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Nickel niobia interaction in non-classical Ni/Nb$_2$O$_5$ catalysts

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Abstract

Non-classical Ni/Nb$_2$O$_5$ catalysts [Ni introduced by the simple (SIM) or EDTA-double impregnation (DIM) methods] were prepared by aqueous hydrazine reduction at 353 K. Their structural and surface properties were investigated by XRD, TEM, XPS techniques, and by H$_2$-TPR, H$_2$- or O$_2$-adsorption and isopropanol decomposition measurements. The results obtained confirmed that niobia is a typical SMSI oxide. Indeed, the hydrazine reduced the support and not the supported Ni^{2+} ions due to the SMSI effect. Reduction proceeded only in case of a layer of Ni^{2+} ions weakly bonded to a sub-layer of Ni^{2+} ions strongly attached to the support. This was achieved by stepwise impregnation with the nickel precursor. A very strong nickel–niobia interaction plays a crucial role in the passivation phenomenon of nickel active sites towards hydrogen or in gas phase hydrogenation of benzene. The SMSI effect was in parallel studied on classical catalysts prepared by the SIM or DIM method for comparison.
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1. Introduction

Supported metal catalysts find a variety of applications in the petrochemical and environmental industries [1]. Especially nickel catalysts are commonly used in many industrial processes including hydrogenation, hydrotreating, hydrogenolysis of hydrocarbons, methanation and steam-reforming. The activity and selectivity of a supported metal catalyst are strongly influenced by the amount of metal, the size of dispersed metal particles, the preparation method and the support composition [1–3]. Evidence has been found that in many systems the carrier exerts a marked influence on the properties of the metal particles supported on it [2]. The application of H$_2$Na$_2$EDTA in the stage of nickel catalysts preparation favored a high dispersion of an active phase [4–6]. Nickel nanoparticles have been successfully prepared by chemical reduction in the presence of a surfactant [7] or a support [8] which prevents from an agglomeration. Hydrazine was used [8,9] because it is a good reducing agent in aqueous medium for noble and transition metals ions [9–11].

In the previous work [12] we studied nickel (1 wt.%) classical and non-classical catalysts supported on Al$_2$O$_3$, SiO$_2$ and Nb$_2$O$_5$ oxides. The metal precursor was deposited on the support using simple (SIM) or EDTA-double impregnation (DIM) methods. Non-classical catalysts were obtained by pretreatment of the SIM or DIM nickel precursors in aqueous hydrazine at 353 K. The catalysts prepared exhibited various nickel species due to the existence of various metal–support interaction strengths. As a consequence, the reducibility, surface or hydrogenating properties changed as a function of the nature of the support or method of preparation. The metal–support interactions are the highest when niobium oxide is used as the matrix. It was also shown that hydrazine formed stable complexes with nickel and was adsorbed on the support with a strength depending on the nature of the oxide.

In this paper we focus on nickel catalysts supported on Nb$_2$O$_5$ which exhibited the strongest metal–support interactions. Special attention is paid for non-classical catalysts. Indeed, in this case, SMSI prevents the reduction of supported Ni^{2+} ions by aqueous hydrazine not only for 1% Ni content, as previously reported, but for 5% Ni content also. The SMSI persisted even when EDTA was pre-adsorbed on the support and prevented the reduction of nickel. In contrast, the hydrazine reduced the support and formed stable surface N–H species. We show here

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that the negative effect of the support on Ni^{2+} ions reduction could be overcome by using a stepwise impregnation. We also report a new insight on the structural and surface properties of catalysts by XRD, TEM and XPS measurements not previously used. The catalysts were also investigated by H_2-TPR, H_2-adsorption, O_2-adsorption and isopropanol decomposition. The catalysts were prepared with 1%Ni or 5% loading using, as previously described [12], simple (SIM) or double (DIM) impregnation methods and nickel acetate as a precursor. Non-classical catalysts were also studied for comparison.

2. Experimental

2.1. Catalyst preparation

Procedures for classical and non-classical catalyst preparation were the same as previously described [12]. Recall that hydrazine reduction of the material with 1%Ni content led to the blue $[Ni(N_2H_4)_n]^{2+}$ intermediate complex which was not decomposed to metallic nickel and dinitrogen [12]. The same results were obtained for 5 wt.% nickel content with niobia as the support. Nevertheless, we succeeded when a stepwise procedure was employed for 5 wt.%Ni content. Three successive impregnations of Nb_2O_5 with nickel acetate were carried out in order to obtain 1, 3, then 5 wt.% of Ni. After each impregnation step, the obtained solid was filtrated and then dried. The final 5 wt.%Ni solid was reduced in aqueous hydrazine: the blue color of $[Ni(N_2H_4)_n]^{2+}$ complex was changed to the dark color of metallic nickel whereas dinitrogen evolved in the exit gas. Hydrazine reduction of 3 wt.%Ni supported precursor, obtained by impregnating a 1 wt.% Ni content sample, also failed.

Classical and non-classical catalysts are denoted as xNi/Nb_2O_5 and xNi/Nb_2O_5 (HYDZ), respectively, where x is the nickel content and HYDZ the hydrazine method of preparation.

2.2. Catalyst characterization and testing

H_2-TPR, H_2-adsorption, O_2-adsorption and isopropanol decomposition experiments were previously described in details [12]. We summarize the procedures. The H_2-TPR study was carried out from room temperature to 1123 K using H_2/Ar (1000 ppm H_2) mixture as a reductant. H_2 or O_2-adsorption was performed on reduced samples (0.1 g). H_2-adsorption was carried out by flowing the sample with a mixture of 100 ppm H_2/argon at room temperature. The degree of nickel reduction was determined by O_2-adsorption by injection of a mixture of O_2/Ar (100 ppm O_2) for 1 h at 823 or 723 K for classical and non-classical catalysts, respectively. The reduction was performed by pure hydrogen for 2 h at 773 or 673 K for classical or non-classical catalysts respectively. Isopropanol decomposition was performed at 523 K using 5 μl pulses of isopropanol after activation at 673 K for 2 h.

The XRD patterns were recorded with a classical Θ/2Θ diffractometer using Cu Kα radiation ($\lambda = 1.54056$ nm). The electron microscopy images were obtained with a Phillips CM20

STEM after placing a drop of the catalyst suspension on the carbon coated copper grid. X-ray microanalysis of chemical compositions were determined using energy dispersive X-ray spectroscopy mounted on the Phillips microscope. The XPS spectra were recorded on a KRATOS AxisULTRA spectrometer using Al Kα radiation (150 W). The samples were deposited at room temperature under ultra high vacuum on a copper surface.

The hydrogenation of benzene was carried out in a fixed bed quartz reactor over 0.1 g of catalyst under atmospheric pressure and in the temperature range 348–498 K [12].

3. Results and discussion

### 3.1. Reduction of supported Ni^{2+} ions by aqueous hydrazine

The attempts of reduction of SIM as well as DIM catalysts by hydrazine failed. Indeed, in the reduction of nickel by the hydrazine, the reaction is expected to proceed according to the following equation [8,9]:

$$2Ni^{2+} + N_2H_4 + 4OH^- \rightarrow 2Ni^0 + N_2 + 4H_2O \qquad (1)$$

The green color of Ni^{2+} ions first changes to blue, that of the $[Ni(N_2H_4)_n]^{2+}$ complex intermediately formed, then progressively to dark, that of colloidal Ni^0 particles. In addition, dinitrogen evolves in the exit gas from the reduction flask. The blue complex is formed via the substitution of water ligands by hydrazine ligands and decomposes by heating. For Ni/Nb_2O_5 precursor, these changes did not occur and no gaseous dinitrogen evolved whatever the nickel content used: 1, 3, or 5 wt.%. This is ascribed the formation of a very stable $[Ni(N_2H_4)_n]^{2+}$, firmly attached to the niobia support. For silica supported Ni^{2+} ions, it was previously shown that the reduction occurs in the same hydrazine media with a rate and a conversion depending on the nickel content and reaction conditions [13].

In contrast, we remarkably succeeded in nickel reduction by using a stepwise procedure in case of 5%Ni content catalyst. Indeed, after three successive impregnations (1, 3 and 5 wt.%Ni), the final solid 5%Ni/Nb_2O_5 (HYDZ) was prone to the reduction by aqueous hydrazine at 353 K. The green color of the solid was changed to blue then dark and nitrogen was detected in the exit gas (see Eq. (1)).

It is now well established that stepwise impregnation of Ni/SiO_2 catalysts leads to strongly and weakly adsorbed Ni^{2+} [14]. Nickel in strong interaction is obtained by impregnation of the nickel salt followed by water washing or by ion exchange then calcination. Nickel in weak interaction is obtained by impregnation to Ni^{2+} ions previously strongly attached to silica. The latter ions serves as a "chemical glue" [15] to the former. Nickel in strong interaction is identified as phillosilicates or grafted nickel depending on the preparation conditions. The anchoring of the metal particles onto the support was found to occur via Ni^I or Ni^{II} ions located at the metal-support interface [16]. Basing on these data one can suggest that, for Ni/Nb_2O_5 catalysts, nickel ions are strongly anchored to the support up to 3% content and thus cannot be reduced by the hydrazine.

Fig. 2. XRD pattern of the 5% Ni/Nb$_2$O$_5$ catalyst after H$_2$ treatment at 773 K.
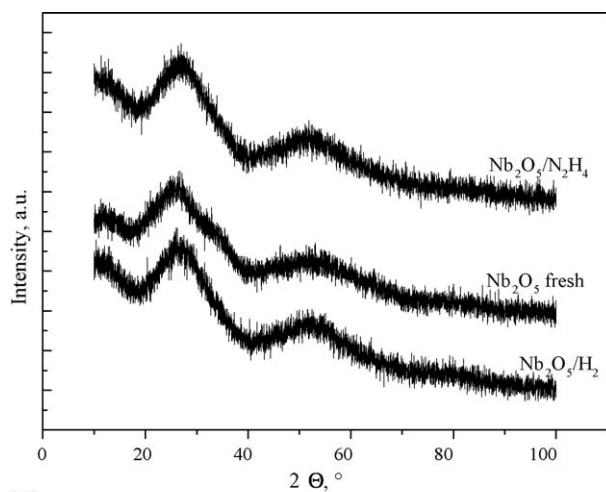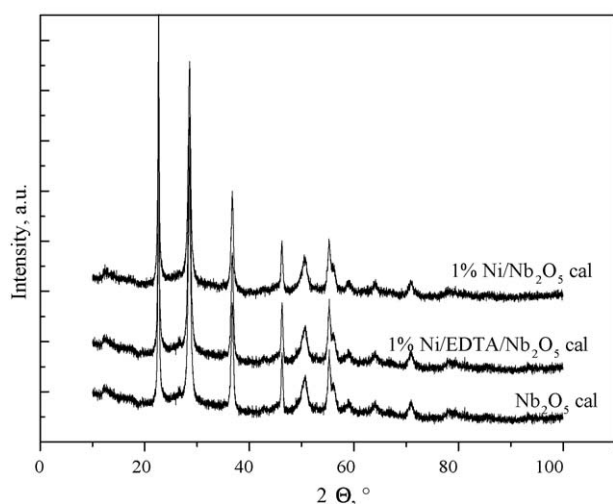
Fig. 1. XRD patterns of the catalysts: (A) Nb$_2$O$_5$ fresh and after H$_2$ and N$_2$H$_4$ treatments; (B) calcined Ni/Nb$_2$O$_5$ classical catalysts.

These ions, in turn, make up an interface on which the excess nickel introduced by the third impregnation weakly adsorbs and, consequently, becomes more reducible and gives rise to metallic nickel phase: the reduction by hydrazine then proceeds via reaction (1).

3.2. Catalyst characterization

3.2.1. XRD study

Fresh hydrated Nb$_2$O$_5$ is amorphous. This was confirmed by the XRD patterns (Fig. 1A). The H$_2$ as well as hydrazine treatment did not change the structure of niobium pentoxide (Fig. 1A). In contrast, the XRD pattern of the calcined Nb$_2$O$_5$ showed a crystallized phase of niobium oxide with the hexagonal structure (Fig. 1B).

Impregnation of the support with 1 wt.% of nickel does not change the hexagonal order of the material. However, at the higher nickel content (5 wt.%), the XRD patterns (Fig. 2) showed two crystallized phases after the hydrogen treatment at 773 K. The first phase with the main reflection peaks at 22.686 and
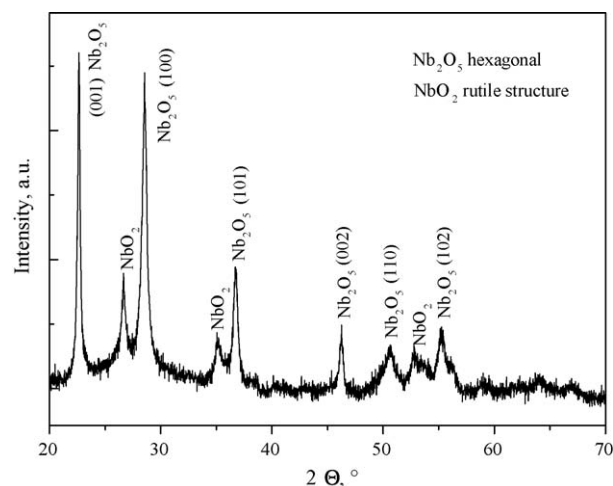
28.585 could be ascribed to hexagonal Nb$_2$O$_5$ and the second with the main peaks at 26.132, 35.336 and 51.954 to the rutile structure of the NbO$_2$ phase [17]. The hydrogen treatment of Nb$_2$O$_5$ provided the change of the sample color from white to gray which could confirm the partial reduction of white Nb$_2$O$_5$ to black NbO$_2$.

XRD patterns for both 1 and 5 wt.% Ni catalysts did not show peaks which could originate from metallic nickel. However, one should remember that XRD technique is not sensitive if the amount of phase is too low (less than 5 wt.%). Moreover, if the particle size of nickel is very small, XRD patterns cannot detect them.

3.2.2. TEM study

The TEM micrographs of the classical 5%Ni/Nb$_2$O$_5$ and non-classical 5% Ni/Nb$_2$O$_5$ (HYDZ) catalysts are shown in Fig. 3. For the former catalyst, the TEM image showed well dispersed nickel particles with the average particle size of 30 nm (Fig. 3A). The TEM image of the non-classical catalyst differs from that of classical one. Indeed, the nickel particles are not visible (Fig. 3B). However, the X-ray microanalysis carried out on this sample showed the presence of the reduced nickel species. Very small nickel particles (∼1 nm) are formed and not detected by the TEM technique used in this study. The method of preparation strongly influences the final metal particle size.

3.2.3. XPS study

3.2.3.1. Niobium oxide. The XPS Nb 3d$_{5/2}$ spectra of the pure Nb$_2$O$_5$ and Nb$_2$O$_5$ (HYDZ) samples (Fig. 4A) show two well defined peaks at 207.1 and 209.5 eV which correspond well to the reported binding energies of Nb$_2$O$_5$ [18]. The O 1s (Fig. 4C) spectra of both samples are also nearly the same. There is one predominant peak at 529.8 eV which originates from the skeleton oxygen from Nb$_2$O$_5$. A second peak at 532.7 eV could be attributed to the formation of hydroxyls groups on the catalyst surface.

Interestingly, the spectra of the Nb$_2$O$_5$ (HYDZ) sample, exhibit a N 1s peak (Fig. 4B) at a binding energy BE = 400 eV due to N$_2$H$_4$ adsorbed on the surface [18].
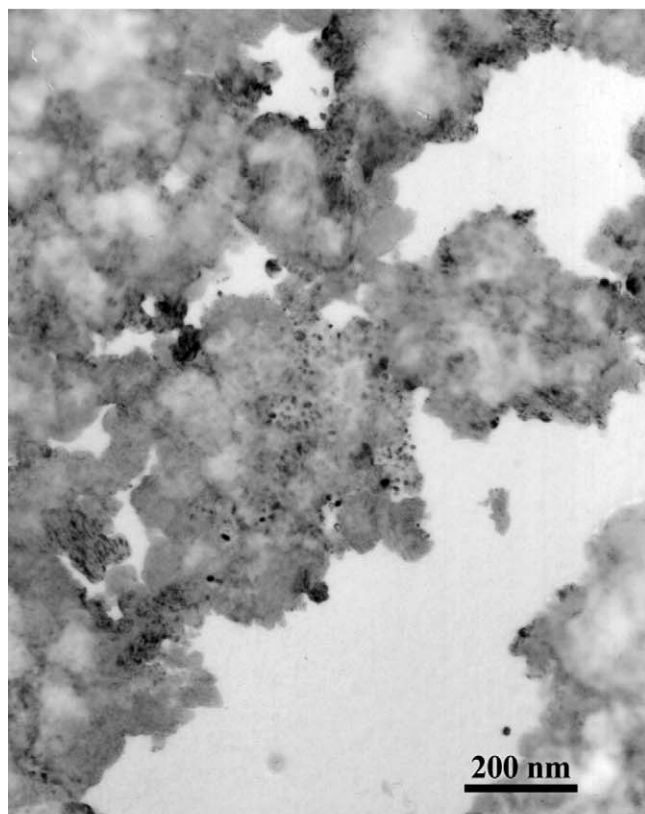
(A)
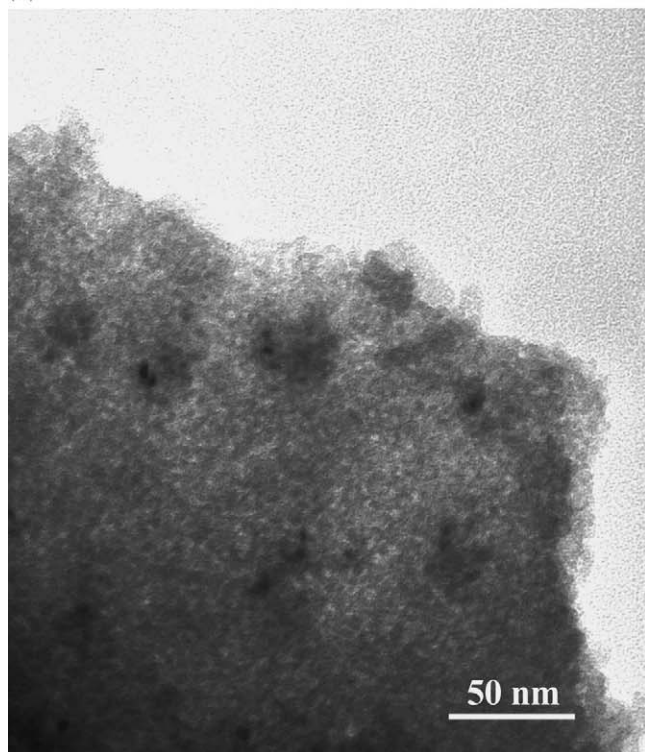
(B)

Fig. 3. TEM images of classical 5% Ni/Nb$_2$O$_5$ (A) and 5% Ni/Nb$_2$O$_5$ (HYDZ) catalysts (B).

3.2.3.2. Ni/Nb$_2$O$_5$ catalysts. The XPS spectra of classical 5%Ni/Nb$_2$O$_5$ and non-classical 5%Ni/Nb$_2$O$_5$ (HYDZ) catalysts were recorded before and after hydrogen reduction at 773 K.

The XPS Nb3d$_{5/2}$ spectra of the calcined classical catalyst and fresh hydrazine treated catalysts (Fig. 4A) are very similar and show the same peaks from niobium oxide. It means that the reduction with hydrazine does not change the structure of the niobium species. Contrary to that, the XPS spectra of catalysts reduced by hydrogen show four peaks at 209.5, 208, 207.1, and 205.5 eV. The peaks at 208 and 205.5 originate from NbO$_2$ oxide [18]. It is known that the high temperature reduction (1073–1573 K) of Nb$_2$O$_5$ with hydrogen gives the bluish–black dioxide NbO$_2$ that has a distorted rutile structure and is diamagnetic. This reduction is reversible [19]. In the case of this work, the temperature of the hydrogen treatment is much lower (773 K) and nevertheless the reduction occurred, although probably for a few superficial oxide layers (gray color instead of dark). This could be ascribed to the presence of nickel in the surface layers which promoted the niobium partial reduction. This reduction is in a good agreement with the XRD study findings.

The O 1s region was also investigated (Fig. 4C). The analysis of the corresponding spectra showed the presence of two peaks at 529.7 and 532.7 eV for classical catalysts calcined or reduced. The main peak at 529.7 eV is related to the oxygen anions, O^{2-}, bound to the metal cations in the lattice [18]. The second peak at 532.7 eV could be attributed to the formation of hydroxyl groups on the catalyst surface. Non-classical 5% Ni/Nb$_2$O$_5$ (HYDZ) catalyst also showed one well defined peak at 529.7 eV which originates from the O^{2-} anions. However, the hydroxyl group peak at 532.7 is much less intense.

The Ni 2p$_{3/2}$ spectrum of the calcined classical catalyst exhibits a peak at 856.1 eV, characteristic of the presence of Ni$_2$O$_3$. The spectrum (not shown here) of H$_2$ reduced classical catalyst shows one very small but detectable peak at 852.5 eV which corresponds to Ni^0 [18]. The spectra of fresh and reduced non-classical catalysts show the presence of the Ni$_2$O$_3$ only, detectable by the peak at 856.1 eV. The absence of Ni^0 on the surface of the catalyst can be explained by the reoxidation of the nickel particles by air during the drying. Note that small nickel particles of the hydrazine treated catalyst are more rapidly oxidized than the larger ones for classical catalyst. Moreover, the low concentration of surface nickel species detected by XPS could confirm the passivation of nickel by niobium. The catalysts were not activated in hydrogen before the XPS study.

The N 1s spectra of the hydrazine catalyst (Fig. 4B) shows one peak at 400 eV due to the N$_2$H$_4$ adsorbed on the surface. The position of the peak, identical to that found for Nb$_2$O$_5$ (HYDZ) alone (Fig. 4B) shows that hydrazine is probably adsorbed only on the niobium oxide support.

3.2.4. Isopropanol decomposition

The acidity of the support plays a crucial role in the chemistry of the supported nickel catalysts [12]. The acidity of the hydrated niobia used as the support and the classical catalysts was estimated on the basis of isopropanol dehydration (Fig. 5). Dehydration towards propene formation as well as reaction pro-
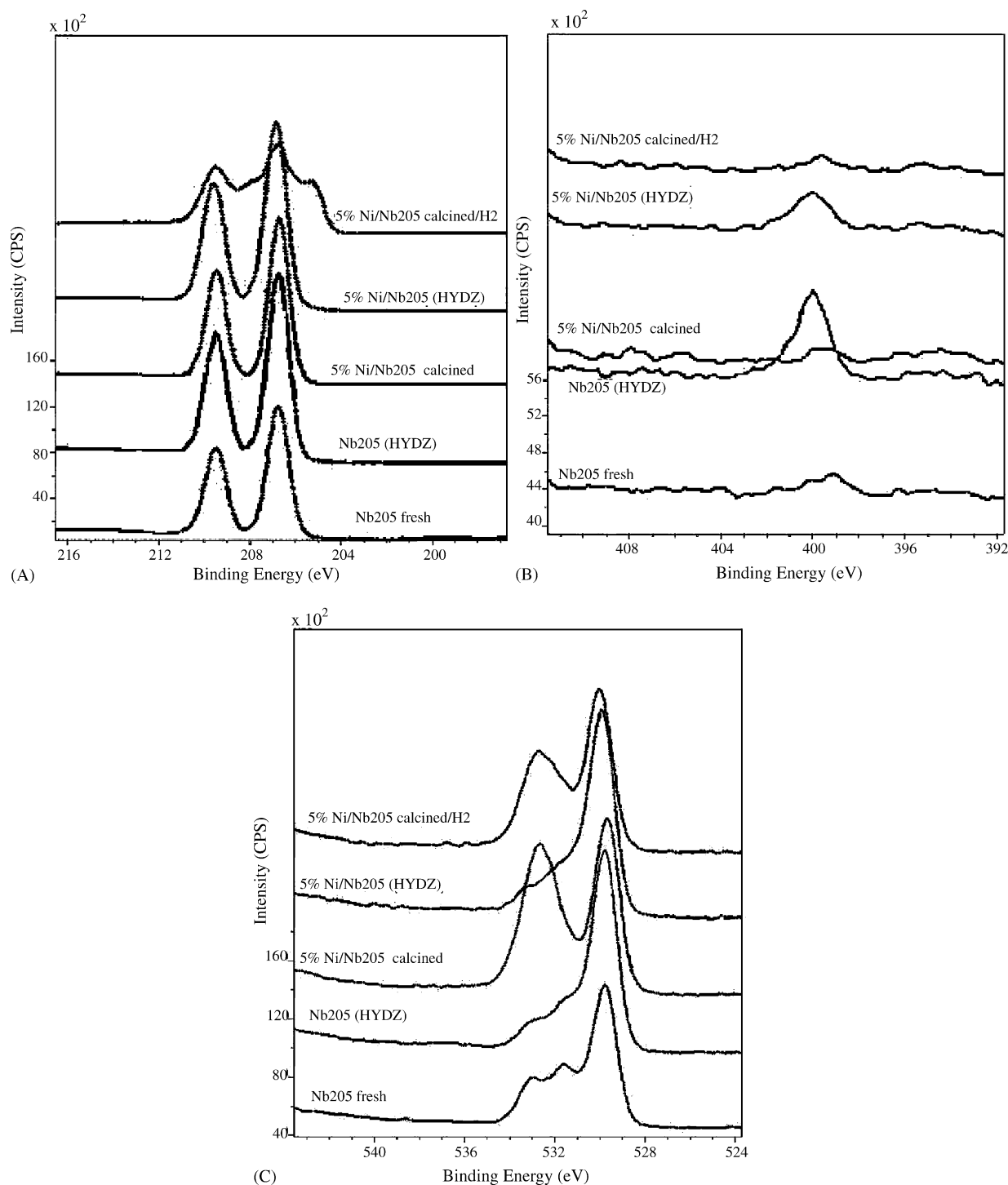
Fig. 4. XPS profiles of Nb $3d_{5/2}$ (A), N 1s (B) and O 1s (C) regions.

ducing diisopropyl ether occurs with the participation of acidic centers on the catalyst surface. For all catalysts tested, propene was the main reaction product indicating acidity of the materials. Moreover, the high conversion of alcohol (>15%) confirmed the high acidity of the niobia oxide materials. Remarkably, in the presence of nickel, the conversion increased. Moreover, the results showed that the impregnation with EDTA salt decreases the acidity of the final material.

Because of the high acidity of the support one can expect the strong interaction of Nb_2O_5 with the nickel salt. In fact, acidic hydrated niobia oxide reacted chemically with Ni-acetate during the impregnation followed by calcination. This was evidenced by IR spectroscopy measurements as previously reported [12]. IR bands in the skeletal region for hydrated Nb_2O_5 and that detected for Ni-impregnated samples were compared. In case of both impregnated methods the final materials exhibit well
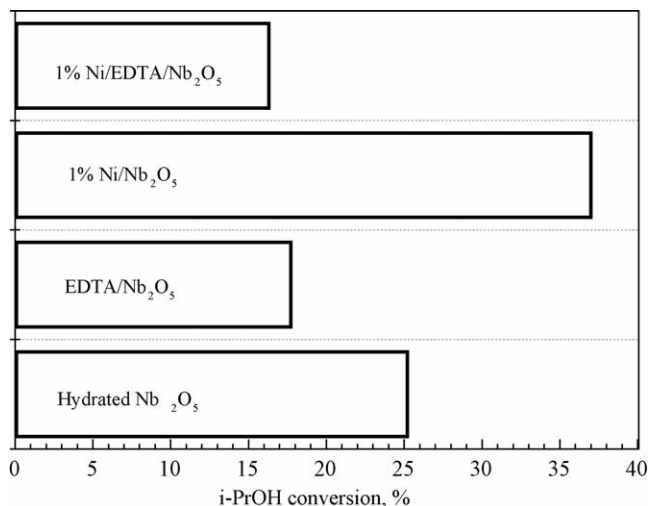
Fig. 5. Isopropanol decomposition at 523 K.

resolved bands in the 500–1000 cm^{-1} region not characteristic for the initial support. It indicates the chemical reaction between nickel species and niobia support leading to the change in the IR spectra.

3.2.5. H$_2$-TPR study

Previous work showed the influence of the method of preparation on the H$_2$-TPR profiles of 1%Ni catalysts [12]. Comparing these results with the H$_2$-TPR profiles of both 5%Ni catalyst and bare support gives more insight on the metal-support interactions involved.

3.2.5.1. Support. The pristine Nb$_2$O$_5$ support, previously calcined, is reduced under hydrogen flow (100 ppm/Ar) at 723 K as shown in Fig. 6A. The main step of reduction occurs at 1023 K and is ascribed to the reduction of bulk niobium oxide, in a good agreement with the XRD and XPS studies presented above. A second peak is also observed from 523 K. It could be due to the reduction of NbOx superficial species. The reduction of the superficial oxide species reduction could also account for the shoulder arising at 750 K. The partial reduction of the support could be confirmed also by the change of the sample color after TPR test from white to gray.

It is worth noting that the H$_2$-TPR of pure Nb$_2$O$_5$ calcined in air at 773 K for 5 h has been reported [20] and did not show any reduction peaks up to 773 K. This may originate from the oxide precursor which was supplied from another commercial source.

The H$_2$-TPR profile of Nb$_2$O$_5$ somewhat changed after a treatment in aqueous hydrazine (Fig. 6A). Pure Nb$_2$O$_5$ support, previously treated in aqueous hydrazine, consumed very small amount of hydrogen which gave rise to a peak at around 1050 K, ascribed to the reduction of bulk niobium oxide. In contrast, the peak at 523 K and a shoulder at 750 K were absent and, in addition, the oxide released gaseous nitrogen at 440 K (Fig. 6D). In the basic aqueous media, the fresh oxide reacted with hydrazine and formed stable NH-surface species. These species were evidenced by the XPS study. They decomposed by the heating under hydrogen during the TPR experiments. Super-

ficial reduction of the support by hydrazine may explain the absence of the reduction peak at 523 K and the shoulder at 750 K. The low consumption of hydrogen during the TPR experiments may be ascribed to the previous reduction of Nb$_2$O$_5$ in hydrazine media. It could also be explained by the formation of superficial Nb^{n+} species which would prevent a high reduction of the oxide.

3.2.5.2. Classical catalysts. The TPR profiles of the calcined classical catalysts comprise two peaks (Fig. 6B). The high temperature peak (900–1050 K) may be ascribed to niobium reduction whereas the lower temperature peak (700–850 K) may be due to the reduction of nickel species strongly interacted with the support [20]. Very strong Ni–niobium oxide interactions are very well known [20–24]. It causes a mutual influence on the reduction of the two components. Thus the temperature of the peak of the support reduction decreases to 978 K for the 1%Ni catalysts whereas it is not changed after the incorporation of 5%Ni nickel (see Fig. 6A and B). Simultaneously, the peak of reduction of nickel is more intensive for the 1%Ni catalysts (783–838 K) as compared to that of the 5%Ni catalyst (695 K) (Fig. 6B). For the 1%Ni catalysts, the DIM preparation gives rise to a higher reduction temperature of nickel as compared to the SIM preparation [12].

These results reflect the various strengths of metal–support interactions in the catalysts. Let us first consider nickel reduction. At a low nickel loading, a great part of nickel atoms is in a close contact with the support, also the high temperature peak prevails for nickel reduction. In contrast, at a higher loading, a part of the Ni precursor not directly or less attached to the support will probably more easily form NiO species, which are reduced at lower temperatures. If one consider the support, its temperature of reduction is lowered by the strong interaction with nickel in the presence of 1% metal loading. At the higher loading of 5% the weakness of metal-interaction does not change the reduction temperature of Nb$_2$O$_5$.

The H$_2$-TPR study of 2–15%Ni/Nb$_2$O$_5$ catalysts was reported [20]. Examination of the profiles showed that the peak of reduction occurred at temperatures depending on the nickel loading. This was ascribed to the existence of a strong metal–support interaction.

3.2.5.3. Non-classical catalysts. The non-classical catalysts exhibit H$_2$-TPR profiles due to presence of unreduced nickel species. These species may arise from an incomplete reduction of the supported Ni^{2+} ions by hydrazine [13] or from reoxidation of Ni^0 species due to moisture contamination. The TPR profiles of the Ni niobia supported catalysts prepared with hydrazine treatment (Fig. 6C) differ from that of classical catalysts (Fig. 6B). There is only a more or less well-defined peak with the maximum at 780–790 K (1 wt.%Ni) or 723 K (5 wt.%Ni) which originates from the reduction of nickel species. Stronger interactions are expected to occur in 1 wt.%Ni catalyst. The small peak at 450 K in case of 5%Ni content can be attributed to isolated NiO particles more easily reduced. The partial reduction of this catalyst is attested by a change of the color from green to gray. The peak of support reduction is not
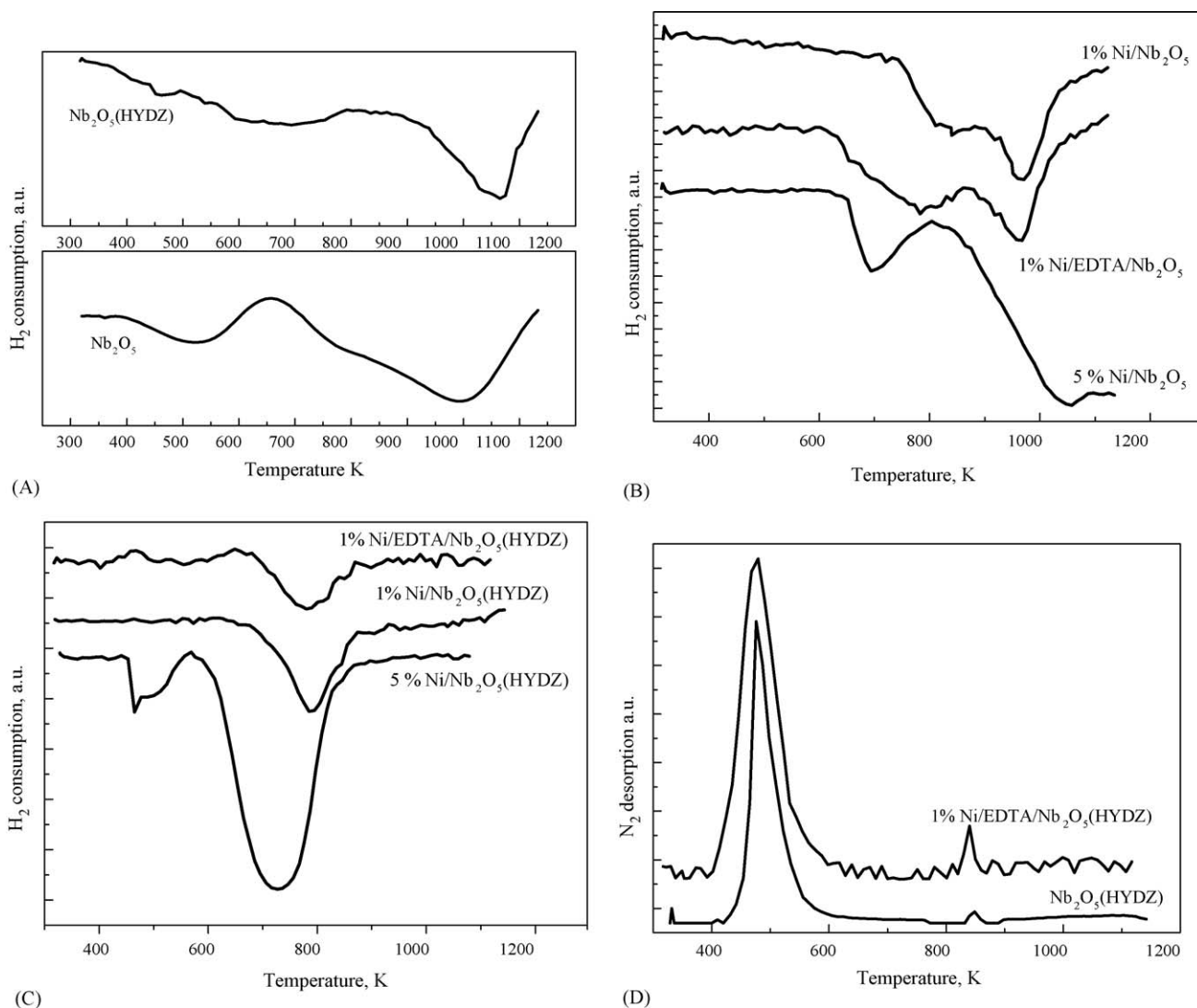
Fig. 6. H_2-TPR profiles: (A) Nb_2O_5 fresh and after N_2H_4 treatment; (B) classical catalysts; (C) non-classical catalysts; (D) N_2 desorption during H_2-TPR study.

observed in the temperature range examined. One may speculate that the support was reduced in the aqueous hydrazine media due to the presence of nickel.

The N_2 desorption, due to the decomposition of hydrazine species adsorbed on the surface, was previously observed for the catalyst with 1 wt.% Ni loading [12]. This is shown in Fig. 6D for DIM catalysts, still not reported. A main peak arises at 440 K (with a shoulder) and a smaller one at 830 K. These peaks are ascribed to different adsorption sites of hydrazine on the niobia support. N_2 desorption was not observed for 5% Ni/Nb_2O_5 (HYDZ) catalyst. Excess nickel ions prevented the reaction of hydrazine with the niobia support.

3.2.6. Degree of reduction

The amount of reduced nickel atoms was measured by oxygen adsorption at 723 or 823 K after a treatment under pure hydrogen for 2 h at 673 and 773 K. The obtained results are reported in Table 1.

It is known that the high temperature reduction of Nb_2O_5 with hydrogen gives the bluish-black dioxide NbO_2 that has a distorted rutile structure [19]. The presence of the NbO_2 phase

with a rutile structure was well confirmed by the results of XPS and XRD studies. This reduction is reversible and the NbO_2 reoxidation gives rise to Nb_2O_5. Taking into account this reaction, the degree of reduction after H_2 treatment at 773 K was calculated as 54.4% for calcined Nb_2O_5 and 27% for Nb_2O_5 treated with aqueous hydrazine (Table 1).

Table 1
Degree of reduction of the Ni/Nb_2O_5 catalysts

Catalyst	Amounts of O_2 consumed (mol g_{cat}^{-1}) $\times 10^{-5}$	Degree of reduction calculated (%)
1% Ni/Nb_2O_5	24.28	78
1% Ni/EDTA/Nb_2O_5	25.22	89
5% Ni/Nb_2O_5	70.11	123
Nb_2O_5	17.63	56
1% Ni/Nb_2O_5 (HYDZ)	17.59	87
1% Ni/EDTA/Nb_2O_5 (HYDZ)	19.26	104
5% Ni/Nb_2O_5 (HYDZ)	47.29	89
Nb_2O_5 (HYDZ)	10.23	27

Pre-treatment: H_2/673 K:2 h.

This reaction was also taken into account for the calculation of the reduction degree of the nickel–niobia catalysts, supposing the same degree of support reduction. This is an approximation since, in the presence of nickel, the reduction of Nb_2O_5 was facilitated according to the TPR study. The values obtained are in fact maximums degree of reduction. From Table 1 it can be seen that the degree of reduction changes with the nickel content and method of preparation.

The classical 1% Ni/EDTA/Nb$_2$O$_5$ catalysts showed a higher degree of reduction than that of the SIM catalyst (89.3% against 78.2%). This is also the case of 1%Ni non-classical catalysts (104% against 87%). One can suppose that EDTA ions could facilitate the reduction of nickel species formed on the surface when Nb_2O_5 support is applied. These results also show an improvement in nickel reduction for hydrazine treated catalysts. This may be due to the existence of smaller nickel particles as showed from the XRD and TEM studies.

Remarkably, 5%Ni/Nb$_2$O$_5$ classical catalyst exhibits a degree of reduction (123%) which exceeds the stoichiometric ratio. This high maximum value may reflect excess reduction of niobium oxide (>56%) in the presence of nickel, not taken into account in our calculations. In contrast, for hydrazine treated materials, increasing nickel content to 5 wt.% does not increase the degree of reduction, although the metal phase became more reducible according to the TPR study (Fig. 6). Recall that 5%Ni/Nb$_2$O$_5$ (HYDZ) comes from a stepwise preparation method which included the intermediate formation of nickel species firmly attached to the support. These species were less prone to reduction.

The method of preparation influences on the interaction of the catalyst surface with hydrogen.

3.2.7. H$_2$ adsorption study

After a H$_2$ thermal treatment, SIM and DIM classical as well as non-classical catalysts did not adsorb hydrogen at room temperature. This is true for 1 or 5 wt.%Ni contents. It could be attributed to a very strong interaction of nickel particles with the matrix [19,22]. As evidenced from the IR spectra, the nickel ions react with the niobium oxide providing the blockage of the hydrogen adsorption capacity of nickel.

Hydrogen adsorption on Nb$_2$O$_5$ supported nickel catalysts has been already reported for higher nickel contents (2–15%) [20]. Very low metal surface areas ($\leq 1\,m^2\,g^{-1}$) were found after a reduction with hydrogen at the temperature of 673 K, i.e. nickel atoms are not easily accessible for hydrogen. SMSI would be responsible for the suppression of hydrogen adsorption. However, it was suggested that, during the reduction and cooling down the sample in flowing hydrogen, the nickel surface remained covered with hydrogen atoms [20,22,23].

3.3. Catalytic activity in benzene hydrogenation

After a H$_2$ thermal treatment, the niobia supported catalysts are not active in the gas phase hydrogenation of benzene to cyclohexane. Only the classical 5%Ni exhibits some activity (1.1% of conversion at 448 K). The absence of activity is ascribed to strong metal–support interactions, which hides the access of

nickel to the reactant molecules [25]. Nickel particles on the niobia surface did not present catalytic activity and are randomly distributed at the surface, and then the catalytic activity decay is expected to be of the same order of magnitude as surface coverage. Another reason of inactivity may reside on the mechanism of benzene hydrogenation. It is admitted that the support can furnish the adsorption sites for the aromatic molecule, in the form of carbonium ions, and in the vicinity of the metal particles, the adsorbed molecule can react with the spilt-over hydrogen from the metal [26–28]. In the case of this work, niobium oxide is acidic and probably strongly adsorbs the benzene molecules and may suppress the catalytic activity. It is worth noting that Ni/Nb$_2$O$_5$ catalysts were found active in hydrogenation of carbon monoxide [22,23]. In this case, the adsorption strength of CO on the support is much weaker than that of benzene and also CO is more easily converted.

4. Conclusion

The results obtained in this work confirmed that niobia is a typical SMSI oxide. The SMSI effect is manifested in the preparation of non-classical catalysts. Indeed, in this case, it prevents the supported Ni^{2+} ions from the reduction by aqueous hydrazine for 1, 3 or 5 wt.% Ni content. The prevention in nickel reduction is also observed when the support is pre-adsorbed with EDTA. Only when stepwise procedure is performed the reduction could proceed: superficial Ni^{2+} ions weakly attached are formed and reduced on a layer of nickel species strongly bonded to the support. In contrast, hydrazine reduced the support and formed stable surface N–H species.

The very strong interaction between niobia surface and metal active phase not always is favorable for the catalytic processes. The interaction of nickel with Nb$_2$O$_5$ caused a high suppression of nickel activity in the hydrogenation reaction. Moreover, it was shown that Ni supported on hydrated niobia was not active towards hydrogen.

It could be proposed that preferential deposition on nickel occurred on the niobia monolayer which is more difficult to reduce and which could favor the formation of nickel niobate compounds. The very strong nickel–niobia interaction could play a crucial role in the passivation phenomenon of nickel active sites.

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