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Catalytic methane steam reforming: novel results

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1. Introduction

Methane interaction with steam is one of the basic reactions in the process of methane oxidative transformations. When studying this reaction kinetics we have found that methane steam reforming proceeds by a hetero–homogeneous mechanism in the presence of supported nickel catalyst [1]. The steam reforming rate was shown to decrease noticeably at reactor filling with the catalyst or with addition of the radical trapping material.

To understand either such mechanism is realized in the case of massive nickel catalyst in the present paper we have studied for a nickel wire the effect of the nickel surface value and the addition of carbon on the steam reforming rate. The data obtained were compared with those for supported nickel catalyst.

2. Experimental

The nickel wire activity was studied in a flow-recycling set up with a stainless reactor (volume 30 cm^3) at 750°C and the concentrations of methane and steam 33 and 67 vol.-%, respectively. The set up scheme, the process conditions, kinetic experiments and catalysts treatment are described elsewhere [1,2].

The surface of the wire (0.1 mm) at full reactor filling came to 0.28 m^2. The samples with a lower value of Ni surface were selected from this one.

The data for supported Ni/Al_2O_3 catalyst (26 wt.-% NiO, 0.25 to 0.5 mm granules) are given in ref. [1]. Ni specific surface was determined by oxygen adsorption after the sample testing. It averages 2.4 m^2/g. The catalyst specific surface is equal to 35 m^2/g.

Spherical carbon sorbent (volume 10 cm^3, 0.5 to 1.0 mm granules with a post-test surface area of 200 m^2/g) was used to dilute the catalyst if necessary. Methane conversion was found [1] to be negligible for an empty reactor and for that filled only with carbon.

Catalytic activity was characterized by the value of rate constant at 750°C.

3. Results and discussion

Previously [1] we have found that at 750°C the rate of methane steam reforming on nickel catalysts is described by the equation of first order for methane. Fig. 1 exemplifies the relationship between the reaction rate of steam reforming and the partial pressure of methane in the reaction mixture for the nickel wire and the Ni/Al_2O_3 catalyst at 750°C.

Fig. 2 presents the comparison of activity for bulk nickel and supported nickel catalyst. The data for Ni/Al_2O_3 catalyst obtained in ref. [1] were amplified with measurements of activity on small and large catalyst amounts.

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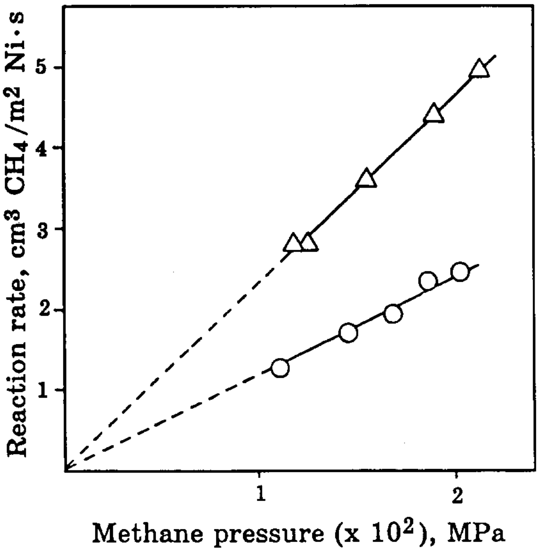

Fig. 1. Reaction rate of methane steam reforming on nickel wire (0.19 m^2) and Ni/Al_2O_3 catalyst (0.25 to 0.50 mm fraction, 0.25 g sample) as a function of P_{CH_4} at 750°C. (△) Ni wire; (O) Ni Al_2O_3.

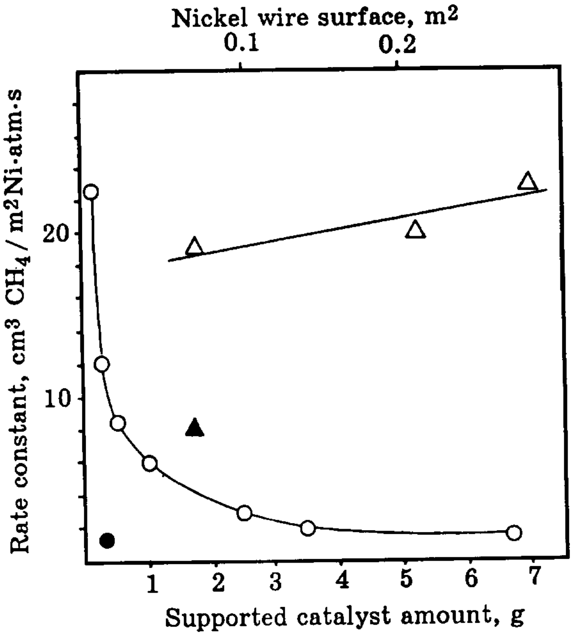

Fig. 2. A comparison of activity for massive (△, ▲) and supported (○, ●) nickel catalysts in methane steam reforming at 750°C. (▲, ●) After carbon addition.

As is seen from Fig. 2, in contrast to supported nickel catalyst, the activity of nickel wire does not change practically if its surface is about 0.07–0.28 m^2. The value of rate constant (20–23 cm^3 CH_4/m^2 Ni atm s) is close to that for Ni foil obtained in ref. [3]. Note, that the equation derived in ref. [3] from the data for Ni foil in terms of the 'pure' heterogeneous mechanism satisfactorily describes the kinetics on the Ni wire [1]. We could accept 'pure' heterogeneous interaction methane with steam on bulk nickel if we had no results of experiments with carbon. Owing to the high specific surface area its pore diameters are smaller than a free path of the species, so it is capable of trapping the radicals from the gas phase suppressing the gas-phase reactions [4,5]. One can see that in the case of massive Ni the rate constant also falls rapidly with the addition of carbon to the wire (Fig. 2). It is restored after carbon removal. The same occurs in the case of Ni/Al_2O_3 but more strongly [1] perhaps because the carbon mixes better with crushed supported catalyst than with twisted wire.

These experiments confirm the occurrence of gas-phase reactions in the presence of massive Ni as well as for supported Ni. Moreover, the activity of the Ni/Al_2O_3 catalyst is maximum and close to that for massive Ni only at the small catalyst amount. In this case the catalyst is placed into the reactor as a thin bed that does not absorb the radicals. Reactor filling with the catalyst suppresses the homogeneous reactions: the overall catalyst surface rises but the free reaction volume between the catalyst granules decreases.

4. References

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