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Development of Stable and Highly Active Bimetallic Ni–Au Catalysts Supported on Binary Oxides $CrAl_3O_6$ for POM Reaction

**Tomasz P. Maniecki · Katarzyna Bawolak ·
P. Mierczyński · Wojciech K. Jozwiak**

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Abstract The resistance of supported Ni catalysts for carbon deactivation in CH_4 partial oxidation (POM) was studied in this work. The 5%Ni/Al_2O_3 catalyst showed only 18% of CH_4 conversion at 900 °C and 23% carbon deposition after 24 h run of POM. Both Au addition and binary support $CrAl_3O_6$ use seem to guarantee high activity (100% at 900 °C), selectivity (97% at 900 °C) and high carbon resistance (<1%). Furthermore the gold doped catalysts revealed only the presence of $C\alpha$ and $C\beta$ whereas the monometallic Ni catalysts showed the presence of graphitic carbon $C\gamma$ responsible for catalysts deactivation.

Keywords Bimetallic Ni–Au catalysts · $CrAl_3O_6$ · POM reaction · Synthesis gas

1 Introduction

Nickel supported catalysts are used in CH_4 reforming processes in industrial practice because of their high activity and low cost. The Ni/support catalysts can be deactivated by both Ni sites oxidation [1] and/or carbon deposition [2], which is a major subject of this work. The reaction conditions (reagents composition, reaction temperature and flow rate of reagents) as well as catalyst structure (metal type, crystallite size, promoter and catalyst support) are responsible for carbon deactivation of catalysts. Many studies are still carried out to optimize catalytic performance of Ni catalysts, particularly to decrease susceptibility to carbon deactivation [3]. The solution of this problem is important because the synthesis gas and hydrogen production on Ni catalysts is very often the most expensive part of very huge and complex processes like Fisher–Tropsh synthesis (F–T) and many others. The syngas factory in those cases is one of the part of bigger industry system, because of that, the decrease of syngas production cost is a major aim of researchers efforts. The technology simplification by application for example partial oxidation against steam reforming of CH_4 and the increase of Ni catalyst long life is consider as more cost-effective for process.

Methane decomposes on active metallic Ni sites to H_2 and Ni_xC, and then Ni_xC could reacts with NiO to CO or CO_2. Unfortunately the nucleation and polymerization of C species also take place on the catalyst surface which cause the formation of carbon deposition being responsible for deactivation. The carbon formation is not observed on noble metals (Ru, Rh), unfortunately they are prohibitively expensive for their application in industrial scale. The several theoretical and experimental works reported that structural changes of Ni sites by second metal introduction could increase the energetic barrier for the CH_4 dissociation simultaneously decreasing carbon formation [4, 5]. Gold seems to be good promoter of Ni catalysts.

Therefore the supported bimetallic Ni–Au systems were used in POM reaction in this work. The Au catalysts found many application in low temperature reactions [6], we also reported in our earlier work that use of gold as a promoter in high temperature process was successful [7]. The increase of carbon formation resistance for Ni–Au/support was observed. In the literature the promoting effect of Au on Ni catalysts performance is not clearly described. The influence of gold addition on carbon formation, kind and reactivity of carbon deposition was studied in this work also we focused on influence of support type ($CrAl_3O_6$, Al_2O_3) on activity and stability of Ni–Au catalysts.

T. P. Maniecki · K. Bawolak (✉) · P. Mierczyński ·
W. K. Jozwiak
Technical University of Lodz, 94-924 Lodz, Poland
e-mail: kbawolak@p.lodz.pl

2 Experimental

Supports Al_2O_3, $CrAl_3O_6$ were prepared by precipitation and co-precipitation of ($Cr(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$) aqueous solution with ammonia. All supports were dried and calcined at 400 °C/4 h/air. 5%Ni and 5%Ni–2%Au catalysts were prepared by wet impregnation method of precursors: $Ni(NO_3)_2 \cdot 6H_2O$ and $HAuCl_4$. The series of 5%Ni–x%Au/Al_2O_3, $x = 2, 1, 0.5, 0.1$ was also prepared. Then obtained catalysts were dried and calcined at 400 °C/4 h/air and catalytic tests were carried out without any preliminary reduction procedure of catalysts before it.

The activity tests in partial oxidation of methane ($CH_4 + ½O_2 \rightarrow H_2 + CO$) were carried out in the temperature range 200–900 °C. The catalyst samples 100 mg were placed in the quartz flow reactor where methane (5%CH_4/He) and oxygen (5%O_2/He) were supplied. All reagents of POM reaction were analyzed using GC technique. Gases: CH_4, O_2, CO_2, CO were detected by GC Varian 3300 (Varian Inc.) instrument, CTR-1 column, temperature 35 °C with TCD detector (130 mA, temperature 120 °C). The analysis of H_2 was carried out using CHROM-4 gas chromatograph (Laboratorni Pristroje Praha), molecular sieve 4A, temperature 110 °C with TCD detector (100 mA, temperature 120 °C). Conversion (X), yield (Y) and selectivities (S) were calculated according to:

$$X_{CH_4} = (CH_{4in} - CH_{4out})/CH_{4in}$$

$$Y_{H_2} = H_{2out}/2CH_{4in}$$

$$S_{CO} = CO_{out}/(CO_{out} + CO_{2out})$$

$$S_{CO_2} = CO_{2out}/(CO_{out} + CO_{2out})$$

The stability tests were carried out during 24 and 72 h run in POM reaction. The carbon deposition was analyzed by TOC measurements and TGA-MS technique. Thermogravimetric TG method, equipped with differential thermal analysis DTA device SETSYS-16/18 (Setaram) combined in line with quadrupole MS mass spectrometer Thermostar (Balzers) were used for temperature programmed decomposition of carbon deposition in oxidative atmospheres 2%O_2–98%Ar. The TG-DTA-MS measurements were carried out applying sample weight about 20 mg, linear heating rate of 10 °C/min, temperature range from 25 up to 1,500 °C.

3 Results and Discussion

The specific area surface of precipitated Al_2O_3 support was $S_{BET} = 237$ m^2/g. The co-precipitated binary oxide $CrAl_3O_6$ ($S_{BET} = 150$ m^2/g) was prepared due to stabilization of Cr_2O_3, which achieved high activity in POM reaction, in spite of very small surface (6 m^2/g). The deposition of metal oxide phase on both supports caused about 25% decrease of S_{BET}. The XRD analysis showed that both supports and catalysts had low crystallization degree regardless of calcinations temperature, which assured high development of specific surface area. The same type of crystal structure for Al_2O_3 and Cr_2O_3 and method preparing (co-precipitation) of support lead to the rise of the spinel like compound $CrAl_3O_6$, which was observed by XRD [8]. The temperature programmed reduction showed the reduction effect coming from reduction of Cr^{x+} ($3 < x < 6$) and also NiO for 5%Ni/$CrAl_3O_6$. The gold addition had not influence on catalyst TPR profiles [9].

The catalytic tests were carried out in partial oxidation of methane in the temperature range 200–900 °C. The example of activity tests (CH_4 conversion, H_2 yield and CO, CO_2 selectivity) of 5%Ni/$CrAl_3O_6$ and 5%Ni–2%Au/$CrAl_3O_6$ in POM reaction is presented in Fig. 1. The total oxidation of CH_4 to CO_2 begins at 300 °C and CO_2 selectivity decreases from 100 to 5% at about 800 °C. The production of synthesis gas is observed above 600 °C for

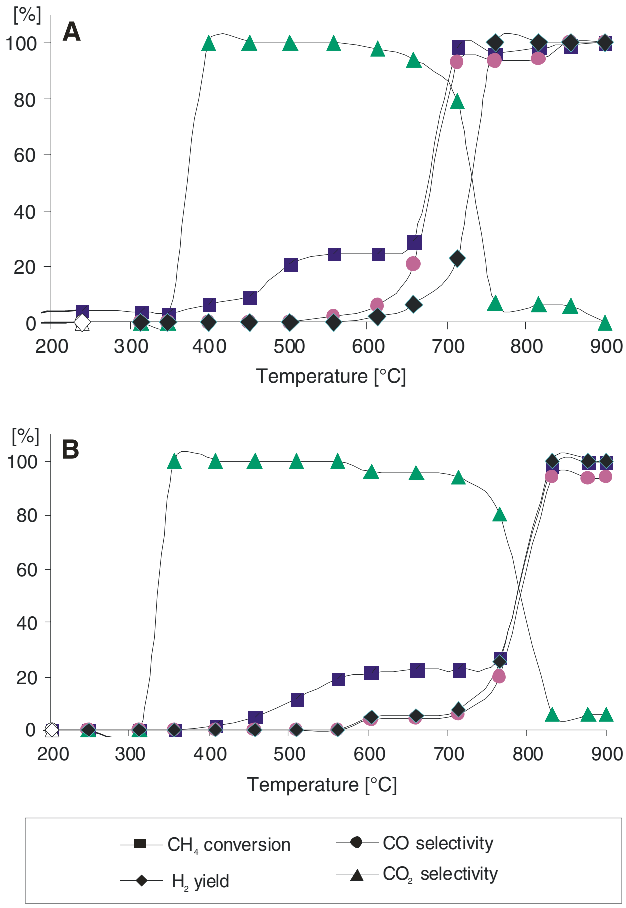

Fig. 1 The CH_4 conversion, H_2 yield and CO, CO_2 selectivity for 5%Ni/$CrAl_3O_6$ (**a**) and 5%Ni–2%Au/$CrAl_3O_6$ (**b**) in POM reaction

both catalysts 5%Ni/$CrAl_3O_6$ and 5%Ni–2%Au/$CrAl_3O_6$ and CH_4 conversion for catalysts was 100% at 900 °C. The CO selectivity was 97% whereas that for CO_2 3% at 900 °C. The improvement of catalytic activity was achieved by support modification, using binary oxide against conventional Al_2O_3. The CH_4 conversion for conventional 5%Ni/Al_2O_3 at 900 °C was 18% whereas for catalyst promoted by gold it was increased two times as reported in our previous work [9].

The gold addition to Ni catalyst does not influence the CH_4 conversion nor temperature start of reaction, but it evidently increases resistance for carbon formation. Even thought, the activity of Ni and Ni–Au catalysts was similar, stability of bimetallic catalyst was higher in POM process. The loss of activity after 24 h was not observed whereas after 72 h of POM for 5%Ni and 5%Ni–2%Au/$CrAl_3O_6$ was observed decrease of CH_4 conversion about 4 and 1%, respectively.

The deactivation of catalysts was caused by carbon deposition on their surface. The Au promoting effect is evident. The carbon deposition was 23% of carbon for 5%Ni/Al_2O_3 catalyst, while 7% for 5%Ni–2%Au/Al_2O_3 and only 1% for 5%Ni–2%Au/$CrAl_3O_6$ as shown in Table 1. It is well know that deep dehydrogenation of CH_4 needs the large ensemble of metal atoms, because of that the structural changes of active sites could limit carbon formation. The improvement of carbon resistance for Ni–Au/support catalyst is connected probably with surface alloying of Ni–Au as reported in theoretical work [10], where the authors supposed that Au entrance to Ni catalyst could cause selective poisoning of active sites. The structure changes increase the energetic barrier for the CH_4 dissociation on Ni atoms, about 16 kJ/mol by every Au atom, which limits carbon deposition growth [11].

The Ni–Au surface alloy, metallic Ni and Au phases are observed on bimetallic supported Ni–Au systems depending on the preparation conditions, i.e., molar ratio of Ni/Au. It is well known that bulk binary phase diagram for Ni–Au has a large miscibility gap, causing that alloying is not observed at low temperature. However the surface Ni–Au alloy is energetically favorable for gold doped Ni (110) and Ni (111), which was confirmed by both theoretical and experimental studies [12]. The process of nickel–gold alloy formation during H_2 reduction and during POM reaction (at high temperature and reductive atmosphere) was affirmed for 5%Ni–2%Au/Al_2O_3 system in our previous work [13], but the alloy it was not observed for 5%Ni–2%Au/$CrAl_3O_6$. The alloy crystallites could be to small for study by XRD technique.

Table 1 The TOC analysis of carbon deposition on catalyst after POM reaction

Catalyst	TOC (%)	Catalyst	TOC (%)
5%Ni/Al_2O_3	23	5%Ni–2%Au/Al_2O_3	7
5%Ni–2%Au/Al_2O_3	7	5%Ni–1%Au/Al_2O_3	7
5%Ni/$CrAl_3O_6$	5	5%Ni–0.5%Au/Al_2O_3	7
5%Ni–2%Au/$CrAl_3O_6$	<1	5%Ni–0.1%Au/Al_2O_3	6

The 24 h run in POM reaction caused about 8% of activity fall for 5%Ni/Al_2O_3. It was a result of 23% of carbon on that catalyst (Table 1). The Au promoted 5%Ni/Al_2O_3 catalyst showed tree times lower carbon deposition, whereas the nickel–gold catalyst supported on binary oxide 5%Ni–2%Au/$CrAl_3O_6$ achieved only about 1% of carbon. The decrease of gold loading from 2 to 0.1% did not influence on an increase of carbon deposition, what suggests that 0.1% of Au is sufficient for limitation of carbon deposition.

The interesting fact seems to be various kinds of carbon deposition forming during reaction. Unfortunately the amount of carbon on 5%Ni–2%Au/$CrAl_3O_6$ was to low to differentiate the form of deposition, because of that the longer tests—72 h were carried out.

The results of carbon deposition oxidation after 72 h run in POM reaction is presented in Fig. 2. The three kinds of carbon deposition are formed during CH_4 decomposition $C\alpha$, $C\beta$ and $C\gamma$ as reported previous works [14, 15]. The $C\alpha$ called as polymeric carbon, is the most active species responsible for syngas formation. The filamentous carbon

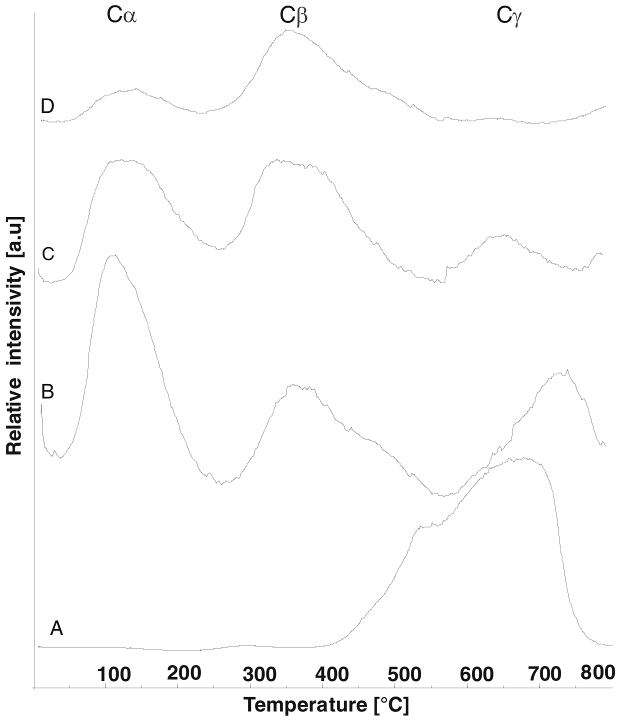

Fig. 2 The oxidation of carbon deposition forming on 5%Ni/Al_2O_3 (**a**), 5%Ni–2%Au/Al_2O_3 (**b**), 5%Ni/$CrAl_3O_6$ (**c**), 5%Ni–2%Au/$CrAl_3O_6$

Cβ and graphitic carbon Cγ are quiet inactive species, which are further transformed to carbon deposition. It is mean that not only quantity of carbon but also the carbon quality is important factor of deactivation catalysts active centers.

The 5%Ni/Al_2O_3 catalyst showed two maximum of CO_2 between 400 and 800 °C assigned to oxidation of hard reducible filamentous Cβ and graphitic carbon Cγ responsible for catalyst deactivation (Fig. 1, curve A). The polymeric carbon Cα (50–250 °C) forming synthesis gas, filamentous Cβ (250–500 °C) and graphitic carbon Cγ were observed for gold doped catalyst (curve B). The effect attributed to Cγ oxidation is relatively lower for bimetallic Ni–Au system than that for 5%Ni/Al_2O_3. The three forms of carbon deposition were showed in a case of 5%Ni/$CrAl_3O_6$ (curve C), but the lower amount of carbon was observed. The bimetallic 5%Ni–2%Au/$CrAl_3O_6$ seemed to be suitable catalyst for POM reaction, because it is resistant for graphitic carbon Cγ formation (curve D).

4 Conclusions

The use of gold promoted Ni catalysts supported on binary oxide $CrAl_3O_6$ allowed to decrease carbon formation from 23 to above 1%. The Cα, Cβ and Cγ species were formed during partial oxidation of methane. The graphitic carbon Cγ carbon responsible for catalyst deactivation was observed for 5%Ni/Al_2O_3, 5%Ni–2%Au/Al_2O_3 and 5%Ni–2%Au/$CrAl_3O_6$. The improvement of carbon resistance was particularly showed for bimetallic 5%Ni–2%Au/$CrAl_3O_6$ and the enhance their performance was a synergic effect of gold addition and use of binary support.

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References

1. Ohi T, Miyata T, Li D, Shishido T, Kawabata T, Sano T, Takehira K (2006) Appl Cat A 308:194
2. Lucredio AF, Jerkiewick G, Assaf EM (2007) Appl Cat A 333:90
3. Nikolla E, Shwank J, Linic S (2007) J Cat 250:85
4. Molenbroek AM, Norskov JK (2001) J Phys Chem B 105:5450
5. Miyata T, Li D, Shiraga M, Shishido T, Oumi Y, Sano T, Takehira K (2006) Appl Catal 310:97
6. Witońska I, Maniecki TP (2007) Przem Chem 86/11:2
7. Maniecki TP, Bawolak K, Mierczyński P, Jóźwiak WK (2008) Polish J Chem 82:2245
8. Maniecki TP, Bawolak K, Gebauer D, Jóźwiak WK (2007) Przem Chem 869:857
9. Maniecki TP, Rogowski J, Bawolak K, Nowosielska M, Jóźwiak W, Polish J (2006) Environ Stud 15.6A:124
10. Besenbacher F, Chorkendorff I, Clausen BS, Hammer B, Molenbroek AM, Norskov JK, Stensgaard I (1998) Science 279:1913
11. Ruban AV, Skriver HL, Norskov JK (1999) Phys Rev B 59:15990
12. Djaidja A, Libs S, Kiennemann A, Barama A (2006) Catal Today 113:194
13. Maniecki TP, Bawolak K, Gebauer D, Mierczynski P, Jozwiak WK, KinCat (in a print)
14. Zhang ZL, Verykios XE (1994) Catal Today 21(2–3):589
15. Guo J, Lou H, Zheng X (2007) Carbon 45:1314