RESEARCH NOTE

Synthesis of Methanol from CO over Ca-Promoted Pt/SiO$_2$

T. C. Watling, A. F. Gusovius, and R. Prins

Laboratory of Technical Chemistry, Swiss Federal Institute of Technology (ETH), 8092 Zürich, Switzerland

Pt/SiO$_2$ and Ca-promoted Pt/SiO$_2$ catalysts were prepared from three different Pt precursors and tested for CO hydrogenation at 280°C and 25 bar. Changing the Pt precursor affects both the activity and selectivity of the resulting catalyst. The measure of activity enhancement for methanol on addition of the promoter increases in the order $[Pt(NH_3)_4](OH)_2 < H_2[Pt(OH)_6] < H_2[PtCl_6]$. A correlation between the activity enhancement on Ca addition and the extent of metal–promoter interaction, as measured by the change in the temperature-programmed reduction profile and loss of chemisorption capacity, was observed. This suggests that the dopant needs to be located on the metal particle in order to promote the reaction. © 1999 Academic Press

Key Words: Pt/SiO$_2$; methanol synthesis; hydrogenation of CO; promoter; TPR; chemisorption; decoration.

INTRODUCTION

Methanol is one of the important raw materials produced from syngas. The current commercial process is based on a Cu/ZnO/Al$_2$O$_3$ catalyst and was introduced by ICI in 1966. Previous studies from our laboratory (1, 2) have shown that promoted Pd/SiO$_2$ catalysts are also active for methanol synthesis, while unpromoted Pd/SiO$_2$ is inactive. A wide range of promoters were considered, of which Ca and La were found to give the most active catalysts, with La being slightly less selective than Ca. The effect of the Pd precursor on the activity of Ca/Pd/SiO$_2$ was also investigated, and it was found that activity of the resulting catalyst increased in the order $Pd(NO_3)_2 \ll PdCl_2 < [Pd(NH_3)_4](NO_3)_2$.

In more recent work the location of the promoter in Ca/Pd/SiO$_2$ catalysts has been investigated (3). From a combination of H$_2$ and CO chemisorption, transmission electron microscopy (TEM), temperature-programmed reduction (TPR), and activity measurements it was concluded that (i) CaO locates itself preferentially on the PdO particles present after calcination, until a maximum coverage is reached, and (ii) CaO species located on (and perhaps also near) the Pd particles formed after reduction give rise to the catalytic activity for methanol. When other promoters were considered, a correlation between the extent of decoration of the promoter on the Pd particles and the activity for methanol was found. Thus, the affinity of the promoter for the metal particle is at least partly responsible for its ability to promote the reaction.

In this paper we extend our study of the methanol synthesis to Pt-based catalysts. Since Pt lies below Pd in the periodic table, it might be expected that promoted Pt catalysts behave similarly to promoted Pd/SiO$_2$ catalysts; both Pd and Pt are poor at dissociating CO (4, 5), which favours methanol formation, in which the C–O bond remains intact, over hydrocarbon formation, which requires dissociation of the CO. To this end Pt/SiO$_2$ and Ca/Pt/SiO$_2$ catalysts have been prepared using three different precursors. These catalysts have been tested for catalytic activity. TPR and H$_2$ chemisorption have been used to measure the extent of Pt–promoter interaction, to see if a correlation between this and activity exists for Pt- as well as Pd-based catalysts.

One key difference between platinum and palladium is that the latter forms its oxide much more readily. This may be important if the preferential location of the promoter on the metal particle, which seems crucial for the activity for methanol, is dependent on the metal being present as an oxide during impregnation of the promoter, e.g., if the preferential promoter location involves adsorption of promoter ions on the noble metal oxide particles during impregnation or compound formation during calcination.

EXPERIMENTAL

Catalyst Preparation

The catalysts (Table 1) were prepared by pore volume impregnation, using ultrapure SiO$_2$ (800 m^2 g^{-1}, 250–350 μm), prepared by hydrolysis of tetraethoxysilane (Fluka, puriss, >99%) (6) as the support. The SiO$_2$ was impregnated with the Pt precursor (Table 1), dried at 120°C (ramp 1°C min^{-1}) for 16 h, and calcined in air at 450°C (350°C for the sample prepared from H$_2$[Pt(OH)$_6$]) (ramp 5°C min^{-1}) for 2 h to give a Pt/SiO$_2$ with 4.5 wt% Pt. The Pt/SiO$_2$ was

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TABLE 1

Catalytic Properties and Chemisorption Results for Pt/SiO$_2$ and Ca/Pt/SiO$_2$ Catalysts Prepared from Different Precursors

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Precursor	wt% Pt	Ca/Pt (molar)	Chemisorption H$_{irr}$/Pt	Activity (mmol$_{CO}$ mol$_{Pt}^{-1}$ s^{-1})	Deactivation[a] (%)	TOF (10^{-3} s^{-1})	Selectivities (%)					MeOH/ DME[b]
							C$_{1\text{-oxo}}$	CH$_4$	C$_{2+}$	C$_{2\text{-oxo}}$	CO$_2$	
[Pt(NH$_3$)$_4$](OH)$_2$	4.50	0	0.56	0.32	61	0.6	14.6	70.5	0.9	0.0	14.0	143
	4.49	0.125	0.55	0.57	29	1.0	70.4	8.8	0.6	0.4	19.9	571
H$_2$[PtCl$_6$]	4.51	0	0.29	0.81	57	2.77	7.4	91.9	0.7	0.0	0.0	11
	4.50	0.23	0.20	2.28	7	11.62	90.1	1.4	0.4	1.1	6.5	1516
H$_2$[Pt(OH)$_6$][c]	4.50	0	0.29	0.06	31	0.22	31.4	14.5	8.0	0.2	45.4	—[d]
	4.49	0.125	0.27	0.53	59	1.97	82.2	2.9	1.1	0.0	13.7	—[d]

Note. The activities and selectivities given are those after 24 h on stream.

[a] Loss of total activity after 24 h relative to total activity after 1 h.

[b] Methanol to dimethyl ether ratio.

[c] Dissolved in 65% nitric acid. Sample calcined and reduced at 350°C instead of 450°C.

[d] No DME detected.

subsequently impregnated with Ca using Ca(NO$_3$)$_2 \cdot$ 4H$_2$O (Fluka, MicroSelect, >99%) as the precursor and the same drying and calcination protocol as before.

Catalyst Characterization

TPR measurements were carried out using an apparatus described previously (7). The sample (120 mg) was cooled to −80°C in flowing Ar. The feed was then switched to 5% H$_2$ in Ar (11 cm^3 min^{-1}), which gave rise to a switch peak. The temperature was ramped at 10°C min^{-1} to 600°C and held for 15 min before cooling back to −80°C. The feed was switched back to Ar and then back to H$_2$/Ar, generating another switch peak. The difference in areas between the first and the second switch peak corresponds to the hydrogen uptake occurring when the hydrogen is first introduced (7, 8). The hydrogen uptakes were quantified using PdO as a standard.

H$_2$ chemisorption was performed using a standard volumetric apparatus. The sample (containing 2 mg Pt) was reduced in flowing H$_2$ at 450°C (350°C for the sample prepared from H$_2$[Pt(OH)$_6$]) (ramp 5°C min^{-1}) for 1 h and then evacuated at 10^{-4} Pa for 1 h at the same temperature. Isotherms were measured at 20°C in the pressure range 0–1200 Pa. After measurement of the first isotherm, the sample was outgassed at 10^{-4} Pa for 35 min before a second isotherm was measured. The linear proportions of the two isotherms were extrapolated to zero pressure and the amount of hydrogen irreversibly adsorbed is given by the difference between these two intercepts. The number of exposed Pt atoms was calculated assuming one H adsorbed per exposed Pt atom.

Activity Testing

Catalysts were tested for CO hydrogenation using a stainless steel reactor equipped with an internal quartz tube (i.d.

9 mm) to avoid contamination of the catalyst with Fe, Ni, or Cr formed from metal carbonyls by reaction with the steel; for the same reason, a γ-Al$_2$O$_3$ trap upstream of the catalyst was used to adsorb such metal carbonyls (9). H$_2$ and CO were fed from mass flow controllers. The catalyst (ca. 620 mg) was diluted with SiC to give a bed volume of 1.5 cm^3. The catalyst was reduced in a flow of H$_2$ (30 cm^3 min^{-1}) at 450°C (350°C for the sample prepared from H$_2$[Pt(OH)$_6$]) (ramp 5°C min^{-1}) for 1 h under atmospheric pressure. After cooling to reaction temperature (280°C), the pressure was increased to working pressure (25 bar) by means of a back pressure regulator, and then CO was added. The feed was H$_2$/CO = 2, flowing at 0.11 mol h^{-1}. Experiments were carried out for 24 h on stream. The reactor effluent was analysed every hour using two online GCs, a Shimadzu GC8A equipped with a HAYESEP D column (SS, 12 ft × 1/8 in.) and a TCD detector for analysis of CO, CO$_2$, and methanol and an HP 5890 equipped with a Chrompack WCOT capillary column (fused SiO$_2$, 50 m × 0.32 mm) and an FID detector for analysis of hydrocarbons and oxygenates. The products will be summarised in five classes, CO$_2$, CH$_4$, C$_{2+}$ (alkanes and alkenes with $n \geq 2$), C$_{1\text{-OXO}}$ (methanol and dimethyl ether), and C$_{2\text{-OXO}}$ (ethanol).

RESULTS

Catalysts from [Pt(NH$_3$)$_4$](OH)$_2$

The Pt/SiO$_2$ and Ca/Pt/SiO$_2$ samples derived from this precursor were both black, indicating the presence of Pt metal and/or PtO (10). The hydrogen uptakes in the TPR corresponded to H/Pt = 1.4, confirming that the Pt was partially reduced. The TPR profiles of both samples (Fig. 1) are very similar, showing that there is little interaction between the Pt and the Ca promoter. (Note that the small apparent peak seen with all samples around −50°C is an artefact caused by the sudden increase in temperature when the
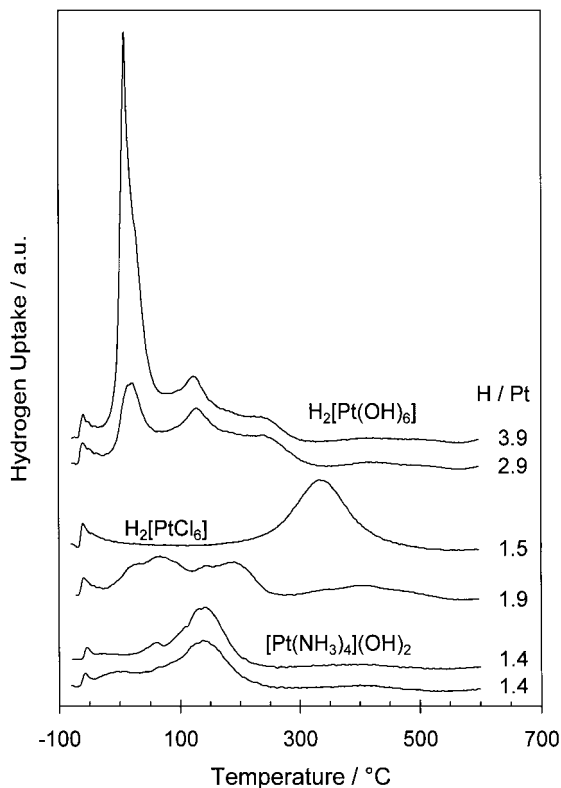
FIG. 1. TPR profiles of Pt/SiO₂ and Ca/Pt/SiO₂ samples prepared from different precursors. In each pair of traces, the upper trace corresponds to the Pt/SiO₂ and the lower to the Ca/Pt/SiO₂. The precursor is indicated above each pair of traces, and the ratio of H uptake to number of Pt atoms is given on the right.

temperature ramp is started.) Similarly, Ca doping resulted in only a slight decrease in the chemisorption capacity from 56 to 55%, indicating negligible decoration of the Pt particles by Ca.

Catalytic results are given in Table 1. The TOF obtained with Pt/SiO₂ is comparable to that of Pd/SiO₂ (0.6×10^{-3} and 0.8×10^{-3} s^{-1} (3), respectively), although the selectivity to $C_{1\text{-oxo}}$ is almost halved (15% compared with 29%). However, unlike the Pd-based catalysts, addition of Ca has little effect on the activity of the Pt/SiO₂; the TOF obtained with a Ca/Pt/SiO₂ sample with a Ca : Pt ratio of 0.125 is less than that of a Ca/Pd/SiO₂ sample with a Ca : Pd ratio of 0.004. The enhancement in activity for $C_{1\text{-oxo}}$ by Ca addition is 8.6, compared with a 49-fold enhancement in going from Pd/SiO₂ to a Ca/Pd/SiO₂ with a Ca : Pd ratio of 0.10 (3). This low enhancement of activity reflects the minimal promoter–Pt interaction.

Catalysts from $H_2[PtCl_6]$

With this precursor the interaction between the Ca promoter and the Pt was clearly greater than that obtained with [Pt(NH₃)₄](OH)₂. The hydrogen chemisorption capac-

ity decreased from 29 to 20% on Ca addition, suggesting that Ca was deposited on the metal particles. In addition, the TPR (Fig. 1) was significantly changed by Ca addition from a broad peak at 333°C to a rather complicated uptake feature between −25 and 560°C. The H/Pt ratios are 1.5 without Ca and 1.9 with Ca, although in the latter case the peak shape makes accurate integration difficult. This suggests that the Pt in the Pt/SiO₂ is not fully oxidised. On the other hand, the Pt/SiO₂ was brown while the Ca/Pt/SiO₂ was black, which suggests the presence of PtO₂ with the former sample and Pt metal and/or PtO in the latter sample (10, 11).

The Pt/SiO₂ and the Ca/Pt/SiO₂ derived from this precursor were the most active of all the Pt samples prepared, both in terms of total activity and TOF. Addition of Ca resulted in a large increase in the selectivity to $C_{1\text{-oxo}}$ from 7 to 90% and a 34-fold enhancement in $C_{1\text{-oxo}}$ activity. This considerable enhancement of activity reflects the significant promoter–Pt interaction.

Catalysts from $H_2[Pt(OH)_6]$

This precursor was found to be insoluble in water and therefore had to be dissolved in 65% nitric acid. The chemisorption capacity, on Ca addition, was reduced by only a small amount, from 29 to 27%, indicating relatively little decoration of Ca on the metal particles. The TPR of both samples (Fig. 1) consist of a series of overlapped bands lying mainly between −20 and 350°C. While the Ca addition results in a large decrease in the band at 8°C, the other bands are essentially unaffected and the hydrogen uptake still occurs over the same temperature range. This precursor gave the highest hydrogen uptakes of the precursors tried; H/Pt values of 3.9 and 2.9 were obtained for the samples without and with Ca, respectively, suggesting that the Pt was present as a mixture of PtO and PtO₂. Similarly, the fact that both samples were brown suggests a predominance of PtO₂ (11).

This precursor produced the least active Pt/SiO₂ sample, although the enhancement in $C_{1\text{-oxo}}$ activity (23-fold), on Ca addition, was greater than that obtained with [Pt(NH₃)₄](OH)₂. Ca addition resulted in the $C_{1\text{-oxo}}$ selectivity increasing from 31 to 82%.

DISCUSSION

As with Pd-based catalysts, a correlation between promoter–noble metal interaction and enhancement of activity on promoter addition was observed. Thus, with the catalysts prepared from [Pt(NH₃)₄](OH)₂, addition of Ca results in no significant change in the chemisorption capacity or TPR profile, and it also results in the smallest activity enhancement. On the other hand, the H₂[PtCl₆]-based catalysts showed the largest decrease in chemisorption capacity, the largest change in the TPR profile, and the greatest activity enhancement on Ca addition. This confirms the model

that the Ca promoter needs to be located on the noble metal particles in order for methanol synthesis to be promoted.

There are, however, differences between the Pt- and Pd-based systems. While the most active $Ca/Pd/SiO_2$ catalyst was prepared from $[Pd(NH_3)_4](NO_3)_2$, the $Ca/Pt/SiO_2$ catalyst prepared from $[Pt(NH_3)_4](OH)_2$ exhibited only low activity. This might be because in the latter case the NH_3 produced by the decomposition of the precursor during calcination is able to reduce the Pt^{2+} cations to the metal. Since platinum metal forms only a surface oxide, the result is a Pt/SiO_2 sample with the platinum predominantly in the metallic form. In contrast, with the palladium system formation of a bulk oxide occurs during calcination. As already mentioned, this may be important if the preferential location of the promoter on the metal particle, which seems crucial for activity for methanol, is dependent on the metal being present as an oxide during impregnation of the promoter. Therefore subsequent catalysts were prepared using $H_2[PtCl_6]$ and $H_2[Pt(OH)_6]$ as precursors in an attempt to prepare Pt/SiO_2 samples in which the platinum was present as an oxide. These precursors do not contain ammine ligands, which bring about reduction of platinum on decomposition, and have the Pt in the $4+$ rather than the $2+$ oxidation state. The resulting Pt/SiO_2 samples were brown, indicating the presence of PtO_2, while the Pt/SiO_2 sample prepared from $[Pt(NH_3)_4](OH)_2$ was black, suggesting the presence of Pt metal and/or PtO. On the other hand, the hydrogen uptakes from the TPR suggest that only the Pt/SiO_2 prepared from $H_2[Pt(OH)_6]$ contains PtO and PtO_2, while with those Pt/SiO_2 samples prepared from $[Pt(NH_3)_4](OH)_2$ and $H_2[PtCl_6]$, the Pt is only partially oxidised. Even though the Pt/SiO_2 sample produced from $H_2[Pt(OH)_6]$ shows nearly the threefold hydrogen uptake of the Pt/SiO_2 prepared from $[Pt(NH_3)_4](OH)_2$, the resulting $Ca/Pt/SiO_2$ catalysts have almost the same catalytic activity for methanol. Thus, it can be concluded that there is no direct correlation between hydrogen uptake in the TPR of the Pt/SiO_2 sample and the activity enhancement on the addition of a Ca promoter.

CONCLUSIONS

Changing the Pt precursor affects both the activity and the selectivity of the resulting catalyst, as well as the extent of interaction between the Ca promoter and the metal particles. The most active and selective catalyst for methanol was obtained using $H_2[PtCl_6]$ as the precursor; while this catalyst was reasonably active, the activity was still not as good as that obtained with the Pd-based system. It was notable that the extent of metal–promoter interaction, as measured by the change in the TPR profile and loss of chemisorption capacity, correlated with the activity enhancement on addition of Ca. This confirms the idea that the dopant needs to be located on the metal particles in order to promote the reaction.

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