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Resistance to coking determination by temperature programmed reaction of *n*-butane with steam

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Resistance to coking is one of the most important characteristics of nickel catalysts used for steam reforming of hydrocarbons, CO_2 reforming or methanation of carbon oxides. Microbalance reactors have for a long time played an important role in catalyst deactivation studies, providing coking and coke gasification rates. However, conventional thermogravimetric microbalances have a number of limitations. The aim of this paper is to compare initial temperatures of coking of Ni and Ni-Mo catalysts (with different resistance to coking) obtained in the temperature-programmed reaction of *n*-butane with steam with the results of coking rates obtained by the traditional thermogravimetric method. The investigations showed great agreement of the results.

KEY WORDS: steam reforming of hydrocarbons; TPReaction; nickel catalysts; resistance to coking; Mo promoter.

1. Introduction

Carbon formation is an unavoidable side-reaction in the catalytic processing of hydrocarbons, e.g., in steam reforming. Microbalance reactors have long played an important role in catalyst deactivation studies, providing coking and coke gasification rates [1,2]. In this technique, carbon deposition is monitored continuously by recording the weight change of a catalyst sample placed in a quartz basket hung on the balance arm in a flow reactor where it contacts gaseous reactants. With the typical hanging pan microbalance, much of the process gas bypasses the catalyst and catalyst temperature can be difficult to control [3–5]. Temperature gradients can play as significant a role in the investigations of endothermic reaction as steam reforming of hydrocarbons [1,5]. Recently, a new technique has been used for measuring sample weight changes during the process of coking or gasification—the so-called the vibrational balance (the tapered element oscillating microbalance (TEOM)), in which weight changes are determined from the changes of vibration frequency of the cell with the catalyst [3–5]. The TEOM, apart from unmistakable advantages [3–5], has one disadvantage, which is its high price [6].

It seems that another way to exclude gradient and diffusion effects on the results of coking experiments is by the application of the temperature programmed reaction (TPReaction) (*e.g.*, steam reforming of *n*-butane) for determination of the minimal temperature at which carbon deposit formation starts.

The formation of the deposit precedes a period of the so-called induction time [1,7] (during which time there is virtually no formation of carbon), the length of which depends on many factors influencing also the rate of coking, *i.e.*, the kind of hydrocarbon [1], the reagent ratio [1,8], and the temperature [9]. After the induction time under stable conditions of the reaction, coking accelerates and the coking rate reaches a constant value shown by a straight line.

Borowiecki *et al.* [10,11] have shown that the introduction of small amounts (0.5–2 wt%) of molybdenum or tungsten compounds to nickel catalysts greatly improved their resistance to coking. It was also shown that a small addition of the promoter increases the induction time of coking [12,13]. The length of the induction period is affected also by the same factors which have an influence on the coking rate of nickel catalysts in the steam reforming of hydrocarbons. High dispersion rates of nickel [14] and increase of MgO content in the support [12,15] cause prolongation of the induction time.

From the practical point of view, length of the coking induction time is more important for a given catalyst than the rate of its coking.

To determine quantitatively the effect of the two most important parameters (temperature and reagent ratio) on the initiation of the coking process, a gravimetric method was applied to observe the deposit formation in the model reaction mixture at a linear temperature increase. We applied the TPReaction of *n*-butane with steam for determination of the initial temperature of carbon formation on the catalysts with varied resistance to coking (Ni/Al_2O_3 and $Ni\text{-}Mo/Al_2O_3$) at different

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Table 1
The characteristics of the catalysts studied

Catalysts	Composition[a] (wt%)		Atomic ratio	Surface area (m^2/g_{cat})		Mean size of Ni crystallites (nm)	
	NiO	MoO_3	Mo/Ni	Total[b]	Active[c]	d_H[d]	d_X[e]
Ni(A)	17.5	–	–	4.2	2.1	36.8	–
Ni(B)	13.6	–	–	3.35	0.80	75.0	50.8
Ni(B)-Mo(0.1)	13.5	0.21	0.008	–	0.86	69.3	52.4
Ni(B)-Mo(0.5)	13.6	0.82	0.031	3.3	0.73	82.5	–
Ni(B)-Mo(1.0)	13.3	1.68	0.065	3.9	0.82	71.5	55.0

[a] Determined by atomic absorption spectroscopy (AAS).

[b] Determined by physical adsorption of argon at the temperature of liquid nitrogen.

[c] Determined by hydrogen chemisorption at 293 K and 100 mm Hg pressure.

[d] Determined from hydrogen chemisorption.

[e] Determined by X-ray line broadening.

reagent ratios ($H_2O:C$). The obtained results were compared with the coking-rate data acquired by conventional thermogravimetric microbalance methods [11].

2. Experimental

2.1. Catalysts

Studies were carried out on an impregnated Ni/α-Al_2O_3 commercial catalyst assigned for steam reforming of natural gas, denoted as Ni(A), and on a series of nickel catalysts containing varied amounts of MoO_3 (≤ 1.7 wt%), denoted as Ni(B)-Mo(−), where the number in parentheses denotes the amount of MoO_3 in wt%. Investigations were carried out after reduction at 800 °C for 2 h in deoxidized and dried hydrogen.

2.2. Methods

The methods used for the determination of catalyst properties are described in detail elsewhere [10,11,13, 15,16].

The coking TPReaction experiments were performed by the gravimetric method in a flow reactor at atmospheric pressure in the TGA-121 Cahn System. The reaction mixture ($C_4H_{10} + H_2O + He$ or $C_4H_{10} + H_2O + H_2 + He$) (5 vol% of H_2) with varied molar reagent ratios of water to n-butane of 1.6–6.0 (which corresponds to the ratio of water-to-carbon of 0.4–1.5 mol/atom), but at a constant flow rate (70 $cm^3\,min^{-1}$), was passed through the reactor at a programmed temperature rise as high as 5 $°C\,min^{-1}$. The examinations of the coking were carried out at a constant partial pressure of C_4H_{10} (60.8 hPa).

After reduction the catalyst was cooled to the initial temperature (250 °C for the catalyst Ni(A) or 350 °C for Ni(B) series catalysts) and the reducing mixture (He + 10% H_2) was replaced by the stream of proper reaction mixture. After 15 min stabilization the reactor was heated at the rate of 5 $°C\,min^{-1}$ by a temperature programmer up to 640 °C.

The coking rates were determined in the steam reforming of n-butane (by the traditional gravimetric method in a flow reactor at atmospheric pressure), at constant temperature (500 °C), at constant partial pressure of n-butane (60.8 hPa) and different reagent ratios $H_2O:C_4H_{10}$ equal to 2.0 or 8.0 [11,15].

3. Results

The properties of the catalysts examined are summarized in table 1. For the applied promoter (Mo) no noticeable changes of total and active surface areas are observed.

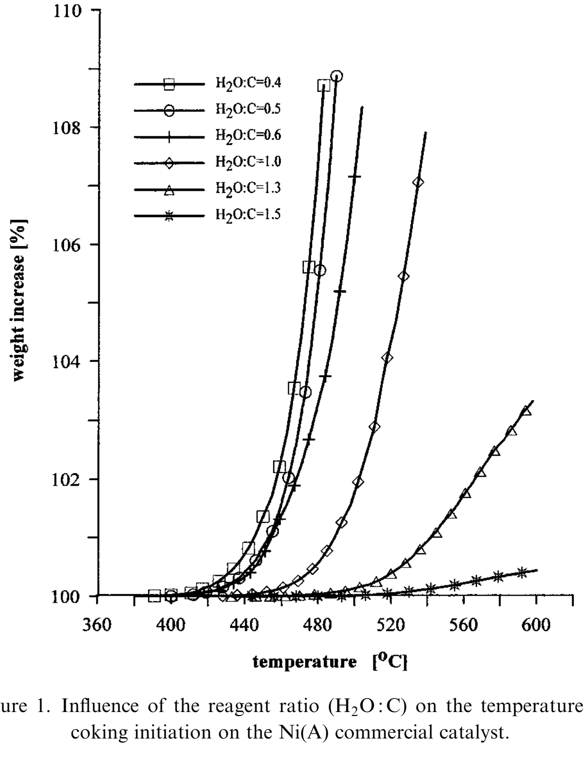

Figure 1. Influence of the reagent ratio ($H_2O:C$) on the temperature of coking initiation on the Ni(A) commercial catalyst.

Table 2
Comparison of the coking results on Ni(A) catalyst

$H_2O:C$ (mol/atom)	0.4	0.5	0.6	0.7	0.9	1.0	1.3	1.5	2.0
T_{in} [a] (°C)	408	415	416	–	–	447	482	518	–
Rate of coking [b] ($\mu g/g_{cat}$ min)	–	7549	–	7086	5607	–	5150	4705	3775

[a] Temperature of coking initiation at different reagent ratios.
[b] Rate of coking in thermogravimetric measurements at 500 °C.

3.1. Commercial nickel catalyst

The influence of the reagent ratio on the changes of weight on the typical commercial catalyst Ni(A) during TPReaction of *n*-butane with steam are shown in figure 1. The shape of the curves indicating weight changes of the samples in time alters with increasing $H_2O:C$ reagent ratio.

To determine the initial temperature of coking one can choose absolute increase of weight resulting from the deposit formation or relative increase of weight in time, *i.e.*, the rate of coking. Both methods are characterized by some disadvantages because in both cases it is necessary to define the criterion quantity which determines the value of reading.

In the case of the phenomenon characterized by large dynamics as observed for the catalysts Ni(A), particularly at lower contents of water vapour—all proposed methods of determining the initial temperature of coking can be a basis for estimation of catalyst resistance to carbon deposit formation. At the high steam to hydrocarbon ratio in the reaction mixture, and for the catalysts resistant to coking, the absolute quantities of weight increase are small and the rate of deposit formation proved to be the best criterion for determination of initial temperature of coking.

The rate of deposit formation was determined using the differential of relative sample weight to time:

$$r = \delta[m_T/m_0]/\delta\tau \tag{1}$$

where m_T is the sample weight during the experiment at temperature T, m_0 is the initial sample weight, and τ is time.

Table 2 presents for the Ni(A) catalyst the temperatures of coking initiation determined by the TPReaction at varied reagent ratios and the results of coking rates determined in the steady-state rate of coking.

The increase of the reagent ratios ($H_2O:C$) causes the temperature increase of coking initiation determined by the TPReaction method and the decrease of coking rate in the thermogravimetric measurements at constant temperature.

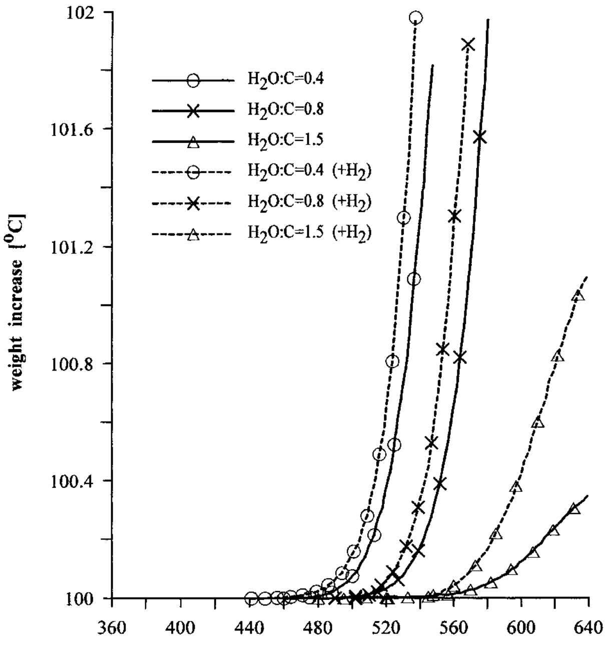

Figure 2. Influence of the reagent ratio and the presence of hydrogen on the temperature of coking initiation, Ni(B) catalyst.

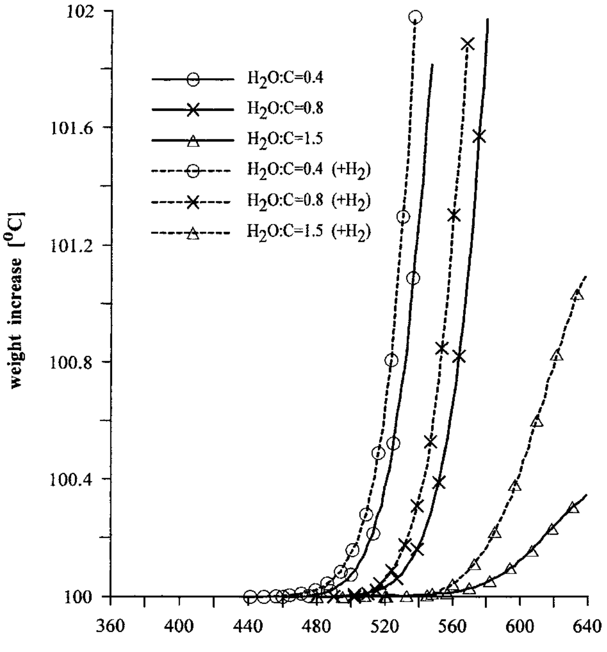

Figure 3. Influence of the reagent ratio and the presence of hydrogen on the temperature of coking initiation, Ni(B)-Mo(0.5) catalyst.

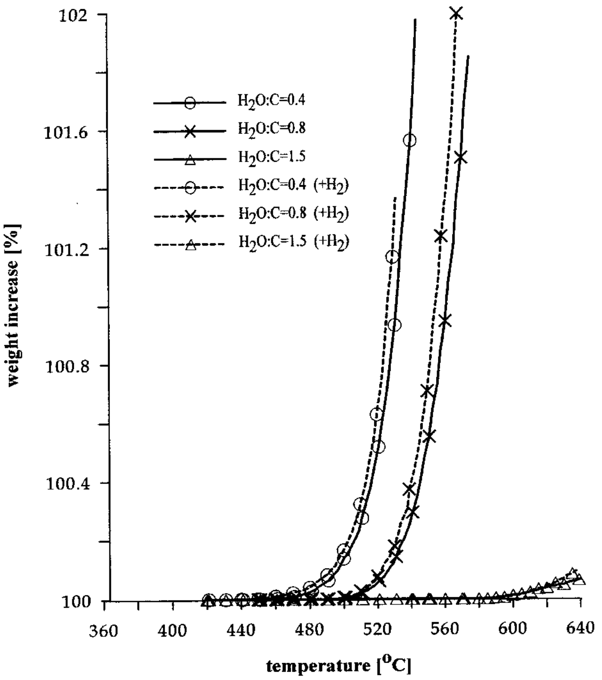

Figure 4. Influence of the reagent ratio and the presence of hydrogen on the temperature of coking initiation, Ni(B)-Mo(1.0) catalyst.

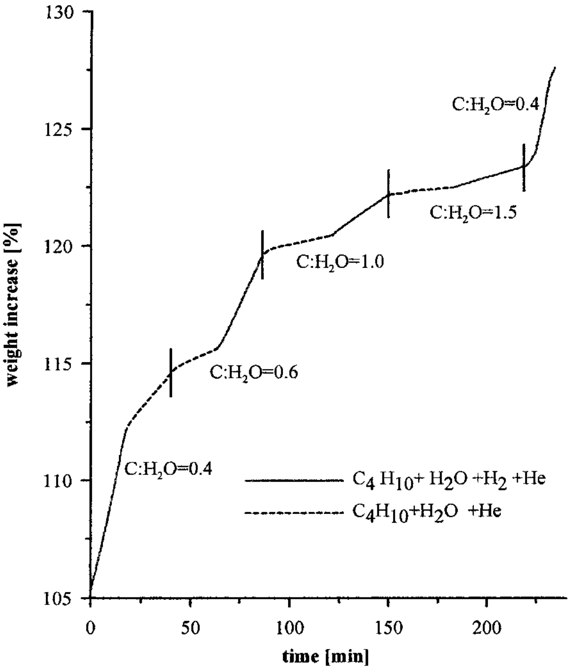

Figure 5. Influence of hydrogen on the changes of weight in the isothermic coking-rate measurements for the steam reforming of *n*-butane (at different $H_2O:C$ ratios from 0.4 to 1.5).

3.2. Nickel–molybdenum catalysts

Investigations were carried out on a series of nickel–molybdenum catalysts on α-Al_2O_3, with different amounts of MoO_3. It was shown recently [11,17] that additions of small amounts of MoO_3 (~1.0 wt%) to $NiAl_2O_3$ catalysts decrease the coking rate in the steam reforming of hydrocarbons significantly. TPReaction measurements were carried out of the initial temperature of coking in the steam reforming of *n*-butane at three different reagent ratios. The TPReaction curves are shown in figures 2–4.

In table 3 the temperatures of coking initiation and the coking rates obtained at analogous reagents ratio are presented.

Hydrogen present in the reaction mixture causes the decrease of the temperature of coking initiation. As shown in ref. [18], small amounts of hydrogen in the reagent mixtures increased the coking rate of the catalysts examined.

For verification of the influence of hydrogen on the resistance of Ni-Mo catalysts to coking, the isothermic coking-rate measurements for the steam reforming of *n*-butane has been carried out (at different $H_2O:C$ ratios, from 0.4 to 1.5). In figure 5 changes in the weight of an Ni(B)-Mo(0.1) sample (in the presence and absence of hydrogen) are presented. For the investigated reagent ratio, the introduction of hydrogen into the reaction mixture causes a coking-rate increase.

When promoter Mo is present in the nickel catalyst, it causes an increase in the initiation temperatures of coking, which is adequate to decrease the coking rate in conventional measurements. The influence of the

Table 3
Temperature of coking initiation and rate of coking on Ni(B) and Ni(B)-Mo/Al_2O_3 catalysts

Catalyst	Type of reaction mixture	Temperature of coking initiation (°C) at different $H_2O:C$ ratios			Rate of coking[a] ($\mu g/g_{cat}$ min) at different $H_2O:C$ ratios	
		0.4	0.8	1.5	0.7	1.5
Ni(B)	$C_4 + H_2O + He$	466	484	509	8225	4939
Ni(B)-Mo(0.5)	$C_4 + H_2O + He$	475	502	557	3650	938
Ni(B)-Mo(1.0)	$C_4 + H_2O + He$	469	499	599	2404	240
Ni(B)	$C_4 + H_2O + H_2 + He$	418	430	471	–	–
Ni(B)-Mo(0.5)	$C_4 + H_2O + H_2 + He$	466	493	542	–	–
Ni(B)-Mo(1.0)	$C_4 + H_2O + H_2 + He$	458	495	593	–	–

[a] In thermogravimetric measurements at 500 °C.

promoter on the coking rate of catalysts depends on the reagent ratio, *i.e.*, the H_2O:C [mol:atom] ratio in the reaction mixture [11,17] (see table 3). The differences of coking initiation temperatures increase significantly with the increase of the reagent ratio H_2O:C to 1.5.

4. Discussion

In the steam reforming of a given hydrocarbon, the factors which have the biggest influence on the coking process are temperature and reagent ratio [1] and properties of the applied catalysts characterized by the "induction coking time" magnitude [1,12,13].

Rostrup-Nielsen, in his important and still valid works [1,19], has shown that an increase of reagent ratio and temperature (in the range 450–600 °C) has a different influence on the length of induction coking time and catalyst coking rate measured by the traditional gravimetric method. For the Ni-MgO catalyst Rostrup-Nielsen [1] found a linear dependence of the coking-rate logarithm as well as of the coking induction time logarithm on the H_2O:C ratios in the reaction mixture. Based on the above he proposed a dependence of the critical steam to hydrocarbon ratio at which deposit appears on the temperature [1]:

$$\left(\frac{p_{\mathrm{H_2O}}}{p_{\mathrm{C}_n\mathrm{H}_m}}\right)_{\mathrm{crit}} = \frac{-a}{T} + b \qquad (2)$$

where a and b are positive constants depending on catalyst type and hydrocarbon.

The critical ratio was found to increase rapidly with the temperature and to be influenced by the type of hydrocarbon and by the catalyst.

In the case of Ni(A) catalyst it was observed that an increase of the H_2O:C ratio in the reaction mixture causes the following:

- the temperature increase of the initiation of coking (measured by the TPReaction method)
- the decrease of coking rate (measured by the isothermic gravimetric method).

For Ni(B) and Ni(B)-Mo(−) catalysts with different resistance to coking (characterized by the varied coking induction time [13]), it was noticed that an increase in the amount of the promoter causes:

- the temperature increase of the initiation of coking (measured by the TPReaction)
- the decrease of coking ratio (measured by the isothermic gravimetric method).

Figure 6 for the Ni(A) catalyst presents the dependence of the coking-rate logarithm and reciprocal of the coking initiation temperature on the H_2O:C ratio in the reaction mixture. As can be seen, both dependencies have a linear character.

The semilogarithmic dependency of the coking rate on the steam-to-carbon ratio (traditional gravimetric method) is in agreement with those presented in the literature [1]. An analogous linear character dependency of the reciprocal of the coking initiation temperature on the steam-to-carbon ratio (TPReaction method) confirms Rostrup-Nielsen's conclusions [1] and indicates the compatibility of results obtained by both methods.

For the Ni(B)-Mo catalysts (figure 7) there are presented dependencies of the coking-rate logarithm and the reciprocal of the coking initiation temperature (determined at the reagent ratio H_2O:C = 1.5) on the

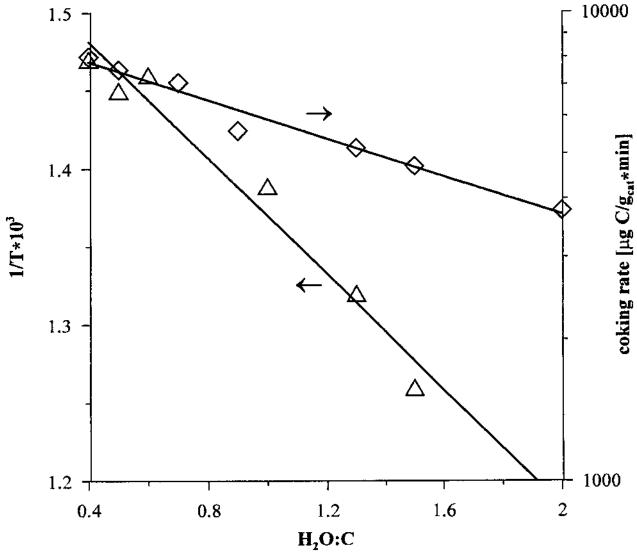

Figure 6. Influence of the reagent ratio on the coking rate determined by the gravimetric method and the initiation coking temperature determined by the TPReaction method for Ni(A) catalyst.

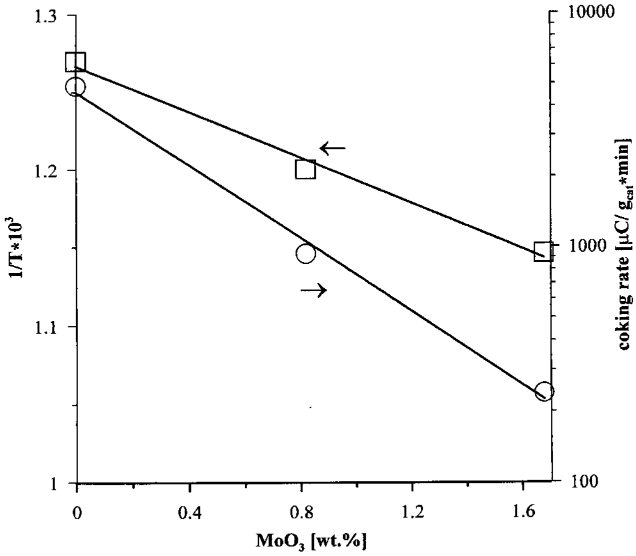

Figure 7. Influence of molybdenum promoter amount on the coking rate determined by the gravimetric method and the initiation coking temperature determined by the TPReaction method for Ni(B)-Mo(−) catalysts.

promoter content. As for the catalyst Ni(A), the presented dependencies also have a linear character.

Results obtained for promoted catalysts confirm all the above deliberations and show the compatibility of the results from both methods.

In the steam reforming of *n*-butane on the nickel and nickel–molybdenum catalysts (in the investigated temperature range) a filamentous deposit is formed [20,21]. As was examined in many studies [*e.g.*, 1,11,20,22,23], in the steam reforming of hydrocarbons it is a dominant form of deposit. The mechanism of its formation causes, in practice, a pure carbon of graphite-like structure with distances of ~0.34 nm between the layers. The amount of hydrogen (in the deposits formed) determined by burning (CHN Perkin–Elmer analyser) was within the method limit [24].

It seems that the temperature-programmed-reaction method gives qualitative results of the resistance to coking analogous to the traditional gravimetric methods of the rate of carbon deposit formation. It shows the possibility of replacing the traditional thermogravimetric method for estimation of catalyst resistance to coking by the simpler and faster TPReaction method of the determination of initial temperature of coking.

Conclusions

1. The increase of the $H_2O:C_nH_m$ ratio causes a temperature increase of coking initiation.
2. A promoter present in a nickel catalyst causes an increase in the initial temperature of coking which is adequate to decrease the coking rate of conventional measurements.
3. Results obtained by both methods indicate that the influence of molybdenum promoter on the resistance of Ni-Mo catalyst to coking in the steam reforming of hydrocarbons depends on the reagent ratio in the reaction mixture.
4. Hydrogen present in the reaction mixture causes a decrease in the temperature of coking initiation. As shown, small amounts of hydrogen in the isothermal measurements showed an increase in the coking rate.
5. It was stated that the traditional thermogravimetric method used for determination of resistance to coking can be replaced by a simple, faster method of measurement of initial temperature of coking on catalysts.

Acknowledgments

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References

[1] J.R. Rostrup-Nielsen, in: *Catalysis—Science and Technology*, Vol. 5, eds. J.R. Anderson and M. Boudart (Springer, Berlin, 1984) p. 1.

[2] C.H. Bartholomew, M.V. Strasburg and H.-Y. Hsieh, Appl. Catal. 36 (1988) 147.

[3] De Chen, A. Gronvold, H.P. Rebo, K. Moljord and A. Holmen, Appl. Catal. A: General 137 (1996) L1.

[4] K. Liu, S.C. Fung, T.C. Ho and D.S. Rumschitzki, J. Catal. 169 (1997) 455.

[5] J.N. Armor and D.J. Martenak, Appl. Catal. A: General 206 (2001) 231.

[6] D.S. Rumschitzki, private information.

[7] D.C. Gardner and C.H. Bartholomew, I&EC Prod. Res. Devel. 20 (1981) 80.

[8] L.S. Lobo and D.L. Trimm, J. Catal. 29 (1973) 15.

[9] R.T.K. Baker and P.S. Harris, in: *Chemistry and Physics of Carbon*, Vol. 14, ed. P.H. Walker Jr. (Marcel Dekker, New York, 1978) p. 83.

[10] T. Borowiecki and A. Gołębiowski, Catal. Lett. 25 (1994) 309.

[11] T. Borowiecki, A. Gołębiowski and B. Stasińska, Appl. Catal. A: General 153 (1997) 141.

[12] T. Borowiecki, A. Machocki and J. Ryczkowski, in: *Catalyst Deactivation 1994*, eds. C.H. Bartholomew and J.B. Butt (Elsevier, Amsterdam, 1994) p. 537.

[13] T. Borowiecki and A. Machocki, in: *Catalyst Deactivation 1999*, eds. B. Delmon and G.F. Froment (Elsevier, Amsterdam, 1999) p. 435.

[14] T. Borowiecki, Appl. Catal. 4 (1982) 223.

[15] T. Borowiecki, Appl. Catal. 10 (1984) 273.

[16] T. Borowiecki, Polish. J. Chem. 67 (1993) 1755.

[17] B. Stasińska, J. Gryglicki and T. Borowiecki, in: *Heterogeneous Catalysis*, eds. A. Andreev *et al.* (Institute of Catalysis, Sofia, 1996) p. 879.

[18] B. Stasińska, T. Borowiecki, A. Gołębiowski, K. Stołecki, Adsorp. Sci. Technol. 16 (1998) 705

[19] J.R. Rostrup-Nielsen, J. Catal. 33 (1974) 184.

[20] E. Tracz, R. Scholz and T. Borowiecki, Appl. Catal. A: General 66 (1990) 133.

[21] L. Kępiński and B. Stasińska, T. Borowiecki, Carbon 38 (2000) 1845.

[22] J.W. Snoeck, G.F. Froment and M. Fowles, J. Catal. 169 (1997) 240.

[23] I. Alstrup, J. Catal. 109 (1988) 241.

[24] T. Borowiecki and A. Hofman, unpublished data.