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NOTES

Methanation and Water-Gas Shift Reactions over Pt/CeO_2

Results on the catalytic activity of platinum supported on ceria (Pt/CeO_2) in methanation and in the water-gas shift (WGS) reactions are reported. We have previously indicated that Pt/CeO_2 is reactive in carbon monoxide hydrogenation and the WGS reactions (*1*, *2*). Also it was reported recently that Pt/CeO_2 was active in the synthesis of methanol from carbon monoxide and hydrogen at high pressures and low temperatures (*3*). Palladium impregnated on lanthanide oxides at atmospheric pressures is active in methane formation (*4*).

The preparation of the catalyst (by the citric acid method) and the experimental procedure were previously described (*1*, *2*). The BET specific area of the Pt/CeO_2 used in the present work was 50 m^2/g and the catalyst contained 1.9% of platinum (*1*). The Pt/CeO_2 showed an identical XRD pattern to ceria. No diffraction pattern for platinum crystallites was obtained, indicating that the sizes of the platinum particles are 4 nm or smaller. In fact, the average size of the platinum particles estimated from hydrogen adsorption measurements was 2.4 nm. Platinum dispersion was 0.35 in the samples pretreated in the temperature region 273–873 K. However, the dispersion decreased to 0.24 at 973 K.

(*A*) $CO + H_2$. Mixtures of carbon monoxide and hydrogen (3 : 4, 3 : 1, and 1 : 1) diluted with helium were reacted over Pt/CeO_2 at temperatures between 473 and 673 K and total pressure of 150–500 Torr (1 Torr ≡ 133.33 $N\ m^{-2}$). Methane was formed and was accompanied by carbon dioxide as shown in Fig. 1. Water was *not* detected.

Mass spectrometric and gas chromatographic measurements did not show the presence of alcohols or other oxygenated products in the effluent.

Ceria was not active in this temperature region in the methanation reaction. Moreover, no carbon dioxide was obtained, in contrast to the reaction where carbon monoxide alone was reacted with ceria (*5*, *6*).

(*B*) *Water-gas shift*. The Pt/CeO_2 catalyst was active also in the WGS reaction. Mixtures of carbon monoxide and water vapor in helium reacted readily at 523–673 K and total pressure 300–700 Torr. Carbon dioxide and hydrogen were detected in the first stage of the reaction. Methane appeared at a second stage (Fig. 2), presumably by a Koelbel–Engelhardt reaction. The time delay in this reaction needs further study.

(*C*) $CO_2 + H_2$. A reaction between carbon dioxide and hydrogen under similar conditions started only at 623 K where methane, carbon monoxide, and water were formed.

It may be suggested that methane is formed here by a consecutive reaction of the hydrogenation of carbon monoxide obtained by either of the two reactions proposed earlier by several workers on other catalysts:

$$CO_2 + H_2 = H_2O + CO \quad (1)$$

i.e., a reverse WGS reaction (where this catalyst is active), or by a dissociative mechanism

$$CO_2 = CO_{ads} + O_{ads} \quad (2)$$

In situ infrared experiments may shed light on the mechanism dominating.

(*D*) *Carbon balance*. It was established from experiments with the pulse reactor that carbon was not retained on the catalyst as carbon oxides or other adsorbed carbon species (see Table 1).

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TABLE 1

Results of Experiments in the Pulse Reactor (Pt/CeO_2)

Pulse injected contains	Treatment before pulse injection	Gases identified by GC	Temperature (K)	Flow rate (cm^3 (STP)/min)	Material balance (μmol ± 0.1)		Basis for the balance
					In	Out	
CO	Vacuum pretreatment	CO, CO_2	523	50	2.3	2.3	Carbon
CO	Vacuum pretreatment	CO_2	623	50	2.3	2.3	Carbon
CO	Pulse of O_2	CO_2	623	50	2.4	2.5	Carbon
O_2	Pulse of CO injected	O_2	623	50	2.3	2.0	Oxygen
H_2	Pulse of CO	H_2	623	50	—	—	—
CO + H_2	Vacuum pretreatment	CO, CO_2, H_2	623	50	2.6	2.5	Carbon
CO + H_2	Vacuum pretreatment	CO, CO_2, CH_4, H_2	623	<5	2.4	2.5	Carbon

The formation of carbon dioxide in the reaction of carbon monoxide and hydrogen can in principle be explained in three different ways. The first is described by the Boudouard reaction

$$2CO = CO_2 + C_{ads} \qquad (3)$$

The second by a dissociation mechanism

$$CO = C_{ads} + O_{ads} \qquad (4a)$$

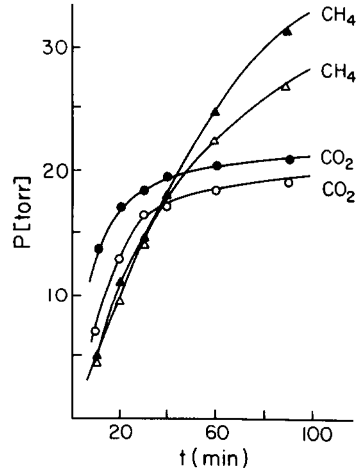

FIG. 1. Reaction of carbon monoxide with hydrogen in the static reactor: (△, ○) at 473 K and 295 Torr total pressure (20% CO, 20% H_2 in He); (▲, ●) at 623 K and 170 Torr total pressure (29% CO, 41% H_2 in He).

$$CO + O_{ads} = CO_2 \qquad (4b)$$

The third by reaction of the oxidic oxygen with carbon monoxide

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \qquad (5)$$

Reaction (3) is not likely because carbon balance (D) shows that all the carbon was recovered (Table 1). If a dissociative mechanism takes place (*7*, *8*) then it may be proposed that methane is produced by the stoichiometric reaction

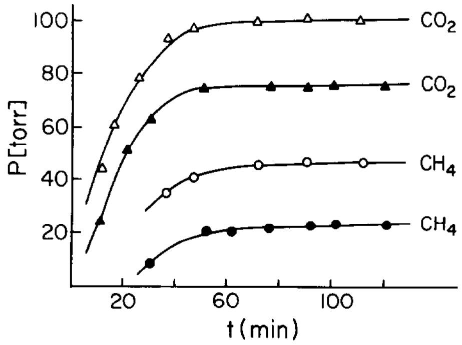

FIG. 2. Reaction of carbon monoxide with water vapor in the static reactor at 623 K (28% CO, 29% H_2O in He): (▲, ●) 400 Torr total pressure; (△, ○) 700 Torr total pressure. A hydrogen evolution curve is not shown because of analytical limitations of the gas chromatographic method.

$$C_{ads} + 2H_2 = CH_4 \qquad (6)$$

The absence of water in the products is in accordance with the proposed pathway. A reaction of hydrogen with adsorbed oxygen [Reaction (4a)] does not seem to take place at the low pressures where our reaction was studied (*7*).

Carbon dioxide can also be formed by Reaction (5), at least in the first stage of the reaction. A possibility that methane is formed also by a reaction between carbon dioxide [formed by Reaction (4b)] and hydrogen is not likely because such a reaction takes place only at temperatures higher than 623 K (Section C) and then the yield of methane is low. A synergetic effect of carbon monoxide on a reaction between carbon dioxide and hydrogen is not plausible because the hydrogenation of carbon dioxide is inhibited in the presence of carbon monoxide (*9*).

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