Influence of molybdenum and tungsten additives on the properties of nickel steam reforming catalysts

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An introduction of small amounts of molybdenum and tungsten compounds into the nickel catalyst of the steam reforming of methane considerably reduces the detrimental effect of carbon deposit formation, while entailing no change in the catalyst activity.

Keywords: steam reforming catalysts; Mo doped Ni/Al_2O_3; W doped Ni/Al_2O_3; catalyst activity; carbon deposition

1. Introduction

The steam reforming of hydrocarbons belongs to a group of some of the most important technological processes of chemical synthesis. One of the significant properties of a good steam reforming catalyst is its resistance to coking.

In recent years there has emerged a tendency to lower the H_2O/C ratio in the reforming process. This procedure brings considerable economic advantages though it simultaneously hinders the prevention of catalyst coking. For that reason there is an evident need to develop new, better nickel catalysts which would ensure stable operation of technological installations under more difficult conditions [1]. Coking resistance can be increased by a selection of an appropriate carrier composition and the manner of catalyst preparation [1–3].

Still, the simplest manner of improving the quality of the catalysts is the introduction of certain additives into them which increase their resistance to coking. Thus, in spite of their lower activity, potassium promoted catalysts have found wide application in industry. An increase in the coking resistance was also obtained after the introduction of considerable amounts (3–15 wt%) of the oxides of metals such as uranium [4], lanthanum [2] and cerium [5] into nickel catalysts.

The aim of the present paper was to examine promoters other than those mentioned above, such as molybdenum and tungsten, which promote nickel catalysts used for steam reforming. These promoters were chosen on the basis of our earlier studies [6] as well as on the literature data [7].

2. Experimental

Experiments were carried out on two series of catalysts containing varied amounts of promoters such as WO_3 (0.2–2 wt%) and MoO_3 (0.2–5 wt%). Samples were prepared by impregnation of a Ni/α-Al_2O_3 commercial catalyst designed for steam reforming of natural gas, with the promoter salts [8].

The total surface area of the samples was determined by measuring argon adsorption at the temperature of liquid nitrogen in a static–volumetric apparatus which ensured a vacuum better than 2×10^{-5} hPa.

The active surface area of Ni was determined by means of hydrogen chemisorption at 20°C and 100 mm Hg pressure (after the reduction of catalysts at temperature 800°C), assuming that chemisorption stoichiometry was $H : Ni = 1 : 1$, and the surface area occupied by one hydrogen atom equalled 0.065 nm^2 [9].

Studies of the coking rates in the steam reforming of *n*-butane were carried out using the gravimetric method in a flow reactor (38 mm in diameter), at temperature 500°C under conditions presented in greater detail elsewhere [3].

The catalytic activity of samples in the steam reforming of methane was measured in a gradientless reactor [10]. Measurements were made (after the reduction of the catalysts) under a pressure of 2.5 MPa at various temperatures, at the molar ratio of $H_2O : C = 4.5–5.0$ (at the reactor inlet). The reaction rate constant was reported as the activity measure (related to 1 g of the catalyst), assuming first order kinetics with respect to methane.

3. Results and discussion

The total surface area of the unpromoted industrial catalyst was 3.4 $m^2 g^{-1}$. The introduction of the promoters practically did not change the total surface area of the samples; it varied in the range of 3.3–3.6 $m^2 g^{-1}$.

However, the presence of the promoters decreased the active surface area of Ni. The decrease was slight and it did not depend on the amount of the tungsten compound introduced. Samples with molybdenum revealed a drop in nickel active surface area, especially after the introduction of 0.2–0.5 wt% of the promoter. Values of nickel active surface area in the catalysts are given in table 1.

Table 1 also contains a comparison of the coking rates of the examined catalysts.

The effectiveness of the promoters increases when their amount in the catalyst rises and when the $H_2O : C$ ratio rises in the gas phase. Fig. 1 presents the effect of the amount of the promoter (WO_3 and MoO_3) on the coking rate with some

Table 1
The effect of WO_3 and MoO_3 on nickel active area and coking rate of the examined catalysts. Temperature of reduction: 800°C. Temperature of coking: 500°C

Promoter	Amount (wt%)	Surface area of nickel ($m^2 g^{-1}$)	Coking rate at different reactant ratios H_2O : C ($\mu g\ g^{-1}\ min^{-1}$)					
			0.5	0.7	0.9	1.2	1.5	2.0
–	–	2.0	4588	4249	3313	2618	2362	1815
WO_3	0.2	1.7	4166	3124	–	1956	1535	1316
WO_3	0.5	1.9	2798	2255	1490	1031	794	596
WO_3	1.0	1.9	2711	1999	1279	823	632	455
WO_3	2.0	1.8	2135	1518	1017	645	458	329
MoO_3	0.2	1.2	2438	833	409	205	145	82
MoO_3	0.5	1.2	1936	640	247	111	81	34
MoO_3	1.0	1.3	1694	649	180	63	37	0
MoO_3	2.0	1.4	1052	242	87	35	−8[a]	−19[a]
MoO_3	5.0	1.4	564	67	0	−46[a]	−119[a]	–

[a] Initial rates of loss in weight.

selected H_2O : C ratios. An addition of $WO_3 > 0.5$ wt% or $MoO_3 > 0.2$ wt% to the catalyst causes a considerable reduction in coking.

An increase in the steam excess in the reaction mixture does not cause any changes in the shapes of the curves of the dependence of the coking rate on the amount of WO_3.

The effect connected with the introduction of MoO_3 to the catalyst increased with higher H_2O : C ratios. In the reaction mixtures in which H_2O : C$\geqslant$0.9, the

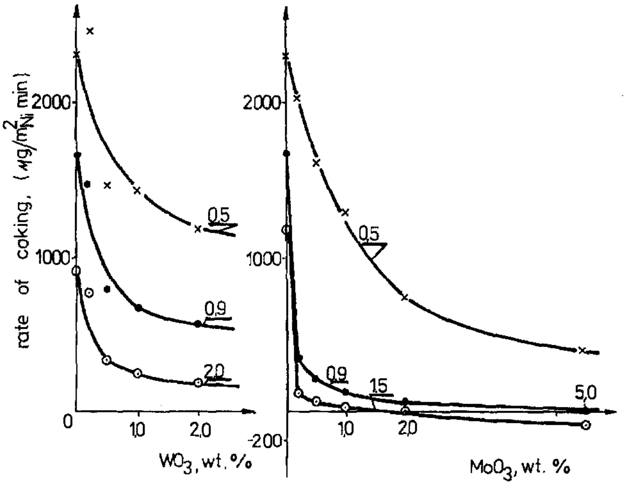

Fig. 1. Influence of amount of promoter on the rate of coking at 500°C in steam reforming of *n*-butane at various ratios of reagents.

coking rate decreased by one order of magnitude for a sample containing only ~ 0.2 wt% of molybdenum oxide.

Such a considerable reduction of the coking rate and the possibility of removing the deposit observed in samples containing ⩾2 wt% MoO_3 (table 1) suggest that a typical catalyst for the steam reforming of natural gas (characterized by a relatively low coking resistance) when promoted with WO_3 or MoO_3 becomes useful for reaction with higher hydrocarbons and is a very interesting object for further studies.

Fig. 2 presents a comparison of the effects of addition of molybdenum and tungsten on the activity of catalysts for steam reforming of methane, expressed as changes in the magnitude of the constant reaction rates as a function of temperature. As opposed to the effects of potassium addition, the nickel catalyst promoted with tungsten or molybdenum retains its catalytic activity for steam reforming of methane.

The literature provides no data on the application of molybdenum or tungsten compounds as additives to reduce coking of nickel catalysts in steam reforming. Dowden [7] merely predicted their advantageous influence on the properties of the catalysts while in the case of Ni/WO_3 [11] and $Rh/MgWO_4$ [12] systems, only the kinetics of the reaction was examined.

The increase of the resistance to sulphur poisoning was the most important aim of previous investigations [13–16] which included introducing molybdenum compounds into nickel catalysts of the hydrogenation of carbon oxide or benzene. In addition, Bartholomew [14] stated that the presence of molybdenum compounds in Ni/Al_2O_3 catalyst (containing 2.5% Ni and 3% MoO_2) increased the rate of carbon deposition in the reaction of CO methanation by one order of magnitude.

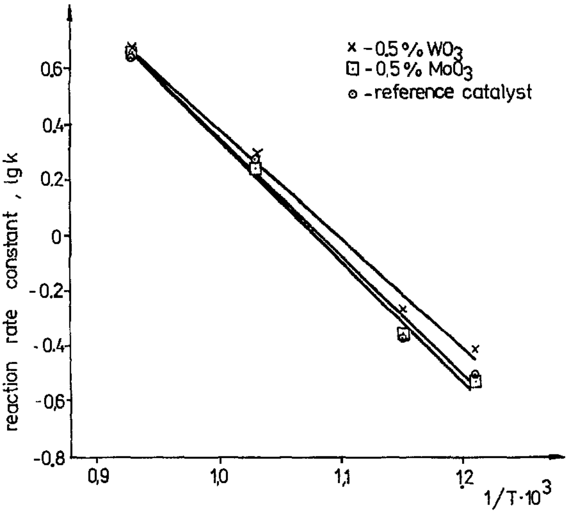

Fig. 2. Influence of temperature on the activity of catalysts in steam reforming of methane.

The difference between the influence of MoO_3 on the coking rate of nickel catalysts in the reactions of steam reforming observed in this study and methanation [14], is quite striking and difficult to explain at the moment. In one of the most fundamental reviews concerning the formation of carbon deposits on nickel catalysts, Bartholomew [17] states that the morphology and mechanism of the formation of carbon deposits in steam reforming of hydrocarbons and carbon oxide methanation are quite similar.

The results obtained seemed quite interesting and for that reason further studies on the promotion of nickel catalysts with WO_3 and MoO_3 were undertaken in order to arrive at a fuller evaluation of their properties and to explain their mechanism of operation.

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