

Gasification of carbon deposited on supported Ni–Cu catalysts*

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The activity of supported Ni–Cu alloy catalysts in the gasification of carbon was studied for a range of copper concentrations. Deposits formed from the decomposition of methane under constant and well-defined conditions were gasified by hydrogen and hydrogen-steam mixtures. The kinetics of hydrogasification were determined under such conditions that the reaction rates did not depend on the extent of carbon burn-off. Comparison of the different catalysts indicates that, similarly to previous results for the decomposition, an ensemble of surface nickel atoms plays a role in the gasification.

(Keywords; gasification of carbon; catalyst; surface deposition)

Carbon formation is an unavoidable side-reaction in the catalytic processing of hydrocarbons. Various methods have been tried to prevent this reaction, namely the control of the operating conditions, the addition of alkali to the catalyst and, when nickel is the active metal, coverage of the metallic surface by sulphur¹. Sulphur passivation depends on the fact that the nucleation of carbon involves a larger number of nickel surface sites than the main reaction¹. Another method of diminishing the deposition of carbon on a nickel-based catalyst is alloying with copper, a metal that shows no activity in the decomposition of aliphatic hydrocarbons below 1070 K².

Various studies and reviews^{3,4} have been devoted to the effect of copper and on the deactivation and activity of nickel catalysts. Barcicki *et al.*⁵ state that the addition of 0.02% (w/w) of copper to alumina-supported nickel catalysts increases significantly the activity for methane-steam reforming. Bajpai *et al.*⁶, however, reported the opposite effect when copper was added to a Ni/Al₂O₃ methanation catalyst.

They also noted a decreased tendency for deactivation. Vass *et al.*⁷ observed a decrease in activity after adding up to 20% Cu to a nickel-kieselguhr catalyst for ethene hydrogenation. Cale and Richardson⁸ found that copper decreases the activity for cyclopropane hydrogenation in alloys with nickel supported on silica. A recent study⁹ of methane decomposition and steam reforming over Ni–Cu/SiO₂ catalysts concluded that the rate of the former reaction decreases more than that of the latter when the copper concentration is increased. It was also observed that methane decomposition rates depended strongly on the concentration of copper in the metallic phase, indicating a possible ensemble effect.

This paper reports a study of the gasification by hydrogen of carbon formed on silica-supported Ni–Cu catalysts. The aim of this study was to contribute to the

elucidation of the mechanism of gasification of carbon on nickel based catalysts.

EXPERIMENTAL

Catalysts

Ni–Cu/SiO₂ catalysts, prepared by a 'dry' impregnation technique^{9,10} contained 20 wt% nickel plus copper, and bulk copper concentrations in the metallic phase of 0, 0.1, 1, 10, 25, 50 and 80 atomic %. The catalysts were characterized by hydrogen chemisorption, hydrogen sulphide chemisorption (sulphur capacity), X-ray diffraction and X-ray photoelectron spectroscopy (XPS)⁹.

X-ray diffraction showed that the catalysts with more nickel than copper contained only one metallic phase, with a composition equal to the nominal one. Two metal alloy phases were observed in the 50 and 80 atomic % Cu catalysts⁹. In all samples a substantial surface copper enrichment was detected by hydrogen chemisorption, and confirmed by XPS. Hence, in the present work, the normalized reaction rates are referred to the capacity of strongly chemisorbed hydrogen.

The reaction system and reactants

The deposition and gasification experiments were performed in a flow reactor associated with a microbalance (CI Electronics, MK2B), a furnace and a temperature controller^{9,11}. When necessary, a constant flow of steam was produced by on-line hydrogen reduction of copper oxide. The composition of the effluent gases was determined by gas chromatography.

A catalysts pellet (cylinder: diameter, 4 mm; ht, 4 mm; wt, ≈ 60 mg) was suspended from the microbalance, in a quartz basket, into the reactor. Prior to the reaction, the reactor was flushed with hydrogen, at the working temperature, until the catalyst was completely reduced.

All experiments were performed at atmospheric pressure, with total gas flow rates from 0.6 to 0.8 mol

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(hour)⁻¹; carbon was deposited from methane (>99.95% pure), under constant conditions: 850 K; $P_{\text{CH}_4} \approx 13 \text{ kPa}$, $P_{\text{H}_2} \approx 7 \text{ kPa}$; N_2 as balance. Under these conditions, mostly whisker carbon (long, thin filaments with a metal particle at the end¹²) is observed in the deposits^{9,11}. For all the catalysts but that with 80% at.Cu, long periods of constant deposition rates were observed leading to massive deposits, whose size was limited only by the sample holder and the microbalance capacities.

RESULTS

The characteristics of gasification

The gasification curves obtained for constant temperature and partial pressure of the gasifying agent were similar to those reported previously for nickel catalysts^{11,13,14}. An initial acceleration was followed by a period of nearly constant gasification rate, which remained at ~15–75% of the total weight loss. Changing the gasification conditions in this period led to a new, constant, value of the rate, thus allowing the determination of kinetic parameters.

A series of experiments was performed to determine the dependence of the rate of the initial weight of the carbon deposits. It was found that, above a minimum weight of deposit (ca. 6.5 mg for the 25 atomic % Cu catalyst), with all other conditions constant, the rate is almost independent of the initial carbon weight. This may result from the fact that, above that minimum, all the metal has been transferred from the catalyst to the deposit. It may also result from the approach to equilibrium conditions for methane decomposition (see ahead).

Scanning electron microscopy observations showed that the 'whisker' carbon deposits gasify in a homogeneous way, without coalescence of the metal

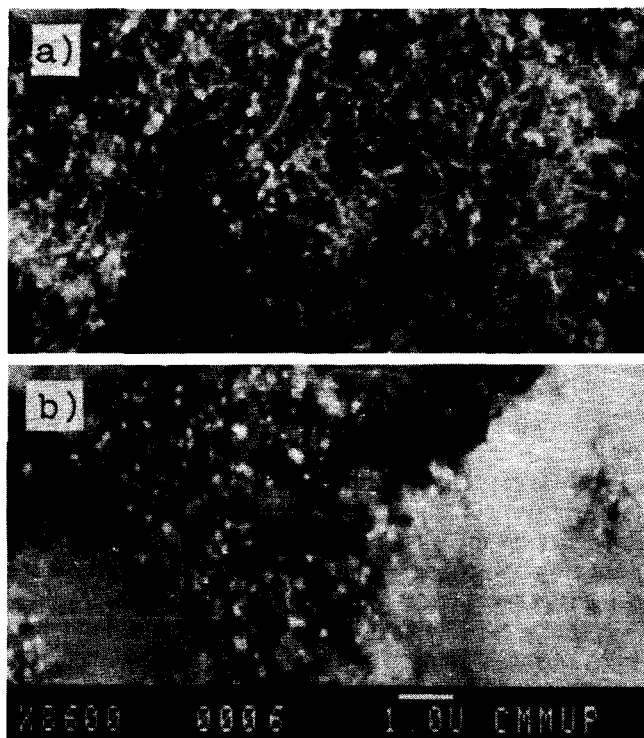


Figure 1 Sequences in the gasification of a 72 mg deposit formed in a Ni-Cu catalyst with 1 at.% Cu, corresponding to: a) 50%, b) 100% burn-off of carbon. 85 mm = 1 μm

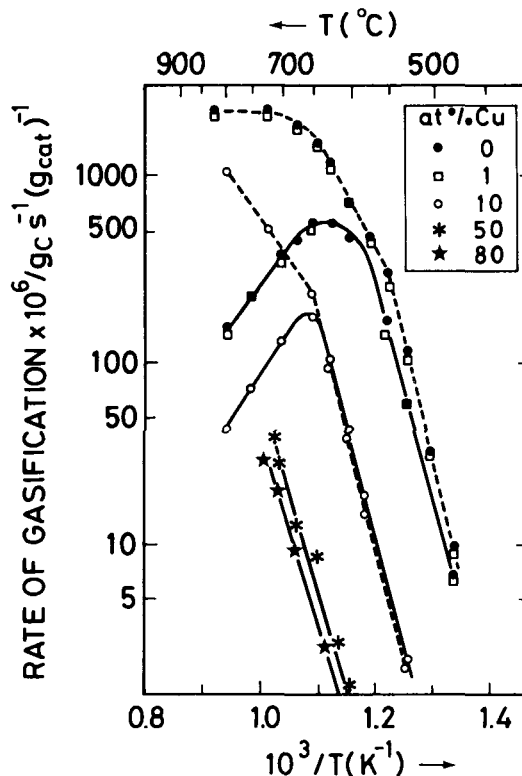


Figure 2 Temperature dependence of the rates of carbon gasification on Ni-Cu/SiO₂ catalysts. Copper concentrations in the metallic phase as indicated. Conditions: Full line— $P_{\text{H}_2} = 42 \text{ kPa}$; broken line— $P_{\text{H}_2} = 38 \text{ kPa}$, $P_{\text{H}_2\text{O}} = 7 \text{ kPa}$, N_2 as balance. Total gas flow ca. 0.7 mol h^{-1}

particles on top of the filaments. This can be observed in *Figure 1b*, in which, after 100% burn-off, the metal particles, whose nature was confirmed by energy dispersive X-ray microanalysis, are clearly seen on the silica support. Their diameters are approximately the same as those of the particles on the filaments (*Figure 1a*).

Determination of kinetic parameters

The temperature dependence of the gasification rates, in the linear gasification period, for fixed partial pressures of the gasifying agent is shown in *Figure 2*.

The hydrogen gasification curves in the figure are similar to those obtained previously for nickel catalysts^{14–16}. The decrease in the rates when the temperature increases above 900–950 K (T_{max}) can be due either to progressive deactivation of the catalyst or to thermodynamic limitations (as the methane concentration in the pores of the carbon approaches the equilibrium values). However, the first explanation should be rejected for two reasons: first, the rates recover to their original values when the temperature is lowered below T_{max} and this effect is reversible; second, when steam is added to the system (broken lines in the figure), the behaviour remains constant below T_{max} , but the rates increase with temperature thereafter. The apparent activation energies determined in the presence of steam, below and above T_{max} (≈ 220 and 110 kJ mol^{-1} , respectively) indicate the possible occurrence of pore diffusion limitations at the higher temperatures.

Orders of reaction with respect to hydrogen were determined at fixed temperatures. These, together with the apparent activation energies measured from *Figure 2*, are presented in *Table 1*.

Table 1 Kinetic data for hydrogen gasification of carbon deposited on Ni-Cu/SiO₂

Temperature (K)	< 900 (500)	> 900 (500)
E _a (KJ mol ⁻¹)	214 ± 6 ^a	-(88 ± 7)
Order of reaction ^b	2 to <1	~2

^aFor 80 at. % Cu this value is unreliable due to the small amount of carbon deposited

^bFor 1 at. % Cu only; N₂ used as balance

The kinetic parameters determined below T_{max} may be explained in terms of a surface reaction involving atomic hydrogen, as in the case of the pure nickel catalyst¹⁵. In fact, the reaction order decreased from ≈2 to below unity when the hydrogen partial pressure was increased above 40 KPa. This indicates that, in spite of the similarity of the rates with and without steam, a common solid state process is not rate controlling below T_{max}.

DISCUSSION

The effect of hydrogen in the deposition of carbon on Ni-Cu alloys was first reported in Nishiyama and co-workers¹⁷, who found that hydrogen suppressed deposition for copper-rich, and accelerated it for nickel-rich alloys. The authors attributed the former effect to surface dilution. To our knowledge no study of carbon gasification on these alloys has been reported since.

The present results show that the hydrogasification of carbon deposited on nickel-based catalysts does not change, in its general and kinetic features, with or without copper alloying. However, by allowing discussion of the effect of the dilution of the active nickel surface, they can help to elucidate the mechanism of gasification of carbon from Ni-Cu/SiO₂ catalysts.

Figure 3 shows the gasification rate, in the non-thermodynamically limited range, expressed per unit catalyst weight (Figure 3a) and referred to the relative capacity for strongly chemisorbed hydrogen (Figure 3b). For this, the hydrogen chemisorption results reported earlier⁹ (see upper curve in Figure 4) were used to determine the capacities of the different alloys, relative to that of the 'pure nickel' catalyst.

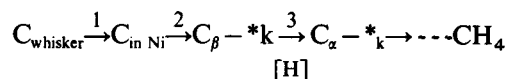
In the alloy catalysts, the nickel surface atoms are surrounded by copper atoms which do not chemisorb hydrogen. In the temperature range in which the hydrogasification is not limited thermodynamically, since no reaction occurs in the Cu sites, this dilution effect can be related to the reaction rate by:

$$r_H = r_H^0 (1 - X_{Cu})^k$$

in which r_H⁰ is the rate in the case of pure nickel, X_{Cu} is the atomic fraction of copper in the alloy surface and k defines the dimension of the ensemble of nickel surface atoms active in the reaction (in the absence of electronic effects). As can be seen in Figure 3, k must be greater than 1, since the rates drop more than the hydrogen chemisorption capacity (nickel area), when the copper concentration is increased. This can also be observed in Figure 4, that shows, additionally, that the gasification rates on the alloys with >10at. % Cu are more than one order of magnitude lower than those on pure nickel. This would mean that the gasification on these alloys is, according to Poniec's classification⁴, a type II reaction, corresponding to the breakage of C-C or C-O bonds. This indicates that

two or more carbon atoms are attached to the same k-size surface ensemble, in a bound state. The scission of the carbon bonds would then be the rate limiting step in the gasification. This supports the results of Dost *et al.*¹⁸, who concluded that the detachment of carbon atoms from β-carbon islands controls the rate of β-carbon hydrogenation on nickel.

In previous publications^{11,13}, a mechanism for the gasification of 'whisker' carbon was proposed, involving the following steps: a) adsorption of the reactant gas at the metal surface; b) reaction of the adsorbed species with carbon atoms (C_α) at the surface; c) supply of carbon atoms to the surface by diffusion through the metal. In view of the above discussion, the hydrogen gasification process can be represented by the scheme:



in which *_k represents the active surface ensemble and

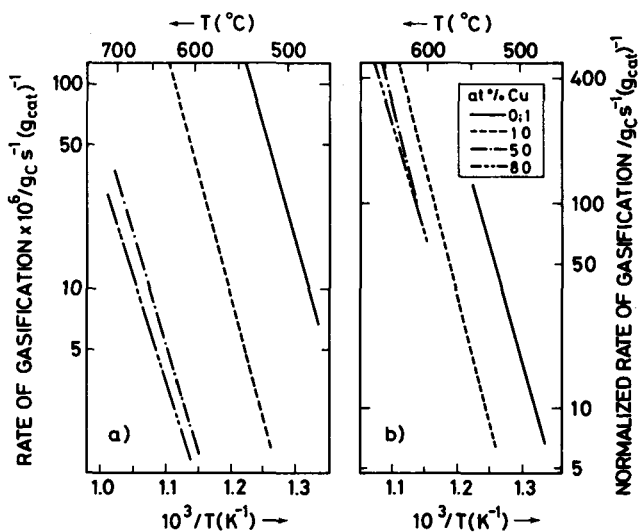


Figure 3 Temperature dependence of the rates of carbon gasification by hydrogen. Rates: a) non-normalized; b) normalized by the relative amount of strongly chemisorbed H₂. Conditions: as in Figure 2

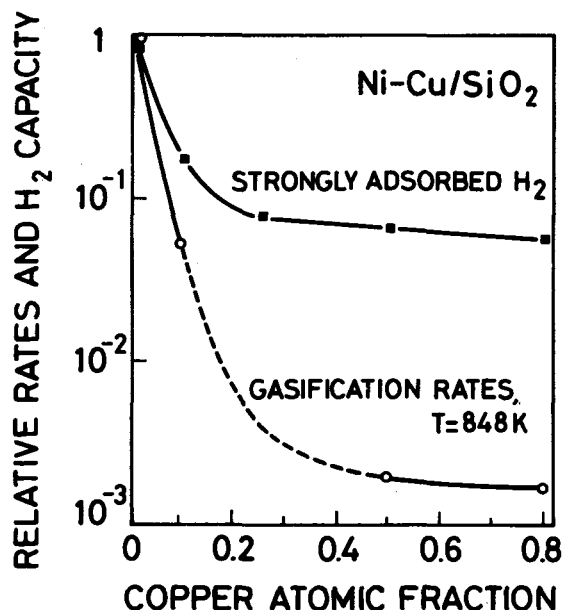


Figure 4 Gasification rates and hydrogen capacities, relative to pure nickel, of the different alloy catalysts. Rates for 50 and 80 at. % Cu extrapolated.

step 3 is rate controlling. According to the present work, in contrast to the conclusion of Dost *et al.*²⁰, absorbed hydrogen should be involved in the detachment of β -carbon atoms, as the gasification rates depend strongly on the hydrogen partial pressure (see *Table 1*).

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