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Catalysis Today 57 (2000) 291–296

CATALYSIS TODAY

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The nickel–niobia–silica interactions at low nickel contents

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Abstract

Nickel was impregnated in two Nb_2O_5/SiO_2 samples. The first one contained small crystallites of niobia dispersed over silica and the second one a niobia monolayer distributed quite uniformly over the silica substrate. These systems were submitted to different treatments (calcination and water vapor) in order to obtain different interactions between the nickel and niobia. A preferential interaction of the nickel with niobia was observed in both niobia–silica samples. The hydrogenation of benzene and dehydrogenation of cyclohexane were used to characterize the reduced surface nickel. Suppression in the catalytic activity was observed due to a strong metal-support interaction (SMSI) and nickel niobate formation. The extension of SMSI and nickel niobate formation depend on the niobia–silica interactions, which are a function of sample preparation and treatment.

Keywords: Nickel; Nb_2O_5/SiO_2; Interaction

1. Introduction

The concept of strong metal-support interaction (SMSI) was proposed by Tauster et al. [1] to explain the suppression in H_2 and CO chemisorption, after reduction at 773 K, or higher, in metals supported on TiO_2 and other reducible oxides. This decrease in the chemisorption capacity was observed without sintering and has been related to electronic or decoration model [2]. The reversible character of this phenomenon, upon calcination, was reported in the literature [2].

The catalytic properties are largely changed when the metal is promoted by an oxide that presents SMSI behavior, or a support modified by the addition of a reducible oxide [2].

The work of Kunimori et al. [3] has proposed the formation of three phases of nickel and rhodium on a niobia support: Nb_2O_5, metallic oxide and metal niobate. The amount of these phases was dependent on the thermal treatment conditions. At 773 K, both Nb_2O_5 and metallic oxide are present. At 973 K, part of the metal was already observed as metal niobate. Under more drastic calcination treatment (1173 K) only metallic niobate was observed.

The TPR technique indicates that nickel niobate is more difficult [4] to reduce than NiO. The reduction of NiO supported on niobia presented an uptake of H_2 between 623 and 973 K, with the major H_2 consumption at 723 K. On the other hand, nickel niobate reduction is observed between 723 and 1273 K, or higher. The SMSI phenomenon was observed when reducing the nickel niobate system. This behavior of the Ni/Nb_2O_5 system indicates that Nb_2O_5 is a good candidate as a nickel trap in fluid catalytic cracking (FCC). The FCC

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PII: S0920-5861(99)00339-9

process occurs in a reducing atmosphere during the reaction and a calcination step at high temperatures during catalyst regeneration [5,6].

Ko et al. [7] compared Nb_2O_5- and Nb_2O_5–SiO_2-supported nickel catalysts. They expected the same extent of SMSI in both systems, since there is a sufficient supply of niobia. However, the catalytic activity of Ni/Nb_2O_5/SiO_2 was 50% greater than the Ni/Nb_2O_5 system. Although they could not totally rule out the possibility of some crystallites sitting on uncovered SiO_2 contributing to the activity, they suggested that such an effect was small and the lower availability of Nb_2O_5 in the Nb_2O_5–SiO_2 was responsible for activity decreased.

Silica is a common component in FCC catalyst [8]. The preferential location of nickel in these systems still remains an area to be studied. This has led us to introduce nickel by using the classical Mitchel [9] impregnation method on different niobia–silica supports. The effects of pretreatment were also verified on each system. The idea to further explore Nb_2O_5/SiO_2 as a Ni trap was the main objective of this work in order to:

- verify the prevailing interaction of Ni with Nb_2O_5 in the ternary system (Ni–Nb_2O_5–SiO_2);
- study the effect of the Nb_2O_5–SiO_2 interaction on the extent of the SMSI in the presence of Ni.

2. Experimental

2.1. Preparation of the systems

– *Nb_2O_5–SiO_2 (NSI)*: The preparation method was based on Asakura and Iwasawa [10] using niobium ethoxide, $Nb(OC_2H_5)_5$, as precursor. Silica (OX50 from Degussa) was treated at 473 K for 30 min to control the silanol concentration at 5 OH nm^2. The reaction between $Nb(OC_2H_5)_5$ and the OH groups was conducted for 2 h in hexane under reflux conditions. The sample was washed with hexane to remove unreacted $Nb(OC_2H_5)_5$. After this step, the sample was evacuated and heated to 473 K to complete the grafting reaction. Then the sample was exposed to H_2O vapor at room temperature and calcined overnight at 773 K. This procedure was repeated successively four more times to cover the SiO_2 surface with niobium oxide. The final Nb_2O_5 concentration was 7.4 wt.%.

– *Nb_2O_5–SiO_2 (NSII)*: The second method used as precursor an ammonium complex of niobium, $NH_4^+[Nb(C_2O_4)_3]^-$, [11]. Silica was added to 200 ml of deionized water containing the precursor at room temperature and kept 4 h. This material was dried at 273 K, washed and calcined overnight at 773 K. The procedure was repeated twice and the final composition was 7.7 wt.% of Nb_2O_5.

– *Nickel niobia–silica*: Nickel was impregnated on niobia–silica systems using the incipient wetness method, with nickel naphthanoate in toluene. The support was previously calcined at 673 K in a furnace for 1 h. After that, the system was calcined at 773 K for 2 h.

2.2. Pretreatment procedures (after nickel impregnation)

The reference sample was considered just after calcination at 773 K. One pretreatment was calcination of the reference sample with air, flowing at 60 ml/min at 1073 K for 2 h. The second pretreatment was done submitting the reference sample to 100% water vapor calcination with a flow rate of 60 ml/min at 1073 K for 2 h. From now on we recall these samples as: NiNSIA and NiNSIIA — reference sample; NiNSIB and NiNSIIB — samples calcinated at 1073 K and NiNSIC and NiNSIIC samples calcinated with water vapor at 1073 K.

2.3. Characterizations

2.3.1. Temperature-programmed reduction (TPR)

The TPR measurements were performed with a Micromeritics 2900 instrument. The profiles were obtained with a mixture of 10% H_2 in N_2, a flow rate of 60 ml/min and raising the temperature at a rate of 10 K/min, up to 1273 K.

2.3.2. Catalytic tests

Before the catalytic tests the samples were reduced as described above up to 773 K. Then, hydrogen was switched passing through cyclohexane in a saturator at 285 K, at 20 ml/min. This reactant mixture was passed through the catalytic bed, containing 100 mg of the catalyst, at a temperature of 743 K.

3. Results

3.1. TPR

The TPR profiles of the NiNSI samples are shown in Fig. 1 with the corresponding H_2 consumption in Table 1. They show that the NS sample did not present any H_2 consumption (Fig. 1(a)), while the NiNSIA sample showed a hydrogen uptake between 623 and 873 K in agreement with the Ni/SiO$_2$ catalyst (Fig. 1B). However, after calcination and vapor treatments (Fig. 1(c) and (d), respectively) these peaks are shifted towards higher temperatures and exhibited an increase of H_2 consumption. This behavior is more pronounced after water vapor treatment (NiNSIC).

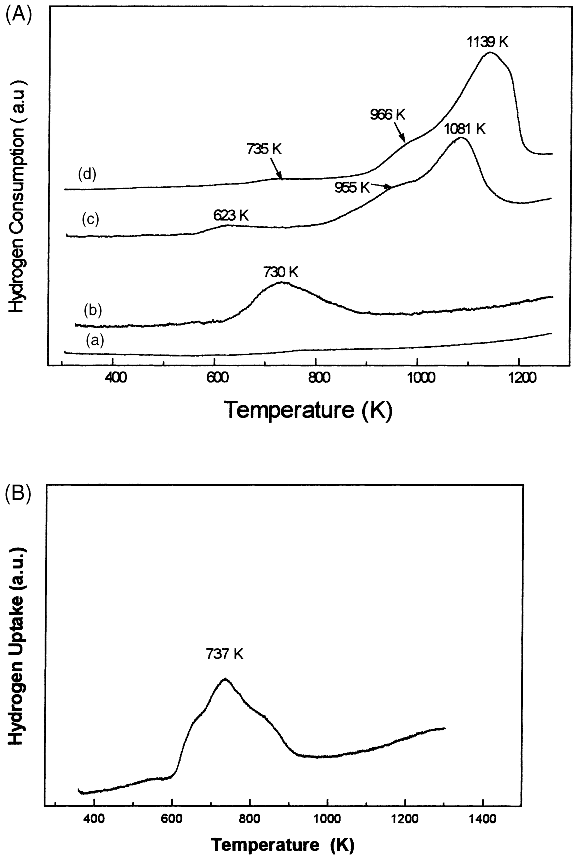

Fig. 1. (A) TPR profiles of NiNSI systems. (a) NSI; (b) NiNSIA (reference); (c) NiNSIB (calcination); (d) NiNSIC (water vapor treatment). (a) TPR profiles of Ni/SiO$_2$ system. (B) TPR profiles of Ni/SiO$_2$ system.

Table 1
Temperature-programmed reduction — H_2 consumption[a]

	Up to 773 K (μmol/g$_{Ni}$)	Up to 1273 K (μmol/g$_{Ni}$)
Ni/NSIA	41	78
NiNSIB	17	151
NiNSIC	14	203
NSIA	0	39
2nd TPR NSIB	4	55
NiNSIIA	33	91
NiNSIIB	31	145
NiNSIIC	4	120
NSIIA	0	0
2nd TPR NSIIB	0	0

[a] NSI and NSII — blanc sample without Nickel. A — calcination at 773 K; B — sample A calcined at 1073 K; C — sample A calcined with water vapor at 1073 K.

Fig. 2 shows the TPR profiles of NiNSII, which exhibits three main regions of H_2 consumption: the first one at 752 K, then an intermediate region and finally around 1123 K, which is also very different from NSI (Fig. 1(a) and Fig. 2(a)). Table 1 presents the corresponding amounts of H_2 consumption, indicating that NSII it was slightly greater than for NSI. After calcination and in the presence of water vapor H_2 consumption at low temperature decreased markedly, while at high temperatures it increased.

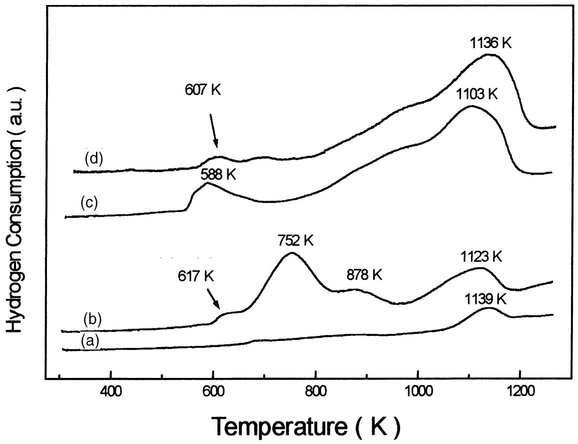

Fig. 2. TPR profiles of NiNSII systems. (a) NSII; (b) NiNSIIA (reference); (c) NiNSIIB (calcination); (d) NiNSIIC (water vapor treatment).

Table 2
Benzene hydrogenation on Ni/Nb_2O_5–SiO_2 systems[a]

System	$mmol_{benzene}$/(min g cat)	Activity ratio related to the Ni/SiO_2 sample (%)
Ni/SiO_2 A[b]	15.6	100
Ni/SiO_2 B	6.8	44
NiNSIA	1.6	10
NiNSIB	0	0
NiNSIIA	1.4	9
NiNSIIB	1.4	9

[a] A — calcination at 773 K; B — sample A calcined at 1073 K; C — sample A calcined with water vapor at 1073 K.

[b] Maximum activity for Nickel used as reference.

3.2. Benzene hydrogenation

The results are presented in Table 2, comparing the reference catalyst to the others as a function of the pretreatment. The NiNSIA and NiNSIIA samples presented the same activity but the NiNSIB sample showed no detectable catalytic activity. On the other hand, the NiNSIIA and NiNSIIB exhibited the same activity.

3.3. Cyclohexane dehydrogenation

Table 3 presents the rates of cyclohexane dehydrogenation results at two different temperatures around 640 K and at high temperature of the NiNS systems under water vapor pretreatment and without pretreatment (reference) besides the industrial catalysts E and F (equilibrium catalysts). The same activity level was reached for the NiNSI and NiNSII systems. For the NiNSIA and NiNSIIA samples the conversions were 11.3 and 13.3%, respectively. For NiNSIC and NiNSIIC samples the conversions decreased drastically.

Aiming for the detection limit of catalytic activity, we diminished the mass of the Ni/SiO_2 catalyst by diluting it with SiO_2, till 100 mg of total weight was reached. Even until 11 mg of Ni/SiO_2 catalyst it was possible to detect measurable catalytic activity. It shows that this reaction is sensitive enough allowing to determine precisely the metallic surface atoms at low concentrations. The industrial catalysts E and F were compared to the nickel dehydrogenation passivation activity. Although the activity level was of the same order the temperature was significantly higher in the NiNSIC and NiNSIIC samples, indicating that the passivated catalysts presented less dehydrogenation capacity.

4. Discussion

4.1. The nickel–niobia and niobia–silica interactions

The TPR profiles of NiNSIA and Ni/SiO_2 were very similar, which suggests a weak interaction between nickel and niobia. After calcination (NiNSIB) these peaks shift to higher temperatures with a considerable increase of the amounts of H_2 consumed (Figs. 1 and 2). This behavior agrees with results in the literature [4,7] an indication of a stronger interaction between nickel and niobia, promoting the reduction of niobia.

Table 3
Cyclohexane dehydrogenation[a]

System	$T_{reaction}$ (K)	W_{cat} (g)	Conversion (%)	$mmol_{benzene}/(min\ g_{Ni})$
F catalyst	641	2.0051	3.1	0.29
E catalyst	642	2.0044	31.9	3.2
Ni/SiO_2 A	642	0.1055	43.1	48.22
Ni/SiO_2 A	761	0.0011	2.4	–
Ni/SiO_2 C	641	0.1036	3.4	3.37
Ni/SiO_2 C	713	0.1036	10.8	10.13
NiNSIA	642	0.101	11.3	11.71
NiNSIC	723	0.604	0	0
NiNSIIA	641	0.1094	13.3	11.79
NiNSIIC	741	0.3347	1	0.29

[a] A — calcination at 773 K; B — sample A calcined at 1073 K; C — sample A calcined with water vapor at 1073 K.

After vapor pretreatment, H_2 consumption was largely increased, which could be attributed to nickel niobate formation. The extent of formation of this compound can be estimated from the stoichiometry of the reaction:

$$NiNb_2O_6 + 2H_2 \rightarrow Ni + 2NbO_2 + 2H_2O$$

The theoretical amount of H_2 consumed for reducing nickel was 102 μmoles/g cat and the observed H_2 consumption was 203 μmoles/g cat Considering that the oxidation number of Nb changes from +5 to +4 and that nickel +2 species are present, the resulting 1:2 stoichiometric value corresponding to the amount of nickel present, suggests that nickel will be present in its majority as a nickel niobate compound. It was observed that the niobia sublayer did not show reduction after calcination at 1073 K.

These results are in agreement with the proposal that the nickel–niobia interaction is a function of the Nb_2O_5–SiO_2 interaction, which affects the availability of Nb_2O_5 to interact with the metal. In NiNSII, with weaker Nb_2O_5–SiO_2 interactions, the surface coverage of silica is estimated to be around 13%. The nickel–niobia interaction without pretreatment was stronger than the nickel–niobia interaction in NiNSI (surface coverage of silica estimated to be 80%) under the same conditions. However, as the calcination and vapor pretreatment changed the niobia–silica, an inversion of interaction was observed.

On the other hand, Fig. 2(b) shows that reduction of NiNSII occurs at higher temperature and H_2 consumption corresponds to reduction of nickel niobate. Upon calcination and vapor pretreatment nickel niobate formation was increased, however, the corresponding amount of H_2 consumed was lower than in the NiNSI system. Therefore, these results suggest that the nickel–niobia interaction is a function of the Nb_2O_5–SiO_2 interaction and of the surface coverage of Nb_2O_5 available to interact with the metal. In NiNSII, which has a surface coverage of silica which is estimated to be around 13%, the nickel–niobia interaction without pretreatment was greater than the nickel–niobia interaction in NiNSI (surface coverage of silica estimated to be 80%) without pretreatment. However, the calcination and vapor pretreatment changed the niobia–silica interaction.

4.2. The Nb_2O_5–SiO_2 systems for nickel passivation

The addition of niobia to silica diminished the catalytic activity of nickel for the benzene hydrogenation and cyclohexane dehydrogenation reactions. The catalytic activity decay was pronounced for both systems NiNSI and NiNSII. Even without pretreatment both systems showed a very similar behavior. Therefore, it seems that the different coverages of silica and the interactions between nickel–niobia are responsible for these behavior. The calcinated pretreated NiNSIB samples did not present catalytic activity, whereas NiNSIIB system presented the same catalytic activity as sample without pretreatment, suggesting that part of the nickel was located on the silica surface.

4.3. The distribution of the nickel precursor

Assuming that the nickel particles on the niobia surface did not present catalytic activity and are randomly distributed at the surface, then the catalytic activity decay is expected to be of the same order of magnitude as the surface coverage. However, the benzene hydrogenation results of the NiNSII system were not consistent with our proposal, since the catalytic activity decay was 90% below the expected value, corresponding to a surface coverage of 13%, as expected in our model.

Otherwise, the catalytic activity decay cannot be attributed to only niobia passivation, but also to coke formation. The coke formation increased [12] in the presence of niobia. However, coking would not explain the drastic decay of catalytic activity for the benzene hydrogenation. On the other hand, as shown in Table 3, the catalytic data for cyclohexane dehydrogenation showed a lower catalytic decay and comparing the activity of the NiNSI and NiNSII systems to the Ni/SiO_2 catalyst the deactivation was of the order of 25%. These results suggest that deposition of coke cannot be the main reason for this drastic decrease of the catalytic activity. Apparently the high surface coverage of silica in the NSI system did not show a preferential deposition of nickel on the niobia sublayer. However, as no benzene hydrogenation and cyclohexane dehydrogenation activities were observed for the NiNSI with more severe pretreatment, it can be proposed that a preferential deposition of nickel occurred on the niobia monolayer.

The preferential deposition of the nickel precursor occur either after the nickel complex formation or by the preferential deposition of nickel on niobia. The first hypothesis can be attributed to the oxide migration, since NiO has low mobility [13]. The nickel compounds on FCC catalysts are stable even at high temperature [14]. The passivation phenomenon, attributed to a Ni–Nb_2O_5 interaction, already observed at low temperatures (773 K — without pretreatment), would eliminate the migration of NiO particles to Nb_2O_5, Nb_2O_5 migration to NiO being the mechanism of passivation [3]. From the above considerations, one can propose that the nickel precursor would be deposited preferentially on the niobia surface. This preferential location can be explained based on the acid character of niobia and oxygen donation.

From the literature it is known that the Bronsted and Lewis acid sites exist at the surface of niobia [15–17] but not in bulk niobia. However, bulk niobia promotes the preferential deposition of nickel.

The difference in electronegativity between Si and Nb [18] can be related directly to oxygen donation from Nb_2O_5 to NiO, which would explain the preferential deposition of nickel precursor on niobia.

5. Conclusions

The nickel compounds seem to present a preferential interaction with niobia when compared to silica. These nickel species favor lower dehydrogenation activity. This behavior suggests the choice of niobia as a nickel trap.

The nickel–niobia compounds and SMSI are correlated with the presence of niobia species. The presence of bulk niobia favors nickel niobate formation and a more intense SMSI state under mild treatment. The niobia monolayer is more difficult to reduce and nickel niobate compounds were observed only at high temperatures. If the Nb_2O_5–SiO_2 interaction is destroyed under severe treatment the passivation of Nb_2O_5–SiO_2, due to the initial configuration, provides complete Ni passivation.

References

[1] S.J. Tauster, S.C. Fung, R.L. Garten, J. Am. Chem. Soc. 100 (1978) 170.
[2] G. Haller, D.E. Resasco, Adv. Catal. 36 (1989) 173.
[3] K. Kunimori, H. Shindo, H. Oyamagi, T. Uchijima, Catal. Today 16 (3/4) (1993) 387.
[4] H. Nakamura, H. Hu, K. Kunimori, Y. Yokoyama, H. Asano, M. Soma, T. Uchijima, J. Catal. 119 (1989) 33.
[5] G.L. Woolery, M.D. Ramos, A.R. Quinomes, Symposium in Advances in FCC Conversion Catalysts, New Orleans, LA, March 1996.
[6] J. Biswas, I.E. Maxwell, Appl. Catal. A 63 (1990) 197.
[7] E.I. Ko, J.M. Hupp, K.J. Foger, J. Catal. 86 (1984) 315.
[8] P. O'Connor, E. Brevoord, H.N. Wijngaards, Symposium in Advances in FCC Conversion Catalysts, New Orleans, LA, March 1996.
[9] B.R. Mitchell, Ind. Eng. Chem. Prod. Res. Dev. 19 (1980) 209.
[10] K. Asakura, Y. Iwasawa, J. Phys. Chem. 95 (1991) 1711.
[11] M.M. Pereira, Ph.D. Thesis, Federal University of Rio de Janeiro, COPPE/UFRJ, 1997.
[12] D.A.G. Aranda, F.B. Passos, F.B. Noronha, M. Schmal, Catal. Today 16 (1993) 397.
[13] E.L. Kugler, D.P. Leta, J. Catal. 109 (1988) 387.
[14] B.K. Speronello, W.J. Reagan, J. Oil & Gas 30 (1984) 209.
[15] J. Datka, A.M. Turek, J.M. Jehng, I.E. Wachs, J. Catal. 135 (1992) 186.
[16] G. Connell, J.A. Dumesic, J. Catal. 105 (1987) 285.
[17] T. Kataoka, J.A. Dumesic, J. Catal. 112 (1988) 66.
[18] J.A. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry: Principles of Structure and Reactivity, 4th Edition, Harper Collins College Publishers, 1993.