

Reaction of Carbon Monoxide over Pt/alumina at High Pressure and Temperature: Control of Carbon Deposition.

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Introduction.

Catalyst loss of activity with time on stream or “deactivation” is one of the major problems associated with heterogeneous catalysis. In the catalysed steam reforming of CH₄, the most significant form of deactivation is fouling of the catalyst surface with carbon from CH₄ cracking or CO disproportionation. Iglesia et al. [1-3] studied CO₂/H₂O reforming and CH₄ decomposition over a range of noble metals and Ni with different metal dispersions. The exclusion of transport and thermodynamic artefacts, the rigorous correction to forward rates and the measurement of rates normalised by the relevant exposed surface metal atoms made these results a fair comparison of each metal. From calculations of CH₄ turnover rates, the results showed a unified order of activity of: Pt > Ir > Ni > Rh > Ru. In this paper we investigate the deposition of carbon from CO over a Pt/alumina catalyst and examine the use of CO₂ as a means of inhibiting the deposition.

Materials and Methods

The catalyst was prepared by impregnating the pre-dried support (alumina heated to 1173 K for 2h, S.A. 104 m²g⁻¹) to incipient wetness with an aqueous solution containing the precursor salt (H₂PtCl₆) to give a weight loading of 0.2 %. The wet catalyst was then oven dried before calcination at 723 K for 2 h. All reactions were carried out in a continuous-flow, high-pressure rig. The reactor was filled with 0.5g of catalyst, which was reduced in situ at 873 K for 2 hours in a flow of 50/50 H₂/Ar at 20 barg pressure. Following reduction the reactor was flushed with Ar at 873 K and 20 barg for 1 h. The flow was then switched the reaction gas(es) and the reaction followed by mass spectrometry (Minitorr, ESS).

Results/Discussion

In the absence of CO₂ in the CO feed there is rapid carbon deposition and transient evolution of CO₂ as shown in Figure 1. The carbon deposition comes from the Boudouard reaction $2\text{CO} \rightarrow \text{C} + \text{CO}_2$. To examine the effect of this carbon on catalytic activity a 1:1 CO/H₂ reaction was performed and no activity was observed. The CO/H₂ reaction over a fresh catalyst gave a conversion of 21 % with methane and carbon dioxide as the main products with a CO₂:CH₄ ratio of 0.6. To examine the effect of CO₂ fresh catalysts were subjected to CO/CO₂ ratios of 10:1, 5:1 and 1:1. The effect of adding the CO₂ was probed by performing a CO/H₂ reaction immediately after each treatment

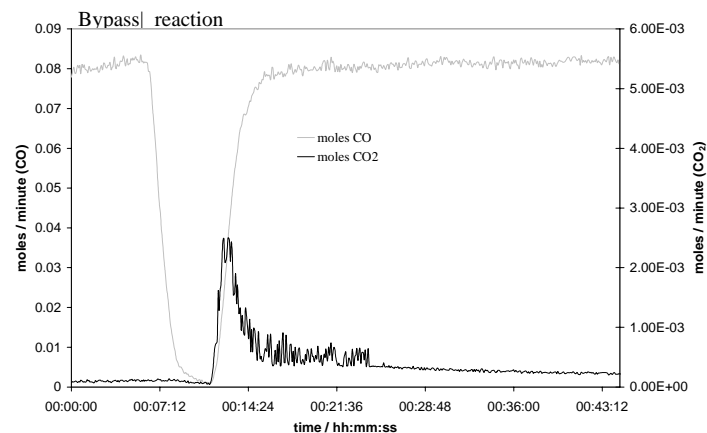


Figure 1. Treatment of Pt/alumina with CO at 873 K and 20 barg.

When CO:CO₂ ratio was 10:1 and 5:1 the CO/H₂ reaction was completely poisoned, although there was some evidence that the hydrogen was reacting with the deposit. At 1:1 CO:CO₂ however the CO/H₂ reaction was in evidence with a conversion of 24 % but the reaction selectivity had changed with a CO₂:CH₄ ratio of 1.6. Hence at 873 K and 20 barg a 1:1 CO:CO₂ ratio inhibits carbon laydown. The detailed processes occurring were further studied using isotopically labeled CO and CO₂.

Significance

Carbon deposition in steam reforming is still a significant issue yet there are few studies on precious metals systems at pressure. This study adds new data to our understanding of carbon laydown and the methodology by which it can be controlled.

References

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