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# DETERMINATION OF THE SURFACE AREA OF NICKEL CATALYST BY A CHROMATOGRAPHIC PULSE METHOD (CARBON MONOXIDE–HYDROGEN TITRATION)

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## SUMMARY

A new, simple chromatographic pulse method (carbon monoxide titration of preadsorbed hydrogen) is useful for determination of the specific surface areas of silica-supported nickel (and rhodium) catalysts. The extent of hydrogen uptake can be measured without drastic thermal treatment. The results demonstrate that the carbon monoxide–hydrogen titration method is suitable for the relatively simple and rapid determination of the specific surface areas of supported nickel (and rhodium) catalysts.

There are several techniques for the measurement of surface areas of supported metal catalysts. The most widely employed methods use the selective chemisorption of gases, usually hydrogen, oxygen and carbon monoxide, and the titration of preadsorbed oxygen with hydrogen (hydrogen–oxygen titration). The advantage of the titration method as compared to direct chemisorption is that the metal surface need not be cleaned. Two different techniques are in common use for measuring adsorption uptakes, the static and the dynamic pulse methods. The pulse method has become a frequently used technique in recent years, because of its experimental simplicity and since it allows the rapid determination of irreversible adsorption on metal surfaces. Previous investigations dealt mainly with platinum, only a few concentrating on other metals from Group VIII of the periodic system[1–4].

Sinfelt[5] and also Brooks and Christopher[6] studied the measurement of the specific surface areas of supported nickel catalysts by static hydrogen and carbon monoxide chemisorption. It seems that a comparison of these methods gives the best result, because of the uncertainty of the adsorption stoichiometry[7,8]. Verma and Ruthven[8] used the dynamic pulse method for the measurement of the surface area of supported nickel by carbon monoxide chemisorption. Dynamic hydrogen chemisorption, however, does not give good results.

The co-adsorption of carbon monoxide and hydrogen on nickel catalysts is studied intensively because of its industrial importance. At room temperature, carbon monoxide sorption on nickel is non-dissociative and reaction products cannot be found. Carbon monoxide is adsorbed more strongly than hydrogen, and at low temperatures (350°K), therefore, carbon monoxide displaces hydrogen from the surface of nickel almost quantitatively[8–11]. On this basis we concluded that chemisorbed

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TABLE I

SURFACE AREAS OF NICKEL CATALYSTS MEASURED BY DIFFERENT METHODS

| *Catalyst* | *Carbon monoxide–hydrogen titration* | *Hydrogen chemisorption* | *Nitrogen adsorption* |
|---|---|---|---|
| 3 % Nickel–silica | 0.068 | 0.067 | |
| 10 % Nickel–alumina | 0.07 | 0.10 | |
| Nickel | 0.004 | | 0.003 |

hydrogen could be measured by a new dynamic method (carbon monoxide–hydrogen titration).

The essence of this method is as follows. A dynamic adsorption apparatus was used, with nitrogen as the carrier gas. The nitrogen was purified by passage through a copper–copper(I) oxide bed at 400°C. The carrier gas flowed over one side of the bridge in the thermal conductivity cell of a Carlo Erba Fractovap Model 1400 gas chromatograph. Carbon monoxide impulses were injected into the carrier gas stream by means of a gas-sampling valve. After passage through the catalyst bed, the carrier gas flowed over the other side of the bridge in the cell. The output of the detector was recorded. Hydrogen gave a large negative peak, but carbon monoxide gave only a very small peak with varying polarity. When the surface area of a 3 % nickel–silica catalyst was measured, it was found that the carbon monoxide displaces the total hydrogen from the surface in one peak. The result was compared with that obtained with hydrogen chemisorption measured by a static method (Table I). It is also possible to measure the hydrogen and carbon monoxide chemisorption at the same time, using helium as the carrier gas and a molecular sieve chromatography column.

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