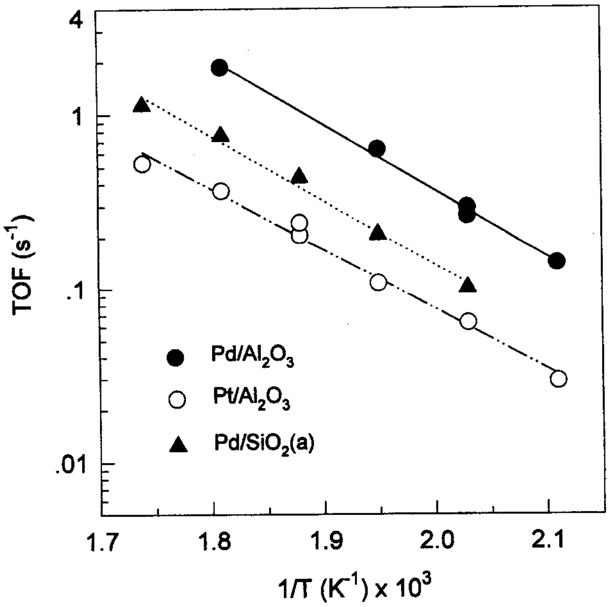

Fig. 2. TOF of methanol decomposition vs. 1/T over the Pd and Pt catalysts prepared from the chloride precursors ($P_{A,in}$= 0.2 atm, total flow rate=100 cm^3/min).

nol decomposition (conversion of methanol to CO and H_2 only) are compared in terms of conversion under the same conditions. The conversion in Fig. 1 does not include the fraction of methanol converted to dimethyl ether. Per g catalyst basis, Pd/Al_2O_3 was much more active than Pt/Al_2O_3, but $Pd/SiO_2(a)$ was less active than Pt/Al_2O_3. However, if the activities were compared in terms of the turnover frequencies (TOFs) based on the hydrogen chemisorption (Fig. 2), Pd/Al_2O_3 was again the most active, $Pd/SiO_2(a)$ the next, and Pt/Al_2O_3 was the least active. Therefore, it can be said that the specific activity per active surface area, or the TOF, of Pd is higher than that of Pt. In addtion, since Pd/Al_2O_3 is more active than $Pd/SiO_2(a)$, a support effect seems to exist.

TOFs for the $Pd/SiO_2(b)$ catalysts prepared from the amine salt with different solution pH(b) are shown in Fig. 3. The specific activity of $Pd/SiO_2(10.0)$ was a little bit higher than that of $Pd/SiO_2(a)$, and the other $Pd/SiO_2(b)$ catalysts showed a little bit lower activities than $Pd/SiO_2(a)$. Since silica is susceptible to dissolve at pH above 9 or 10 [Moulijin et al., 1993], the surface structure of the support may be altered with the pH. This might have caused the different activity with different pH in spite of the similar percentage exposed of the Pd. However, the activity of $Pd/SiO_2(10.0)$ was still somewhat lower than that of Pd/Al_2O_3. Compared with a Ni/SiO_2 catalyst in the literature [Yoon et al., 1993], Pd/Al_2O_3 and $Pd/SiO_2(10.0)$ are more active but Pt/Al_2O_3 is less active, even though some difference in the partial pressure dependence is taken into account. For example, at 473 K and under the partial pressure of methanol of 0.2 atm, the TOFs over Pd/Al_2O_3, $Pd/SiO_2(10.0)$, $Pd/SiO_2(a)$ and Pt/Al_2O_3 are 0.14, 0.098, 0.052 and 0.029 s^{-1}, respectively, while the TOF over the Ni/SiO_2 catalyst is 0.088 s^{-1} under the methanol partial pressure of 0.05 atm at which the rate shows the maximum with respect to the partial pressure.

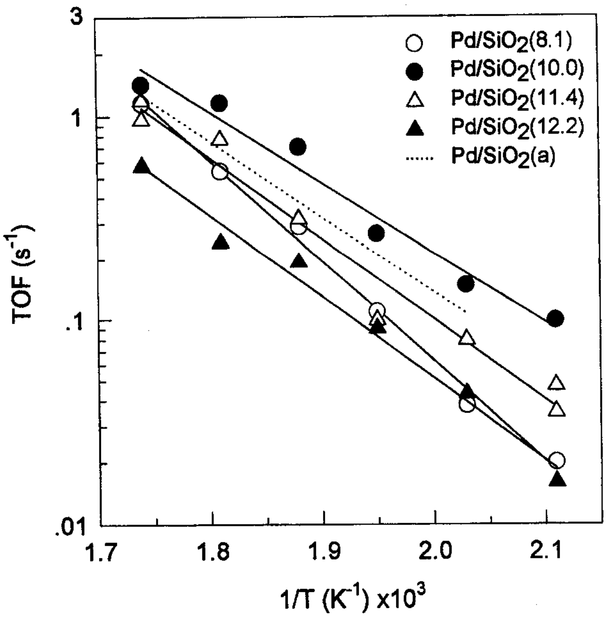

Fig. 3. TOF of methanol decomposition vs. 1/T over Pd/SiO_2 (reaction conditions are same as in Fig. 1).

Although the alumina is more favorable than the silica as the support for the decomposition activity, it catalyzes the dehydration of methanol to dimethyl ether (DME) due to its acidity [Spivey, 1991; Lee et al., 1993], which may be undesirable for some applications of the methanol decomposition. The activities of the alumina-supported catalysts as well as the alumina for the methanol dehydration are shown in Fig. 4 in terms of the conversion of methanol. The alumina tested for this reaction had been treated under the same conditions employed for the calcination of the supported catalysts. Over the alumina only, CO and H_2 were not detected but only DME and H_2O were produced. The dehydration activity of Pd/Al_2O_3

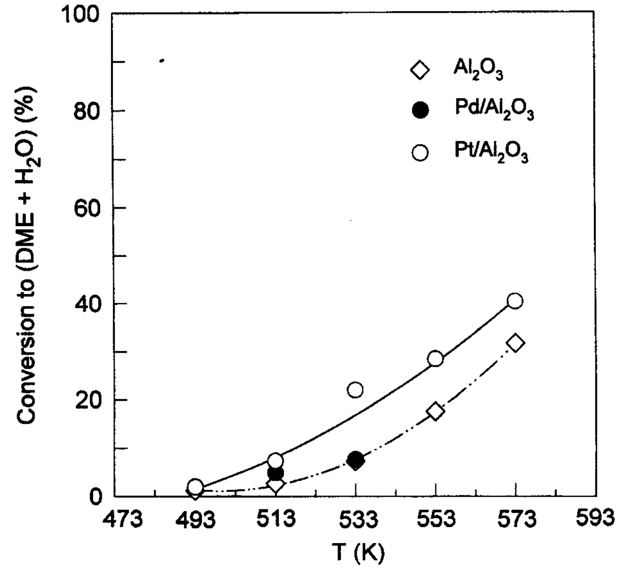

Fig. 4. Conversion for methanol dehydration to DME and H_2O with temperature over Al_2O_3 and Al_2O_3-supported catalysts (reaction conditions are same as in Fig. 1).

up to 533 K was almost the same as that of the alumina only, but that of Pt/Al_2O_3 was considerably higher than that of the alumina up to 573 K. This means that the Pd metal particles on alumina do not affect the dehydration activity of the alumina, but the Pt metal particles on alumina exhibit a significant enhancement of the dehydration activity of the alumina. There seems to be some kind of interaction between the Pt particles and the alumina, and this may be a cause for the relatively lower specific activity of Pt/Al_2O_3 than that of Pd/Al_2O_3 in methanol decomposition. By the interaction Pt may alter the number or the strength of the active sites on the alumina [Spivey, 1991], but since the methanol dehydration is not a subject of main interest in this work, no further detailed study or discussion will be given afterwards.

Product selectivities over Pt/Al_2O_3, Pd/Al_2O_3 and Pd/SiO_2(a) with temperature are given in Table 2. As mentioned above, comparable amounts of CO and DME were produced over Pt/Al_2O_3 at above 513 K, and over Pd/Al_2O_3 the selectivity to CO is much higher than that to DME even at high conversions. No DME was produced over Pd/SiO_2(a), and this is due to the nearly neutral character of the silica. Methane formation was observed at high temperatures (or high conversions) over both Pt/Al_2O_3 and Pd/Al_2O_3. Due to different conversions and S_{CO} as well as from the limited experiments in this work, it is not clear which of Pd and Pt is more active for the formation of methane. Over Pd/SiO_2(a), no methane formation was observed even at 573 K, but the methane conversion was considerably low. If the conversion becomes higher, the possibility for methane formation cannot be ruled out. On the other hand, the methanation activity of Pd or Pt is clearly lower than that of Ni when compared with the result in an earlier work [Yoon et al., 1993], which reported that methane formation was observed at as low as 493 K with a lower methane conversion.

Table 2. Product selectivities with temperature

($P_{A,in}$=0.2 atm, total flow rate=100 cm^3/min, catalyst wt =200 mg)

Catalyst	Temp. (K)	Overall conv. (%)	Selectivity (%)[1]		
			S_{CO}	S_{DME}	S_{CH4}
Pt/Al_2O_3	473	2.1	100	-	-
	493	6.5	70.9	29.1	-
	513	15.1	51.6	48.4	-
	533	39.5	44.4	55.6	-
	553	55.9	47.8	51.0	1.2
	573	79.8	48.3	50.5	1.1
Pd/Al_2O_3	453	5.1	100	-	-
	473	10.2	100	-	-
	493	21.5	90.9	9.1	-
	513	40.8	88.1	11.9	-
	533	65.2	88.3	11.7	-
	573	98.3	90.7	-	9.1
Pd/SiO_2(a)	473	0.6	100	-	-
	493	2.0	100	-	-
	513	4.0	100	-	-
	533	8.5	100	-	-
	553	14.8	100	-	-
	573	22.1	100	-	-

[1] Si(%)=100×(moles of carbon in product i)/(total moles of methanol converted), i=CO, DME or CH_4.

From the discussion above, Pd/Al_2O_3 seems to be an excellent catalyst for methanol decomposition provided that the dehydration activity of alumina is effectively suppressed. This may be done by neutralizing the acid sites without affecting the activity of Pd adversely. Another possible method is use of other supports which do not catalyze side reactions but help Pd retain the high activity. These suggestions may be tested in future work.

3. Apparent Reaction Orders and Activation Energies

Dependence of the activity of methanol decomposition on the partial pressure of methanol was investigated and the results are given in Figs. 5 and 6. The methanol conversions were maintained below 20 % in these experiments, and the conversions became lower with increasing partial pressure. Although the partial pressure dependence over Pd/Al_2O_3 at 553 K was observed to be similar to that at lower temperatures, the conversions were considerably high (30-60 %) and therefore the partial pressure dependence at this temperature should be used with some reservation. The partial pressure given was the average value between the reactor inlet and outlet, and the reaction rate, only for the decomposition to CO and H_2, was also the average value in the bed. As shown in the Figures, patterns of the dependence on the partial pressure look alike regardless of the catalyst and temperature. Therefore, the dependence over Pd/SiO_2(b) is considered to be similar to that over Pd/SiO_2(a) and was not investigated in this work. At low partial pressures below about 0.4 atm, the reaction orders were around 0.3. As the partial pressure increased, the orders became near zero or slightly negative. The relatively low reaction orders and their decrease with the partial pressure may be explained by adsorption inhibition [Kim and Yoon, 1996]. Although the detailed reaction mechanism is not investigated in this work, a great portion of the surface is considered to be covered with adsorbed species including methanol and in-

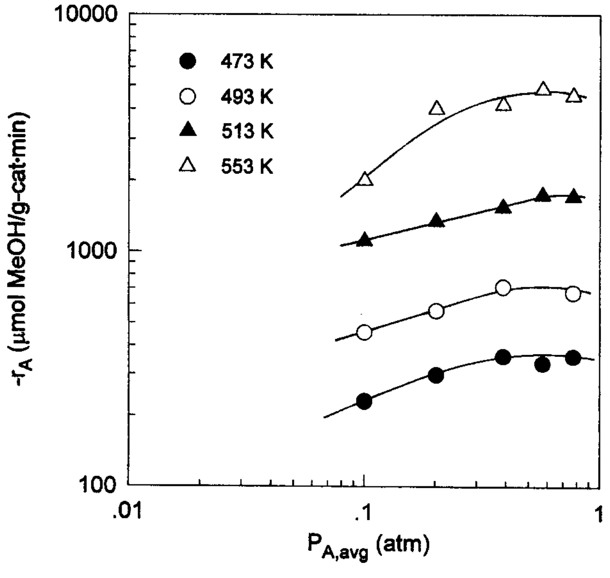

Fig. 5. Rate of methanol decomposition vs. partial pressure of methanol over Pd/Al_2O_3.

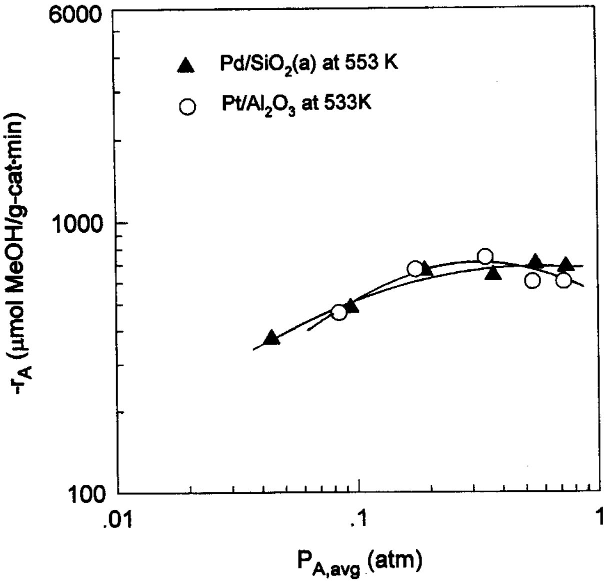

Fig. 6. Rate of methanol decomposition vs. partial pressure of methanol over Pd/SiO$_2$(a) and Pt/Al$_2$O$_3$.

termediate species, and due to the presence of these species adsorption of methanol and subsequent decomposition steps may be inhibited. With the increase of the partial pressure the surface coverage will become greater, which results in lowering of the reaction order. In fact, negative reaction orders have also been observed over a nickel catalyst with increasing partial pressure of methanol [Yoon et al., 1993].

The apparent activation energies (E_{app}'s) were estimated from Figs. 2 and 3 and the results are given in Table 3. Except for Pd/SiO$_2$(8.1), the values were about the same ranging from 66 to 77 kJ/g-mol. Although the exceptionally high activation energy for Pd/SiO$_2$(8.1) is not well understood, it largely appears that the activation energy is little affected by the metal, the support or the preparation method. The value for a Ni catalyst in an earlier work [Yoon et al., 1993] was also similar to them.

For Pd, Pt and Ni, the rate determining step in the mechanism of methanol decomposition is generally considered to be the formation of methoxy species on the surface. Contrary to Cu on which methoxy is stable at high temperatures, the methoxy is rapidly decomposed to CO and H_2 on Pd, Pt and Ni without producing formaldehyde and methyl formate [Gates and Kesmodel, 1983; Bare et al., 1985; Yoon et al., 1993; Lee and Bell, 1996]. Similar partial pressure dependence and apparent activation energies for the supported Pd catalysts in this work suggest that the rate determining step is the same and the inherent catalytic property of the metal is altered only to a small extent, but different activities depending on the support may be considered due to the support effect. Although the nature of the support effect is not clearly understood, some speculations may be proposed. As it has been reported that the formation of methoxy species is facilitated by adsorbed oxygen on Pd while the methoxy species is difficult to form on a clean surface [Gates and Kesmodel, 1983], the oxygen on the support at the periphery of the metal particles may facilitate the methoxy formation to a different extent depending on the support. Another speculation is that an adsorbed intermediate of methanol or methoxy species formed on the support near the metal particles may be readily decomposed by the metal. The concentration of the adsorbed intermediate on the support may be different depending on the support, and that on the alumina may be considered to be the highest. Although the support effect may result in changes of the apparent activation energy to some extent, it did not come out to be large for the catalysts in this work.

CONCLUSIONS

The specific activity of Pd for methanol decomposition was higher than that of Pt. Although alumina-supported Pd produced dimethyl ether as a by-product and silica-supported Pd did not, the former is more active than the latter. A silica-supported Pd catalyst prepared from the tetraamine salt solution with a proper pH exhibited higher activity than the other silica-supported Pd catalysts. These suggest that a support effect on the activity of methanol decomposition may be present. Dependence of the rate on the partial pressure of methanol was similar to one another regardless of the metal, the support or the preparation method. The apparent reaction orders were near 0.3 at low pressures below about 0.4 atm and became near zero or slightly negative at higher pressures. The apparent activation energies were about the same for most of the catalysts and were in the range from 66 to 77 kJ/g-mol.

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NOMENCLATURE

DME: dimethyl ether
E_{app} : apparent activation energy [kJ/g-mol of methanol]
$P_{A,avg}$: average partial pressure of methanol between reactor inlet

Table 3. Apparent activation energies of methanol decomposition

Catalyst	Pt/Al$_2$O$_3$$^{a)}$	Pd/Al$_2$O$_3$$^{a)}$	Pd/SiO$_2$(a)	Pd/SiO$_2$(8.1)
E_{app} (kJ/g-mol)	66.6	72.5	71.2	94.5
Catalyst	Pd/SiO$_2$(10.0)	Pd/SiO$_2$(11.4)	Pd/SiO$_2$(12.2)	Ni/SiO$_2$$^{b)}$
E_{app} (kJ/g-mol)	66.2	75.9	77.2	63

a) Dehydration of methanol occurred simultaneously, but only the rate data for the methanol decomposition were used in the data analysis.
b) From Yoon et al. [1993].

and outlet [atm]

$P_{A,in}$: partial pressure of methanol at reactor inlet [atm]

$-r_A$: reaction rate of methanol decomposition [μmol/(g-cat·min)]

S_i : selectivity of i based on carbon balance, i=CO, DME or CH_4 [−or %]

T : temperature [K]

TOF : turnover frequency [s^{-1}]

W : catalyst weight [mg]

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