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# A study of the promoting effect of noble metal addition on niobia and niobia alumina catalysts

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## Abstract

The catalytic activity of $Nb_2O_5$ and $Nb_2O_5/Al_2O_3$-supported metal catalysts was evaluated in the *n*-heptane conversion, CO hydrogenation and butadiene hydrogenation. After high temperature of reduction (HTR), the metal adsorption capacity decreases on all the samples, due to the reduction of $Nb_2O_5$ with subsequent blocking of metal atoms and bimetallic effect.

It was also observed that the activity decay caused by metal-support interaction was remarkably inhibited on the bimetallics with respect to the monometallics by comparing reaction rates after HTR. Thus, the addition of Rh to Co, Cu to Pd and Sn to Pt on niobia catalysts significantly altered the product distribution in Fischer–Tropsch synthesis (FTS) and in the hydrogenation and dehydrogenation of hydrocarbons, respectively. In addition, an unusual bifunctional effect was obtained in $Pt/Nb_2O_5/Al_2O_3$ catalyst.

*Keywords:* $Nb_2O_5/Al_2O_3$ catalysts; High temperature reduction; *n*-Heptane; Bimetallic effect; Fischer–Tropsch effect

## 1. Introduction

Since Tauster et al. [1,2] reported the SMSI phenomena, there has been much interest to study group VIII metal catalysts supported on reducible oxides such as niobium oxide. After reduction at high temperature, the migration of reduced species of the support onto the metallic particles led to remarkably modification of catalytic and adsorptive properties of the metal. Several reactions have been studied on metal-supported reducible oxides, like titanium and niobium oxides [3–6] and the main observation was that the product selectivity changed, depending on the reduction temperature.

The niobia-supported catalysts showed a higher selectivity toward saturated hydrocarbons in the FTS compared to the alumina supports, after reduction at high temperatures [7]. These results demonstrate strong interaction of cobalt with the support, suggesting the presence of new sites to explain the increase of the selectivity toward hydrocarbons with longer chains. Moreover, the addition of a noble metal can also change the cobalt properties [8–11]. Kapoor et al. [9] reported data of the CO hydrogenation with Ru, Pd and Pt added to $Co/Al_2O_3$ catalysts and found that they are also more selective in $C_5^+$ hydrocarbons.

Recently, $Nb_2O_5$ has also been used as a promoter in metal catalysts supported on $SiO_2$ or $Al_2O_3$ [12].

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The catalytic and adsorptive properties of the catalysts were also drastically modified by the oxide promoter. It has been also reported that $Nb_2O_5$ promoted catalysts exhibit the SMSI effect [4]. However, the metal–$Nb_2O_5$ interaction will be function of the molecular structure of the surface metal oxide species and the surface coverage of the metal oxide overlayer.

The main objective of this review is to present unusual promoting effects involving noble metals on $Nb_2O_5$ and $Nb_2O_5/Al_2O_3$ catalysts and this is displayed through catalytic performances for different reaction like FTS, hydrogenation of 1,3-butadiene and *n*-heptane dehydrogenation.

### 1.1. Fischer–Tropsch synthesis

Fischer–Tropsch synthesis (FTS) is an alternative route to produce long chain hydrocarbons from hydrogen and carbon monoxide. However, one of the most important problems in the FTS is the selectivity limitation [8]. Several studies have been done aiming to overcome these restrictions through the development of new catalysts. These works focus attention on (i) reducible supports, (ii) alloy formation, and (iii) addition of promoters.

Niobium pentoxide as a support material for CO hydrogenation metal catalysts was the subject of a few studies [7,13–17]. These studies have reported that the use of $Nb_2O_5$ as a support results in better CO hydrogenation activities for $Rh/Nb_2O_5$ in comparison to Rh supported on $ZrO_2$, $Al_2O_3$, $SiO_2$, or MgO [16], and for $Ni/Nb_2O_5$ in comparison to $Ni/SiO_2$ [17].

In our laboratory, several studies dealing with niobia-supported cobalt catalysts were performed [7,14,15]. Cobalt catalysts were prepared with 5 wt.% cobalt supported on alumina and niobia by incipient wetness impregnation in order to study the effect of the support on the activity and selectivity of the FTS [7]. As expected, after reduction at high temperature, the hydrogen adsorption and the selectivities of the $Co/Al_2O_3$ catalyst did not change (Table 1). On the other hand, the reduction at 773 K led to a strong suppression of the hydrogen adsorption capacity of the $Co/Nb_2O_5$ catalyst. This chemisorption ability was recovered after high temperature treatment under oxygen followed by reduction at low temperature. These results agree well with SMSI behavior. Furthermore, $Co/Nb_2O_5$ catalyst reduced at 773 K presented a very low methanation activity and a high selectivity towards long chain hydrocarbons in FTS. These results were interpreted in terms of the presence of SMSI effect after reduction at 773 K. Moreover, the effect of the preparation method of niobia-supported cobalt catalysts (containing 5 wt.% Co) was studied in the FTS [15].

Table 1
Selectivity in Fisher–Tropsch synthesis

| Catalyst | $T_{red.}$ (K)[a] | $D$ (%)[b] | Selectivity (%) | | | |
|---|---|---|---|---|---|---|
| | | | $CH_4$ | $C_2$–$C_4$ | $C_5^+$ | $CO_2$ |
| $Co/Al_2O_3$ | 573 | 4.6 | 54.5 | 24.1 | 12.8 | 8.5 |
| $Co/Al_2O_3$ | 773 | 4.5 | 56.2 | 23.6 | 11.4 | 8.8 |
| $Co/Nb_2O_5$ | 573 | 3.8 | 52.3 | 29.3 | 16.1 | 2.3 |
| $Co/Nb_2O_5$ | 773 | 1.0 | 14.1 | 34.8 | 48.8 | 2.3 |

[a] Temperature of reduction.

[b] Cobalt dispersion calculated from hydrogen adsorption at 423 K.

Recently, characterization of niobia-supported cobalt catalysts was performed in order to determine the different types of cobalt species present [18]. XPS and DRS analysis revealed the presence of $Co_3O_4$ particles and $Co^{2+}$ species represented by a mixture of cobalt niobates. According to these authors, after reduction at 773 K, the mixture of cobalt niobates was reduced and the formation of $NbO_2$ led to the SMSI effect that was responsible for the observed selectivity behavior.

The addition of noble metals to a supported cobalt catalyst can also affect the activity and selectivity as described elsewhere [8–11]. It has been proposed that the addition of a noble metal promotes the cobalt oxide reduction. Moreover, the addition of a second metallic element leads to an alloy formation which also affect the catalytic and adsorptive properties.

In principle, the addition of a second metal allows changes in the electronic structure, arrangement and size of atom clusters, and in the adsorption properties [19]. This is beneficial to the CO hydrogenation reaction in particular because carbon chain growth would progress more efficiently on large atom clusters. These positive features of the bimetallics catalysts have been described as “synergistic effects” by several authors. For instance, Co–Ru bimetallic interactions were found to increase reaction rate and selectivity towards $C^{5+}$ hydrocarbons in CO hydrogenation and to improve catalyst regeneration [20–25], reducibility

[26–29] and alcohol synthesis [30]. It is claimed that Co properties in the CO hydrogenation reaction are complemented by adding a noble metal, to lower the reduction temperature and promote better regenerability, both very attractive features for commercial applications. There have been a few studies on Co–Rh catalysts [31–35]. These are promising candidates for improved oxygenate selectivities from the CO/$H_2$ reaction because of the combination of Co's ability in promoting carbon chain growth with Rh's versatility in adsorbing CO molecules either in molecular or dissociate forms [36,37].

A series of Co–Rh/$Nb_2O_5$ catalysts is investigated with respect to their performance in the CO hydrogenation reaction, as an attempt to improve the $C^{2+}$ alcohol selectivity of Co-based catalysts. To this date, there are no catalytic data for Co–Rh/$Nb_2O_5$ catalysts and characterization has not been presented until recently [38]. TPR characterization of these catalysts is discussed and correlated with the XPS characterization results reported elsewhere [38].

Figs. 1 and 2 show that the Rh/Nb catalyst presented a quite diversified and an uncommon product distribution for a Rh-based catalyst. Among the products, we detected high molecular weight olefins, alcohols from ethanol to butanol, and saturated hydrocarbons from 1 to 27 carbon atoms in the chain. Iizuka et al. [16] also observed a considerable amount of heavy hydrocarbons produced from CO hydrogenation on a Rh/$Nb_2O_5$ catalyst.

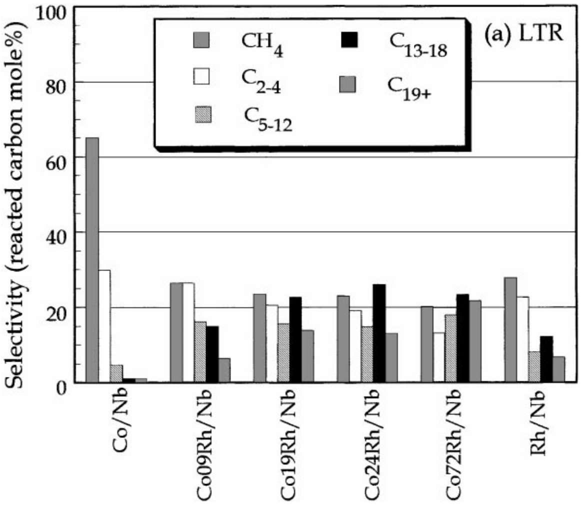

Fig. 1. Hydrocarbons selectivities (based on mol% of C reacted) for the CO hydrogenation reaction (at 423 K and 0.1 MPa, $H_2$/CO=2) as a function of the catalyst sample reduced at 573 K (low temperature reduction — LTR).

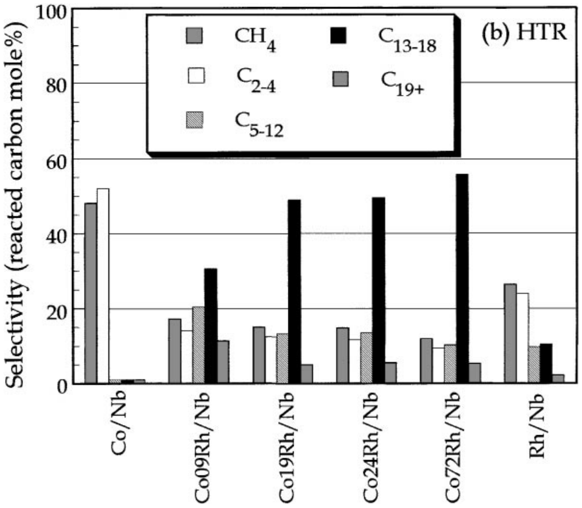

Fig. 2. Hydrocarbons selectivities (based on mol% of C reacted) for the CO hydrogenation reaction (at 423 K and 0.1 MPa, $H_2$/CO=2) as a function of the catalyst sample reduced at 773 K (high temperature reduction — HTR).

The product distributions of these bimetallic catalysts from the CO hydrogenation reaction clearly showed a significant change upon the addition of Rh to Co as opposed to the study of Van't Blik [33] who did not observe a significant difference for Co–Rh on $Al_2O_3$ or $TiO_2$ in the CO/$H_2$ reaction at 523 K, and 1 atm with [$H_2$/CO]=3. Their selectivities towards methane and $C^{4+}$ hydrocarbons were ∼50–70 and ∼10–25%, respectively, consistent with their higher reaction temperature and higher $H_2$/CO ratio which would favor methanation and disfavor the formation of long chain hydrocarbons. In addition, Van't Blik [33] did not observed a noticeable change in product distribution after reduction of their Co–Rh bimetallics at 773 K compared to the reduction at 523 K. Our Co–Rh bimetallics presented a significant alteration of the products selectivities compared to the monometallic Co/Nb. The selectivity towards methane dropped from 65% on the Co/Nb to 20–27% on the bimetallics, depending on the Rh content. The selectivity towards lighter hydrocarbons in the $C_{2-4}$ range also dropped for the bimetallics compared to Co/Nb. A considerable increase of the selectivity in the gasoline range

($C_{5–12}$) was observed, changing from ~5% on the Co/Nb to 13–20% on the bimetallics. However, the most significant effect occurred in the heavier product range, diesel ($C_{13–18}$) and $C_{19+}$, plus the oxygenated compounds (ethanol and propanol).

Increasing the Rh content of the HTR bimetallic catalysts gives a pronounced promotion of the selectivity towards long chain hydrocarbons, specifically in the diesel range. The diesel range selectivity increased from zero on the Co/Nb to 14–25% on the LTR bimetallics, and 31–56% on the HTR bimetallics. Figs. 1 and 2 clearly show that the selectivity towards heavy hydrocarbons, mainly in diesel range, goes through a maximum of around 56% for the Co72Rh/Nb HTR catalysts. An increase on the selectivity towards heavy hydrocarbons was also obtained for a 5% $Co/Nb_2O_5$ catalyst after reduction at 773 K [7]. In that work, this effect was attributed to formation of new active sites from metal-support interactions as discussed earlier. However, the lower Co content and the lower mass of sample tested here suggest that the formation of special species originating from the support were not entirely responsible for the production of heavy hydrocarbons, but also a bimetallic effect must be involved. Increased selectivity for heavy hydrocarbons was also detected on other bimetallic catalysts such as Fe–Co, Co–Ni and Ni–Fe in the CO hydrogenation reaction at 523 K and 10 atm [39]. Iglesia et al. [20] obtained $C^{5+}$ hydrocarbons selectivities in the range 85–91% on $Co–Rh/TiO_2$ catalysts.

The bar diagrams of Figs. 1 and 2 clearly point out that the selectivity towards methane and $C_2$–$C_4$ hydrocarbons for the bimetallics did not vary noticeably with increasing Rh content. Olefins, except $C_4$=, were not detected on the Co-containing catalysts. The $C_4$= content increased relative to butane on the bimetallics, compared to the Co/Nb catalyst. In contrast, the Rh/Nb catalyst was active for the formation of long chain olefins $C_{5–12}$= and $C_{13–18}$= [40]. Villeger et al. [37] had already shown that the addition of Rh to Co catalysts results in increased selectivities towards $C_2$= and $C_3$= in the CO hydrogenation reaction. However, these olefins were not detected in the present study.

We have previously determined from XPS and TPR [38] that the preferred model for the support surface of these bimetallic catalysts after calcination is that of $Co_3O_4$ islands covered by a thin film of $Rh_2O_3$. Therefore, during the reaction, CO promotes the ionic state of $Me^{n+}$ and $Co^{n+}$ forming sites for the insertion of methylene and CO to account for the growth of carbon chains and oxygenates. However, with increasing loading of noble metal it induces agglomeration of the particles, blocking the ionic sites.

### 1.2. Butadiene hydrogenation

The selective hydrogenation of 1,3-butadiene present as an impurity in $C_4$ alkenes cut is a process for production of linear low density polyethylene polymer [41]. However, this process requires high 1-butene purity. Palladium is generally used to hydrogenation of diolefins. But, palladium can also hydrogenate the desired olefins which stimulated several studies to develop more selective catalysts.

Recently, we performed the 1,3-butadiene hydrogenation over $Pd–Cu/Nb_2O_5$ catalysts [42]. The addition of copper increased the 1-butene selectivity and the *trans*/*cis*-2-butene ratio. Furthermore, both bimetallic catalysts were fully selective for the partial hydrogenation, whereas the $Pd/Nb_2O_5$ catalyst was only 90% selective. Copper addition decreased both $H_2$ and CO adsorption capacities and the linear/bridged ratio of the adsorbed carbon monoxide. We attributed these results to a modification of the electronic structure of palladium in $Pd–Cu/Nb_2O_5$ catalysts [43]. Thus, the palladium–copper interaction on niobia-supported catalysts improved the partial hydrogenation selectivity of 1,3-butadiene.

### 1.3. Dehydrogenation of alkanes

Catalytic dehydrogenation processes have presented increasing interest because the high demand for the production of oxygenated compounds in reformulated gasoline and $C_9$–$C_{14}$ mono-oleflns for obtaining biodegradable detergents [44,45]. These processes have also been performed on Pt–Sn catalysts. In summary, the ensemble effect caused by dilution of platinum particles by tin and the ligand effect related to changes in the electronic density of metals are the usual models for explaining the good stability and selectivity obtained for these catalysts. On niobia support, bimetallic and SMSI effects can be important and both ligand and geometric phenomena can modify the structure and the properties of plat-

Table 2
Selectivity in *n*-heptane dehydrogenation at 773 K[a]

| Catalysts | Selectivity (%) | | | |
|---|---|---|---|---|
| | $C_1$–$C_6$ | *i*-$C_7$ | $C_7$= | Aromatics |
| 1% Pt/$Al_2O_3$ | 10 | 11 | 37 | 42 |
| 1% Pt–1% Sn/$Al_2O_3$ | 4 | 15 | 63 | 18 |
| 1% Pt/$Nb_2O_5$ | 7 | 23 | 65 | 5 |
| 1% Pt–1% Sn/$Nb_2O_5$ | 4 | 7 | 78 | 11 |

[a] WHSV=7 $h^{-1}$, conversion ∼5–12%, stationary conditions [4].

inum clusters, the active phase to dehydrogenation. In addition, the acidity of calcined niobia surface is lower than alumina, the standard support to Pt–Sn catalysts. Thus, the usual addition of alkaline metals to decrease the alumina acidity and avoid reactions like hydrocracking, aromatization and isomerization would not be necessary.

In fact, Pt/$Nb_2O_5$ and Pt–Sn/$Nb_2O_5$ catalysts have shown good results in the selectivity for dehydrogenation reactions [46–48]. Table 2 displays the selectivity in *n*-heptane reaction. Light hydrocarbons were negligible in all niobia-supported catalysts, even in the monometallic Pt/$Nb_2O_5$ catalyst. On these catalysts, both the SMSI effect and weak acidic sites were confirmed as observed by $H_2$ and CO chemisorption and TPD of $NH_3$, respectively [47,49]. The suppression of parallel reactions induced Pt/$Nb_2O_5$ and Pt–Sn/$Nb_2O_5$ catalysts to promote a high selectivity towards olefins, the main product.

For these new materials, determination of promoting effect is more complex than on Pt–Sn/$Al_2O_3$. On niobia, both bimetallic and SMSI effect can be important and specific experiences are necessary to evaluate the main mechanism. Ensemble effect was evidenced by decreasing in the turnover frequency of sensitive reactions [47,49]. In fact, the dilution of platinum particles by tin or by reduced $NbO_x$ species observed after reduction at 773 K is largely discussed in the literature [50,51]. The confirmation of electronic effects is more difficult. However, two characterization techniques have suggested an increasing in the electronic density of platinum atoms on Pt/$Nb_2O_5$ and Pt–Sn/$Nb_2O_5$ catalysts.

The maximum desorption peak of CO from the metallic surface of niobia promoted catalysts occurred at 300 K instead of 500 K observed in Pt/$Al_2O_3$ catalyst. The anticipated desorption of CO due to the addition of tin on platinum was discussed by Sachtler and Van Santen [51] for Pt–Sn alloys who used this example to describe the ligand effect. Therefore, these results indicate a probable Pt–Sn alloying on niobia after reduction at high temperature, in agreement with our previous TPR measurements [46]. This explains the different adsorption properties, where CO is weaker bonded to the surface and easier desorbed during the initial heating of the samples.

Moreover, the extrapolation of vibration frequency of linear bonded CO adsorbed at zero surface coverage makes commonly possible a less complex interpretation of the CO–metal interaction by exclusion of CO intermolecular vibrational coupling [52]. For well dispersed platinum catalysts, the extrapolated frequency of CO linearly adsorbed has been observed around 2040–2050 $cm^{-1}$ [53–55]. The results summarized in Table 3 has presented an unambiguous change in the vibration frequency of CO bonded to Pt and Pt–Sn systems supported on niobia. The particle size effect on the CO singleton vibration frequency is not discarded. However, the high differences observed for the values of $\lambda$ ($\theta \Rightarrow 0$) between niobia-supported catalysts and usual platinum surfaces indicates a more elaborate phenomenon. The value obtained for CO singleton vibration frequency (2025 $cm^{-1}$) on Pt/$Nb_2O_5$ is the same attributed to CO adsorbed on platinum which interacts with the support according to Barth et al. [53]. In fact, the shift to lower frequencies is related to increasing of C–O bond strength due to increasing of metal–CO back-bonds [53], so we can propose the electron transfer from partially reduced niobia to platinum particle producing a higher electron density one. Pt–Sn/$Nb_2O_5$ catalysts have also presented alteration in the $\lambda$ ($\theta \Rightarrow 0$) values. Besides, this value has increased with the temperature of reduction which can be related to a stronger Pt–Sn interaction and probably due to alloying process. According to the literature,

Table 3
CO singleton vibration frequency for platinum catalysts [6]

| Catalysts | Temperature of reduction (K) | $\lambda$ ($\theta$=0) ($cm^{-1}$) |
|---|---|---|
| 1% Pt/$Al_2O_3$ | 773 | 2045±3 |
| 1% Pt–1% Sn/$Al_2O_3$ | 773 | 2045±3 |
| 1% Pt/$Nb_2O_5$ | 573 | 2025±3 |
| 1% Pt–1% Sn/$Nb_2O_5$ | 573 | 2052±3 |
| 1% Pt–1% Sn/$Nb_2O_5$ | 773 | 2058±3 |

the higher value for the singleton vibration frequency is ascribed to weaker interaction between carbon monoxide and platinum [55]. These results have induced a different interpretation than on Pt–Sn/$Al_2O_3$ FTIR studies. Balakrishnan and Schwank [55] have shown that ligand effect between platinum and ionic tin promoted a shift towards lower frequencies caused an increase in the electronic density of platinum. Pt–Sn alloying on niobia surface must be rationalized on the basis of competition for d electrons between metal–CO back-bonds and metal–metal bonds. This is in rough agreement with TPD results for CO release, which has showed a easier CO desorption for the bimetallic catalysts supported on niobia.

The Pt–Nb interaction was also studied for Pt/$Nb_2O_5$/$Al_2O_3$ catalysts, aiming to follow the interaction effects on the selectivity towards olefins formation [12]. The Nb content was varied until the monolayer was reached. Furthermore, the $Nb_2O_5$/$Al_2O_3$ catalysts were obtained by a new method of niobium oxalate impregnation on alumina. Jehng and Wachs [56] used niobium oxalate for coating on alumina support and observed that the monolayer is reached for 19% of $Nb_2O_5$. Surface niobia species on alumina exhibit peculiar and specific properties [57]. However, the potentialities of a metal-like platinum supported on this type of support were not yet well characterized in the literature. The influence of the preparation method on the structure of metallic particles, the degree of SMSI and catalytic properties of Pt/$Nb_2O_5$ and Pt/$Nb_2O_5$/$Al_2O_3$ were investigated.

The conversion of *n*-heptane results are presented in Fig. 3. The Pt/$Nb_2O_5$ samples show a low initial activity that deactivates quite fast. The $Nb_2O_5$/$Al_2O_3$-supported catalysts present higher initial activities and are more stable than the $Nb_2O_5$-supported catalysts. Furthermore, the samples with higher niobia loading showed a high selectivity towards olefins. As compared to Pt–Sn/$Al_2O_3$ catalysts [47] Pt/$Nb_2O_5$/$Al_2O_3$ catalysts presented a higher olefin to aromatics ratio. The low initial conversion is attributed to the lower dispersion of platinum and the partial coverage by reduced $NbO_x$ species.

However, the higher stability observed in the Pt/$Nb_2O_5$/$Al_2O_3$ catalysts compared to the Pt/$Nb_2O_5$ needs a better explanation model. The deactivation by

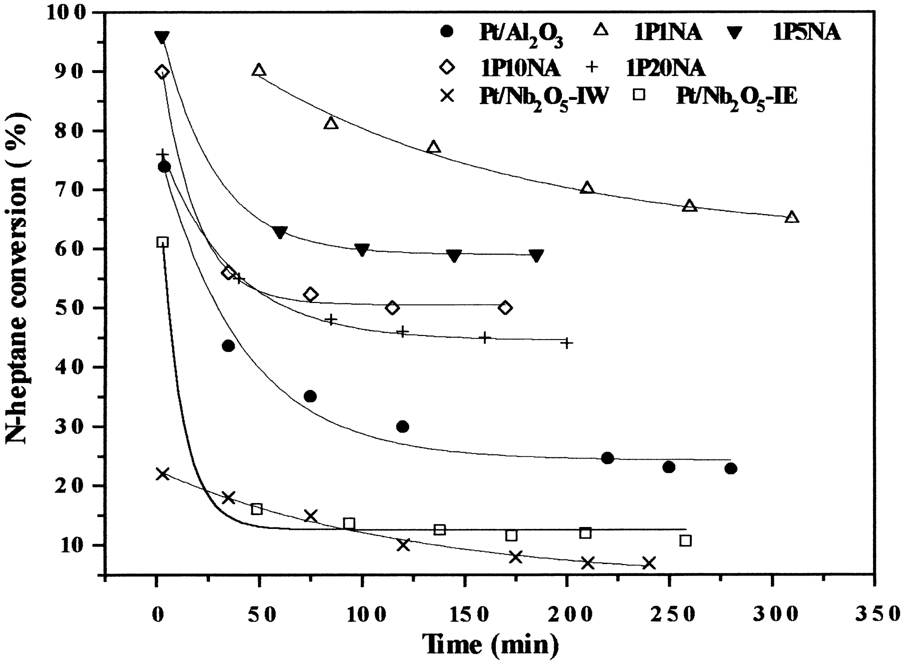

Fig. 3. *n*-Heptane conversion at 773 K (*y*P*x*NA, *y* and *x* are the platinum and niobia loading on alumina, respectively; Pt/$Nb_2O_5$ IE=catalyst prepared by ion exchange method; Pt/$Nb_2O_5$ IW=catalyst prepared by incipient wetness method) [12].

Table 4
Selectivity of *n*-heptane conversion at 773 K on platinum catalysts ($P$=1 atm; $H_2/C_7H_{16}$=16) [12]

| Catalyst | Hydrog.[a] | Hydrocrack.[b] | $C_7$ olef.[c] | Tol.[d] | Isom.[e] | $R$[f] |
|---|---|---|---|---|---|---|
| $Pt/Nb_2O_5$ IW | 7 | – | 65 | 5 | 23 | 13 |
| $Pt/Nb_2O_5$ IE (calc. 773 K) | 17 | 3 | 68 | 3 | 9 | 22.7 |
| $Pt/Al_2O_3$ | 32 | 13 | 17 | 32 | 6 | 0.5 |
| 1P1NA | 18 | 15 | 48 | 12 | 7 | 4 |
| 1P5NA | 14 | 15 | 48 | 12 | 11 | 4 |
| 1P10NA | 4 | 1 | 82 | 6 | 7 | 13.7 |
| 1P20NA | 3 | 2 | 78 | 8 | 9 | 9.8 |
| 1Pt1SnA | 2 | 2 | 63 | 18 | 15 | 3.5 |

[a] Selectivity to hydrogenolysis products.

[b] Selectivity to hydrocracking products.

[c] Selectivity to $C_7$ olefins.

[d] Selectivity to toluene.

[e] Selectivity to heptane isomers.

[f] Ratio between the selectivity to olefins and the selectivity to toluene (*y*P*x*NA, *y* and *x* are the platinum and niobia loading on alumina, respectively; $Pt/Nb_2O_5$ IE=catalyst prepared by ion exchange method; $Pt/Nb_2O_5$ IW=catalyst prepared by incipient wetness method) [12].

coke in the hydrocarbon conversion is described by two main mechanism: the poliene and the C1 routes [58]. The former route favors the olefins coupling promoted by acidic sites, while the C1 mechanism favors the carbon deposition on metallic sites from light molecules, as methane. The low selectivity towards hydrogenolysis products (Table 4) indicates that the C1 route is less probable on niobia-based catalysts. This indicates that the deactivation process is related to the acidity of the support. It has been shown that the Brönsted acidity of $Nb_2O_5/Al_2O_3$ samples increases with the niobia loading. This increase is attributed to the tetrahedral or octahedral niobia units containing Nb=O bands [59] dispersed on alumina surface. On the other side, the niobia calcined at 773 K displays few and weak acidic sites [47]. Davis et al. [60] presented a model which indicates that the Brönsted acidic sites are very important to "drain-off" the coke precursors produced on metallic sites cleaning up the surface. The $Pt/Nb_2O_5$ catalysts show high selectivity towards olefins, as presented in Table 4. The hydrogenolysis selectivity decreases, since the SMSI effect causes dilution of metallic particles. Besides, the lower acidity of this support promotes lower amounts of hydrocracking, isomerization and aromatization products. However, the higher olefin density localized on metal sites, as observed by TPO of deactivated catalysts [61] is responsible for a faster deactivation.

The $Pt/Nb_2O_5/Al_2O_3$ catalysts present two different possibilities:

1. At low niobia contents (1–5%), hydrocracking occurs on Lewis acidic sites decreasing the selectivity towards olefins. Furthermore, hydrogenolysis occurs on larger ensembles of platinum.
2. At high niobia loading (10–20%), the SMSI intensity is higher and the diluted metallic ensembles allow to minimize the hydrogenolysis reactions. In addition, the Lewis acidity decreases preventing hydrocracking, while the Brönsted sites attract coke precursors to the support and therefore free metallic sites for the dehydrogenation, thus resulting more stable catalysts.

## 2. Summary

Niobia-supported catalysts present specific properties related to the well-known SMSI effect. However, bimetallic catalysts supported on niobia showed higher intermetallic interaction than on alumina catalysts. In fact, Rh–Co, Pd–Cu and Pt–Sn particles dispersed on niobia surface presented interesting catalytic properties related to a preferential bimetallic interaction than typical metal–$Nb_2O_5$ SMSI effect.

On the other hand, the results of $Pt/Nb_2O_5/Al_2O_3$ catalysts in *n*-heptane reaction is a particular type of niobia promoted catalyst, since simultaneous dilution of the metallic particles associated to new acidic sites on $Nb_2O_5/Al_2O_3$ support produced a very interesting dehydrogenation catalyst.

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