METHANOL SELECTIVITY OF SILICA-SUPPORTED PtFe

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Adding Fe to Pt/SiO_2 catalysts improves activity for methanol synthesis from $3H_2/CO$ at 523 K and 3.19 MPa. Over 90% methanol selectivity can be achieved at low conversion, depending on the metal composition and dispersion. *In situ* Mössbauer measurements after reduction in hydrogen at 673 K and during steady-state reaction show the presence of PtFe alloy and Fe^{3+} phases only. The amount of PtFe alloy increases as catalysts activate to produce methanol with higher activity and selectivity.

High pressure CO hydrogenation studies by Poutsma et al. have shown that silica-supported Group VIII noble metals (Ir, Pd, and Pt) are catalysts for C_1 and C_2 oxygenates [1]. Rh/SiO_2 also catalyzes production of C_2 oxygenates [2]. Addition of Fe to Rh modifies the oxygenate product distribution causing ethanol to become the major C_2 oxygenated product and increasing the methanol selectivity [2]. Iron also enhances methanol production over Pt, Ir, and Pd [3–6]. Meriaudeau et al. showed that the oxide support used can strongly influence the selectivity and activity for methanol [7], and that addition of Mo, Co, Hi, and Cr can enhance methanol activity of supported Pt [8–10]. Fukuoka et al. showed that 100% methanol selectivity can be achieved with a Pt_3Fe_3 cluster-derived catalyst [3] and Fukushima et al. reported methanol selectivity of over 95% with $PdFe/SiO_2$ [4]. In these cases, the primary effect of Fe is to improve activity [3,4]. Fukushima et al. also showed that with addition of small amounts of Fe, the methanol selectivity of $FeIr/SiO_2$ is superior to that of Ir/SiO_2 [5]. Koningsberger et al. have found that $FeIr/SiO_2$ with Fe/Ir atomic ratios greater than 1 is a highly active methanol-producing catalyst, but only after times of 20 to 40 hours on stream needed to fully activate the catalyst [6].

In light of the high initial rates of methanol production with Fe-noble metal bimetallic catalysts [2–6], we have paid particular attention to this effect in a general study of PtFe/SiO_2 catalysts. In this communication, we report high initial rates of methanol versus hydrocarbon production obtained with PtFe/SiO_2, and that this selectivity is dependent on the metal dispersion percentage exposed) of the catalysts. To investigate the nature of the methanol selective catalysts, Mössbauer spectroscopy was used to characterize the chemical state of Fe, X-ray photoelectron spectroscopy (XPS) was used to characterize the surface chemical state of the catalysts, and H_2 desorption was used to determine metal dispersions.

Catalysts were prepared, by the incipient wetness impregnation of $H_2PtCl_6 \cdot 4.5H_2O$ (Sigma) and $Fe(NO_3)_3 \cdot 9H_2O$ (Fischer Scientific) solutions onto previously dried Cab-O-Sil silica (EH5, 390 m^2/g). The impregnated catalysts were dried by raising the temperature from room temperature to 413 K in 20 to 25 K increments spread over 8 hours and then holding at 413 K for 24 hours. The detailed drying procedure is described elsewhere [11]. The catalysts for Mössbauer spectroscopy experiments were prepared with appropriate amounts of ^{57}Fe (93.31%, Oak Ridge) and $Fe(NO_3)_3 \cdot 9H_2O$ dissolved in 3N HNO_3 solution. All catalysts were pretreated in H_2 at 673 K for 2 hours prior to reaction. CO hydrogenation reactions at 3.19 MPa were carried out at 523 K with $3H_2/CO$ reactant ratio in a stainless steel U-tube reactor at conversions between 0.1 and 1% and flow rates of 100 std cc/min of reactant gas. The empty reactor was checked periodically to ensure that it had no activity. The constant acceleration Mössbauer spectroscopy experiments were performed in an *in situ* high-temperature absorber cell capable of withstanding 0.87 MPa pressure with an Austin Science S-600 spectrometer controller, a $^{57}Co/Rh$ source, and a Nuclear Data model 62 multichannel analyzer. All spectra reported have isomer shift referenced to a 25 μm NBS Fe foil and have the contribution of Fe in the Be windows of the cell subtracted. The procedures for Mössbauer experiments and the computer analysis of the spectra by non-linear least squares fitting are described in detail elsewhere [11,12]. The XPS experiments were performed in a PHI 5300 ESCA spectrometer using AlK_α radiation. The catalysts were treated *in situ* in a reaction chamber and transferred to XPS analysis chamber without exposure to air. A low energy electron gun was used to minimize the charging effects and electron binding energy is referenced against Si 2p at 103.1 eV. The procedures for XPS experiments and analysis of data will be described elsewhere [13]. The H_2 desorption measurements were conducted by reducing the catalysts in hydrogen at 673 K for 2 hours, cooling to room temperature over at least an 8 hour period, and then desorbing the chemisorbed hydrogen at 673 K using a procedure similar to that of Amelse et al. [14].

Table 1 lists the metal dispersion, turnover frequency (TOF) normalized to the metal surface area determined from H_2 desorption, and selectivity of the catalysts. The TOF and selectivity are values obtained after approximately 20 hours of reaction when all catalysts were at steady state. For the Pt-only catalysts, both methane and methanol production deactivate to reach the steady state while for the bimetallic catalysts, methanol activity increases from trace amounts after 10

Table 1

Dispersion, methanol activity, and product selectivity of Pt and PtFe catalysts, at 523 K, 31.6 atm, and $3H_2/CO$

Catalyst	Dispersion (%)	TOF CH_3OH (×1000) (sec^{-1})	Product selectivity (CO_2 free)		
			CH_3OH	CH_4	C_{2^+}
2% Pt/SiO_2	75	1.1	79.1	20.9	0.0
2% $3Pt1Fe/SiO_2$	73	2.5	94.6	5.4	0.0
2% $1Pt1Fe/SiO_2$	50	7.5	90.1	9.7	0.2
10% Pt/SiO_2	50	0.48	67.3	32.7	0.0
10% $3Pt1Fe/SiO_2$	25	15.0	92.8	7.1	0.1
10% $1Pt1Fe/SiO_2$	23	15.0	64.2	29.6	6.2

minutes, to measureable amounts after one hour and then by a factor of about 3 during continuing activation. Methane activity of the bimetallic catalysts is stable during the activation period. The selectivity is the mole percentage of total product excluding CO_2 and H_2O. The 2 wt% PtFe catalysts have higher dispersion, produce methanol with higher selectivity than the 10 wt% catalysts with identical metal ratios, but have a lower TOF. For the 2 wt% catalysts, the high methanol selectivity (over 90%) is maintained as the atomic ratio changes from 3 to 1. The methanol selectivity of 10 wt% $1Pt1Fe/SiO_2$, on the other hand, is 64%, comparable to that of 10 wt% and 2 wt% Pt/SiO_2. The lower CH_3OH selectivity of 10 wt% $1Pt1Fe/SiO_2$, compared to the other bimetallic catalysts, is due to increased methane and higher hydrocarbon production, with a hydrocarbon product distribution similar to that of Fe/SiO_2. In addition to high methanol selectivities, all bimetallic catalysts have higher TOFs to methanol than those of the Pt-only catalysts. Even though selectivity is low for 10 wt% $1Pt1Fe/SiO_2$ catalyst, the TOF of this catalyst to methanol is much higher than that of the Pt-only catalysts and is as high as all other bimetallic catalysts. Thus, methanol activity enhancement by the addition of Fe to Pt/SiO_2 is shown for all bimetallic catalysts.

As indicated in table 1, a large selectivity difference was observed between 10 wt% $1Pt1Fe/SiO_2$ and 2 wt% $1Pt1Fe/SiO_2$. These two catalysts provide an opportunity to look for chemical or physical differences that might identify active phases for methanol enhancement and hydrocarbon production. One difference between the two catalysts shown in table 1 is the metal dispersion. The 10 wt% $1Pt1Fe/SiO_2$ catalyst has a metal dispersion of 25% while that of 2 wt% $1Pt1Fe/SiO_2$ is 50%. For additional characterization of these two catalysts we turn to Mössbauer spectroscopy and XPS.

Figure 1 shows Mössbauer spectra of 10 wt% 1Pt1Fe and 2 wt% $1Pt1Fe/SiO_2$ reduced at 673 K for 2 hours in H_2 and measured *in situ* in H_2 at 523 K and during reaction at 523 K and 0.87 MPa with a $3H_2/CO$ reactant ratio. The

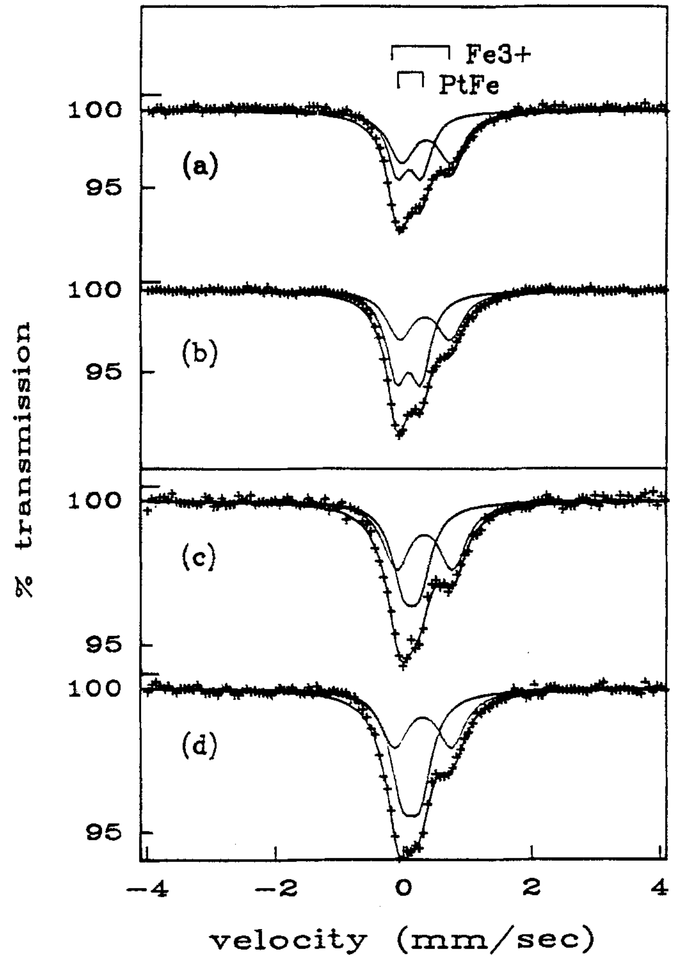

Fig 1. Mössbauer spectra of 10 wt% and 2 wt% PtFe/SiO_2 at 523 K. (a) 2 wt% 1Pt1Fe after 673 K H_2 for 2 hours, (b) 2 wt% 1Pt1Fe during reaction at 8.6 atm and $3H_2$/CO, (c) 10 wt% 1Pt1Fe after 673 K H_2 for 2 hours, (d) 10 wt% 1Pt1Fe during reaction at 8.6 atm and $3H_2$/CO.

bimetallic catalysts required a typical activation period of 6 to 12 hours. Spectra taken during reaction were collected over a period of 6 to 24 hours after the catalysts reached steady state. The crosses in the figure 1 represent the data while the solid lines represent the computer fitted total envelope of the spectra and the individual phases contributing to the envelope. The Mössbauer parameters from the computer analysis of these figures are given in table 2. The best fit of the spectra was obtained with two doublets corresponding to data for PtFe alloy and high spin Fe^{3+} ions. Bartholomew and Boudart [15] and Niemantsverdriet et al. [16] also obtained better fits to their data for PtFe alloy catalysts using a doublet for the PtFe alloy phase. The presence of Fe^{3+} ion in PtFe/SiO_2 catalysts after reduction in H_2 has been confirmed by Martens et al. using electron spin resonance [17].

Table 2
Mössbauer parameters for catalysts measured at 523 K, fig. 1.

Catalyst	Phase	IS *	QS *	Γ *	% dip	Area **
(a) 2% $1Pt1Fe1SiO_2$						
673K H_2	PtFe	0.16	0.22	0.45	3.13	3.60
	Fe^{3+}	0.30	0.85	0.50	3.48	4.44
(b) 2% $1Pt1Fe/SiO_2$						
523 K $3H_2/CO$	PtFe	0.10	0.32	0.45	4.22	4.84
	Fe^{3+}	0.32	0.85	0.46	2.61	3.06
(c) 10% $1Pt1Fe/SiO_2$						
673 K H_2	PtFe	0.12	0.27	0.45	2.43	8.28
	Fe^{3+}	0.32	0.88	0.53	2.25	9.04
(d) 10% $1Pt1Fe/SiO_2$						
523 K $3H_2/CO$	PtFe	0.11	0.28	0.45	3.08	10.54
	Fe^{3+}	0.31	0.89	0.53	1.94	7.82

* IS (isomer shift), QS (quadrupole splitting) and Γ (line width) in units of mm/sec.
** Absolute area (% dip·mm/sec·10^{-5}/mol ^{57}Fe).

The results for 10 wt% $1Pt1Fe/SiO_2$, shown by fig. 1 (c) and (d), indicate that there is no visible contribution of unalloyed Fe^0 or iron carbide prior to and during reaction that could account for the hydrocarbon production observed. Recently, Clausen et al. pointed out the difficulties in observing small contributions of superparamagnetic species in Mössbauer spectra of Fe/SiO_2 [18]. Although it is difficult to rule out small contributions from both superparamagnetic Fe and carbides, a number of previous studies with Group VIII noble metal-Fe alloy catalysts at cryogenic temperatures indicated the absence of such species with bimetallic catalysts [19,20]. Furthermore, the CO/H_2 reaction data for 2% $1Pt1Fe/SiO_2$ suggest that superparamagnetic species are not present. Because of its relatively high activity, Fe carbide that was phase separated from Pt or PtFe alloy phases would have contributed substantially higher hydrocarbon production.

During steady-state reaction, both catalysts show an increased PtFe alloy contribution to the spectra at the expense of Fe^{3+}, as indicated by a comparison of the area contributions from the PtFe and Fe^{3+} phases present in the post-reduction catalysts to those for the catalysts during reaction (table 2). Although changes in the PtFe and Fe^{3+} contributions to the Mössbauer spectra were observed for both catalysts after methanol activation, the quantification of this result is not straight-forward because of the dispersion dependence of the recoil-free fraction indicated by the change in the total absolute area per mole of ^{57}Fe for the two catalysts. However, reduction of Fe^{3+} to PtFe alloy during reaction is clearly shown by Mössbauer spectroscopy.

The presence of metallic and irreducible Fe in the two catalysts after 703 K reduction in H_2 for 2 hours is further illustrated by XPS, as shown in fig. 2.

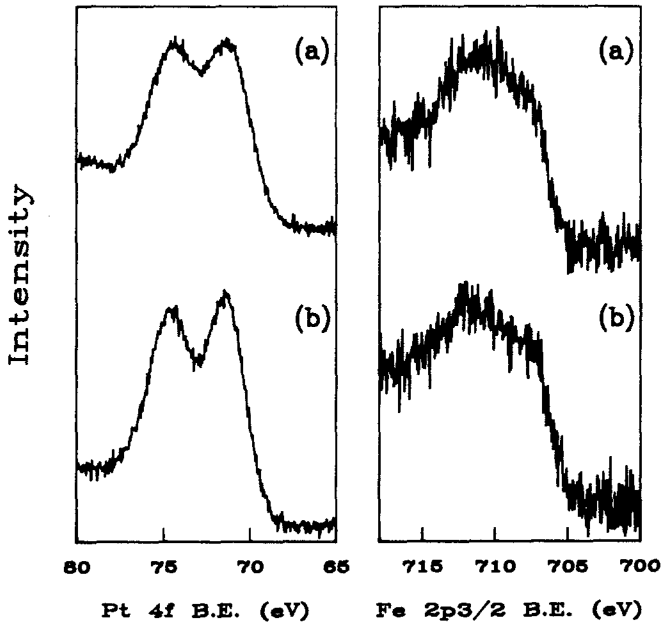

Fig. 2. XPS spectra of Pt 4f and Fe $2p_{3/2}$ regions for $1Pt1Fe/SiO_2$ after 703 K reduction in H_2 for 2 hours a) 2 wt% b) 10 wt%.

Quantitative analysis of the spectra shows substantial Fe reduction to Fe^0 (707.0 eV) and complete reduction of Pt to Pt^0 (71.0 eV). These binding energies for both catalysts agree well with reported values for metallic Pt and Fe [21,22]. The presence of irreducible Fe is indicated by the range of fitted parameters falling well within reported values for both Fe^{2+} and Fe^{3+} (709.0 to 711.0 eV) [21]. The 2 wt% $1Pt1Fe/SiO_2$ sample has a measured Pt/Fe atomic ratio of 0.8,while 10 wt% $1Pt1Fe/SiO_2$ has ratio of 1.0 showing that both catalysts have surface metal ratios close to the nominal value. The surface Pt^0/Fe^0 ratios calculated from the fitted lines are 2.5 for 10 wt% $1Pt1Fe/SiO_2$ and 2.2 for 2 wt% $1Pt1Fe/SiO_2$. The average surface ratios of Pt to Fe are thus not sufficiently different to account for differences in methanol selectivity and hydrocarbon activity. Lateral segregation of Fe on the alloy surface to form an isolated ensembles of Fe could account for the higher hydrocarbon activity of 10% $1Pt1Fe/SiO_2$, however.

In summary, we observe that PtFe bimetallic catalysts have high intrinsic rates for methanol versus hydrocarbon production and that the selectivity depends on the metal dispersion and composition. *In situ* Mössbauer spectroscopy shows that a PtFe phase increase accompanies the methanol TOF increase after activation. The kinetic data show that iron addition to Pt enhances the MeOH production rate. Loss of selectivity occurs when the CH_4 and higher hydrocarbon rates increase, suggesting enhanced iron-like behavior of the non-optimum catalyst. XPS could not quantify this effect in this work, but further studies of the system are in progress.

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