Catalysis Today 178 (2011) 132–136

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

The effect of potassium on the activity and stability of Ni–MgO–ZrO$_2$ catalysts for the dry reforming of methane to give synthesis gas

Bhari Mallanna Nagaraja[a,b], Dmitri A. Bulushev[a,b], Sergey Beloshapkin[b], Julian R.H. Ross[a,*]

[a] *Charles Parsons Initiative, Chemical & Environmental Science Department, University of Limerick, Limerick, Ireland*
[b] *Materials & Surface Science Institute, University of Limerick, Limerick, Ireland*

ARTICLE INFO

Article history:
Available online 4 October 2011

Keywords:
Dry reforming of methane
Ni–MgO–ZrO$_2$ catalyst
Promotion with K
H_2 production
Synthesis gas
Deactivation

ABSTRACT

It has been found that the addition of 0.5 wt.% potassium to a catalyst consisting of 8 wt.% Ni supported on a MgO–ZrO$_2$ support prepared by co-precipitation improved both the activity and stability of this material for the dry reforming of methane. Increasing the content of potassium caused a decrease in the catalytic activity but the stabilities of the resultant catalysts were still higher than those for the undoped catalyst. The BET surface areas of the catalysts increased with potassium content.

1. Introduction

One of David Trimm's early research interests and one in which he made significant contributions was in the deposition of carbon on nickel catalysts, particularly for those used in the steam reforming of naphtha for hydrogen production [1]. Partly through his association with David during David's period in Imperial College, London, in the 1970s, the senior author of this paper developed an interest in the preparation and properties of Ni catalysts used for steam reforming and methanation [2], an interest that he has maintained ever since. In the context of the present paper, it is interesting to note that several successful catalysts formulations from that period used for hydrocarbon reforming to produce either methane or syngas contained K additions to reduce carbon deposition.

In the early 1990s, the subject of the dry reforming of methane:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

became a topic for research in this laboratory, our work being concerned largely with the use of zirconia-supported metals for the reaction. It was shown that platinum on zirconia, with and without promoters such as alumina or rare earth oxides, was particularly effective for the reaction [3–5]. Catalyst deactivation during the reaction is often due to the deposition of carbon on the catalysts and this can be minimised by the addition of either steam or oxygen to the feed [6]. The problem of carbon deposition becomes much more serious when the cheaper nickel-containing catalysts are used and, despite many efforts to modify these catalysts to minimise carbon deposition, this problem of carbon deposition is one of the main reasons why the reaction is not used commercially for syngas production. In our early work, we examined the use of Ni/zirconia catalysts for dry reforming and found that carbon deposition was significantly reduced, particularly at low Ni loadings, if the nickel crystallites used were very small [7]. We have recently embarked on a new programme having the aim on the development of stable Ni/zirconia based catalysts.

Several authors have reported that Ni/MgO catalysts form NiO–MgO solid solutions and that these exhibit good stability in the dry reforming methane because of their pronounced surface basicity and high metal dispersions [8–11]. However, only a small number of authors have reported the use of Ni/MgO–ZrO$_2$ samples in the dry reforming of methane. Gocmez and Fujimori [12] synthesized ZrO$_2$–MgO by a citrate sol–gel method and showed that the samples after calcination at 1073 K consisted of MgO and a metastable tetragonal ZrO$_2$ phase. Trakarnpruk and Sukkaew [13] synthesized Ni/MgO–ZrO$_2$ samples by the same method and showed that these can possess high surface areas (120–140 m^2 g^{-1}) after calcination at 1073 K. Garcia et al. [14] reported the effect of small additions of MgO on the basicity of Ni/ZrO$_2$ and confirmed that these additions prevented the deactivation of the catalyst in the dry reforming of methane.

It has been reported by a number of authors that the alkali metals (Li, Na and K) can act as promoters or modifiers of catalysts with different supports when used for the dry reforming of

---

* Corresponding author. Tel.: +353 061234628; fax: +353 061202734.
E-mail address: Julian.Ross@ul.ie (J.R.H. Ross).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.08.040

Table 1
Physico-chemical characteristics of the Ni catalysts with different potassium contents and estimated rates of methane conversion.

Catalysts	From AAS (wt.%)		S_{BET} of reduced catalysts ($m^2 g^{-1}$)	Rate × 10^5, at 823 K (mol CH_4 s^{-1} g cat^{-1})
	Ni	K		
NM_5Z_2	8.8	0.03	29	6
0.5K–NM_5Z_2	7.8	0.46	34	9[a]
0.9K–NM_5Z_2	7.6	0.92	42	5
1.4K–NM_5Z_2	7.4	1.42	46	5
1.9K–NM_5Z_2	7.7	1.91	57	3

[a] Equilibrium was reached.

methane. Juan-Juan et al. [15] reported that different amounts of K (0.2–5 wt.% K_2O) promoted Ni/Al_2O_3 catalysts for this reaction; a catalyst containing 0.2 wt.% K_2O gave very low coke deposition and the catalytic activity at 973 K was stable for 24 h. Luna and Iriarte [16] studied the influence of K, Sn, Mn and Ca on a $Ni–Al_2O_3$ catalyst for CO_2 reforming of methane. A material with 0.5 wt.% of K was slightly less active as compared to the original ($Ni–Al_2O_3$) sample, but the potassium modified catalyst showed only low levels of carbon deposition. Luna and Quiroga [17] reported the effect of modifiers (0.5 wt.% Li and K) on Ni-based catalysts on different supports (Al_2O_3, CeO_2, La_2O_3, ZrO_2) for dry reforming of methane. A 10% Ni/ZrO_2 catalyst showed stable activity and lower coke deposition. A 10% Ni/CeO_2 catalyst also had a relatively good activity but it deactivated with time on stream. The addition of 0.5 wt.% Li and K to this material led to stable activity with time on stream but the catalytic activity was lower than that for the unmodified 10% Ni/CeO_2 sample. Frusteri et al. [18,19] studied a series of 19% Ni/MgO catalysts doped with different amounts of K and found that these had stable activity at 923 K.

This paper reports that the addition of small amount potassium to catalysts consisting of Ni supported on co-precipitated $MgO–ZrO_2$ support brings about significant improvement of catalytic activity and stability in dry reforming of methane reaction. The dry reforming of methane reaction was studied at different temperatures (823–1023 K) and stability tests were performed at 1023 K for 14 h.

2. Experimental

A $MgO–ZrO_2$ support material (5:2 mole ratio) was prepared by a co-precipitation method. Stoichiometric quantities of $Mg(NO_3)_2·6H_2O$ and $ZrO(NO_3)_2·xH_2O$ were dissolved in distilled water and an aqueous solution of $(NH_4)_2CO_3$ (1 M) was added dropwise to the mixture at 333 K with constant stirring to maintain the value of the pH at about 9.5. The resultant precipitate was then cooled and washed thoroughly several times with distilled water at room temperature; the resulting slurry was dried at 393 K overnight and then calcined at 1073 K for 5 h in air. The calcined $MgO–ZrO_2$ material was designated as M_5Z_2.

The supported nickel catalyst without added K was prepared by impregnation of the M_5Z_2 support with a nickel nitrate solution to give approximately 10 wt.% nickel in the final catalyst. A concentrated nickel nitrate solution was placed in a 50 ml beaker and the appropriate quantity of M_5Z_2 support was added with continuous stirring. The remaining water was then evaporated on a hot plate and the residue was dried at 393 K overnight. The catalyst without calcination in air was designated as NM_5Z_2. All the chemicals were supplied by Sigma–Aldrich.

Samples of the support material containing different amounts of potassium were prepared by adding the appropriate quantities of aqueous solutions of KOH (Merck) to M_5Z_2 so that the final resultant materials contained 0.5, 0.9, 1.4 and 1.9 wt.% of K; after drying the samples at 393 K overnight, each was then impregnated with solutions of nickel nitrate as described above and dried once more before using the sample for the reaction. The potassium and Ni contents of the samples (see Table 1) were determined by atomic absorption spectroscopy (AAS) following extraction with a diluted $HCl:HNO_3$ (3:1) mixture for 12 h. The samples were designated as: (a) 0.5K–NM_5Z_2, (b) 0.9K–NM_5Z_2, (c) 1.4K–NM_5Z_2 and (d) 1.9K–NM_5Z_2.

The BET specific surface areas of the materials (Table 1) were determined by nitrogen adsorption at 77 K using a Micromeritics Gemini II 2370 surface area analyzer. Prior to the analysis, the samples were outgassed in N_2 flow at 473 K for 2 h. Scanning electron microscopy (SEM) was performed with a JEOL JEM-6400 with the accelerating voltage 30–35 kV range. X-ray Photoelectron Spectroscopy (XPS) studies were performed with a Kratos Axis 165 spectrometer using monochromatic Al K_α radiation ($\lambda\nu$ = 1486.58 eV) and a fixed analyzer pass energy of 20 eV.

The CH_4–CO_2 reaction was carried out at 823–1023 K at atmospheric pressure using 20 mg of the catalyst in a fixed bed tubular quartz reactor of 4 mm internal diameter and the catalyst bed length between the quartz wool layers in the reactor was approximately 2–3 mm. The products and reactants were analyzed by a micro gas chromatograph (Agilent-3000) equipped with two-columns (Porapak Q and Molsieve 5A) and TCD detectors. Before each experiment, the sample was reduced in a 5% H_2/Ar flow; the temperature during reduction was increased slowly from room temperature to 1023 K, the final value being maintained for 2 h. The catalyst was then cooled to the lowest reaction temperature (823 K) in Ar before exposing it to a reaction mixture consisting of CH_4, CO_2 and Ar in the ratio of 1:1:8, the total flow rate being 50 ml/min. The reaction was carried out at a series of temperatures, each being maintained for 30 min before increasing the temperature once more by 50 K. When the final temperature of 1023 K had been attained, this value was maintained for 14–15 h to give an indication of the stability of the sample.

3. Results and discussion

Table 1 shows the K and Ni contents, BET surface areas and the estimated rates of conversion of methane (mol CH_4 s^{-1} g cat^{-1}) at 823 K (see further below) for each of the catalysts. The Ni contents in all the catalysts were about 8 wt.%, rather less than expected (10 wt.%). The BET surface area of the unpromoted reduced NM_5Z_2 catalyst was 29 $m^2 g^{-1}$ and the surface area increased with potassium content, reaching 57 $m^2 g^{-1}$ for the catalyst with 1.9 wt.% K.

Fig. 1 shows scanning electron microscopy (SEM) images of the reduced NM_5Z_2 and 1.9K–NM_5Z_2 samples, indicating that the appearance of the surface of the samples changed considerably when doped with potassium. The sample without potassium (Fig. 1a) had a plate-like structure while that with K had spherical grains with a size of about 20–50 nm (Fig. 1b). This growth of smaller crystallites is consistent with the change in BET surface area (Table 1). The alkali metal could etch the support, forming new pores and giving a higher surface area.

The catalysts were characterized by X-ray photoelectron spectroscopy (Table 2) in order to obtain information about the chemical

Table 2
X-ray photoelectron spectroscopy results for the reduced NM_5Z_2 catalysts prepared with different potassium loadings.

Catalyst	Binding energy (eV)		Atomic surface ratio		
	Ni $2p_{3/2}$, Ni $2p_{1/2}$	K $2p_{3/2}$	Ni/Mg	K/Mg	Zr/Mg
NM_5Z_2	855.5, 861.3	–	0.016	0	0.01
0.5K–NM_5Z_2	855.2, 861.1	293.4	0.048	0.002	0.02
0.9K–NM_5Z_2	855.0, 861.1	292.7	0.044	0.004	0.01
1.9K–NM_5Z_2	855.3, 861.5	292.8	0.034	0.011	0.02

states of the Ni and K and the chemical compositions of the surfaces of the samples. Although the samples were pre-reduced, they were most probably re-oxidised during the transfer to the spectrometer as the spectra contained two maxima at 855–855.5 and 861.1–861.5 eV, these being indicative of the presence of Ni^{2+} compounds. Two peaks of Zr 3d (not shown) correspond to Zr $3d_{5/2}$ (181.8 eV) and Zr $3d_{3/2}$ (184 eV) which must be assigned to the Zr^{4+} state [20]. The atomic surface ratio of Zr to Mg was very small (0.01–0.02). This indicates that the surface of the support was considerably enriched with Mg in all the samples. The K $2p_{3/2}$ peak was very weak and it was found in the range of 292.7–293.4 eV, this being characteristic of K^+. The surface atomic K/Mg ratio as expected increased with the K content. The atomic ratio of surface concentrations of Ni to Mg was higher for the catalysts with potassium but decreased for the K-containing samples with an increase of K content from 0.5 wt.% to 2 wt.% (Table 2). The higher Ni/Mg ratio appears to be consistent with a higher dispersion of Ni in the K-modified samples.

The results of the catalytic measurements at temperatures in the range 823–1023 K are shown in Fig. 2a and b for both the unpromoted material and the promoted samples. The highest conversions of both methane and CO_2 obtained were, with the exception of the conversion of methane for the sample with 0.5 wt.% K (see below), lower than the calculated equilibrium values. It should be noted that the calculated equilibrium conversions of CO_2 were somewhat higher than those of methane at all temperatures as a consequence of the existence of the reverse water-gas shift reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O$$

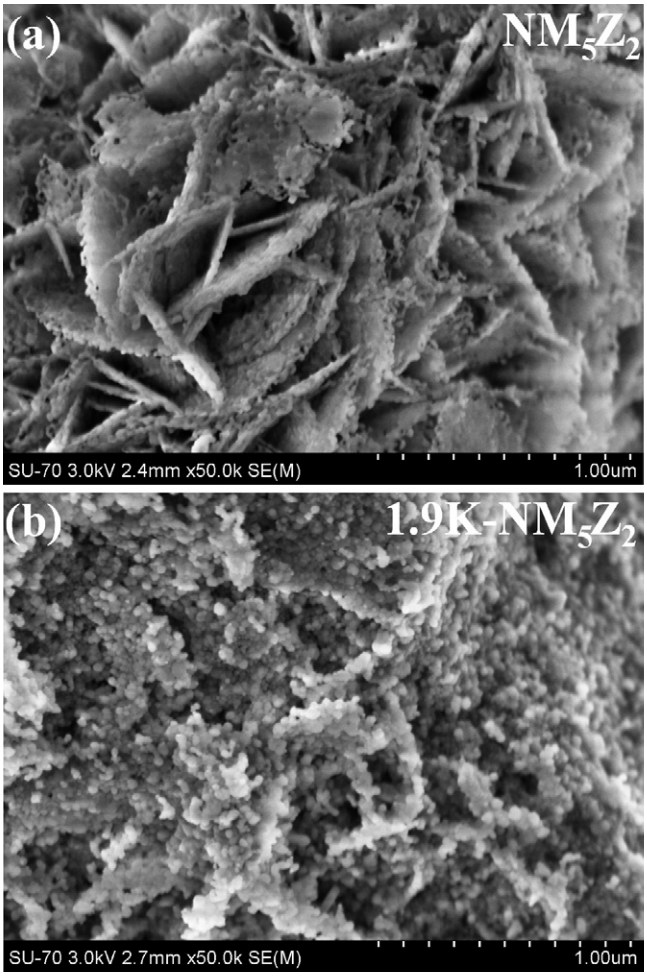

Fig. 1. SEM images of the reduced 8% Ni/MgO–ZrO_2 catalysts without (a) and with 1.9 wt.% of potassium (b).

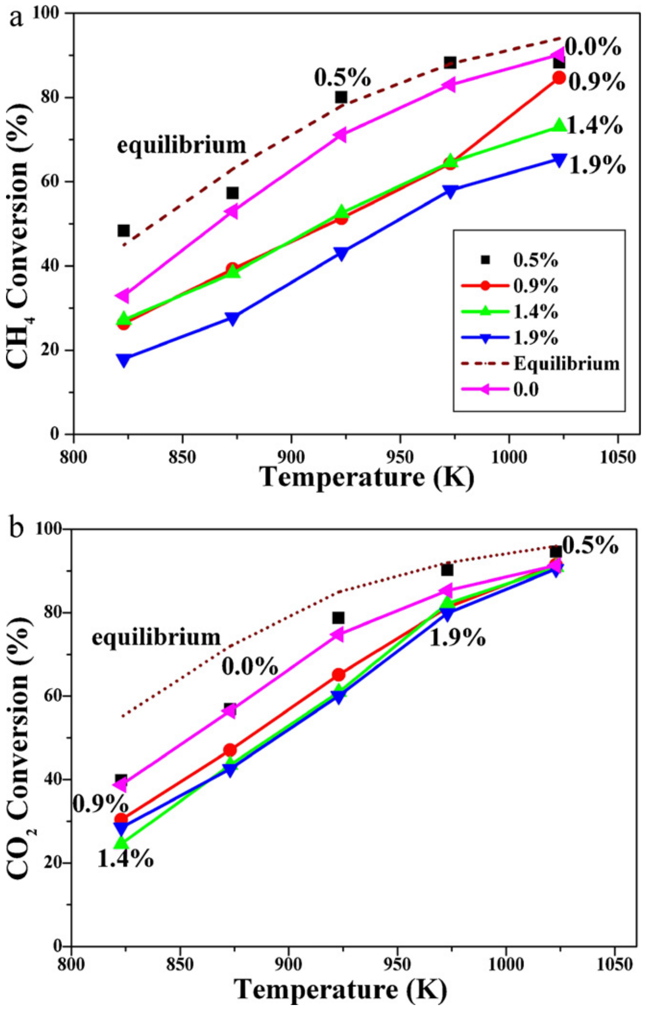

Fig. 2. (a) CH_4 conversion and (b) CO_2 conversion vs. temperature obtained for the dry reforming of methane over the NM_5Z_2 catalysts with different potassium loadings. (Reaction conditions: catalyst weight: 20 mg, reduction conditions: 1023 K/2 h; $CH_4/CO_2/Ar$ ratio: 1:1:8; total flow rate: 50 ml/min.)

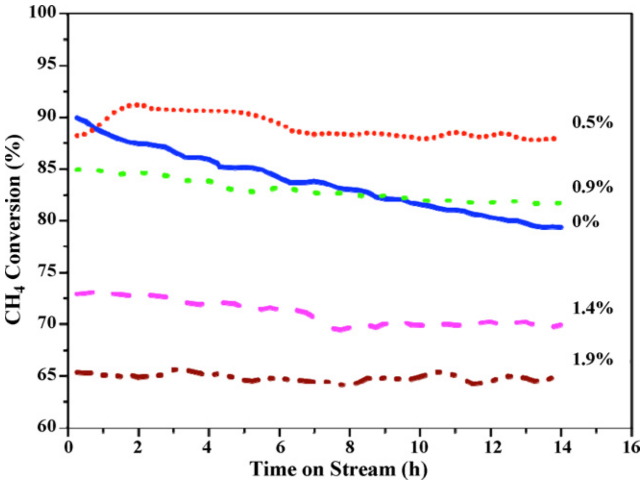

Fig. 3. CH_4 conversion vs. time on stream at 1023 K in the dry reforming of methane over the NM_5Z_2 catalysts with different potassium loadings; reaction conditions as in Fig. 2.

For the unpromoted sample, the CO_2 conversions seem to be further from equilibrium than the CH_4 conversions, indicating that the reverse water gas shift reaction may not have been fully equilibrated for this material.

There was a very significant change in the catalytic conversions when K was added to the formulation, the difference being particularly significant for the sample containing 0.5 wt.% K. The methane conversions for this sample (Fig. 2a) were now close to the equilibrium values at all temperatures while the CO_2 conversions were slightly below the equilibrium values, especially at lower reaction temperatures (Fig. 2b). With higher K content, there was a decrease in the conversions of both methane and CO_2 compared with the unpromoted material at all temperatures (see Fig. 2). This may reflect a decrease in the Ni dispersion (probably due to the Ni being covered by K species) with an increase in the K contents. What is remarkable however is that the conversions at the highest temperature are now much more stable with all the samples, there being very small decreases in conversion with time on stream, particularly for the highest K content of 1.9 wt.%.

Fig. 3 shows the methane conversions as a function of time on stream at 1023 K for all the samples. For the unpromoted material, the conversion dropped from about 90% to about 80% over a period of 14 h, indicating that significant deactivation occurred, probably as a result of carbon deposition. The difference in behaviour at 1023 K between the unpromoted and promoted samples was particularly marked. Although the methane conversion was slightly lower (0.5% of K) than that of the unpromoted sample at the beginning of the period (see Fig. 3), the conversion became higher after several hours and thereafter remained almost constant for more than 10 h.

It is difficult to make a comparison between the behaviour of these catalysts and of other similar materials reported in the literature as the conditions used for each investigation differ (different catalyst weights, flow conditions, reactor geometries) and the results are often obtained under conditions in which the conversions are close to equilibrium values. Without a detailed knowledge of the kinetics of the reaction on each catalyst, it is therefore not possible to estimate a true rate of reaction (or rate constant) for each catalyst for the data at high conversion. Table 1 gives the rates of conversion of methane at the uppermost temperature of 823 K for the different catalysts studied here expressed as numbers of moles s^{-1} g cat^{-1}, these values being lower limits for the actual values. The values of estimated rates of conversion range from about 3 to 9×10^{-5} mol s^{-1} g cat^{-1}.

Kiennemann and his group [21] have recently reported results for the CO_2 reforming of methane using a number of Ni-promoted ceria-zirconia catalysts (Their CeZrRh and CeZrRu catalysts were prepared by a pseudo sol–gel method; nickel (II) nitrate hexahydrate (5 wt.% of Ni) was then added to the CeZrRh and CeZrRu by wet impregnation and the resultant materials were dried at 393 K before calcination in air at 1023 K for 4 h). They found that the estimated rate of methane conversion on 5%Ni/Ce–Zr–O catalysts with and without the Rh and Ru additives was about 1×10^{-5} mol s^{-1} g cat^{-1}, these values being significantly lower than those obtained for our samples. Garcia et al. [14] used Ni/ZrO_2 and $Ni–ZrO_2/MgO$ catalysts for dry reforming of methane. The estimated rate of methane conversion over a $Ni–ZrO_2$–0.4% MgO sample (2×10^{-4} mol s^{-1} g cat^{-1}) was higher than that over a Ni/ZrO_2 (1.6×10^{-4} mol s^{-1} g cat^{-1}) material. It should be noted that their reaction conditions were somewhat different from ours (CH_4:CO_2:Ar = 1:1:2; reaction temperature 873 K, total flow rate 200 ml/min, 0.050 g catalyst).

Snoeck et al. [22] have proposed that the most important effect of potassium addition to a Ni-containing catalyst is a decrease of the value of the lumped forward rate coefficient for methane cracking and that there is also a higher surface oxygen coverage. The lower rate of methane cracking is explained by a decrease of the number of sites available for methane decomposition. The higher surface oxygen concentration of an alkalized catalyst results from a higher rate of the water gas shift reaction. This is due to a reduction of the number of sites available for methane decomposition as a consequence of the presence of potassium on the metal surface. Bengaard et al. [23] have reported that the methane sticking probability on Ni is strongly diminished by the presence of potassium. Juan-Juan et al. [15] reported that the addition of potassium to a $Ni–Al_2O_3$ catalyst increased the reducibility of the nickel species by hydrogen by modifying the interaction of the nickel oxide with the support; potassium also catalyses the gasification of the coke formed during reaction without modification of its structure; potassium migrates from the support to the Ni surface and neutralises a fraction of the active sites but it does not modify the size and structure of the Ni particles.

The results presented in this brief paper show quite clearly that the performance of Ni-containing catalysts for use in dry reforming can be improved significantly by the inclusion of K in the catalyst formulation. We will report elsewhere [24] more detailed results which take advantage of this conclusion in which a series of novel nickel-containing catalysts based on zirconia and having potassium in their formulation exhibit extremely good performances in the dry reforming reaction.

4. Conclusions

Potassium promoted $Ni/MgO–ZrO_2$ catalysts are suitable for the production of synthesis gas by the dry reforming of methane provided that small concentrations of K are added. Addition of K species to a $MgO–ZrO_2$ support increased the thermal stability of the catalysts and increased the resistance of the catalysts to deactivation. The best results were obtained with the addition of 0.5 wt.% of potassium.

Acknowledgements

We thank the financial support of the Irish Research Council for Science, Engineering and Technology (IRCSET) in the frame of the ERA-chemistry project. This publication has also emanated from research conducted with the financial support of Science Foundation Ireland under Grant Number 06/CP/E007. This work was also conducted under the framework of the INSPIRE programme, funded by the Irish Government's Programme for Research in Third Level Institutions, Cycle 4, National Development Plan 2007–2013. The authors thank Prof. A. Kiennemann, Dr. A.-C. Roger and Dr. A. Pietraszek (University of Strasbourg) for their kind support with thermodynamic calculations at different temperatures and valuable discussion of the results.

References

[1] (a) D.L. Trimm, Catal. Rev. Sci. Eng. 16 (1977) 155;
(b) J.R. Rostrup-Nielsen, D.L. Trimm, J. Catal. 48 (1977) 155;
(c) Catal. Today, this issue.
[2] J.R.H. Ross, in: M.W. Roberts, J.M. Thomas (Eds.), Surface and Defect Properties of Solids, vol. 4, Chemical Society, 1975, p. 34.
[3] A.N.J. van Keulen, M.E.S. Hegarty, J.R.H. Ross, P.F. van den Oosterkamp, Stud. Surf. Sci. Catal. 107 (1997) 537.
[4] M.E.S. Hegarty, A.M. O'Connor, J.R.H. Ross, Catal. Today 42 (1998) 225.
[5] J.R.H. Ross, A.N.J. van Keulen, M.E.S. Hegarty, K. Seshan, Catal. Today 30 (1996) 193.
[6] A.M. O'Connor, J.R.H. Ross, Catal. Today 46 (1998) 203.
[7] W. Hally, J.H. Bitter, K. Seshan, J.A. Lercher, J.R.H. Ross, Stud. Surf. Sci. Catal. 88 (1994) 167.
[8] E. Ruckenstein, Y.H. Hu, Appl. Catal. A 133 (1995) 149.
[9] O. Yamazaki, K. Tomishige, K. Fujimoto, Appl. Catal. A 136 (1996) 49.
[10] F. Meshkani, M. Rezaei, Int. J. Hydrogen Energy 35 (2010) 10295.
[11] F. Meshkani, M. Rezaei, Catal. Commun. 12 (2011) 1046.
[12] H. Gocmez, H. Fujimori, Mater. Sci. Eng. B-Adv. Funct. Solid-State Mater. 148 (2008) 226.
[13] W. Trakarnpruk, C. Sukkaew, J. Alloys Compd. 460 (2008) 565.
[14] V. Garcia, J.J. Fernandez, W. Ruiz, F. Mondragon, A. Moreno, Catal. Commun. 11 (2009) 240.
[15] J. Juan-Juan, M.C. Roman-Martinez, M.J. Illan-Gomez, Appl. Catal. A 301 (2006) 9.
[16] A.E.C. Luna, M.E. Iriarte, Appl. Catal. A 343 (2008) 10.
[17] A.E.C. Luna, M.M.B. Quiroga, Int. J. Hydrogen Energy 35 (2010) 6052.
[18] F. Frusteri, L. Spadaro, F. Arena, A. Chuvilin, Carbon 40 (2002) 1063.
[19] F. Frusteri, F. Arena, G. Calogero, T.P. Torre, Catal. Commun. 2 (2001) 49.
[20] S. Tsunekawa, K. Asami, S. Ito, M. Yashima, T. Sugimoto, Appl. Surf. Sci. 252 (2005) 1651.
[21] A. Pietraszek, B. Koubaissy, A.C. Roger, A. Kiennemann, Catal. Today, doi:10.1016/j.cattod.2010.12.015, in press.
[22] J.W. Snoeck, G.F. Froment, M. Fowles, Ind. Eng. Chem. Res. 41 (2002) 3548.
[23] H.S. Bengaard, I. Alstrup, I. Chorkendorff, S. Ullmann, J.R. Rostrup-Nielsen, J.K. Norskov, J. Catal. 187 (1999) 238.
[24] B.M. Nagaraja, D.A. Bulushev, S. Beloshapkin, J.R.H. Ross, unpublished work.