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Effect of platinum on the hydrogenation activity of nickel catalysts

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Abstract

Ni, Pt and Ni-Pt supported on SiO_2 and TiO_2-SiO_2 catalysts containing about 5 wt.% of the active phase were characterised using BET, ICP, TPR, XRD and TOF-SIMS methods and tested in the reaction of toluene hydrogenation to methylcyclohexane. XRD and TOF-SIMS results show that nickel oxide is better dispersed on the binary support than on SiO_2. TPR indicates that platinum promotes the reducibility of supported NiO. Transformations of metallic phase in the successive TPR–TPO cycles have been discussed. Catalysts supported on binary support show considerably higher catalytic activity in the reaction of toluene hydrogenation than those supported on silica. The bimetallic catalysts containing ca. 0.5 wt.% Pt are more active than related monometallic platinum catalysts, containing comparable amount of platinum.

Keywords: Silica and silica-titania supports; Ni-, Pt- and Ni-Pt catalysts; Toluene hydrogenation

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1. Introduction

In recent years, the development of cleaner burning fuels has been of very high priority. The trend towards improvement of air quality by reducing levels of tropospheric ozone, NO_x and particulate matter has resulted in the proposal of stringent specifications on the aromatic and sulphur contents of gasoline and diesel fuel. Consequently, fuel fraction require severe hydrotreatment to meet the product specifications for the year 2005. According to the World Wide Fuel Charter January 1999 specifications for the 2000–2005, the maximum of permissible total aromatic, polyaromatic and sulphur content of diesel fuel are 15 wt.%, 2.0 wt.% and 30 ppm, respectively [1]. World Wide Fuel Charter and European automobile manufactures association (ACEA) [2] have proposed slightly different requirements from those expected by Auto Oil [3] and Comitee European de Normalisation (CEN) [4], but the direction is the same. Applying only hydrorefining catalysts (CoMo, NiMo, NiW on Al_2O_3), the product quality is very dependent on the operating conditions and feedstock. However, because aromatic hydrogenation is an exothermic reaction, there are thermodynamic equilibrium limitations at high temperature operation. Therefore sophisticated processes, technologies and catalysts will be needed to meet these specifications.

Supported nickel and platinum catalysts are used for hydrogenation reactions of industrial interest, like hydrogenation of aromatics. Commonly, nickel and platinum are deposited on alumina and silica. However, because noble metal catalysts are easily poisoned by small amounts of sulphur, the hydrodesulfurisation catalyst in the first stage reactor reduces the level of sulphur upto a few ppm. It was found that sulphur poisoned Pt catalyst has a significant activity for dehydrogenation [5]. Therefore, in recent years, extensive studies have been performed to develop metal catalysts for two-stage process by various petroleum and catalyst manufacturing companies [6–8]. For example MAKFining dearomatisation technology (HDAr technology) is a two-step aromatics saturation process. Feedstock with sulphur levels upto 250 ppm can be treated with KF-200 catalyst in the HDAr section [8].

The modification or replacement of alumina or silica supports can change the interaction with the active phase

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and consequently the activity and resistance to sulphur poisoning of catalysts. In earliest works the higher tolerance towards sulphur poisoning of noble metals was related to electron deficiency of metal deposited close to strong acidic sites [9]. Actually, the higher hydrogenation activity of solid acids containing catalysts was attributed to the presence of hydrogen spillover in the metal–support interfacial region. For aromatics could be adsorbed on acid sites as carbonium ions, which tend to react with the spillover hydrogen. The influence of solid acids (US-SSY; dealuminated and water steam treated HY zeolite and HAlMCM-41) on the benzene, toluene and *o*-xylene hydrogenation over Pt/Al_2O_3 was discussed in [10]. Higher hydrogenation activity over platinum or palladium supported on acidic supports compared to that non-acidic ones was also reported by Lin and Vannice [11]. The results obtained for benzene and toluene hydrogenation showed that hydrogenation activity was highly improved in the presence of F and Cl [12]. The higher activities may be due to improved hydrogen spillover as well as to increased dispersion of the metal on the support [13]. The effect of the carriers (Al_2O_3, SiO_2(20%)-Al_2O_3) was studied for Pt–Pd catalysts. It was found that Pt-Pd/SiO_2-Al_2O_3 catalyst was the most active for aromatic hydrogenation in light cycle oil [14]. In addition to solid acid it has been verified that n-type semiconductors show excellent capability of accepting spillover hydrogen [15,16]. The results obtained for Rh/TiO_2 doped with W^{6+}, proved that metal–support interaction of the electronic type (electron transfer from the doped support to the Rh crystallite) is a taking effect on hydrogenation activity [17].

The influence of the metal and of the support on the stability of bifunctional catalysts for toluene hydrogenation was discussed in [18,19].

TiO_2 and TiO_2-containing mixed oxides are regarded as very promising supports of many industrial catalysts [20–24].

Recently we published a series of papers, devoted to characterisation and catalytic performance of Ni/SiO_2-TiO_2 catalysts in hydrogenation of toluene and diesel oil fraction [25–27]. It was observed that Ni/SiO_2-TiO_2 catalysts show higher dearomatisation activity in aromatics hydrogenation than nickel catalysts supported on silica, alumina, titania and alumina-titania. Among different preparation methods, the deposition of TiO_2 on SiO_2 by hydrolysis of titanium(IV)isopropoxide leads to the support improving the catalytic activity of nickel catalysts. TiO_2 form (anatase, rutile) influences the reducibility and activity of nickel catalysts supported on SiO_2-TiO_2. The results confirm that the optimal content of TiO_2 in the supports is 25 wt.% and of Ni 5 wt.% in the catalysts.

The aim of this work was to characterise the nature of the oxide precursors of some Ni, Pt and Ni-Pt catalysts supported on SiO_2 and TiO_2-SiO_2, to investigate their susceptibility to reduction and activity in the reaction of toluene hydrogenation to methylcyclohexane.

2. Experimental

2.1. Preparation of catalysts

A support containing 25 wt.% of TiO_2 was prepared by deposition of TiO_2 on surface of silica. SiO_2 (Aldrich, $S_{BET} = 370\,m^2/g$, grain size of 0.05 mm) was added to titanium(IV)isopropoxide dissolved in isopropyl alcohol. Then, during continuous mixing at room temperature, water was added to obtain a molar ratio of H_2O:TIPOT = 4:1. The sol was gelated at room temperature. Next, the samples were placed in a dryer and heated up at stepwise increased temperature: 30 °C, 0.5 h; 50 °C, 0.5 h; 70 °C, 0.5 h; 90 °C, 0.5 h; 110 °C, 12 h. Metals were deposited on the supports before the forming process. Monometallic Ni and Pt catalysts were prepared by wet impregnation method using of $Ni(NO)_2 \cdot 6H_2O$ or $H_2PtCl_6 \cdot 6H_2O$, respectively. Bimetallic Ni-Pt catalysts were performed by two-step impregnation, the Pt precursor being impregnated as a second one. After impregnation catalysts were peptised with 3% nitric acid and then extruded; extrudates of diameter 1.2 mm were obtained. The extrudated catalysts were dried at room temperature for 24 h then the temperature was increased slowly (40 °C) to 110 °C at which the extrudates were

Table 1
Composition and BET surface of the catalysts

No.	Catalysts denotation	Nominal content (wt.%)		Real content (wt.%)		BET surface (m^2/g)
		Ni	Pt	Ni	Pt	
1	5Ni/SiO_2	5	–	5.60	–	340
2	4.5Ni-0.5Pt/SiO_2	4.5	0.5	4.98	0.59	331
3	2.5Ni-2.5Pt/SiO_2	2.5	2.5	2.83	2.57	335
4	5Pt/SiO_2	–	5	–	3.18	323
5	0.5Pt/SiO_2	–	0.5	–	0.64	355
1a	5Ni/SiO_2-TiO_2	5	–	5.47	–	318
2a	4.5Ni-0.5Pt/SiO_2-TiO_2	4.5	0.5	4.85	0.51	315
3a	2.5Ni-2.5Pt/SiO_2-TiO_2	2.5	2.5	3.55	2.88	311
4a	5Pt/SiO_2-TiO_2	–	5	–	4.48	301
5a	0.5Pt/SiO_2-TiO_2	–	0.5	–	0.52	309

heated for 12 h and next calcined for 4 h at a temperature of 450 °C.

2.2. Characterisation of catalyst

Specific surface area of the catalysts was determined by a chromatographic method (heat desorption of argon). The reference was SiO_2 (Aldrich) with surface area of 370 m^2/g.

Phase composition was measured with a Siemens D5000 diffractometer using Cu Kα radiation (scanning step: 0.02°, 2θ range 24–81°). The X-ray patterns were compared to those of known standards taken from JCPDS index.

In the TPR and TPO courses, the mixtures of 95 vol.% Ar and 5 vol.% H_2 or O_2, respectively were used at a gas flow-rate of 20 cm^3/min and at a linear temperature increase of 10°/min. After reaching the maximum temperature, the process of reduction/oxidation was continued isothermally

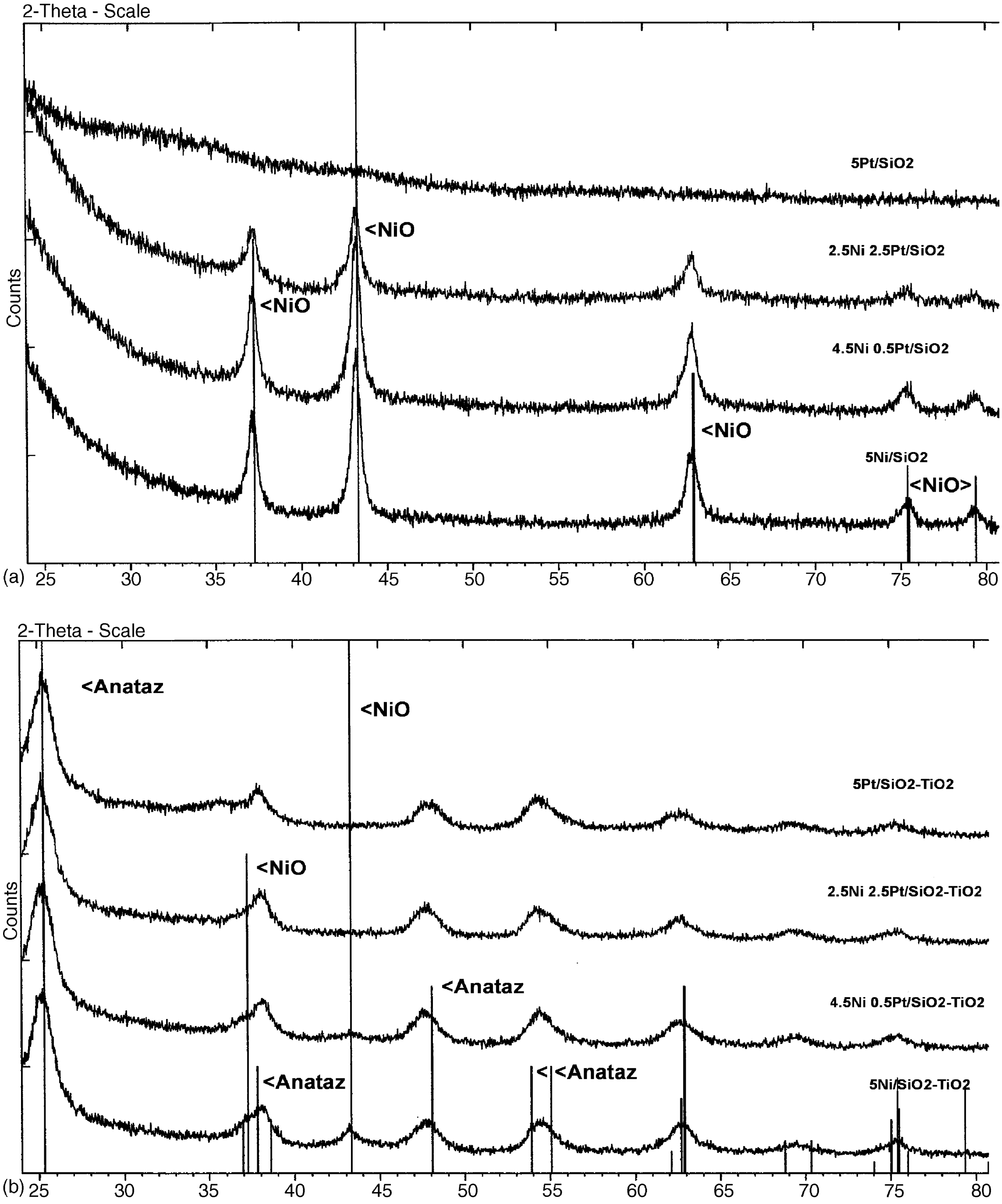

Fig. 1. XRD patterns of the catalysts supported on: (a) SiO_2 and (b) TiO_2-SiO_2, calcined at the temperature 450 °C.

for 1 h and finally the catalyst was cooled in a stream of argon. TPR was performed in the temperature range of 20–900 °C. Calibration of the hydrogen uptake was done by referring to the TPR peak of known amounts of a standard (pure NiO) taken in identical conditions.

The TOF-SIMS investigations were performed in the static mode using an ION-TOF instrument (TOF-SIMS IV) equipped with a 25 kV pulsed $^{69}Ga^{+}$ primary ion gun. Powder catalysts samples were compressed into tablets before measurements. The analysed area corresponded to a square of 68.3 μm × 68.3 μm.

Hydrogenation of toluene was carried out within the temperature range of 80–200 °C, using conventional continuous flow-type reactor. The catalyst sample (4 cm^3, grain size of 0.75–1 mm) was placed in the reactor (0.8 cm in diameter, 20.5 cm long) and activated in a hydrogen stream at the temperature 340 °C for 2 h under pressure of 3 MPa. After activation, the reactor was adjusted to the desired reaction temperature. Liquid reactant was fed from the nozzle and dispersed on the corundum located above the bed of the catalyst. At each temperature under study, parameters (p: 3.5 MPa; LHSV: 3 h^{-1}; H_2:CH = 350 Nm^3/m^3) were stabilised for 1 h, the reaction was continued for 0.5 h. Applied parameters keep the reaction free from mass transfer limitations. The analysis of products was carried using GC (FID detector, capillary column of the RTX-1 type 100% dimethyl polysiloxane, temperature of 70 °C, helium as the carrier gas with flow-rate of 50 cm^3/min).

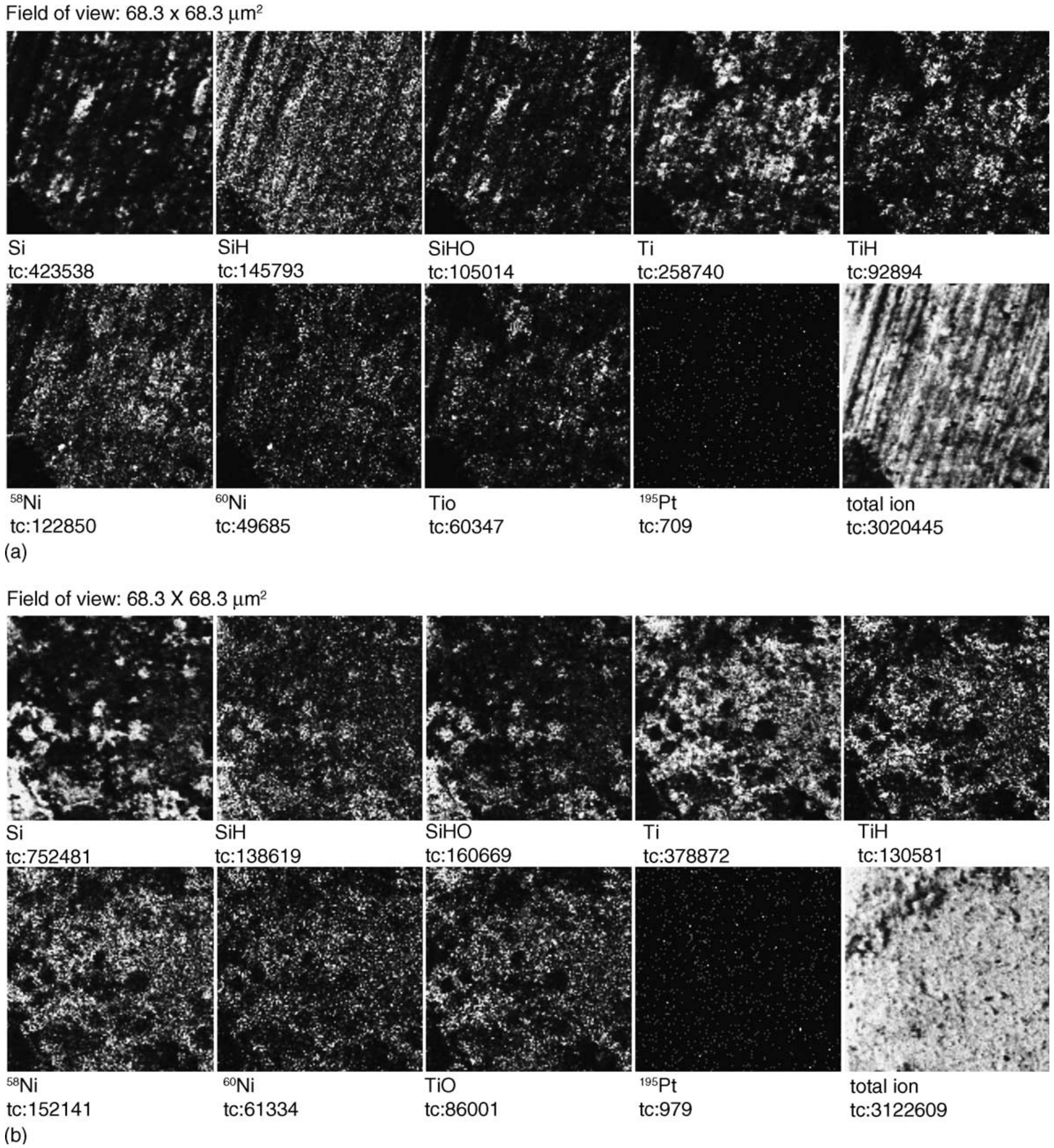

Fig. 2. TOF-SIMS images of the catalysts: (a) 2a-4.5Ni-0.5Pt/TiO_2-SiO_2; (b) 3a-2.5Ni-2.5Pt/TiO_2-SiO_2.

3. Results and discussion

In Table 1 nominal and real (determined by ICP) composition of the catalysts and their BET surface area are given. Deposition of both TiO_2 and metals on SiO_2 slightly (from 4 to 16%) decreases the surface area of the catalysts compared to the pure SiO_2. A more pronounced decrease is observed for the catalysts supported on binary oxide. In Fig. 1 XRD patterns of the catalysts calcined at the temperature 450 °C supported on SiO_2 (a) and TiO_2-SiO_2 (b), are presented. In a binary support TiO_2 exists in a form of anatase. The catalysts supported on both supports differ in the size of NiO crystallites. In the case of TiO_2-SiO_2 supported catalysts, NiO is observed only for the catalysts 1a and 2a and forms relatively small crystallites (a mean size of 8.8 and 4.6 nm, respectively). For the catalyst 3a, NiO crystallites are small enough to be "invisible" for XRD method (<4 nm). Catalysts supported on silica are characterised by much bigger crystallites of NiO (12–15 nm). Such differences prove that the oxide nickel phase is better dispersed on the binary TiO_2-SiO_2 support than on SiO_2. No platinum lines are observed for all, containing platinum, catalysts under study. TOF-SIMS images of the calcined catalysts 2a and 3a (Fig. 2) confirm a good dispersion of platinum. Although platinum signal is weak because of a high ionisation energy of this metal, it seems to be uniformly distributed on the support surface (bright colour on the images indicates an existence of the pointed ion). TOF-SIMS pictures also show an affinity of nickel to titania rather than to silica (bright spots of nickel and titanium ions occur in the same area).

TPR profiles of the catalysts, calcined at 450 °C, are presented in Fig. 3. The monometallic nickel catalyst supported on SiO_2 (Sample 1) is completely reduced in the temperature range 290–580 °C. One can observe maximum at 450 °C and two "shoulders" at the temperatures 400 and 550 °C which can reflect a diversity of NiO crystallites on silica surface. TPR run of the platinum catalyst supported on SiO_2 (Sample 4) is characterised only by a small peak with maximum at the temperature ca. 30 °C. It is possible that calcination of the catalyst at 450 °C leads to a great extent of decomposition of PtO_2 to the metallic platinum. PtO_2 decomposes to Pt and O_2 just about 400 °C at normal pressure [28]. Some of

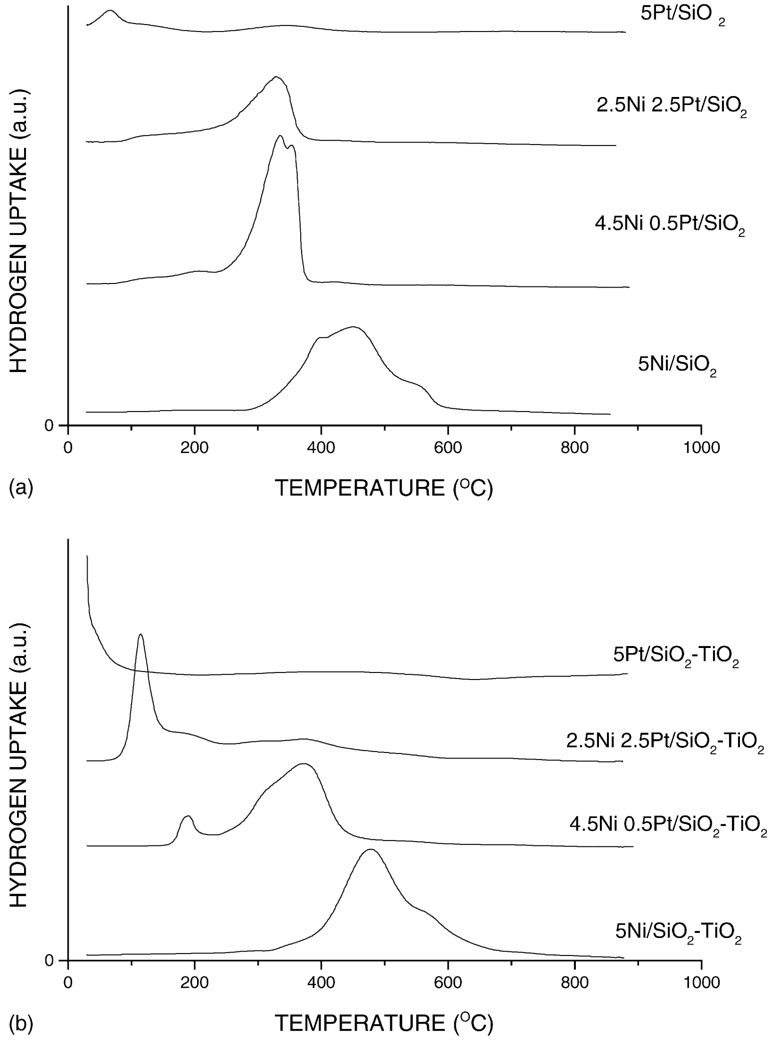

Fig. 3. TPR profiles of the catalysts supported on: (a) SiO_2 and (b) TiO_2-SiO_2, calcined at the temperature 450 °C.

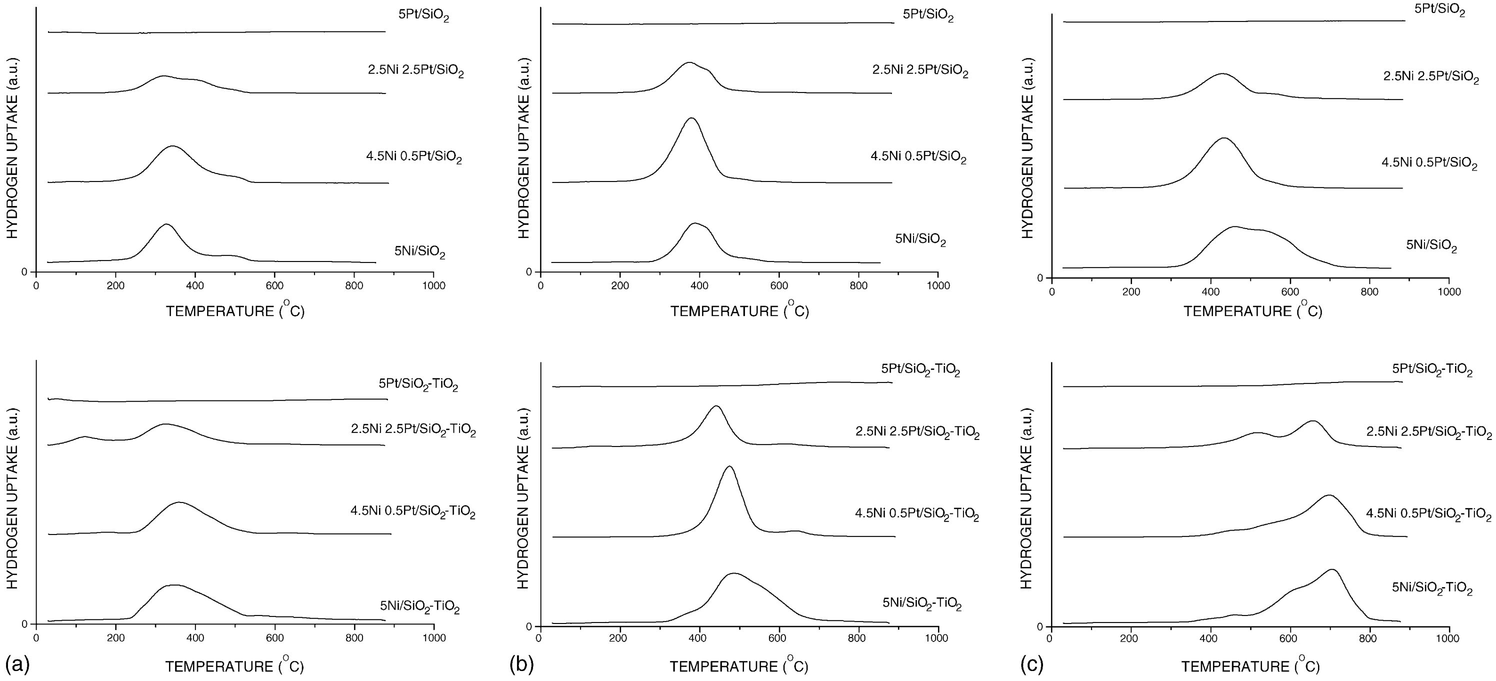

Fig. 4. TPR profiles of the catalysts, reoxidised at the temperatures: (a) 400 °C, (b) 700 °C and (c) 900 °C.

the platinum oxide may, however be stabilised by SiO_2 and reduced at room temperature during standardisation of the catalyst in the reducing atmosphere before the temperature programme starts. TPR profiles of the bimetallic catalysts supported on SiO_2 show that reduction takes place mainly in the temperature range of 250 and 380 °C. It indicates that the rate of nickel oxide reduction is promoted by the presence of platinum. Such behaviour may suggest that both metal precursors are in a close contact with each other after calcination. Initially reduced platinum acts as a catalyst for the reduction of NiO. It is also very likely that bimetallic platinum-nickel particles are formed during reduction. TPR profile of the nickel catalyst supported on binary oxide (Sample 1a) is in fact similar to that supported on SiO_2. However, the temperature range of reduction (330–640 °C) is shifted towards higher temperatures, what can be attributed to the higher dispersion of NiO and some interactions between NiO and TiO_2. On the TPR profile of platinum catalyst supported on binary support (Sample 4a), the descent line up to about 80 °C, reflecting the final stage of PtO_2 reduction, can be clearly seen. TPR profiles of the bimetallic catalysts are more complex comparing to those of silica-supported catalysts. Also in this case the promotion of NiO reduction by platinum is evident but additional low temperature peaks with maxima at ca. 180 and 110 °C (Samples 2a and 3a) are observed. It is difficult to attribute these peaks to some specific species but much more diversified TPR courses of bimetallic catalysts supported on binary support reflect more complex character of interaction between the active phase components and titania. The catalyst 2.5Ni-2.5Pt/TiO_2-SiO_2 (Sample 3a) is definitely easier reducible than the related catalyst supported on silica (Sample 3).

Fig. 4 presents TPR profiles of the catalysts obtained in a series of successive TPR-TPO measurements, after reoxidation of the catalysts in the TPO regime with the final temperatures (a) 400 °C, (b) 700 °C and (c) 900 °C, respectively. Such investigations are useful to have insight into the possible transformations, which the catalysts may undergo during their regeneration in the oxidative atmosphere. TPR profiles of the nickel catalysts (Samples 1 and

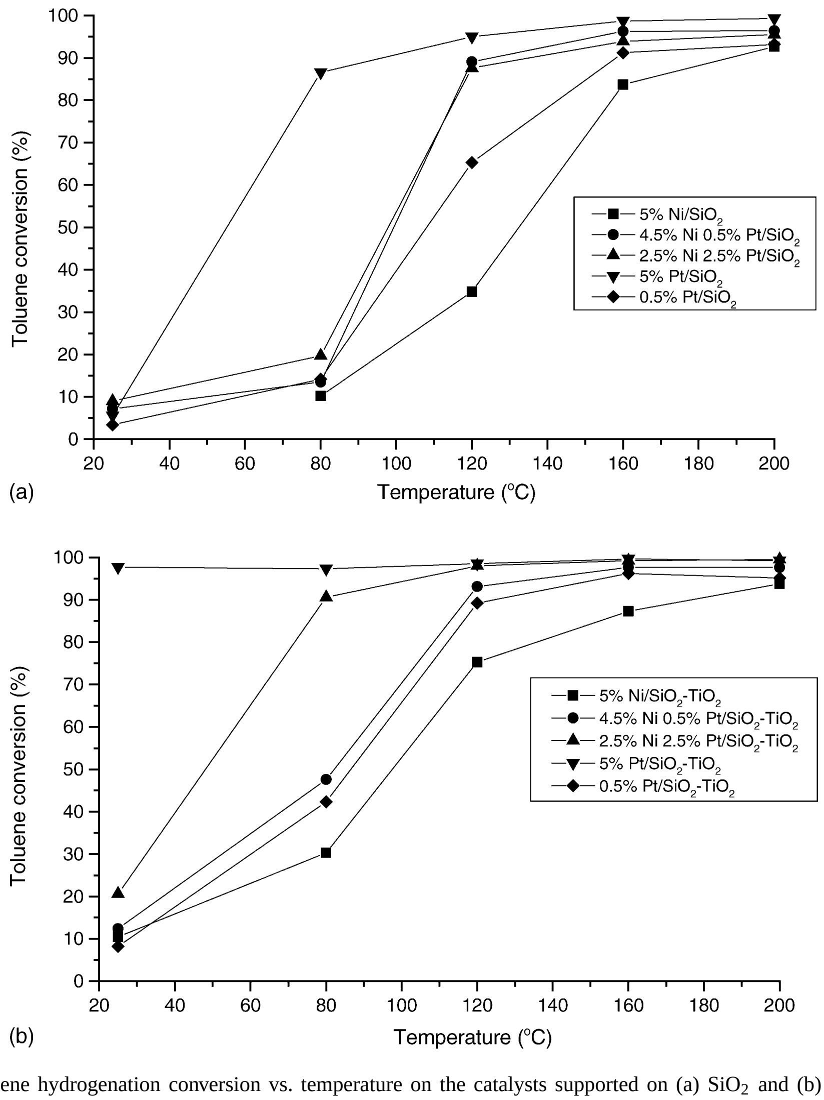

Fig. 5. Toluene hydrogenation conversion vs. temperature on the catalysts supported on (a) SiO_2 and (b) TiO_2-SiO_2.

1a) after TPO to 400 °C (Fig. 4a) show that reoxidation in such conditions is not complete (hydrogen uptake is less than needed to stoichiometric oxidation of Ni to NiO), so in the following TPR, reduction is promoted by unreoxidated metallic nickel. That is why the TPR profiles of the bimetallic samples are similar to nickel one. The increase of the reoxidation temperature to 700 °C (Fig. 4b) results in the shift of the following TPR maxima towards higher temperatures. This shift is much more pronounced for the catalysts supported on binary supports confirming the stronger interaction between oxide nickel phase with titania. Some promoting effect of platinum on NiO reduction is observed but less significant that in the case of calcined catalysts precursors. TPR profiles obtained after TPO to 900 °C (Fig. 4c) reveal the creation of hardly reducible nickel titanates (maximum of TPR peak about 700 °C), which have been already discussed in our previous paper [25]. A small amount of platinum (Sample 2a) does not enhance reduction of such species. Only for the bimetallic catalyst containing 2.5 wt.% Pt (Sample 3a), a promoting effect of platinum on reduction of nickel titanates is clear. What concerns silica supported catalysts, a broaden TPR peak is observed for the nickel catalyst (Sample 1), hydrogen uptake was observed up to reduction temperature of 700 °C. It indicates a strong interactions of NiO with SiO_2 or even a transformation of the part of nickel in nickel silicates during the high temperature reoxidation. Reduction of the bimetallic catalysts is complete at much lower temperatures (about 500 °C).

Toluene conversion, as a function of reaction temperature up to 200 °C over silica and silica-titania-supported nickel, platinum and bimetallic Ni-Pt catalysts is shown in Fig. 5. It can be observed that at lower temperatures (80 and 120 °C) catalysts supported on binary oxide show considerably higher activity than those supported on silica. The hydrogenation activity of nickel catalyst is deeply modified by addition of 0.5 wt.% Pt. The bimetallic catalysts of nominal composition 4.5 wt.% Ni and 0.5 wt.% Pt (Samples 2 and 2a) are more active than monometallic platinum catalysts, containing a comparable amount of platinum (Samples 5 and 5a). The difference between toluene hydrogenation activity of bimetallic catalysts containing 0.5 and 2.5 wt.% of platinum is much more pronounced in the case of the catalysts supported on TiO_2-SiO_2. It can be related to the TPR results —catalyst 3a reduces in the much lower temperature range than the catalyst 2a, whereas the reducibility of the catalysts 2 and 3 is comparable.

4. Conclusions

- Platinum promotes the reduction of NiO in the catalysts supported both on SiO_2 and TiO_2-SiO_2.
- TPR results may suggest formation of Ni-Pt bimetallic particles during the reduction.
- Catalysts supported on TiO_2-SiO_2 show considerably higher catalytic activity in the toluene hydrogenation than those supported on SiO_2.
- Bimetallic Ni-Pt catalysts containing ca. 0.5 wt.% Pt are more active than related monometallic platinum catalysts, containing comparable amount of platinum.

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