Activity and Mechanism of CO Methanation on Activated Carbon-supported Nickel

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Summary At moderate temperatures (475—775 K) activated carbon-supported nickel in the presence of hydrogen shows rapid hydrogenative support gasification while under CO-methanation conditions the support is stable towards hydrogen, resulting in a time-independent activity.

METHANATION, the hydrogenation of carbon monoxide to methane, over nickel catalysts has been studied extensively[1-7] because of its commercial application in producing substitute natural gas from synthesis gas and in eliminating carbon monoxide from hydrogen-rich gases to prevent catalyst poisoning. Surprisingly no recent work involves the study of activated carbon-supported nickel as a methanation catalyst although the application of nickel as a catalyst in carbon gasification reactions has been thoroughly examined.[8,9]

The application of activated carbons as catalyst supports is interesting because of their thermal stability, high specific surface area, capacity for simple active phase recovery, and low cost. The use of activated carbon supports can also lead to extra mechanistic information. In spite of extensive research there are still two different theories of the mechanism of CO methanation over nickel catalysts, one involving oxygenated intermediates,[1-4] and the other assuming surface carbon species as active intermediates.[5-7]

This work presents some results on the methanation activity of highly dispersed nickel (3·5 wt%, prepared by precipitation *via* urea thermolysis[10]) on purified activated carbon as a function of thermal treatment, reaction temperature, and degree of gasification of the support.

In the temperature region 475—775 K the methanation activity was studied in a recirculating batch reactor operated at (H_2 + CO)-pressure of *ca.* 0·5 bar. Nickel surface area was determined *via* hydrogen chemisorption saturation measurements at 300 K and 5 × 10^4 Pa assuming H/Ni-surface = 1

The activation energy (80 kJ $\mathrm{mol^{-1}}$) and turnover frequency per surface nickel atom (T O F) (0·02 $\mathrm{s^{-1}}$ at 545 K) assuming the rate equation (1)[4] agree well with

$$r(\mathrm{CH_4}) = kp^0(\mathrm{CO})p^1(\mathrm{H_2}) \qquad (1)$$

reported values for silica- and alumina-supported nickel under atmospheric conditions [1–4] Calcining for 20 h at 775 K *in vacuo* did not lower the methanation activity significantly, in contrast to calcination at 975 K which obviously leads to sintering and nickel penetration into the carbon bulk [8] Catalysed gasification of the carbon carrier with hydrogen (in the absence of carbon monoxide) at 775 K and 0 5 bar (T O F $10^{-3}\ \mathrm{s^{-1}}$, E_a 200 kJ $\mathrm{mol^{-1}}$) to a maximum conversion of 30 wt%[8] leads to a decrease in methanation activity by a factor of 6 while the Brunauer–Emmet–Teller (B E T) surface area decreases by a factor of 2 A striking feature of methanation at 775 K is that the turnover frequency and the B E T surface area remain constant for several hours This obviously indicates that in the presence of carbon monoxide no reaction of hydrogen with the bulk carbon takes place

It is well known that exposure of CO to nickel surfaces results in the formation of carbon with different reactivities towards hydrogen [5–7] Although our carrier is probably similar to the least reactive type of carbon found by Wise *et al* [6] the possibility of an oxygenated active intermediate cannot be excluded by our experiments From the stability of the carrier during CO methanation we conclude that the hydrogenation of the various types of carbon-containing species occurs with different mechanisms As hydrogenative bulk-carbon gasification involves dissociative hydrogen chemisorption,[9] CO probably blocks the active sites for hydrogen dissociation

In conclusion, whether a surface carbide or $\mathrm{CH_2O_{ads}}$ is the active intermediate in the CO methanation reaction, the subsequent methane formation does not take place *via* mobile atomic hydrogen, as might be inferred from the literature [2,7] Practically, the stability of the carbon carrier under methanation conditions results in a high time-independent activity

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[1] G M Kozub, M T Rusov, and V M Vlasenko *Kinetika i Kataliz*, 1965, **6**, 244, J L Bousquet, P Gravelle, and S J Teichner, *Bull Soc chim France*, 1969, 2963, T van Herwijnen, H van Doesburg, and W A de Jong, *J Catalysis*, 1973, **28**, 391

[2] P Schouby, *J Catalysis*, 1969, **14**, 238, R Fontaine, Ph D Thesis, Cornell University, 1973

[3] M A Vannice, *J Catalysis*, 1975, **37**, 449

[4] M A Vannice, *Catalysis Rev* , 1976, **14**, 153

[5] V Ponec, *Catalysis Rev* , 1978, **18**, 151, M Primet, J A Dalmon, and G A Martin *J Catalysis*, 1977, **46**, 25

[6] J G McCarty and H Wise, *J Catalysis*, 1979, **57**, 406

[7] A E Zagli, J L Falconer, and C A Keenan, *J Catalysis*, 1979, **56**, 453

[8] T Wigmans and J A Moulijn, to be published

[9] R T Rewick P R Wentrek and H Wise, *Fuel*, 1974, **53**, 274, A Tomita and Y Tamai, *J Catalysis*, 1972, **27**, 293

[10] J A van Dillen, J W Geus, L A M Hermans, and J van der Meijden, Proc 6th Internat Congress on Catalysis, The Chemical Society, London, 1976, p 677