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Effect of metal dispersion on CO hydrogenation over Pd/HZSM-5 catalysts

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Pd/HZSM-5 catalysts prepared by ion-exchange method using $Pd(NH_3)_4^{2+}$ were calcined and reduced at different temperatures to provide different metal dispersions. The effect of Pd dispersion on CO adsorption characteristics and acidity were observed through FT-IR study. Methanol and dimethyl ether were the main products in CO hydrogenation over Pd/HZSM-5 catalyst with small Pd particles on which CO was weakly adsorbed, while the selectivity to methane increased with metal sizes.

Keywords: carbon monoxide hydrogenation; palladium; HZSM-5; dispersion; selectivity (oxygenate); catalyst characterization (IR)

1. Introduction

The catalytic hydrogenation of carbon monoxide to hydrocarbons and/or oxygenates has attracted much attention with the need to develop alternatives to petroleum feedstocks. Since Poutsma et al. [1] demonstrated that supported Pd/SiO_2 catalyzes the synthesis of methanol from CO and H_2, methanol synthesis from CO hydrogenation over supported Pd catalysts has been widely investigated [2–8].

Although the activity and selectivity could be changed by altering the supports and promoters, there are some ambiguities concerning the influence of metal dispersion on the catalytic behavior and reaction mechanism. Especially for the Pd/zeolite system, conflicting evidences regarding the effect of the dispersion have been reported for the CO hydrogenation. Jaeger et al. [9,10] reported that the selectivity to oxygenates was higher on smaller crystallites over Pd/X zeolite as well as over Pt or Rh/X zeolite, while Cavalcanti et al. [11] reported the opposite result over Pd/Y zeolite.

In this work, the Pd/HZSM-5 catalysts prepared by ion-exchange method using $Pd(NH_3)_4^{2+}$ were calcined and reduced at different temperatures to provide differ-

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ent metal dispersions. The influence of Pd dispersion on the methanol selectivity in CO hydrogenation was investigated under moderate pressure. The characterization of catalyst samples was made through H_2–O_2 titration, FT-IR of adsorbed CO, and FT-IR of adsorbed pyridine.

2. Experimental

2.1. CATALYST PREPARATION

Samples of NaZSM-5 were obtained by hydrothermal synthesis at 170°C for 3 days in a Teflon-lined 450 ml Parr bomb by following the procedures of ref. [12]. The zeolites were washed and calcined in air overnight at 550°C. The calcined NaZSM-5 samples were converted to the NH_4^+ forms by ion exchanging three times with 1 M NH_4Cl solutions at room temperature. $Pd(NH_3)_4^{2+}$ was exchanged into the above NH_4ZSM-5 samples by stirring in aqueous solution of $Pd(NH_3)_4(NO_3)_2$ (Aldrich) at 25°C for 48 h. These samples were filtered, washed with deionized distilled water and dried under a dynamic vacuum at 80°C.

2.2. PRETREATMENT (CALCINATION AND REDUCTION)

The catalyst was calcined in a flowing gas mixture of Ar(160 cm^3/min)–O_2 (40 cm^3/min) at a temperature increasing from room temperature to the specified calcination temperature (T_C) at a rate of 0.2°C/min. After holding the temperature for 2 h at the calcination temperature, the reactor was cooled to room temperature in Ar. The calcined sample was reduced in a blend of flowing Ar(160 cm^3/min)–H_2(40 cm^3/min) gases at a temperature increasing to the specific reduction temperature (T_R) at a rate of 0.2°C/min, then held at this temperature for 2 h.

2.3. CATALYST CHARACTERIZATION

The structures of the ZSM-5 samples [13] were confirmed by their powder X-ray diffraction (XRD) pattern. The amount of Si, Al and Pd metals in the Pd/HZSM-5 catalysts was measured with an inductively coupled plasma spectrophotometer (ARL-3510). The sample had a silica/alumina ratio of 66 and the Pd loading was 1.8 wt%.

The hydrogen–oxygen titration method [14,15] was applied to the pre-reduced Pd/HZSM-5 catalysts to determine the Pd dispersion. This experiment was carried out in a conventional Pyrex vacuum system. After calcination and reduction through the aforementioned procedure, the samples were exposed to oxygen at room temperature. The catalyst chamber was then evacuated at 100°C for 1 h before the titration was made. The amount of hydrogen titrating the catalyst at 100°C was measured after equilibrium was reached. The titration stoichiometry used to calculate the Pd dispersion was $3H_2 : 2Pd\text{–}O$ [14,15]. The advantage of this method over the hydrogen chemisorption technique is that it does not require the pretreatment at high temperature that may lead to sintering.

For the EXAFS measurements self-supporting wafers were calcined and reduced in an in situ EXAFS cell. The EXAFS measurements were carried out at beam line 10B of the Photon Factory at the National Laboratory for High Energy Physics in Tsukuba, Japan, with a synchrotron energy of 2.5 GeV, ring currents between 200 and 300 mA. Data were collected at the Pd K edge (24348 eV). Data analysis was performed with the University of Washington package. The k range from 2 to 12 in χ data was used for the Fourier transform. The R window used for inverse transform was from 2 to 3 Å. A 0.0125 mm Pd foil was used as reference structure for the EXAFS analysis. The coordination number (CN) of Pd in the reference foil was taken as 12, and the Pd–Pd bond distance (r) in the foil was assigned to 2.75 Å.

2.4. CATALYTIC ACTIVITIES

The CO hydrogenation reaction was performed in a continuous-flow fixed bed reactor system operating at 225°C, 21 bar, and a H_2/CO ratio of 2. Products were passed through a heated transfer line to a gas chromatograph (Hewlett-Packard 5890 series II) with TCD and FID detectors. Products were separated in a cross-linked methyl-silicon capillary column (i.d. = 0.2 mm, length = 50 m, He carrier) and Porapak Q column (o.d. = 1/8 inch, length = 1.8 m, He carrier).

2.5. FOURIER TRANSFORM INFRARED SPECTROSCOPY

FT-IR spectroscopy of adsorbed CO on the catalysts was carried out in a stainless-steel high-pressure transmission IR cell similar to that described by Hicks et al. [16]. Pd/HZSM-5 samples of 13 mg were pressed into a wafer of 13 mm diameter which was loaded in a stainless-steel IR cell. After pretreatment, a background spectrum in the absence of CO was recorded with a Bomem MB 102 Fourier transform IR spectrometer. The sample was then exposed to a flow of CO for 20 min at 25°C under atmospheric pressure. It was subsequently exposed to a flow of Ar at 25°C. The spectra were taken as a function of time-on-stream in Ar.

In order to study acidity of the catalysts, FT-IR spectra of adsorbed pyridine were obtained over the catalyst calcined and reduced through a method similar to that described by Topsøe et al. [17].

3. Results and discussion

3.1. Pd DISPERSION FROM THE H_2–O_2 TITRATION AND EXAFS

Table 1 shows the Pd dispersion of Pd/HZSM-5 catalysts obtained after calcination and reduction at various temperatures. For example, the Pd dispersion of the

Table 1
Metal dispersion by H_2–O_2 titration and EXAFS of 1.8 wt% Pd/HZSM-5 catalysts

Pretreatment temperature (°C)		Dispersion by H_2–O_2 titration	Dispersion by EXAFS coordination number [a]
calcination	reduction		
250	200	0.65	0.60
250	250	0.41	–
250	300	0.37	0.53
350	200	0.31	0.46
350	300	0.26	–

[a] Calculated by the method of Kip et al.[18] assuming the shape of metal particles is spherical.

Pd/HZSM-5 catalyst ($T_C = 250$°C, $T_R = 200$°C) was 0.65 (corresponding to the particle size 17 Å). The increase in the calcination and/or reduction temperature resulted in poor dispersion of Pd particles.

EXAFS was also carried out to measure the Pd dispersion. The Pd dispersion of the catalyst ($T_C = 250$°C, $T_R = 200$°C) estimated from EXAFS coordination number 8.7 is 0.60, which is very close to the value of 0.65 obtained from H_2–O_2 titration. Subsequent increase in the calcination and reduction temperature resulted in the increase in coordination number and the decrease in Pd dispersion.

The XRD gave no indication on the range of particle sizes present in the sample, which seemed to be caused by small particles that produced diffraction peaks too broad to be observed and/or by Pd loading of 1.8 wt% which is too small to be detected.

3.2. FT-IR SPECTROSCOPY OF ADSORBED CO OR PYRIDINE

In fig. 1 the FT-IR spectra of adsorbed CO on Pd/HZSM-5 ($T_C = 250$°C, $T_R = 200$°C) and Pd/HZSM-5 ($T_C = 350$°C, $T_R = 300$°C) are plotted during Ar purge. After Ar purging for 120 min, the peak intensity around 1900–2100 cm^{-1} decreases slightly. This indicates that a 120 min purging time is sufficient to remove gaseous and weakly adsorbed CO.

Three bands at 2086–2092 cm^{-1}, 1965–1969 cm^{-1} and 1928–1925 cm^{-1} were obtained in our experiments. The first band could be assigned to linearly adsorbed CO, and the second and the third band assigned to bridged CO [19–21]. They are denoted by L, B_1 and B_2 respectively.

In order to evaluate the effects of pretreatment conditions, IR spectra of adsorbed CO after Ar purge for 120 min on differently pretreated catalysts are shown in fig. 2. An increase in the calcination temperature and/or in the reduction temperature seems to reduce the relative intensity ratio of linearly adsorbed CO to the bridge-bonded CO. The relative abundance of linear and bridged species on Pd/HZSM-5 catalysts can be expressed in terms of the abundance ratio defined by Tessier et al. [21]. Table 2 shows that the ratio of linear CO species to bridged spe-

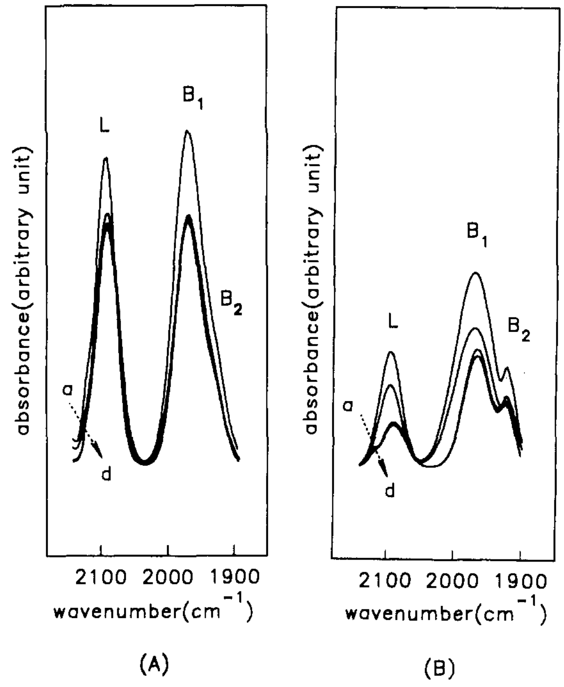

Fig. 1. FT-IR spectra of CO adsorbed on (A) Pd/HZSM-5 (T_C = 250°C, T_R = 200°C) and (B) Pd/HZSM-5 (T_C = 350°C, T_R = 300°C); purging time: (a) 20 min, (b) 40 min, (c) 80 min, (d) 120 min.

cies decreases with pretreatment temperatures, i.e., with increasing particle size. This trend seems to be resonable because a portion of low-coordinated atoms on the surface of metal particles decreases with particle size. It should be noted that the band positions of linear CO species on Pd/HZSM-5 catalysts shifted to lower frequencies at higher temperatures of pretreatment.

The extent of acidity modification with Pd dispersion was investigated through pyridine adsorption. Fig. 3 shows that the acidic characteristics of HZSM-5 i.e., Brønsted and Lewis sites at 1546 and 1451 cm^{-1} respectively, were suppressed as the Pd dispersion (or particle size) improves (or decreases). It seems that the presence of smaller Pd metals in HZSM-5 suppressed the acidic characteristics of zeolites.

3.3. CATALYST ACTIVITY IN CO HYDROGENATION

The catalytic behaviors of Pd/HZSM-5 catalysts were observed for the CO hydrogenation. As shown in table 3, a strong influence of pretreatment condition on product distribution was found. Over the Pd/HZSM-5 catalyst (T_C = 250°C, T_R = 200°C), the selectivity to oxygenates, i.e., methanol and dimethyl ether (DME), was higher than the selectivity to methane. Over the catalyst calcined at 250°C, the selectivity to oxygenates decreased with increasing reduction tempera-

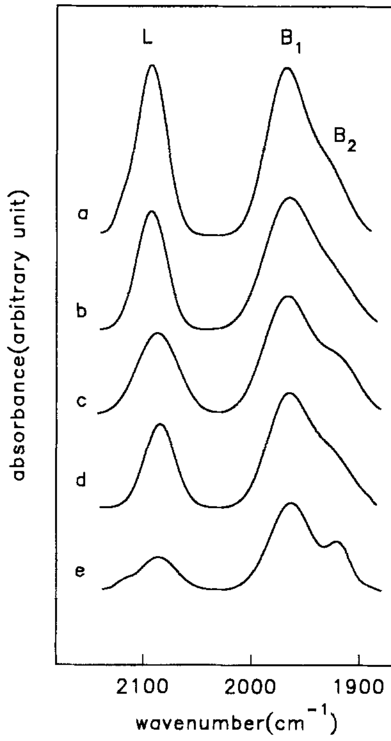

Fig. 2. FT-IR spectra of adsorbed CO after Ar purge for 120 min on Pd/HZSM-5 pretreated at (a) $T_C = 250°C$, $T_R = 200°C$; (b) $T_C = 250°C$, $T_R = 250°C$; (c) $T_C = 250°C$, $T_R = 300°C$; (d) $T_C = 350°C$, $T_R = 200°C$; (e) $T_C = 350°C$, $T_R = 300°C$.

ture. The main product over the Pd/HZSM-5 calcined at 350°C was methane and the selectivity to oxygenates was very low.

The results of the FT-IR study of adsorbed CO over Pd/HZSM-5 catalysts showed that the abundance ratio of adsorbed CO increased (accordingly the fraction of adsorbed CO with strong C–O bond strength increased) with palladium dis-

Table 2
Peak position and relative abundance of linear and bridged CO species over 1.8 wt% Pd/HZSM-5 catalysts

Pretreatment temperature (°C)		ν_{CO} (cm^{-1})			Abundance ratio (L/B)[a]
calcination	reduction	L	B_1	B_2	
250	200	2092	1969	1927	0.58
250	250	2091	1967	1921	0.45
250	300	2087	1966	1921	0.43
350	200	2083	1967	1922	0.40
350	300	2081	1967	1922	0.22

[a] The abundance ratios were estimated from the integrated intensities L to ($B_1 + B_2$)

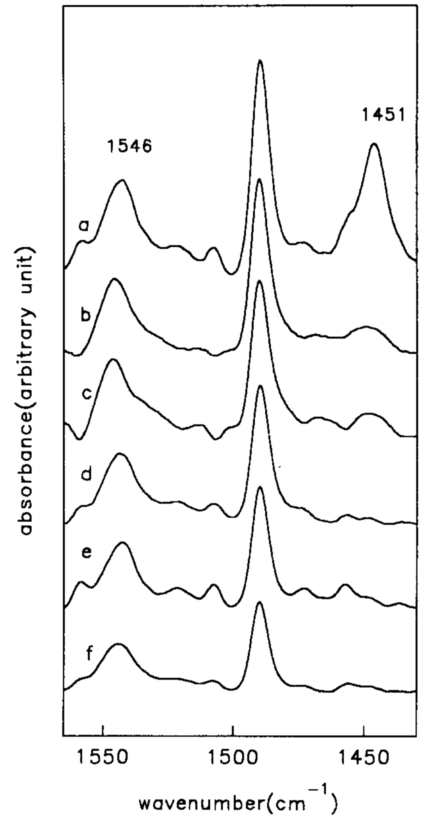

Fig. 3. FT-IR spectra of pyridine adsorbed on HZSM-5 and Pd/HZSM-5. (a) HZSM-5; (b) Pd/HZSM-5 ($T_C = 350°C$, $T_R = 300°C$); (c) Pd/HZSM-5 ($T_C = 350°C$, $T_R = 200°C$); (d) Pd/HZSM-5 ($T_C = 250°C$, $T_R = 300°C$); (e) Pd/HZSM-5 ($T_C = 250°C$, $T_R = 250°C$); (f) Pd/HZSM-5 ($T_C = 250°C$, $T_R = 200°C$).

Table 3
Activity and selectivity in CO hydrogenation over 1.8 wt% Pd/HZSM-5 catalysts at 225°C, 21 bar and GHSV = 4050 h^{-1}

Pretreatment temperature (°C)		TOF ($s^{-1} \times 10^3$)	Product distribution (mol%)					
calcination	reduction		C_1	C_2	C_3	C_{4+}	MeOH	DME
250	200	1.21	35.9	10.1	4.5	–	31.5	18.0
250	250	1.98	49.2	13.4	5.5	3.8	16.7	11.5
250	300	2.04	61.0	17.9	7.2	5.0	4.4	4.7
350	200	3.50	70.7	17.4	7.6	2.7	0.6	1.0
350	300	4.79	72.3	17.6	6.9	1.6	0.5	1.1

persion (table 2). The strengthening in the carbon–oxygen bond leads to the lowering of carbon monoxide dissociation, which favors the formation of methanol. Methanol must be formed on the Pd/HZSM-5 catalysts with small metal crystallites and on which CO is weakly adsorbed. The present result of the metal dispersion effect on methanol selectivity is in agreement with those over the palladium catalysts supported on silica gel [2,7,8] and X zeolite [9,10]. On the other hand, the selectivity to methane increased with decreasing dispersion. Rieck and Bell [22] have shown that CO dissociation occurs preferentially from bridged sites and proceeds more readily with decreasing dispersion over Pd/SiO_2.

The formation of DME over the Pd/HZSM-5 catalysts could be attributed to the dehydration of methanol on acid sites of the HZSM-5 support. Ono and Mori [23] reported that the formation of DME from methanol on acidic zeolites proceeds on weak acid sites, while the formation of higher hydrocarbon formation from methanol and DME requires stronger acid sites. As shown in a FT-IR study of adsorbed pyridine (fig. 3), the Brønsted acidity was suppressed with palladium dis-

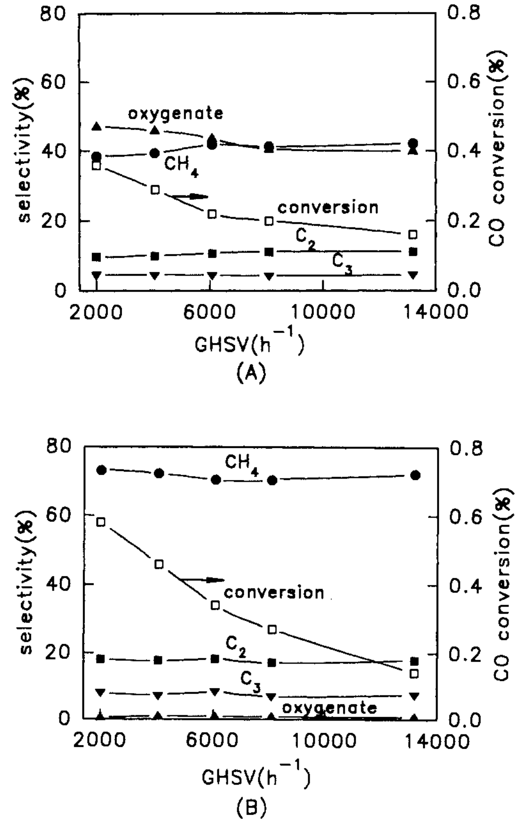

Fig. 4. Effect of space velocity on selectivity in CO hydrogenation at 225°C and 21 bar over (A) Pd/HZSM-5 ($T_C = 250°C$, $T_R = 200°C$) and (B) Pd/HZSM-5 ($T_C = 350°C$, $T_R = 300°C$).

persion. The Pd/HZSM-5 ($T_C = 250°C$, $T_R = 200°C$) showed a low selectivity to higher hydrocarbon as expected.

In fig. 4, the product distribution was plotted against the space velocity. If the oxygenate compounds were converted into hydrocarbon, the oxygenate selectivity should have increased with space velocity. The product distribution was not affected by the change of space velocity, and it seems that the oxygenates were not converted into the hydrocarbons over the Pd/HZSM-5 catalyst.

4. Conclusion

Methanol and dimethyl ether were the main products in CO hydrogenation over Pd/HZSM-5 catalysts with small Pd particles on which CO was weakly adsorbed, while the selectivity to methane increased with metal sizes. The ratio of linearly adsorbed CO species to bridged species increased with metal dispersion on Pd/HZSM-5 catalysts, which favored the formation of methanol due to the inhibition of C–O dissociation.

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References

[1] M.L. Poutsma, L.F. Elek, P.A. Ibarbia, A.P. Risch and J.A. Rabo, J. Catal. 52 (1978) 157.
[2] F. Fajula, R.G. Anthony and J.H. Lunsford, J. Catal. 73 (1982) 237.
[3] Y. Kikuzono, S. Kagami, S. Naito, T. Onishi and K. Tamaru, Faraday Discussions Chem. Soc. 72 (1982) 135.
[4] J.M. Driessen, E.K. Poels, J.P. Hindermann and V. Ponec, J. Catal. 82 (1983) 26.
[5] R.F. Hicks and A.T. Bell, J. Catal. 90 (1984) 205.
[6] C. Sudhakar and M.A. Vannice, J. Catal. 95 (1985) 227.
[7] G. Lietz, M. Nimz and J. Völter, Appl. Catal. 45 (1988) 71.
[8] H.S. Hahm and W.Y. Lee, Appl. Catal. 65 (1990) 1.
[9] N.I. Jaeger, G. Schulz-Ekloff and A. Svensson, in: *Catalysis and Adsorption by Zeolites*, Studies in Surface Science and Catalysis, Vol. 65, eds. G. Öhlmann, H. Pfeifer and R. Fricke (Elsevier, Amsterdam, 1991) p. 327.
[10] A. Martin, B. Lücke, N.J. Jaeger, G. Schulz-Ekloff, D. Gutschick and H. Miessner, Catal. Lett. 13 (1992) 247.
[11] F.A.P. Cavalcanti, C. Dossi, L.L. Sheu and W.M.H. Sachtler, Catal. Lett. 6 (1990) 289.
[12] R.J. Argauer and G.R. Landolt, US Patent 3,702,886.
[13] H. van Koningsveld, J.C. Jansen and H. van Bekkum, Zeolites 10 (1990) 235.
[14] J.E. Benson, H.S. Hwang and M. Boudart, J. Catal. 30 (1973) 146.

[15] D.J. Suh, T.J. Park and S.K. Ihm, J. Catal. 149 (1994) 486.
[16] R.F. Hicks, C.S. Kellner, B.J. Savatsky, W.C. Hecker and A.T. Bell, J. Catal. 71 (1981) 216.
[17] N.Y. Topsøe, K. Pedersen and E.G. Derouane, J. Catal. 70 (1981) 41.
[18] B.J. Kip, F.B.M. Duivenvoorden, D.C. Koningsberger and R. Prins, J. Catal. 105 (1987) 26.
[19] A.M. Bradshaw and F.M. Hoffmann, Surf. Sci. 72 (1978) 513.
[20] N. Sheppard and T.T. Nguyen, in: *Advances in Infrared and Raman Spectroscopy*, Vol. 5, eds. R.J.H. Clark and R.E. Hester (Heyden, London, 1980) p. 67.
[21] D. Tessier, A. Rakai and F.B. Verduraz, J. Chem. Soc. Faraday Trans. 88 (1992) 741.
[22] J.S. Rieck and A.T. Bell, J. Catal. 103 (1987) 46.
[23] Y. Ono and T. Mori, J. Chem. Soc. Faraday Trans. I 77 (1981) 2209.