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 $\gamma$-$Al_2O_3$-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