

Short Communication

Hydrogenation of CO₂ to CH₄ 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 CO₂ [3, 6 - 9].

In the present work we report on the catalytic efficiencies of alumina-supported noble metals in the CO₂ + H₂ reaction. In order to obtain a reliable basis for the comparison of the catalytic activities of the metals in the H₂ + CO₂ reaction with those reported recently for the H₂ + 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: H₂PtCl₆ · 6H₂O, PdCl₂, RhCl₃ · 3H₂O, H₂IrCl₆ and RuCl₃ · 3H₂O. 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 H₂.

The gases used were of commercial purity. They were purified by fractional distillation (CO₂) 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 H₂/CO₂ 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⁻¹ were used. The CO₂ 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 ($5 \times 10^{-3} - 8 \times 10^{-3} \mu\text{mol}$ 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 ± 0.7	181	325	24.2
Rh	30.2	113*	113*	16.2 ± 0.4	13	17	24.0
Pt	16.2	2.3	21	17.5 ± 1.0	2.7	3.4	16.7
Ir	64.1	1.3	1.5	19.3 ± 1.0	1.8	2.6	16.9
Pd	19.1	0.9	1.1	23.3 ± 0.8	12	13	19.7

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

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

*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°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 $Ru > Rh > Pt \sim Ir \sim Pd$. This order is somewhat different from that found by Vannice ($Ru \gg Rh \sim Pd > Pt \sim Ir$) 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 CO₂ 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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