

## Short Communication

### Hydrogenation of CO<sub>2</sub> to CH<sub>4</sub> over Alumina-supported Noble Metals

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The catalytic hydrogenation of carbon monoxide to methane and other hydrocarbons has again become of great practical interest since the current energy shortage and the rediscovery of coal as an energy source. A number of excellent reviews have summarized the results and also discussed them in great detail [1 - 5]. Less attention has been paid so far to the hydrogenation of CO<sub>2</sub> [3, 6 - 9].

In the present work we report on the catalytic efficiencies of alumina-supported noble metals in the CO<sub>2</sub> + H<sub>2</sub> reaction. In order to obtain a reliable basis for the comparison of the catalytic activities of the metals in the H<sub>2</sub> + CO<sub>2</sub> reaction with those reported recently for the H<sub>2</sub> + CO reaction [10, 11], rates per unit surface area of metals have been determined at low conversion using a differential reactor.

The catalysts were prepared by impregnating the alumina support (Degussa P 110 C1) with solutions of the noble metals to yield a nominal 5 wt.% metal. The following salts of noble metals were used: H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O, PdCl<sub>2</sub>, RhCl<sub>3</sub> · 3H<sub>2</sub>O, H<sub>2</sub>IrCl<sub>6</sub> and RuCl<sub>3</sub> · 3H<sub>2</sub>O. The impregnated powders were dried at 100 °C and decomposed in vacuum at 300 °C and 400 °C. Before any measurements were taken, small fragments of pellets made from the catalyst were oxidized for 30 min and reduced for 60 min at 400 °C *in situ*. After oxidation and reduction, the sample was cooled to the reaction temperature in flowing H<sub>2</sub>.

The gases used were of commercial purity. They were purified by fractional distillation (CO<sub>2</sub>) or by adsorbing the impurities with a molecular sieve at the temperature of liquid air.

Catalytic investigations were carried out in a flow micro-reactor. The amount of catalysts used was 0.3 - 0.6 g. The ratio of H<sub>2</sub>/CO<sub>2</sub> in the reacting gas mixture was 4:1. Analyses of the exit gases were performed with a Hewlett-Packard 5750 gas chromatograph equipped with a 3370 electronic digital integrator. The system was operated at a total pressure of 1 atm. High space velocities of 3000 - 6000 h<sup>-1</sup> were used. The CO<sub>2</sub> conversion was in general less than 6 - 10%. The absence of diffusional limitation was confirmed. Experimental details are described elsewhere [12].

Pulse experiments were conducted in a micro-catalytic pulse system [13]. The micro-reactor was incorporated between the sample inlet and the analytical column of the gas chromatograph. One pulse contained 0.125 ml of  $H_2 + CO_2$  gas mixture in a 1:4 mole ratio.

The dispersity of the supported metals was determined by  $O_2 - H_2$  titration at 25 °C by use of dynamic impulse methods [14 - 16].

The supported noble metals exhibited very different catalytic behavior for the  $H_2 + CO_2$  reaction. The main hydrogenation product was in all cases  $CH_4$ . Before kinetic measurements were taken, the catalyst samples were treated with the reacting gas mixture at the highest reaction temperature (10% conversion) until a steady-state activity was obtained. The development of this stage was also followed in separate experiments by pulse methods. In general, it can be stated that the conversion of  $CO_2$  and the selectivity towards  $CH_4$  formation increased during this treatment. The formation of a carbonaceous deposit was already observed in the first pulse. Its amount increased with the number of pulses of  $H_2 + CO_2$  mixture up to 5 - 10 pulses. The amount of carbonaceous deposit after 10 pulses, determined by oxidation after desorption of adsorbed gases at 400 °C, was relatively low ( $5 \times 10^{-3} - 8 \times 10^{-3} \mu mol$  for Pt, Pd, Ru and Rh) compared to that obtained by using the  $H_2 + CO$  mixture. Ir/ $Al_2O_3$  was an exception; in this case the amount of carbonaceous deposit was almost two orders of magnitude larger than on the other catalysts.

The hydrogenation of  $CO_2$  occurred in the lowest temperature range, 170 - 270 °C, on Ru and Rh. On Ru, small amounts of  $C_2H_4$  and  $CH_3OH$  (less than 0.2% of the  $CH_4$ ) were also formed. While the amount of  $C_2H_4$  slightly increased with rising temperature, the amount of  $CH_3OH$  decreased. Below 240 °C, CO was detected (3 - 4% of the  $CH_4$ ). The selectivity of  $CH_4$  formation approached 100% above 240 °C.

Rh/ $Al_2O_3$  also exhibited a high activity and selectivity in the above temperature range; no other CH compounds were detected.

Ir/ $Al_2O_3$  was less active than the previous catalysts. In the temperature range 215 - 290 °C, only CO was formed besides  $CH_4$ . CO appeared first at 245 °C and its amount increased with rising temperature. Accordingly, the selectivity for  $CH_4$  decreased from 100% to 75%.

On Pd/ $Al_2O_3$ , the formation of  $CH_4$  and CO was identified first at 230 °C. With rise in temperature, the amount of CO formed decreased greatly, and as a result the selectivity with regard to  $CH_4$  was more than 90% at 300 °C.

Pt/ $Al_2O_3$  was a less selective catalyst for the hydrogenation of  $CO_2$ . In the conversion range 1 - 10% (230 - 320 °C), the selectivity relating to  $CH_4$  was less than 15%. It increased slightly up to 290 °C and then decreased. The main product of the  $H_2 + CO_2$  reaction was CO, and small amounts of  $C_2H_4$ ,  $C_3H_6$ ,  $CH_2O$  and  $CH_3OH$  (less than 1 - 5% of  $CH_4$ ) were also identified. Their amounts increased with elevation of the temperature.

Variation of the  $H_2/CO_2$  ratio exerted very little influence on the selectivity of the active catalysts (Rh, Ru, Ir). The conversion of  $CO_2$  increased

TABLE 1  
Some characteristic data for  $H_2 + CO_2$  and  $H_2 + CO$  reactions

Catalysts	Dispersity (%)	$H_2 + CO_2$ reaction			$H_2 + CO$ reaction [10]		
		$N_{CH_4}$ ( $\times 10^3$ )	$N_{CO_2}$ ( $\times 10^3$ )	$E_{CH_4}$ (kcal/mol)	$N_{CH_4}$ ( $\times 10^3$ )	$N_{CO}$ ( $\times 10^3$ )	$E_{CH_4}$ (kcal/mol)
Ru	3.6	194	194	$16.1 \pm 0.7$	181	325	24.2
Rh	30.2	113*	113*	$16.2 \pm 0.4$	13	17	24.0
Pt	16.2	2.3	21	$17.5 \pm 1.0$	2.7	3.4	16.7
Ir	64.1	1.3	1.5	$19.3 \pm 1.0$	1.8	2.6	16.9
Pd	19.1	0.9	1.1	$23.3 \pm 0.8$	12	13	19.7

$N_{CH_4}$ ,  $N_{CO_2}$ ,  $N_{CO}$  = turnover numbers given by:

$$\left( \frac{\text{Molecules formed (or reacted)}}{\text{metal site(s)}} \right) \text{ at } 275 \text{ }^{\circ}\text{C}$$

\*Extrapolated value.

with the partial pressure of  $H_2$  on all catalysts. In the case of  $Pt/Al_2O_3$  the selectivity with regard to  $CH_4$  also increased slightly.

The specific activities of noble metals in terms of turnover numbers ( $N_{CH_4}$  and  $N_{CO_2}$ , rates per unit surface area of metals) at 275  $^{\circ}\text{C}$  are shown in Table 1. For comparison, data obtained by Vannice [10] for the  $H_2 + CO$  reaction are also included.

It appears that the specific rates for the formation of  $CH_4$  in  $H_2 + CO_2$  reaction decrease in the order Ru > Rh > Pt ~ Ir ~ Pd. This order is somewhat different from that found by Vannice (Ru > Rh ~ Pd > Pt ~ Ir) for the formation of  $CH_4$  from a  $CO + H_2$  gas mixture at the same temperature and under very similar conditions.

If we compared our data further with those obtained by Vannice, the following can be established: the specific activities ( $N_{CH_4}$ ) of Ru, Pt and Ir agree strikingly in the two reactions. The activation energies differ appreciably only on Ru.

The catalytic behavior of Rh and Pd, however, are markedly different in the two processes. In the case of the  $H_2 + CO$  reaction, their specific activities are the same, and about one order of magnitude less than that of the most active Ru. In contrast, the specific activity of Rh for the hydrogenation of  $CO_2$  is two orders of magnitude higher than that of Pd, and about eight times higher than in the production of  $CH_4$  from the  $H_2 + CO$  mixture. The activity of Pd, which was found to be the least effective catalyst for the formation of  $CH_4$  in the  $H_2 + CO_2$  reaction, is more than one order of magnitude lower than in the  $H_2 + CO$  reaction.

In conclusion we can state that the hydrogenation of  $CO_2$  on supported noble metals produces  $CH_4$  with much higher selectivity than that of  $CO$ .

The catalytic behavior of supported Ru and Rh deserves further attention as the hydrogenation of CO<sub>2</sub> on these catalysts occurs at a faster rate and/or with a lower activation energy than in the case of CO.

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