Physico-chemical properties of cobalt (ruthenium) supported (SiO$_2$, Al$_2$O$_3$ and TiO$_2$) catalysts for Fischer-Tropsch synthesis

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Monometallic 10% Co and bimetallic 0.5% Ru – 10% Co phases dispersed on different support: SiO$_2$, Al$_2$O3 and TiO$_2$ were prepared by wet impregnation and co-impregnation methods. The physico-chemical properties: support surface area and porosity, metallic phase dispersion, reducibility of dispersed metal oxide phase were studied by TG-DTA, BET, temperature-programmed reduction TPR-H$_2$, and H$_2$ chemisorption methods.

Cobalt phase was found to exist as Co$_3$O$_4$ on the support surface after catalyst calcination in air and its reduction takes places as two-step process Co$_3$O$_4$ → CoO → Co. When Co$_3$O$_4$ was supported on Al$_2$O$_3$, a third reduction peak was observed in TPR profile and it was attributed to a very strong chemically interacting phase between CoO and Al$_2$O$_3$. The addition of promoting ruthenium shifts the reduction of supported cobalt oxidic phase to lower temperature range.

1. INTRODUCTION

Cobalt catalysts have been widely employed for Fischer–Tropsch synthesis of long chain hydrocarbons mixture from synthesis gas of carbon monoxide and hydrogen, which can be finally used for the manufacture of diesel fuel.

Because of increasing demands for the high-quality diesel fuel, many studies on both fundamental and technological aspects of Co-based Fischer-Tropsch synthesis catalysts have been made in order to improve their physico-chemical properties, activities and selectivities [1]. The catalyst activity mainly depends

on the density of surface metallic cobalt sites, which is usually corelated to its dispersion and reducibility of cobalt metal oxide. The selectivity to C_{5+} (C_5 and higher hydrocarbons) is affected by the type of support and the promoter. The structure of cobalt catalysts is controlled by both textural and surface chemical properties of support, as well as metal precursor identity and preparation method [1].

It is well known that the type and structure of support influence on the dispersion, particle size and reducibility. The choice of support largely determines the number of active sites stabilized after reduction.

Conventional Fischer-Tropsch cobalt catalysts are usually prepared via impregnation of supports (silica, alumina, titania) with aqueous solutions of many cobalt compounds (especially hydrated cobalt nitrates). After impregnation step the catalysts are calcined in an oxidizing atmosphere and then they are reduced in hydrogen stream [2, 3].

The promotion of Fischer-Tropsch cobalt catalysts with metals such as Ru or Pt increases the surface concentration of metal sites due to enhanced cobalt reducibility. Addition of small amount of ruthenium or platinum shifts the reduction temperature of cobalt oxide and cobalt species interacting with the support to lower temperatures. The use of additives to modify the metal-support interaction has been widely investigated. The modification by Ru, Pt or Zr leads to metal dispersion affected by changing the interaction between the metal catalytic phase and the support [4, 5].

In this study the physicochemical properties of monometallic Co and bimetallic Ru-Co catalysts supported on SiO_2, TiO_2 and Al_2O_3 were investigated:

- the influence of support kind on thermal stability of cobalt and ruthenium precursors $Co(NO_3)_2 \cdot 6H_2O$ and $Ru(NO)(NO_3)_3$,
- specific surface area and porosity of supported Co and Ru-Co catalysts,
- influence of Ru on reducibility of supported cobalt oxide phase,
- influence of Ru addition on dispersion degree of supported metallic cobalt phase.

Fischer-Tropsch synthesis is a part of gas to liquids (GTL) technology, which produces clean fuels from synthesis gas. It is well known that the catalysts for the conversion of natural gas are usually based on metallic cobalt dispersed on an oxide pours support (i. e. silica) and promoted with the small amounts of metals (ruthenium). The research of the physico-chemical properties of the catalysts are necessary to find other, better catalysts for this reaction and these catalysts will be used in the future.

2. EXPERIMENTAL

1.1. Preparation of the catalysts

Monometallic 10% Co and bimetallic 0.5% Ru – 10% Co supported catalysts were prepared by wet impregnation and coimpregnation of different support: SiO_2, Al_2O_3 and TiO_2 with aqueous solutions of cobalt(II) nitrate $Co(NO_3)_2 \cdot 6H_2O$ and ruthenium(III) nitrosyl nitrate $Ru(NO)(NO_3)_3$. The following commercial supports were applied: Al_2O_3 (136 m^2/g, Fluka), SiO_2 (271 m^2/g, Aldrich), TiO_2 (49.5 m^2/g, Degussa, type P25). After wet impregnation the catalysts were dried in air at 120 °C for 3 h and then calcined at 400 °C for 4 h.

2.2. Characterization techniques

Thermal measurements TG-DTA-MS were carried out in a helium atmosphere (99.998% He) up to 900 °C with heating rate of 5 °C/min using a Setaram thermo-balance unit (Setsys 16/18) connected to Balzers quadrupole mass spectrometer (Thermostar). The samples about 10 mg of powdered catalyst precursors were applied: 0.5% Ru – 10% Co/SiO_2, 0.5% Ru – 10% Co/TiO_2, and 0.5% Ru – 10% Co/Al_2O_3.

BET surface area measurements of catalyst samples were determined by Sorptomatic 1900 Carlo-Erba using low-temperature nitrogen adsorption-desorption method.

Temperature programmed reduction TPR_{H2} measurements were carried out in AMI system from Altamira Instruments (USA) equipped with a thermal conductivity detector (TCD). In TPR_{H2} experiments mixture of 5% H_2 and 95% Ar was used with volume velocity 60 cm^3/min and linear growth of the temperature 5°C/min. The samples of catalysts were preliminary oxidized for 30 minutes in a mixture of 5% O_2 in Ar at the temperature of 400 °C.

Hydrogen chemisorption uptakes were measured by static equilibrium H_2 chemisorption method at the temperature of 100 °C using ASAP 2010C apparatus from Micromeritics (USA). All catalysts were degassed and reduced *in situ* prior to hydrogen chemisorption. The catalyst surface purification procedure of ca. 1 g catalyst was performed in flowing helium at 375 °C for 1 h and reduction was carried out in flowing hydrogen at 375 °C for 1 h.

3. RESULTS AND DISCUSSION

3.1. Thermal decomposition of hexahydrate cobalt(II) nitrate(V) and ruthenium(III) nitrosyl nitrate

The decomposition of commercial compound – hexahydrate cobalt(II) nitrate(V) $Co(NO_3)_2 \cdot 6H_2O$ in helium atmosphere is presented in Figure 1 and

appropriate curves TG, DTG, DTA and MS profiles (m/z, respectively 18 H_2O, 30 NO, 32 O_2) are included. Sample decomposition starts at about 30 °C occurring as at least five–step complicated process being accomplished up to 300 °C. TG mass loss $\Delta m \approx 38\%$ up to about 200 °C represents four-step dehydration whereas $\Delta m \approx 33\%$ is attributed to anhydrous cobalt nitrate decomposition. Among detectable nitrogen oxides NO_x (x = 0 is N_2, 0.5, 1, 2) the dominant gaseous products were nitrogen(II) oxide NO (m/z = 30) and molecular oxygen O_2 (m/z = 32). Above 700°C one can anticipate the decomposition of Co_3O_4 with the accompanying evolution of gaseous oxygen and this process is illustrated by TG, DTG changes (Δm about 2%) and DTA weak endothermic effect [6]. The entire loss of sample mass (about 73%) appeared close to that characteristic of theoretical value (about 74%). The following sequence of successive events described by reaction equations can be postulated [7]:

• (1) sample dehydration

$$[Co(H_2O)_p](NO_3)_2 \cdot (6\text{-}p)H_2O \rightarrow Co(NO_3)_2 + 6H_2O \qquad (1)$$
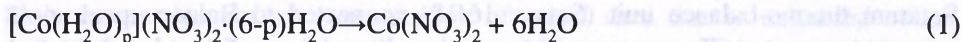
• (2) oxidative decomposition of anhydrous cobalt nitrate

$$Co(NO_3)_2 \rightarrow 1/3Co_3O_4 + 2NO_x + (7/3\text{-}x)O_2 (x = 0, 0.5, 1, 2) \qquad (2)$$
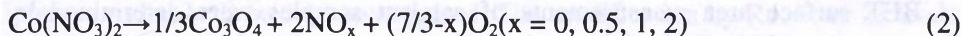
• (3) reductive decomposition of cobalt oxide Co_3O_4

$$1/3Co_3O_4 \rightarrow CoO + 1/6O_2 \qquad (3)$$

The thermal decomposition results for appropriate supported precursors 30%Co/(SiO_2, TiO_2, Al_2O_3) catalysts in helium atmosphere are presented in another article in *Polish Journal of Chemistry* (in press) and decomposition processes runs in similar way to that characteristic of unsupported precursor of cobalt.

The decomposition of starting material – ruthenium(III) nitrosyl nitrate in inert atmosphere of helium is presented in Figure 2 and MS profiles (m/z = 18 H_2O, 30 NO, 32 O_2) and curves TG, DTG and DTA are included. The sample decomposition appears rather complicated four–step process taking place in temperature range 70–400 °C. The evolution of water (m/z = 18) considerably overlaps the region of remaining gaseous products NO_x and O_2. In the temperature range of 150–400 °C ruthenium(III) nitrosyl nitrate decomposes manifesting the evolution of primarily NO (m/z = 30) and O_2 (m/z = 32).

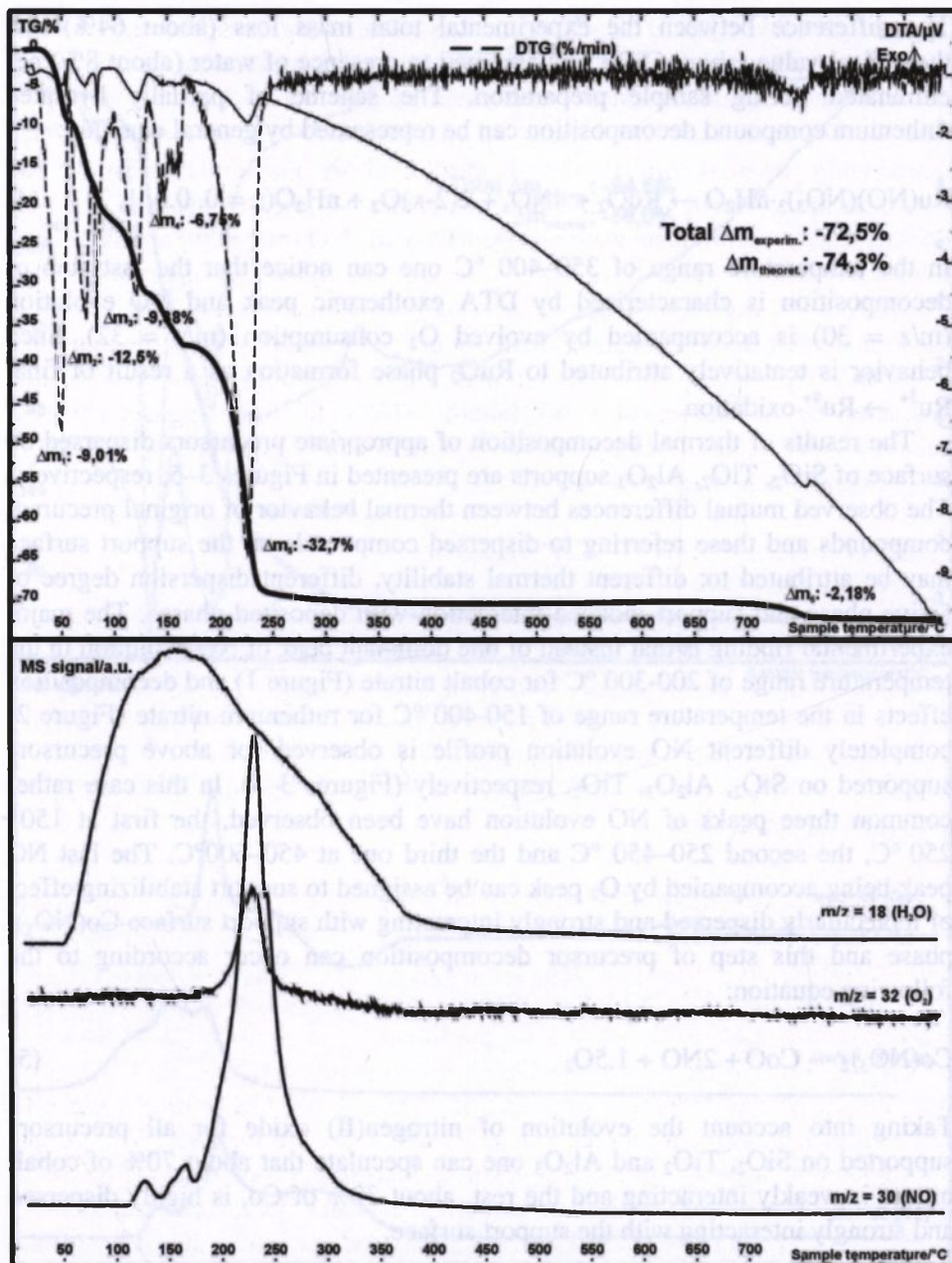Fig. 1. The TG, DTG, DTA and MS profiles of thermal decomposition of $Co(NO_3)_2 \cdot 6H_2O$ compound in helium atmosphere.

The difference between the experimental total mass loss (about 64%) and theoretical value (about 58%) was assigned to presence of water (about 8%) not eliminated during sample preparation. The scheme of partially hydrated ruthenium compound decomposition can be represented by general equation:

$$Ru(NO)(NO_3)_3 \cdot nH_2O \rightarrow RuO_2 + 4NO_x + 2(2-x)O_2 + nH_2O \,(x = 0, 0.5, 1, 2) \qquad (4)$$
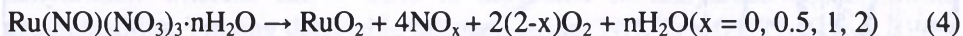
In the temperature range of 350–400 °C one can notice that the last step of decomposition is characterized by DTA exothermic peak and NO evolution ($m/z = 30$) is accompanied by evolved O_2 consumption ($m/z = 32$). Such behavior is tentatively attributed to RuO_2 phase formation as a result of final $Ru^{3+} \rightarrow Ru^{4+}$ oxidation.

The results of thermal decomposition of appropriate precursors dispersed on surface of SiO_2, TiO_2, Al_2O_3 supports are presented in Figures 3–5, respectively. The observed mutual differences between thermal behavior of original precursor compounds and these referring to dispersed compounds on the support surface may be attributed to: different thermal stability, different dispersion degree of active phase and support induced interaction with deposited phases. The major experimental finding is that instead of one dominant peak of NO evolution in the temperature range of 200-300 °C for cobalt nitrate (Figure 1) and decomposition effects in the temperature range of 150-400 °C for ruthenium nitrate (Figure 2) completely different NO evolution profile is observed for above precursors supported on SiO_2, Al_2O_3, TiO_2, respectively (Figures 3–5). In this case rather common three peaks of NO evolution have been observed, the first at 150–250 °C, the second 250–450 °C and the third one at 450–600°C. The last NO peak being accompanied by O_2 peak can be assigned to support stabilizing effect of molecularly dispersed and strongly interacting with support surface $Co(NO_3)_2$ phase and this step of precursor decomposition can occur according to the following equation:

$$Co(NO_3)_2 \rightarrow CoO + 2NO + 1.5O_2 \qquad\qquad\qquad (5)$$

Taking into account the evolution of nitrogen(II) oxide for all precursors supported on SiO_2, TiO_2 and Al_2O_3 one can speculate that about 70% of cobalt nitrate is weakly interacting and the rest, about 30% of Co, is highly dispersed and strongly interacting with the support surface.
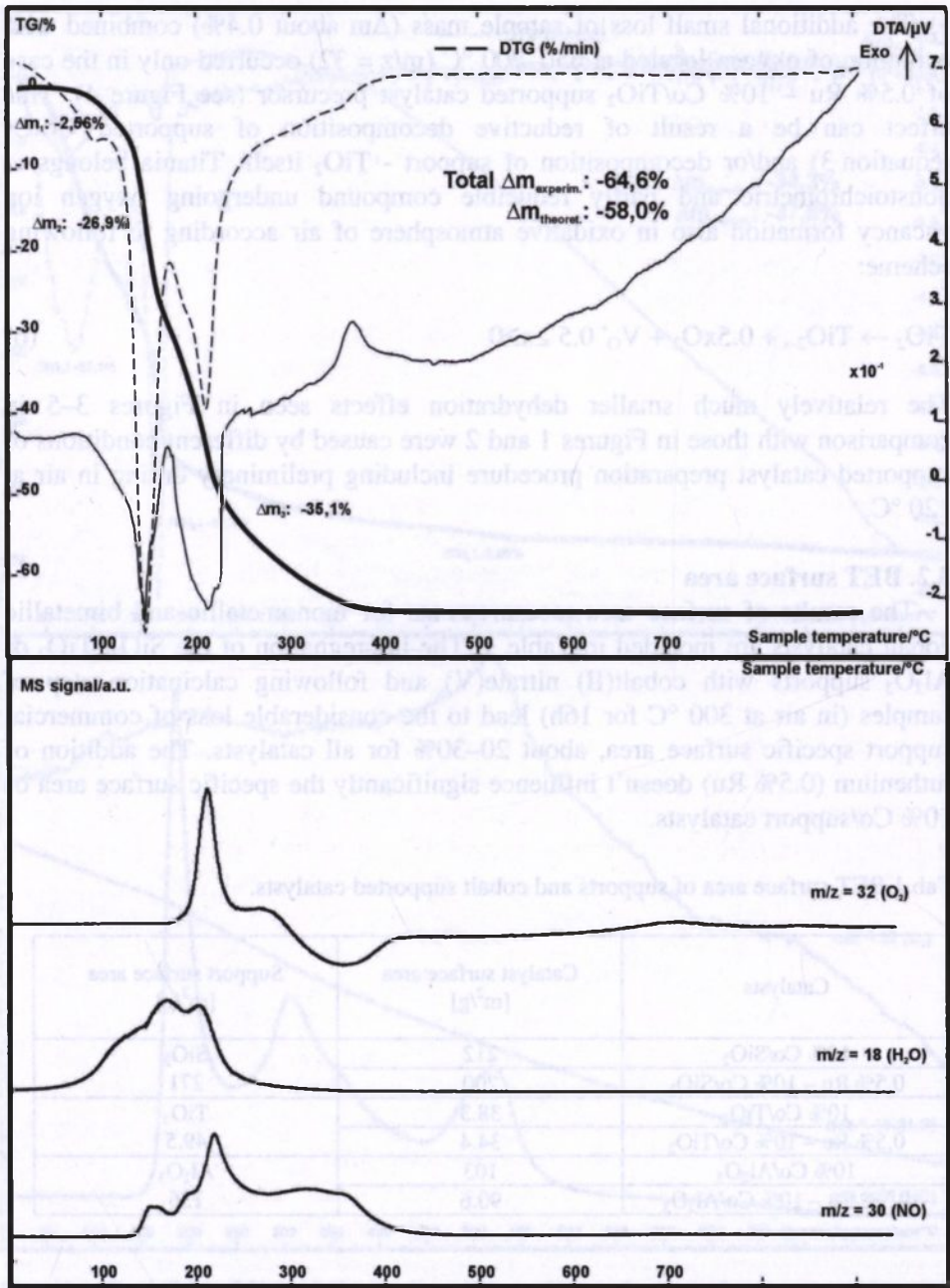
Fig. 2. The TG, DTG, DTA and MS profiles of thermal decomposition of Ru(NO)(NO₃)₃ compound in helium atmosphere.

The additional small loss of sample mass (Δm about 0.4%) combined with evolution of oxygen located at 650–700 °C (m/z = 32) occurred only in the case of 0.5% Ru – 10% Co/TiO$_2$ supported catalyst precursor (see Figure 4). This effect can be a result of reductive decomposition of supported Co$_3$O$_4$ (equation 3) and/or decomposition of support - TiO$_2$ itself. Titania belongs to nonstoichrometric and partly reducible compound undergoing oxygen ion vacancy formation also in oxidative atmosphere of air according to following scheme:

$$TiO_2 \rightarrow TiO_{2-x} + 0.5xO_2 + V_O^- \quad 0.5 \geq x \geq 0 \tag{6}$$
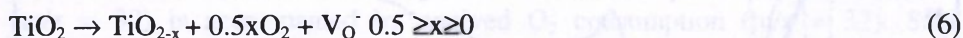
The relatively much smaller dehydration effects seen in Figures 3–5 in comparison with those in Figures 1 and 2 were caused by different conditions of supported catalyst preparation procedure including preliminary drying in air at 120 °C.

3.2. BET surface area

The results of surface area measurements for monometallic and bimetallic cobalt catalysts are included in Table 1. The impregnation of the SiO$_2$, TiO$_2$ or Al$_2$O$_3$ supports with cobalt(II) nitrate(V) and following calcination step of samples (in air at 300 °C for 16h) lead to the considerable loss of commercial support specific surface area, about 20–30% for all catalysts. The addition of ruthenium (0.5% Ru) doesn't influence significantly the specific surface area of 10% Co/support catalysts.

Tab.1 BET surface area of supports and cobalt supported catalysts.

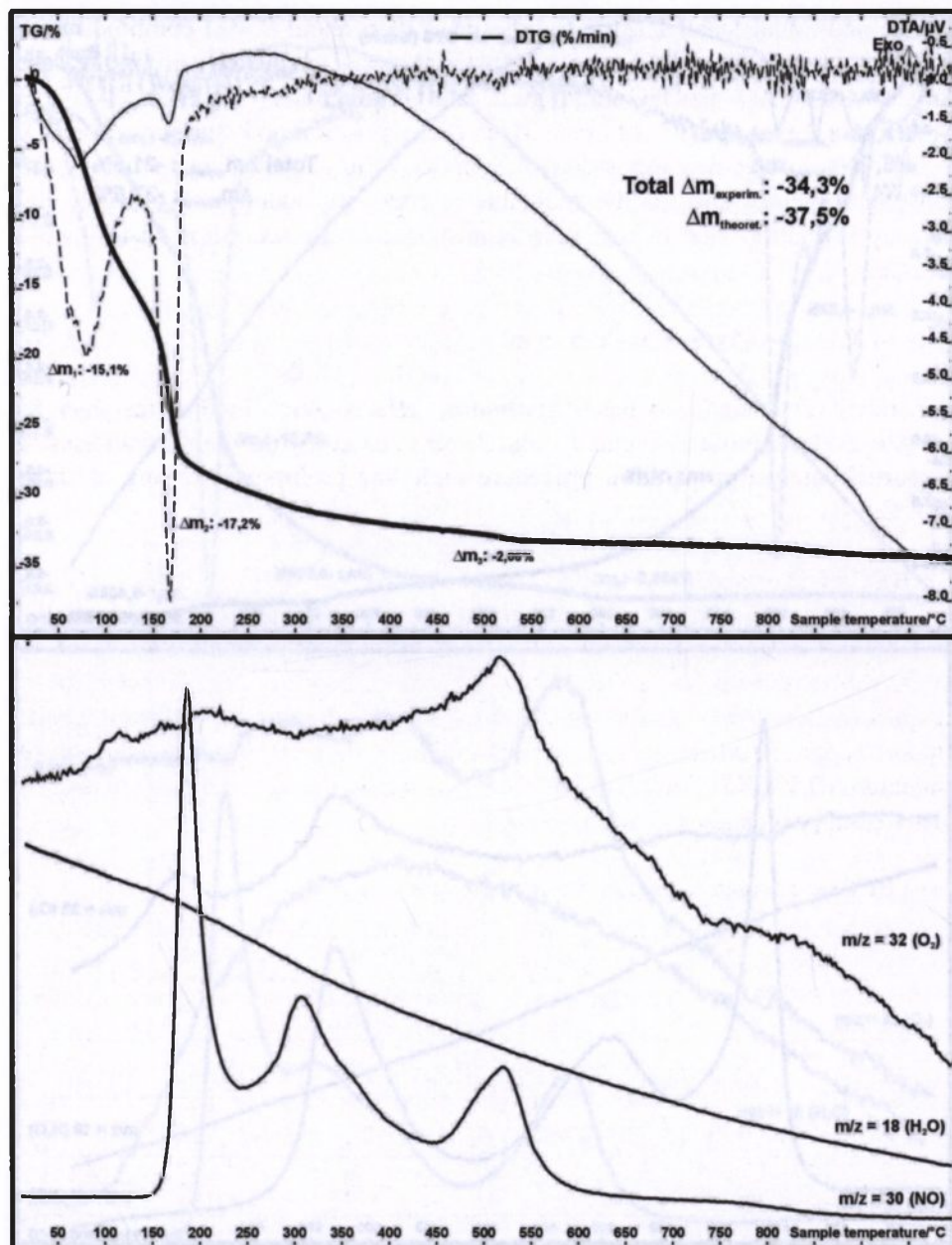| Catalysts	Catalyst surface area [m^2/g]	Support surface area [m^2/g]
10% Co/SiO$_2$	212	SiO$_2$
0.5% Ru – 10% Co/SiO$_2$	200	271
10% Co/TiO$_2$	38.3	TiO$_2$
0.5% Ru – 10% Co/TiO$_2$	34.4	49.5
10% Co/Al$_2$O$_3$	103	Al$_2$O$_3$
0.5% Ru – 10% Co/Al$_2$O$_3$	90.6	136

Fig. 3. The TG, DTG, DTA and MS profiles of thermal decomposition of 10% Co(0.5% Ru)/SiO$_2$ supported catalyst precursor in helium atmosphere.

TG/%

DTG (%/min)

DTA/µV

Exo/ -0.5,

-1.0,

Δm_1: -1,93%

-2.5

-1

Total $\Delta m_{experim.}$: -21,9%

$\Delta m_{theoret.}$: -37,5%

-2.0,

-5.0

-7.5

-2.5,

-3.0,

-10.0 Δm_2: -4,32%

-12.5

-3.5,

-4.0,

-15.0

-4.5,

Δm_3: -14,4%

-17.5

-5.0,

-20.0

-5.5,

Δm_4: -0,800%

Δm_5: -0,438%

50   100   150   200   250   300   350   400   450   500   550   600   Sample temperature/°C

m/z = 32 (O₂)

m/z = 18 (H₂O)

m/z = 30 (NO)

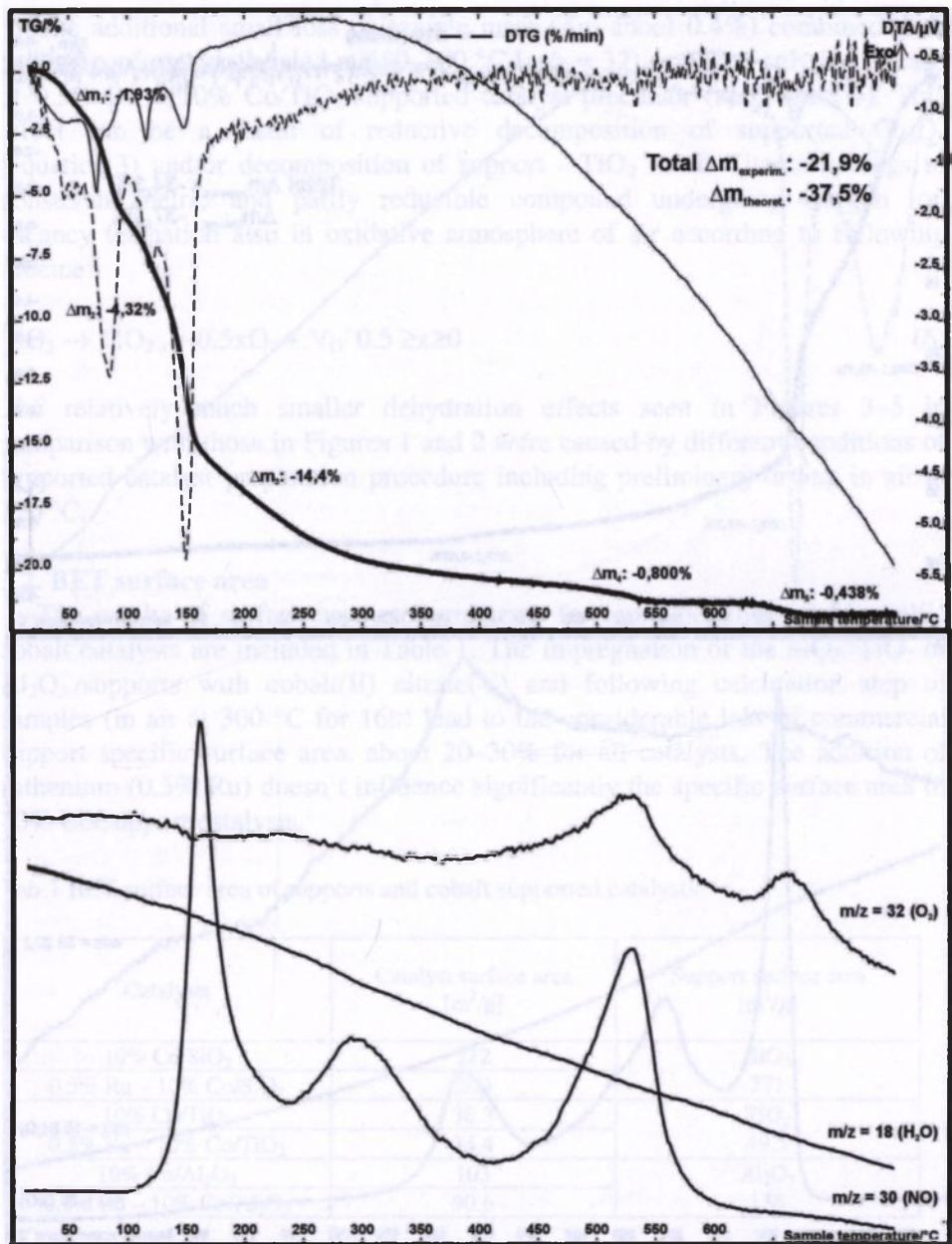50   100   150   200   250   300   350   400   450   500   550   600   Sample temperature/°C

Fig. 4 The TG, DTG, DTA and MS profiles of thermal decomposition of 10% Co(0.5% Ru)/TiO₂ supported catalyst precursor in helium atmosphere.
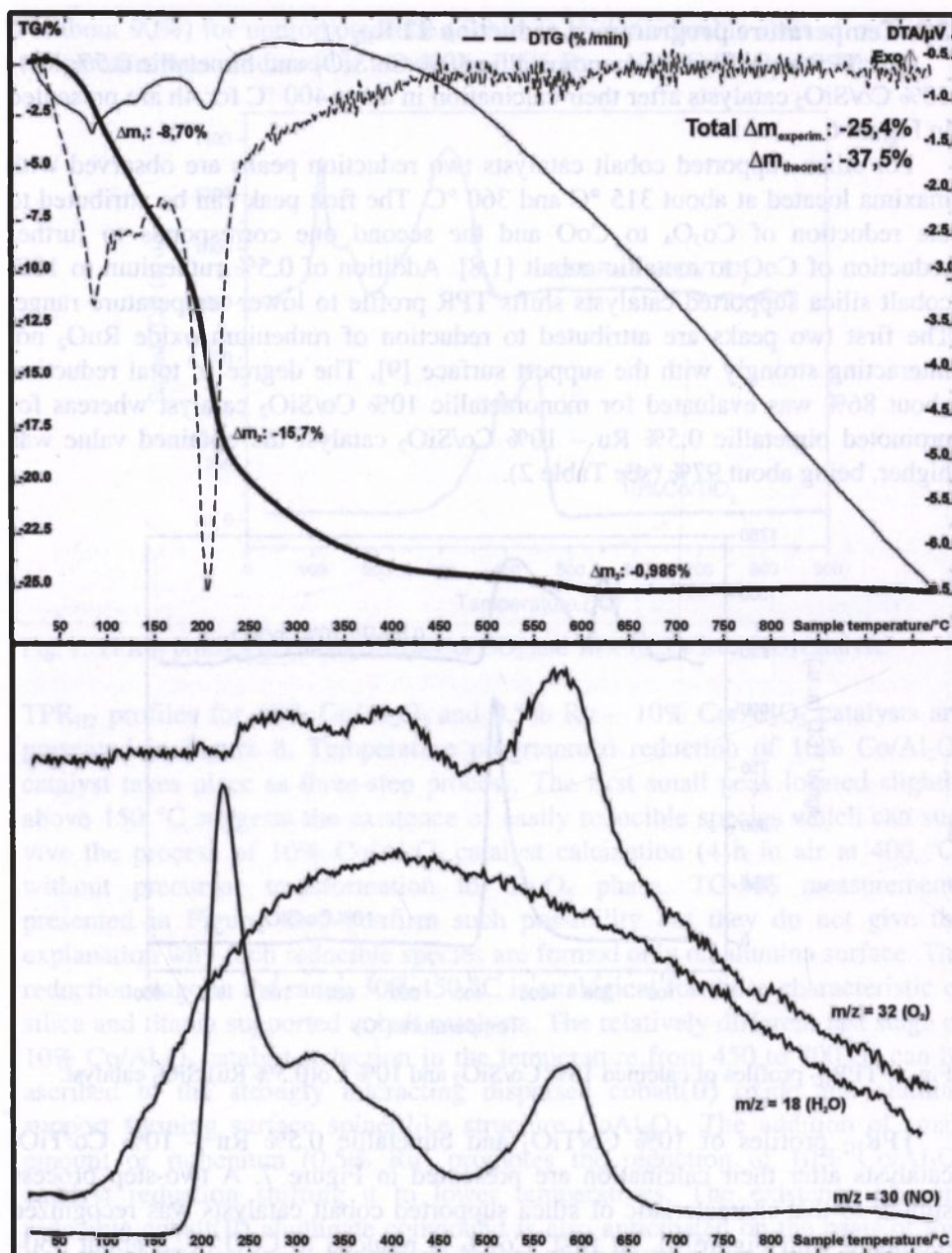
Fig. 5 The TG, DTG, DTA and MS profiles of thermal decomposition of 10% Co(0.5% Ru)/Al_2O_3 supported catalyst precursor in helium atmosphere.

3.3. Temperature programmed reduction TPR$_{H2}$

The TPR$_{H2}$ profiles for monometallic 10% Co/SiO$_2$ and bimetallic 0.5% Ru – 10% Co/SiO$_2$ catalysts after their calcination in air at 400 °C for 4h are presented in Figure 6.

For silica supported cobalt catalysts two reduction peaks are observed with maxima located at about 315 °C and 360 °C. The first peak can be attributed to the reduction of Co$_3$O$_4$ to CoO and the second one corresponds to further reduction of CoO to metallic cobalt [1,8]. Addition of 0.5% ruthenium to 10% cobalt silica supported catalysts shifts TPR profile to lower temperature range. The first two peaks are attributed to reduction of ruthenium oxide RuO$_2$ not interacting strongly with the support surface [9]. The degree of total reduction about 86% was evaluated for monometallic 10% Co/SiO$_2$ catalyst whereas for promoted bimetallic 0.5% Ru – 10% Co/SiO$_2$ catalyst the obtained value was higher, being about 97% (see Table 2).
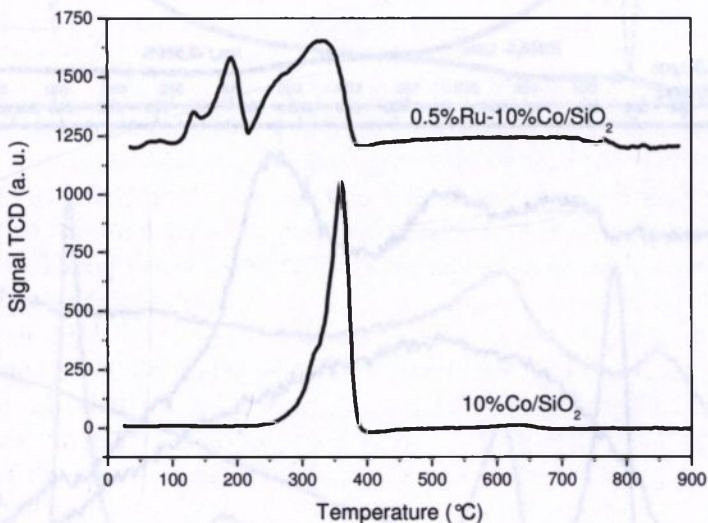

Fig. 6. TPR$_{H2}$ profiles of calcined 10% Co/SiO$_2$ and 10% Co(0.5% Ru)/SiO$_2$ catalyst.

TPR$_{H2}$ profiles of 10% Co/TiO$_2$ and bimetallic 0.5% Ru – 10% Co/TiO$_2$ catalysts after their calcination are presented in Figure 7. A two-step process similar to that characteristic of silica supported cobalt catalysts was recognized (compare with Figure 6). At first, Co$_3$O$_4$ is reduced to CoO (T$_{max}$ about 350–380 °C) and then CoO is reduced to Co (T$_{max}$ about 440 °C) [10]. In the case of 10% Co/TiO$_2$ catalyst reduction a bimodal distribution of cobalt oxide phase Co$_3$O$_4$ phase is inferred and small and large cobalt oxide crystallites can be formed. The reducibility of promoted catalyst (α about 99%) is higher then that

(α about 90%) for unpromoted one (Table 2). A considerable shift of reduction temperature was observed for bimetallic 0.5% Ru – 10% Co/TiO$_2$ catalyst.
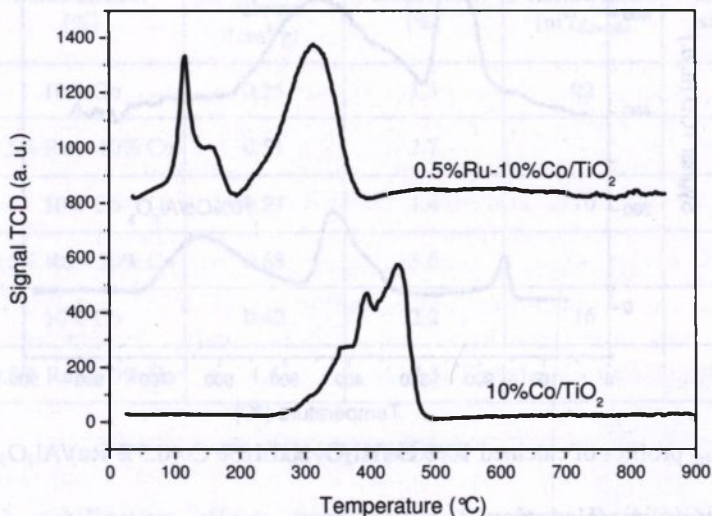

Fig. 7. TPR$_{H2}$ profiles of calcined 10% Co/TiO$_2$ and 10% (0.5% Ru)/TiO$_2$ catalyst.

TPR$_{H2}$ profiles for 10% Co/Al$_2$O$_3$ and 0.5% Ru – 10% Co/Al$_2$O$_3$ catalysts are presented in Figure 8. Temperature programmed reduction of 10% Co/Al$_2$O$_3$ catalyst takes place as three-step process. The first small peak located slightly above 150 °C suggests the existence of easily reducible species which can survive the process of 10% Co/Al$_2$O$_3$ catalyst calcination (4 h in air at 400 °C) without precursor transformation to Co$_3$O$_4$ phase. TG-MS measurements presented in Figures 3–5 confirm such possibility but they do not give the explanation why such reducible species are formed only on alumina surface. The reduction stage in the range 300–450 °C is analogical for those characteristic of silica and titania supported cobalt catalysts. The relatively different last stage of 10% Co/Al$_2$O$_3$ catalyst reduction in the temperature from 450 to 700 °C can be ascribed to the strongly interacting dispersed cobalt(II) oxide and alumina support forming surface spinel-like structure CoAl$_2$O$_4$. The addition of small amount of ruthenium (0.5% Ru) promotes the reduction of 10% Co/Al$_2$O$_3$ catalyst reduction shifting it to lower temperatures. The existence of non-reducible cobalt(II) aluminate compound is also anticipated on the basis of low degree of reduction – about 67% for monometallic 10% Co/alumina catalyst and 70% for bimetallic 0.5% Ru – 10% Co/alumina catalyst (Table 2).
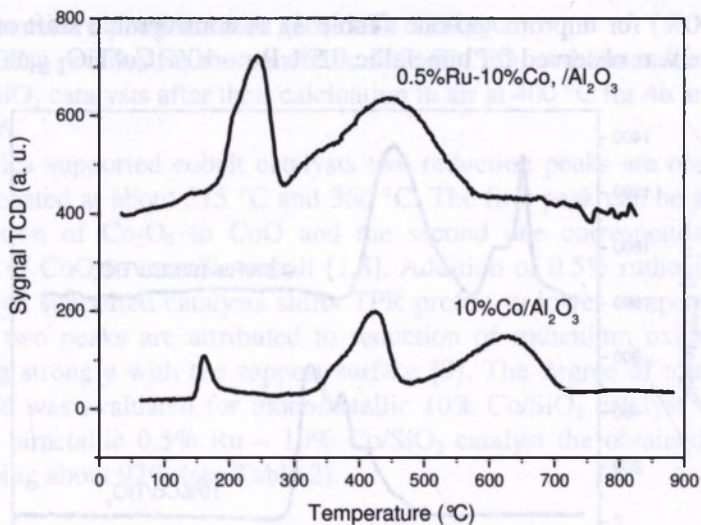
Fig. 8. TPR$_{H2}$ profiles of calcined 10% Co/Al$_2$O$_3$ and 10% Co(0.5% Ru)/Al$_2$O$_3$ catalyst

3.4. Hydrogen chemisoption

H$_2$ chemisorption results are shown in Table 3 as volume of adsorbed hydrogen. The degree of cobalt dispersion, metallic surface area and crystallite size are also given and they refer to reduced cobalt catalysts at 375 °C in pure hydrogen. The obtained monometallic 10% Co/support catalysts appeared in a moderately dispersed system in the range 1.3–2.2%. Two-three times higher degree of metallic phase dispersion can be anticipated taking into account the volume of chemisorbed hydrogen for bimetallic 0.5% Ru – 10% Co/support catalysts. The evaluation of dispersion degree for bimetallic phase of 0.5% Ru – 10% Co/support catalysts requires the additional assumption referring to bimetallic phase surface composition and surface stoichiometry coefficient H/Me$_s$. The highest effect (volume of adsorbed hydrogen) is observed for bimetallic 0.5% Ru – 10% Co catalysts supported on alumina.

Tab. 2. Degree of reduction for cobalt/support catalysts.

Catalysts	Degree of reduction [%]
10% Co/SiO$_2$	85.7
0.5%Ru – 10% Co/SiO$_2$	96.6
10% Co/TiO$_2$	90.0
0.5% Ru – 10% Co/TiO$_2$	99.2
10% Co/Al$_2$O$_3$	67.0
0.5% Ru – 10% Co/Al$_2$O$_3$	70.1

Tab. 3. Hydrogen chemisorption at 25 °C for investigated catalysts.

Support	Metal content [%]	Hydrogen volume [cm³/g]	Dispersion [%]	Metallic surface area [m²/g_metal]	Crystallite size [nm]
SiO₂	10% Co	0.25	1.3	92	98
	0.5% Ru – 10% Co	0.51	2.7	-	-
TiO₂	10% Co	0.27	1.4	10	67
	0.5% Ru – 10% Co	0.68	3.6	-	-
Al₂O₃	10% Co	0.42	2.2	16	43
	0.5% Ru – 10% Co	1.4	7.3	-	-

3. CONCLUSIONS

- Thermal stabilization effects were found for both $Ru(NO)(NO_3)_3$ and $Co(NO_3)_2 \cdot 6H_2O$ compounds dispersed on SiO_2, Al_2O_3 and TiO_2 supports;
- Cobalt (10%) and ruthenium (0.5%) phase deposited on SiO_2, Al_2O_3 and TiO_2 diminishes the specific surface area of the support by about 20–30%;
- Hydrogen reduction of cobalt oxide phase takes place as two-step process $Co_3O_4 \rightarrow CoO \rightarrow Co$; when Co_3O_4/Al_2O_3 was calcined a third reduction step was assigned to reduction of spinel-like $CoAl_2O_4$ phase; Ruthenium promotes the reduction of dispersed cobalt oxide phase; its addition shifts the reducibility to lower temperature range and increases the degree of cobalt oxide reduction;
- Addition of ruthenium improves dispersion degree of supported cobalt especially for alumina supported cobalt catalyst.

Fischer–Tropsch synthesis is a part of gas to liquids (GTL) technology, which produces clean fuels from synthesis gas. It is well known that the catalysts for the conversion of natural gas are usually based on metallic cobalt dispersed on an oxide pours support (i. e. silica) and promoted with small amounts of metals (ruthenium). The research of the physico-chemical properties of the catalysts are necessary to find other, better catalysts for these reaction and these catalysts will be used in the future.

4. REFERENCES

[1] C. H. Bartholomew, J. F. Farrauto, *Fundamentals of Industrial Catalytic Processes*, wyd. Wiley Interscience, New York (2006).
[2] J.-S. Girardon, A. Constant-Griboval, L.Gengembre, *Catalysis Today* 106, 161 (2005).
[3] J.-S. Girardon, A. S. Lermontov, L. Gengembre, *Journal of Catalysis* 230, 339 (2005).
[4] S. A. Hosseini, A. Taeb, F. Feyzi, *Catalysis Communications* 6, 233 (2005).
[5] G. Jacobs, T. K. Das, P. M. Petterson, *Applied Catalysis A: General* 247, 335 (2003).
[6] E. Szubiakiewicz, W. K. Jóźwiak, T. Maniecki, *Przemysł Chemiczny* 82/3, 156 (2003).
[7] C. Ehrhardt, M. Gjikaj, W. Brocker, *Termochimica Acta* 432, 36 (2005).
[8] W. K. Jóźwiak, E. Szubiakiewicz , J. Góralski, *Kinetics and Catalysis* 45/2, 247 (2004).
[9] M. A. Ermakova, D. Y. Ermakov, G. G. Kuvshinov, *Journal of Catalysis* 187, 77 (1999).
[10] J. Li, G. Jacobs, Y. Zhang, T. Das, *Applied Catalysis A: General* 223, 195 (2002).

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