Catalysis Today 137 (2008) 433–438

Contents lists available at ScienceDirect

Catalysis Today

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

Effect of TiO_2 content and method of titania–silica preparation on the nature of oxidic nickel phases and their activity in aromatic hydrogenation

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ARTICLE INFO

Article history:
Received 31 July 2007
Received in revised form 10 March 2008
Accepted 12 March 2008
Available online 29 April 2008

Keywords:
Ti–Si mixed oxides
Nickel catalysts
TPR
TPO
XRD
SEM

ABSTRACT

Ni catalysts (5 wt.% of Ni) supported on titania–silica were studied. The aim of the study was to examine how the TiO_2 (10, 25 and 50 wt.%) content influences the nature of oxidic nickel species on titania–silica supports which were prepared in the following mode: (i) by deposition of TiO_2 on the silica surface via hydrolysis of titanium isopropoxide or via hydrolysis of titanium tetrachloride, and (ii) by sol–gel method. Titania distribution in the titania–silica support depends on the method of support preparation and influences the reducibility and distribution of nickel oxide; as the quantity of titanium increases, so does the quantity of nickel. The results indicate that the deposition of TiO_2 on the silica surface via hydrolysis of titanium isopropoxide (TiO_2/SiO_2) improves the hydrogenation activity of nickel catalysts. The use of TiPOT for the preparation of TiO_2/SiO_2 increases the reducibility of nickel oxide, as well as the acidity and specific surface area of the catalyst.

1. Introduction

Recent environmental legislation on diesel fuels focuses on sulphur content, polynuclear aromatics (PNA), and cetane number (CN). CN improvement needs deep hydrogenation of aromatics and/or ring opening as additional steps in diesel fuel upgrading [1]. A problem inherent in γ-Al_2O_3-supported Ni catalysts is that nickel aluminates are formed, which are not reducible below 600 °C. Thus, to obtain bulk NiO and highly dispersed Ni^{+2} species, it is necessary to apply Ni loading of 10–15 wt.% [2,3]. We have assumed that if we use Si–Ti oxides as supports for hydrogenating catalysts, it will be possible to incorporate a lower amount of Ni. The benefit of using SiO_2TiO_2 supports is that TiO_2 modifies the metal–surface interaction, and silica is characterised by a sufficiently high surface area and thermal stability. The properties of SiO_2TiO_2, however, depend not only on the chemical composition but also on a number of factors which can be modified at the stage of preparation. The most common methods used for the preparation of SiO_2TiO_2 involve sol–gel method. In this method, the difference in reactivity between Ti and Si precursors influences the formation of Si–O–Ti bonds. The reactivity of TiPOT can be modified using acetic acid, acetylacetone and ethylene glycol, which leads to the formation of chelated titanate [4]. The modification of titanium alkoxide does not significantly influence the rate of TiPOT condensation, but lowers the rate of hydrolysis [5]. TiO_2 deposition on the SiO_2 surface is obtained by impregnation [6,7], precipitation [8] and chemical vapour deposition [9]. The preparation methods, as well as the characterisation and applications of titania–silica oxides, can be found elsewhere [10].

The aim of the work was to prepare a highly active catalyst with a low (5 wt.%) nickel content for the hydrogenation of aromatic hydrocarbons. For this purpose, the applicability of titania–silica as a support for such a catalyst was examined. Catalytic activity was tested in the HDA of the diesel oil fraction and in toluene hydrogenation. Our study focuses on the problem of how the quantity of titanium and the method of preparing titania–silica supports contribute to the nickel–support interaction. Emphasis is placed on the surface morphology and reducibility of the catalysts. Experiments are also conducted with Ni/SiO_2 and Ni/TiO_2 catalysts.

2. Experimental

Samples A: Calculated amount of titanium(IV)isoproposide (equivalent to the desired loading percentage), diluted in isopropanol (1:3), was added to suspended silica (SiO_2:i-PrOH = 1:1.5). The solution was stirred for 1 h. Hydrolysis was performed by addition of ammonia, H_2O:TiPOT molar ratio being 4:1. The sol was made subject to gelation at 25 °C (20 h). Next, the

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doi:10.1016/j.cattod.2008.03.007

Table 1
Chemical composition, physicochemical properties and activity of Ni-catalysts in hydrogenation of aromatics

Catalyst	Composition of support	Ni amount (wt.%)	S_{BET} (m^2/g)	Acidity (mmol/g)	TPR experiments			Activity	
					Reducibility[a] (a.u.)	$T_{MAX(1)}$ (°C)	$T_{MAX(2)}$ (°C)	Toluene conversion (%)	HDA[b] (%)
AK10	TiO_2/SiO_2	5.2	360	0.11	264	470	–	–	77.3
AK25		4.7	318	0.22	245	490	625	91.5	88.1
AK50		4.3	286	0.36	140	510–550	680	–	83.9
DK10	TiO_2/SiO_2	5.4	315	0.07	196	415	555	–	66.1
DK25		4.6	221	0.10	204	430	565	79.6	78.1
DK50		4.8	161	0.12	135	490	605	–	72.4
EK10	$TiO_2–SiO_2$	5.3	246	0.25	114	490	–	–	58.3
EK25		4.7	170	0.46	121	–	590	66.2	61.3
EK50		4.9	139	0.55	60	–	565	–	54.1
SK	SiO_2	5.0	360	0.06	355	410	530	28.4	–
TK	TiO_2	5.1	57	0.18	258	380	520	66.8	–

[a] Hydrogen uptake up to 500 °C.

[b] HDA efficiency calculated on the basis of %C_A drop.

samples were dried at 30, 50, 70 and 90 °C for 0.5 h, and at 110 °C for 12 h. TiO_2/SiO_2 was labelled A10, A25 and A50 according to the wt.% of TiO_2 added. *Samples D*: Hydrolysis of $TiCl_4$ was carried out at room temperature. Water volume depended on the sorptive capacity of silica, a fourfold excess being maintained. Sol was aged at 25 °C for 24 h. Silica was mixed for 1 h with titanium hydrogel and was dried under the same conditions as were for the A supports. TiO_2/SiO_2 was labelled D10, D25 and D50. For the samples A and D use was made of silica marketed under the brand name of Sigma (S_{BET}, 370 m^2/g; r, 2.2 nm; V_{H_2O}, 1.9 cm^3/g). *Samples E*: TiPOT was dissolved in isopropyl alcohol (TiPOT:i-PrOH = 1:2 - vol.%), heated up to 70 °C with a reflux condenser, and then treated (1 h) with a solution of ethylene glycol and i-PrOH (1:1 vol.%). Ethylene glycol was used to reduce TiPOT reactivity towards hydrolysis. The samples were aged at 20 °C for 20 h. Titanium alkoxide chelate was mixed with a TEOS and i-PrOH solution (1:1 vol.%) at 25 °C (0.5 h), then 25% NH_4OH was added (TiPOT:-TEOS:H_2O = X:Y:4 ($X + Y$)). Gelation was conducted at 25 °C (20 h). Samples $TiO_2–SiO_2$ containing 10, 25 and 50 wt.% of TiO_2 are referred to as E10, E25 and E50, respectively.

Catalysts with 5 wt.% of Ni (AK, DK and EK) were obtained by wet impregnation of the extruded supports, using nickel nitrate. For comparison, Ni/SiO_2 (SK) and Ni/TiO_2 (TK) catalysts were prepared using SiO_2 (Sigma) and TiO_2 (Degussa P25).

In TPR (95 vol.% Ar and 5 vol.% H_2) and TPO (95 vol.% Ar and 5 vol.% O_2) experiments, a gas mixture was used at 20 cm^3/min and temperature rise of 10 °C/min. Phase composition was determined with a Siemens D5000 diffractometer (CuKα). SEM examinations involved a Jeol JSM 5888LV electron microscope with an X-ray analyser. In the material contrast, bright spots and dark spots indicate the location Ti and Si, respectively.

Acidity was determined by adsorption of ammonia (NH_3–TPD) in a through-flow system equipped with a thermal conductivity detector. The sample was pre-treated in the stream of argon at 550 °C for 2 h and afterwards cooled to 180 °C. After desorption of physically adsorbed ammonia (180 °C) the sample was heated at a rate of 10 °C/min up to 550 °C.

Catalyst activity was examined in a flow reactor. Hydrogenation of toluene was carried out at 160 °C and 3.5 MPa (LSHV, 3 h^{-1}; H_2:CH, 350 Nm^3/m^3). HDA (hydrodearomatisation) of light diesel oil fraction (IBP, 141 °C; 90 vol.%, 248 °C; S, 0.002 wt.%; %C_A, 16.8%; aromatics, 25 wt%; monoaromatics, 23.3 wt.%; polyaromatics, 1.7 wt.%) was performed at 290 °C and 6.0 MPa (LSHV, 2 h^{-1}; H_2:CH, 500 Nm^3/m^3). Catalyst activity was compared, considering the carbon percentage in aromatic structures (%C_A) by IR (1610 cm^{-1}) [11]. Aromatics content was determined by HPLC according to the PN-EN 12916.

3. Results

Chemical composition, textural parameters and acidity of Ni catalysts are summarised in Table 1. As shown by these data, the S_{BET} of all catalysts decreased as the quantity of titania was increased. The differences in the S_{BET} between titania–silica and silica depend on the support preparation methods used. For catalysts supported on TiO_2/SiO_2 prepared by deposition of TiO_2 via hydrolysis of TiPOT, as well as hydrogel ageing on SiO_2 (AK), the differences are less distinct (3–21%) than for the catalysts prepared via hydrolysis of $TiCl_4$, where hydrogel was deposited onto SiO_2 upon ageing (DK) (13–55%). When $TiO_2–SiO_2$ prepared by the sol–gel method (EK) was used as a support, the S_{BET} of the catalysts obtained decreased by 30–60%, amounting to 246 mm^2/g (for EK10) and 139 mm^2/g (for EK50). The results of NH_3–TPD experiments show that the acidity of all Ni catalysts increases with TiO_2 content, but the increase is more distinct for EK than for the other catalysts. The acidity of the catalysts can be ordered in the following sequence: EK > AK > DK.

Fig. 1a shows the TPR profiles of the Ni catalysts supported on titania–silica, calcined at 450 °C (TPR I). For the AK catalysts, there is a peak with a maximum within the range of 470 °C (AK10) to 510–550 °C (AK50). The TPR I profiles for the DK catalysts contain two distinct maxima: a low-temperature one, $T_{max(1)}$, ranging from 415 °C (DK10) to 490 °C (DK50), and a high-temperature one, $T_{max(2)}$, within the range from 555 °C (DK10) to 605 °C (DK50). The two distinct ranges of reduction indicate that, in the case of DK catalysts, metal–support interactions are varied. For the EK catalysts there is one main reduction peak with a maximum at 490, 590 and 565 °C for EK10, EK25 and EK50, respectively; the profiles also show that the Ni–support interaction is stronger for EK25 and EK50 than for EK10.

The TPR II profiles for the catalysts after reoxidation at 400 °C indicate that Ni reduction occurs over the temperature range of 200–500 °C (Fig. 1b). As in the case of the TPR I, the reduction of reoxidised DK catalysts occurs in two stages. The shape of the TPR II profiles shows that reoxidability is lower for catalysts with a 50 wt.% TiO_2 content.

To gain better insight into the interaction between nickel and titania–silica, SiO_2 and TiO_2 were made subject to reduction. The TPR profiles for the Ni/SiO_2 catalyst (SK) and Ni/TiO_2 catalyst (TK) are shown in Fig. 1c and d, respectively. The TPR I profile for the SK

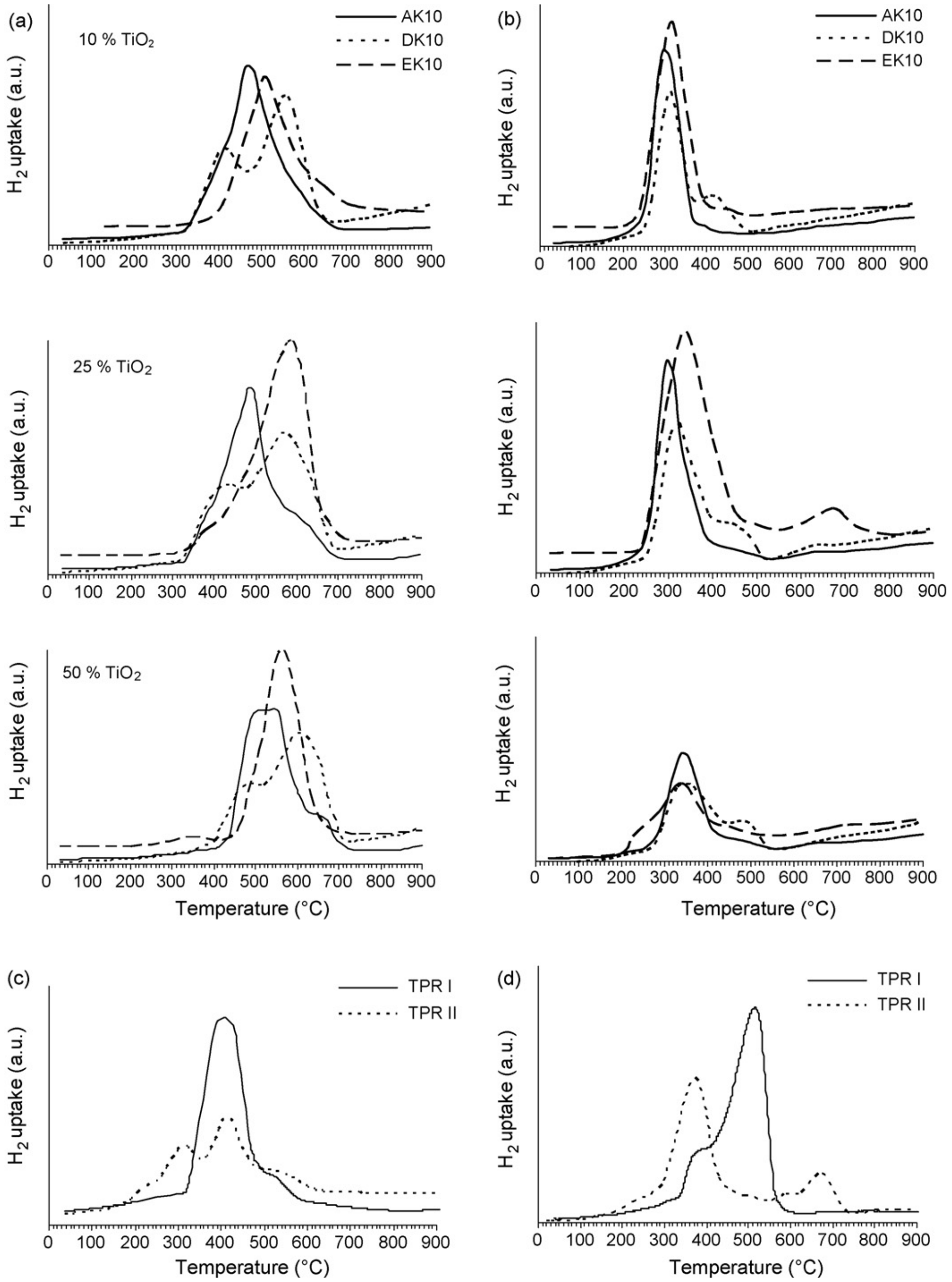

Fig. 1. TPR profiles of Ni catalysts. Effect of TiO_2 amount and of the titania–silica preparation method on TPR I (a) and TPR II (b). TPR I and TPR II patterns for SK (c) and TK (d) catalysts.

catalyst makes it clear that reduction commences at 300 °C and occurs in a single stage, with a maximum at 410 °C and a shoulder at 530 °C. In the TPR II for the same catalyst (reduced in TPR I and reoxidised at 400 °C in TPO) reduction occurs in two, partly overlapping steps. The reduction of NiO species in TPR II starts at a lower temperature (180 °C) as compared to TPR I (320 °C). In the TPR I profile for the Ni/TiO_2 catalyst (TK) a peak is present at 520 °C with a shoulder at 380 °C. The TPR II profile for the TK catalyst shows that after TPR I and TPO some NiO species have formed, whose reducibility is higher as compared to the fresh catalyst. Fig. 2a presents the SEM micrographs of nickel catalysts with a TiO_2 content of 25 wt.%. Thus, when the support was obtained via hydrolysis of TiPOT on the silica surface (AK25), the distribution of TiO_2 was more uniform than when hydrolysis involved $TiCl_4$ (DK25). The surface of the TiO_2–SiO_2 catalyst prepared by co-precipitation (EK25) shows a uniform distribution of TiO_2. Analysis of the Si, Ti, O and Ni content at selected points of the catalyst surface (X-ray analyser) has revealed that DK25 is characterised by a highly varied, nonuniform Ti and Ni distribution. As for DK25, AK25 and EK25, nickel content varies over the range of 3.3–7.9, 2.2–5.5 and 6.2–8.1 at.%, respectively. The spots where Ti atoms occurred in increased amounts also feature increased amounts of Ni atoms (Fig. 2b).

XRD analysis was carried out for catalysts calcined at 450 °C, with a 25 wt.% TiO_2 content. The diffractograms (Fig. 3) display

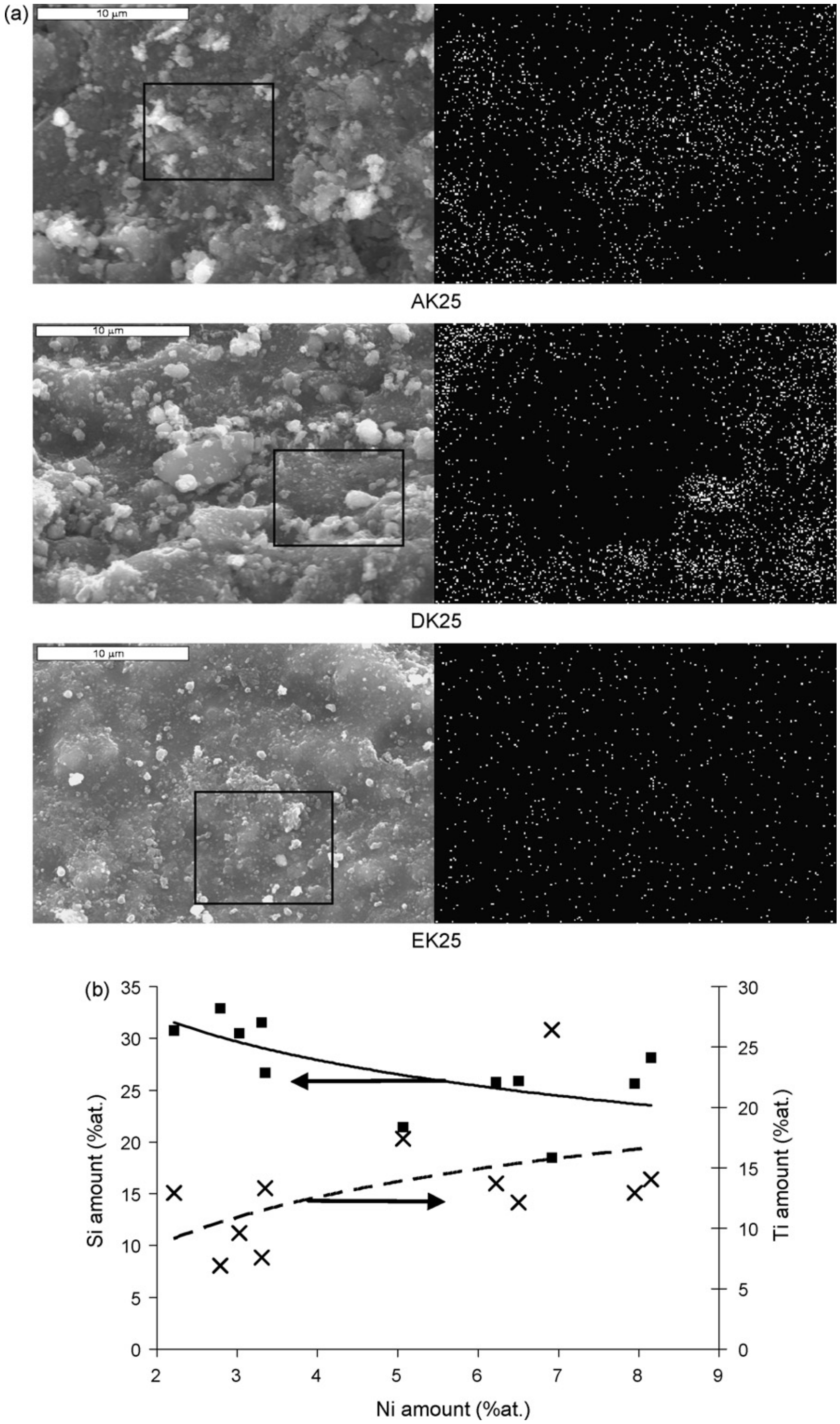

Fig. 2. Effect of the support preparation method on surface morphology of the catalysts. (a) titania distributions and (b) correlation between TiO_2 amount and Ni amount on the catalyst surface.

reflections characteristic for two TiO_2 crystalline forms (anatase, 2θ of 25.3, 48, 54, 55 and 75°; rutile, 2θ of 27.5, 36, 41, 54.5 and 56.5° [12], indicating that TiO_2 crystallisation has commenced), as well as reflections typical of NiO crystals (2θ of 37.3, 43.3, 62.8 and 75.5°). The comparison of AK25 and DK25 has revealed that when the support A is used (AK25), some part of TiO_2 takes the form of anatase. When use is made of sample D (DK25), a portion of TiO_2 has the form of rutile. The XRD pattern for EK25 does not show any reflections typical of crystalline TiO_2.

The results of diesel oil fraction hydrogenation (Table 1) make it clear that AK catalysts display activities higher than those of DK and EK catalysts. HDA efficiency (computed in terms of $\%C_A$ drop) for AK, DK and EK catalysts was 77–88, 66–78 and 54–61%, respectively. Regardless of the preparation method used, catalysts with a 25 wt.% TiO_2 content displayed the highest activity. Considering the decreasing of toluene conversion of catalysts containing 25 wt.% of TiO_2, they can be ordered as follow: AK25 (91%) > DK25 (80%) > EK25 (66%). The HDA efficiency of the Ni/SiO_2 catalyst

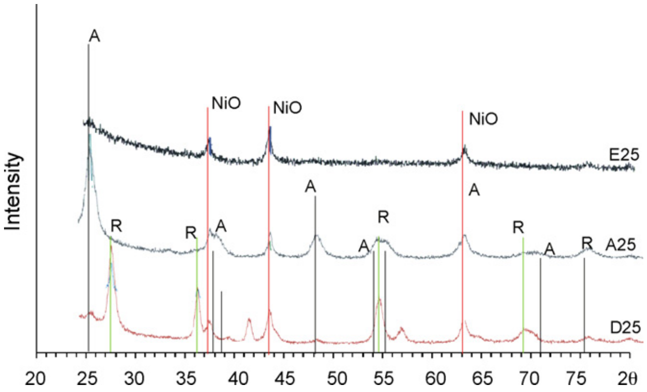

Fig. 3. XRD patterns for AK25, DK25 and EK25 catalysts. R-rutyle; A-anatase.

(SK) was found to be by 39% lower than that of the Ni/TiO_2 catalyst (TK).

4. Discussion

Our TPR experiments have revealed that the reduction of Ni-oxide species on SiO_2 (SK) occurs at 300–600 °C. NiO reduces mainly at 300–450 °C, with a maximum at 410 °C. From the literature [13] it follows that bulk NiO, as well as NiO which weakly interacts with the SiO_2 surface, undergo reduction over the temperature range mentioned. The presence of a shoulder at 550 °C suggests that the interaction of NiO with silica is stronger than at 300–450 °C. The reduction of nickel(II)silicates is induced by temperatures higher than 500 °C [14,15].

The TPR profile of the Ni/TiO_2 catalyst (TK) shows a large peak at 420–580 °C. However, there is some part of NiO that weakly interacts with the surface and undergoes reduction at 300–400 °C, as suggested by the smaller peak in the relevant TPR profile. NiO reduction is also influenced by the phase composition of TiO_2. For the preparation of TK we used TiO_2 Degussa (75% anatase, 25% rutile). In the literature, Ni/TiO_2 (anatase) reduction occurs at 290–500 °C with a maximum at 450 °C [2] or 400 °C [16], while Ni/TiO_2 (rutile) reduction takes place at 300–580 °C with a maximum at 430 °C [17].

During reduction of Ni/TiO_2, also titania can be reduced to TiO_x ($x < 2$) species. In a reducing atmosphere, some Ti^{4+} ions are reduced to Ti^{3+}; their reduction commencing at approx. 400 °C [18]. Owing to their mobility, the TiO_x species create additional active sites [19]. Several explanations have been proposed regarding the origin of enhanced activity of TiO_2 catalysts: (i) a localised electronic promoter effect of the TiO_x species on the adjustment of metal atoms, which remain as the active sites [16], or (ii) the creation of new active sites of the type M–Ti^{+3} and/or M–oxygen vacancy in the metal–support interfacial region [20,21].

Our results show that Ni/TiO_2 (TK) and Ni/SiO_2 (SK) catalysts show a lack of correlation between activity and reducibility. The higher HDA efficiency of TK (as compared to SK) can be due to the following factors: a higher acidity and the occurrence of new active sites that form in the course of reduction.

The TPR I profiles of the catalysts with Ni deposited onto TiO_2/SiO_2 show that for AK and DK the temperatures at which the first peak, $T_{max(1)}$, occurs (Fig. 1a) are higher than the temperature of $T_{max(1)}$ for the Ni/SiO_2 catalyst (SK) (Fig. 1c). As for the DK catalysts, the presence of a second maximum ($T_{max(2)}$) in the TPR I profiles suggests that the interaction between Ni and support surface is less uniform than that for the AK catalysts. This suggestion is additionally confirmed by the TPR II profiles. Seemingly, the less uniform Ni–support interaction in the DK catalysts is attributable to the extent of SiO_2 surface coverage with TiO_2 because the SEM micrographs show that for the DK25 the extent of coverage is notably lower (TiO_2 agglomerates) than for AK25 (Fig. 2a). Taking this all into account, we can assume that a greater quantity of Ni is deposited on the SiO_2 surface of DK as compared to that of AK.

As for the catalysts prepared via co-precipitation (Ni/TiO_2–SiO_2), it is advisable to consider the interaction of Ni with SiO_2 or TiO_2 and Ni with the TiO_2–SiO_2 phase. The noticeably high proportion of SiO_2TiO_2 in E25 and E50 is an indication of their higher acidity (Table 1). SEM micrographs show a uniform distribution of titanium (Fig. 2a).

The higher activities of AK compared to DK are due to a higher reducibility they display up to 500 °C (probably owing to the phase composition of the support), i.e. to the temperature used for catalyst activation before activity tests (500 °C in H_2 flow). The higher activity of AK catalysts can also result from higher acidity (as reported in the literature [22]) and higher S_{BET}. SEM measurements (X-ray analyser) of catalysts with a 25 wt.% TiO_2 content have disclosed agglomerates on the AK25 surface, which contain lower amounts of Ni atoms (2.2–5.3 at.%) than those found on the DK25 surface (3.3–7.9 at.%). When the supports are prepared by co-precipitation (EK), this leads to the formation of the SiO_2TiO_2 phase. Our results show that the co-precipitation method fails to be advantageous in terms of activity. Despite their higher acidity, EK catalysts display a lower activity than do AK and DK catalysts. Surface analysis makes its clear that at the spot of Ti detection the amount of Ni atoms is higher (6.2–8.1 at.%) as compared to AK and DK. Additionally, owing to the formation of the separate TiO_2SiO_2 phase, EK catalysts are characterised by a lower amount of the TiO_2 phase. This implies that the formation of active sites as a result of TiO_2 reduction may be lower in EK than in AK or DK catalysts. The diffractograms of AK25 and DK25 catalysts (reduced at 400 °C) have revealed a very small quantity of Ni/TiO_x (results not shown). Summing up, the catalysts with a 25 wt.% TiO_2 content were found to display the highest hydrogenating activity, irrespective of the preparation method applied. The activity and reducibility of these catalysts can be ordered as follows: AK25 > DK25 > EK25. When use was made of the AK25 catalyst in the HDA of the light diesel oil fraction, the content of aromatics decreased from 25 wt.% (feed) to 1.5 wt.% (product). The product was found to contain primarily monoaromatics.

5. Conclusions

The study enables the following conclusions to be drawn:

1. Titania distribution in the titania–silica support depends on the method of support preparation and influences the reducibility and distribution of nickel oxide; as the quantity of titanium increases, so does the quantity of nickel.
2. Titania–silica supports obtained by deposition of TiO_2 onto silica surfaces (TiO_2/SiO_2) via TiPOT (AK catalysts) and $TiCl_4$ (DK catalysts) are more efficiently used in the preparation of hydrogenating catalysts than titania–silica supports prepared by the sol–gel method (TiO_2–SiO_2; EK catalysts). The use of TiPOT for the preparation of TiO_2/SiO_2 increases the reducibility of nickel oxide, as well as the acidity and specific surface area of the catalyst.
3. The TPR profiles provide evidence supporting the bimodal nature of the Ni species fixed to the TiO_2/SiO_2 supports that were obtained via hydrolysis of $TiCl_4$ (DK catalysts).
4. According to the precursor of titanium and the method used for the preparation of the TiO_2/SiO_2 supports, the catalysts contain anatase (AK) or rutile (DK).

5. The increase in the TiO_2 content brings about a reduction in the S_{BET} and an increase in the acidity of the catalysts, regardless of the method used for the preparation of the supports.
6. The catalytic properties of nickel catalysts supported on titania–silica were found to depend on the quantity of incorporated TiO_2. Thus, the catalysts of a 25 wt.% TiO_2 content were characterised by the highest hydrogenating activity.
7. It has been demonstrated that using a support containing 25 wt.% of TiO_2, prepared by deposition of TiO_2 on the silica surface via hydrolysis of titanium isopropoxide, it is possible to obtain a hydrogenating catalyst characterised by a high activity at a low content of the active ingredient (5 wt.% Ni).

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