

EXAFS investigations of Ni/ γ -Al₂O₃ and Ni/AlPO₄ catalysts and their precursors

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Abstract. *In-situ* EXAFS investigations have been carried out on Ni/ γ -Al₂O₃ catalysts with different metal loadings and prepared from different precursors. When the calcined precursors are reduced in hydrogen, the proportion of nickel metal formed varies with the nature of the precursor employed; NiAl₂O₄ is the unreduced product. The metal loading does not have any significant effect on the proportion of metal formed except in the case of the catalyst prepared by wet-impregnation, where appreciable metal is obtained only when the loading is greater than 10 wt%. Ni/AlPO₄ catalysts do not show the formation of NiAl₂O₄ and reduction to metal is complete, unlike with the Ni/ γ -Al₂O₃ catalysts which show only partial reduction to metal.

Keywords. Ni/ γ -Al₂O₃; Ni/AlPO₄; NiAl₂O₄; EXAFS.

1. Introduction

Supported nickel catalysts have a wide range of applications. It is of interest to compare nickel catalysts prepared from different precursors with varying metal loadings. This is because, in the commonly employed Ni/Al₂O₃ and Ni/SiO₂ catalysts, all the nickel is not reduced to the metallic state due to the formation of NiAl₂O₄ and NiSiO₃ respectively, which are stable towards reduction (Bartholomew and Farrauto 1976; Narayanan and Uma 1985; De Bokx *et al* 1987; Kulkarni *et al* 1991; Clause *et al* 1992; Rao *et al* 1992). It is also noteworthy that in Ni/TiO₂ catalyst there is strong indication of metal-support interaction, wherein, progressive reduction of the support leads to the burial of the metal particles, thereby rendering them unavailable for gas adsorption (Tauster *et al* 1978; Arunarkavalli *et al* 1993). We have investigated Ni catalysts with different metal loadings prepared from wet-impregnation of nickel acetylacetonate and nickel nitrate on γ -Al₂O₃, as well as by coprecipitation of the nitrates of nickel and aluminium. These catalyst precursors as well as the reduced catalysts have been examined by Ni K-edge Extended X-ray Absorption Fine Structure (EXAFS). We have also prepared different metal loadings of nickel on AlPO₄ and compared these catalysts with the corresponding Ni/ γ -Al₂O₃ catalysts, prepared under similar conditions. AlPO₄ which is isostructural with SiO₂ has been used as a support in a number of catalytic reactions (Alba *et al* 1986; Campelo *et al* 1986, 1988; Bautista *et al* 1989; Rebenstore *et al* 1991).

2. Experimental

Ni/ γ -Al₂O₃ catalyst precursors with Ni loadings of 3, 5 and 10 wt% were prepared starting with γ -Al₂O₃, which has a surface area of 200 m²/g, by employing three different precursors.

(a) Nickel acetylacetonate, containing the required amount of Ni by weight %, was deposited on γ -Al₂O₃ in alcohol medium, The excess solvent was vacuum evaporated at room temperature.

(b) An aqueous solution of Ni(NO₃)₂ was wet-impregnated on γ -Al₂O₃ in the required proportions.

(c) Ni-Al₂O₃ gels were prepared by adding excess ammonia under stirring to a solution containing appropriate quantities of the metal nitrates (Subbanna and Rao 1986). All the above mentioned catalyst precursors were dried at 350 K and calcined at 625 K for 4 h. The calcined precursors were reduced at 773 K for 3 h in flowing hydrogen to obtain the catalysts.

AlPO₄ was prepared by the procedure of Campelo *et al* (1986a) wherein an aqueous solution of AlCl₃·6H₂O and H₃PO₄ (85% by wt) was taken such that the Al/P ratio was unity. The solution was neutralized by adding aqueous ammonia solution dropwise with vigorous stirring, taking care to maintain the final pH at 6.1. The resulting gel was filtered, washed with isopropyl alcohol and dried at 373 K for 24 h. It was then calcined at 873 K for 3 h and stored in a dessicator.

The solution of nickel nitrate was deposited on γ -Al₂O₃ and AlPO₄ by wet-impregnation so as to get Ni loadings of 5, 10 and 20 wt%. These precursors were calcined at a higher temperature (namely at 875 K) than the previous systems. The calcined samples were reduced in flowing hydrogen at 773 K. In order to compare the behaviour of Ni/AlPO₄ catalysts with that of Ni/Al₂O₃ catalysts, we have prepared the latter under similar conditions.

EXAFS spectra were recorded at room temperature under *in-situ* conditions using an X-ray absorption spectrometer with a rotating anode X-ray generator (RU-200B, Rigaku, Japan). A Ge(220) crystal was used as the monochromator with a 0.2 mm slit. The precursor catalysts were pressed into self-supporting wafers after mixing with boron nitride fine powder (Merck) and a drop of PVA. The thickness of the wafer was adjusted such that the edge jump (μ .d) was 1.5 in every case. The wafers were mounted in a locally fabricated all-quartz *in-situ* cell, details of which are given elsewhere (Kulkarni *et al* 1991). Reduction was carried out in dry, pure hydrogen (passed through

Table 1. Coordination number (*N*) and inter-atomic distance (*R*) in the reference compounds.

Compound	Atom-pair	<i>N</i>	<i>R</i> (Å)
NiO	Ni-O	6	2.08
	Ni-Ni	12	2.94
NiAl ₂ O ₄	Ni-O	4	1.83
	(tetrahedral)		
	Ni-O	6	1.97
	(octahedral)		
Ni metal	Ni-Ni	12	2.48

BASF R-3-11) at atmospheric pressure. After reduction, the samples were cooled to room temperature under flowing hydrogen.

EXAFS spectra of the reference compounds, NiO, Ni metal and NiAl₂O₄ were also recorded under similar conditions. The structural parameters of the reference compounds are listed in table 1. Fourier transforms (FT) of the EXAFS data were obtained with $k_{\min} \sim 2.4$ and $k_{\max} \sim 12.2 \text{ \AA}^{-1}$ after weighting the data by k^3 . EXAFS data were treated using the multiphasic model involving the additive relationship of EXAFS function (Kulkarni *et al* 1989).

3. Results and discussion

The Fourier transforms (FT) of Ni(acac)₂/γ-Al₂O₃ catalyst precursors with metal loadings of 3, 5 and 10 wt%, calcined at 625 K are shown in figure 1a. All the three catalyst precursors show a peak around 1.72 Å, which on curve-fitting (*r*-window: 1.5–1.9 Å) using Ni–O parameters from NiO gives a Ni–O coordination of ~4 at a distance of 2.07 Å. This has to be compared with the first coordination of NiO at 2.08 Å with a coordination of 6. The precursor with 3 wt% nickel loading shows an additional peak around 2.7 Å, which on curve-fitting (*r*-window: 2.4–3.0 Å) using

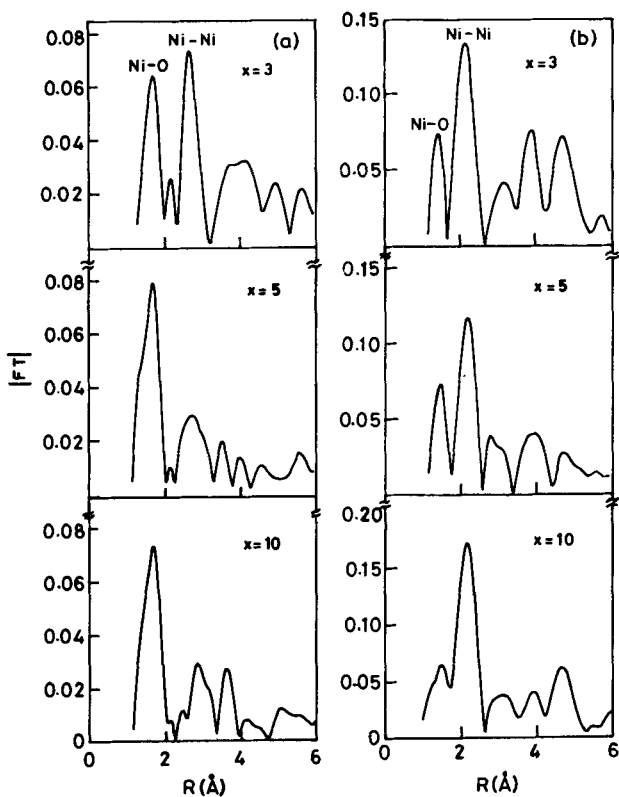


Figure 1. (a) Fourier transforms (FT) of the Ni K-EXAFS of Ni(*x* wt%)/γ-Al₂O₃ catalysts, obtained from Ni(acac)₂/γ-Al₂O₃ precursor, after calcination at 625 K. (b) FT of the same catalysts, after reduction in hydrogen at 773 K.

Table 2. Structural parameters of Ni(x wt%)/ γ -Al₂O₃ catalysts obtained from Ni(acac)₂ precursor.

x	Atom pair	After calcination at 625 K		After reduction in H ₂ at 773 K	
		N	R(Å)	N	R(Å)
3	Ni-O	4	2.07	4	1.88
	Ni-Ni	6	2.97	9	2.47
5	Ni-O	5	2.06	4	1.92
	Ni-Ni	—	—	7	2.48
10	Ni-O	4	2.06	4	1.93
	Ni-Ni	—	—	12	2.48

Ni-Ni parameters from the bulk Ni metal gives a Ni-Ni distance of 2.97 Å, corresponding to that in NiO. We, however, do not see this feature in the FT of precursors with 5 and 10 wt% nickel loadings which may be due to good dispersion in these two precursors. Structural parameters of these calcined catalyst precursors are listed in table 2.

The calcined Ni(acac)₂/ γ -Al₂O₃ precursors were reduced at 773 K in a stream of hydrogen and the FT of the reduced catalysts are given in figure 1b. All three samples, independent of the metal loading, show a feature at 2.22 Å, which on curve-fitting (*r*-window: 1.9–2.5 Å) gives an Ni-Ni distance of 2.48 Å, corresponding to the bulk nickel metal. The coordination number varies between 7 and 12. The theoretical value of 12 is found in the 10 wt% catalyst. Table 2 shows the structural parameters of these catalysts after reduction. All these reduced catalysts show an additional feature at ~1.46 Å which on curve-fitting using Ni-O parameters from NiO gives an Ni-O distance varying from 1.88 to 1.93 Å with metal loading. This cannot be due to Ni-O. Furthermore, this Ni-O species has a coordination of 4 in all three catalysts, which suggests the formation of the NiAl₂O₄ phase. The formation of NiAl₂O₄ is indeed known in Ni/Al₂O₃ systems (Kulkarni *et al* 1991). It is also known from the literature that the distribution of nickel ions among the octahedral and tetrahedral vacancies of the spinel is a function of the nickel content and the tetrahedral vacancies get preferentially occupied at lower loadings (De Bokx *et al* 1987). The Ni-O distances of the tetrahedral and octahedral sites in NiAl₂O₄ are known to be 1.83 and 1.97 Å respectively (table 1). As the nickel content increases, the proportion of the octahedral Ni species also increases, which explains the increase in the Ni-O bond length. The fraction of nickel metal formed does not alter significantly with the metal loading, although it is highest in the 10 wt% catalyst. The structural parameters of the reduced catalysts prepared from the acetylacetonate precursors are summarized in table 2.

In figure 2a we show the FT of the calcined catalyst precursors prepared by the wet-impregnation of nickel nitrate on γ -Al₂O₃. The 3 wt% shows two peaks at 1.4 and 1.86 Å, which, on curve-fitting give two Ni-O distances of 1.86 and 2.16 Å with coordinations of 4 and 5 respectively. The shorter distance at 1.86 Å could be due to the presence of a surface NiAl₂O₄ species. The 2.16 Å distance is longer than the Ni-O bond length in NiO. This could arise from the presence of surface hydroxyl species. We do not, however, see this feature in the 5 and 10 wt% precursors. Both the 5 and 10 wt%

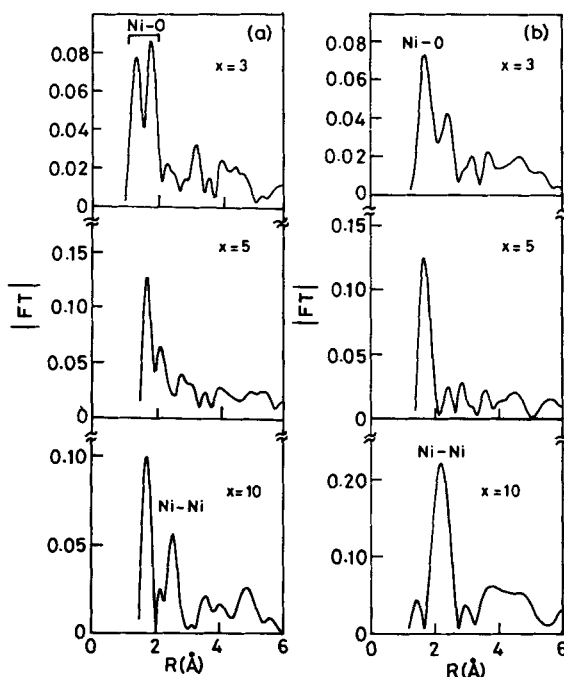


Figure 2. (a) Fourier transforms (FT) of the Ni K-EXAFS of Ni(x wt%)/ γ -Al₂O₃ catalysts, obtained from Ni(NO₃)₂/ γ -Al₂O₃ precursors, after calcination at 625 K. (b) FT of the same catalysts, after reduction in hydrogen at 773 K.

Table 3. Structural parameters of Ni(x wt%)/ γ -Al₂O₃ catalysts obtained from Ni(NO₃)₂·6H₂O precursor.

x	Atom pair	After calcination at 625 K		After reduction in H ₂ at 773 K	
		N	R(Å)	N	R(Å)
3	Ni-O	4	1.86	2	1.87
		5	2.16	4	2.13
5	Ni-O	6	2.08	6	2.07
10	Ni-O	6	2.1	—	—
	Ni-Ni	5	2.92	12	2.49

catalysts show a peak around 1.72 Å in their FTs, which on curve-fitting gives a Ni-O bond length of ~2.08 Å with a coordination of 6, indicating the presence of NiO. The 10 wt% sample has an additional feature at ~2.7 Å, which on curve-fitting gives an Ni-Ni bond length of 2.92 Å, corresponding to the second coordination in NiO. Structural parameters of these calcined catalyst precursors are listed in table 3.

The FT of the above catalysts, reduced in hydrogen at 773 K are shown in figure 2b. Even after reduction, the FT of the 3 wt% catalyst shows two different Ni-O distances, as in the precursor, although there is a slight shortening of the second Ni-O distance. The presence of the 1.87 Å distance even after reduction confirms the formation of the

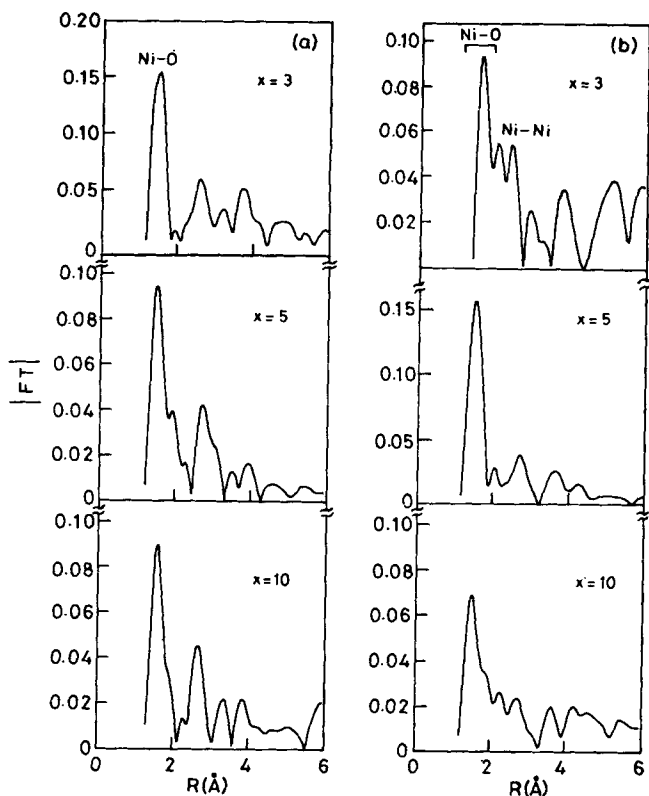


Figure 3. (a) Fourier transforms (FT) of the Ni(x wt%)-Al₂O₃ catalysts, obtained by coprecipitation, after calcination at 625 K. (b) FT of the same catalysts, after reduction in hydrogen at 773 K.

Table 4. Structural parameters of Ni(x wt%)-Al₂O₃ catalysts obtained by coprecipitation

x	Atom pair	After calcination at 625 K		After reduction in H ₂ at 773 K	
		N	R(Å)	N	R(Å)
3	Ni-O	4	1.83	5	2.03
	Ni-Ni	—	—	3	2.46
		—	—	6	2.89
5	Ni-O	6	1.96	6	1.95
	Ni-Ni	4	3.06	—	—
10	Ni-O	6	1.98	4	1.96
	Ni-Ni	4	3.03	—	—

NiAl₂O₄ phase. Apparently, reduction to metallic Ni does not occur. We do not see any evidence for the reduction of NiO to Ni metal in the 5 wt% catalyst either. With 10 wt% loading, however, NiO is reduced to Ni metal almost completely. The presence of an Ni-Ni distance of 2.49 Å with a coordination number of 12 is comparable to

that in metallic nickel. Structural parameters of these reduced catalysts are given in table 3.

In figure 3a, we show the FT of the calcined Ni-Al₂O₃ catalyst precursors prepared by coprecipitation. The three calcined samples show a single Ni-O distance, which increases from 1.83 Å to 1.97 Å along with the percentage of nickel loading (table 4). At lower loadings of nickel, Ni appears to prefer to occupy tetrahedral vacancies of the nickel aluminate spinel and octahedral vacancies get filled up only at higher loadings. The 5 and 10 wt% samples show a second shell Ni-Ni distance of 3.03 Å with a coordination of 4. These observations are in agreement with those of Clause *et al* (1992) on coprecipitated Ni-Al₂O₃ catalysts, where the Ni(II) and Al(III) ions occupy a brucite-type lattice after calcination.

Reduction of the catalyst precursors (prepared by coprecipitation) at 773 K shows the presence of Ni metal in the 3 wt% sample (figure 3b). Reduction is however partial and some unreduced oxidic phase with an Ni-O coordination of 5 at 2.03 Å is also present. The third peak in this FT occurring at 2.7 Å corresponds to Ni-Ni bonding at 2.9 Å, comparable to that in NiO. The 5 and 10 wt% catalysts do not exhibit much changes in the FT as can be seen in figure 3b, except for the disappearance of the second shells due to a good dispersion. The nature of the oxidic phase remains the same as that in their respective calcined states. The structural parameters of these reduced catalysts are given in table 4.

In figure 4a we compare the fraction of NiO obtained after calcination of the catalyst precursors prepared by the three procedures. NiO is formed entirely when the acetylacetonate precursor is used, independent of the percentage of the metal loading. In the case of wet-impregnation, both 5 and 10 wt% precursors show the presence of NiO, whereas the lower loading of 3 wt% shows the formation of only the NiAl₂O₄ species. The coprecipitated catalysts contain no NiO. From figure 4b we see that acetylacetonate precursors, on reduction, give the metal at all loadings. Wet-impregnated precursors give negligible metal at 3 and 5 wt% loadings and an appreciable amount of reduction occurs only at higher loadings. The coprecipitated catalysts give no metal at all except in the case of very low metal loadings, where there is a partial reduction to give metallic nickel. It appears that in order to get a high proportion of Ni metal on reduction, the acetylacetonate route is the best. If wet-impregnation is employed, metal loading should be sufficiently high (~ 10 wt%).

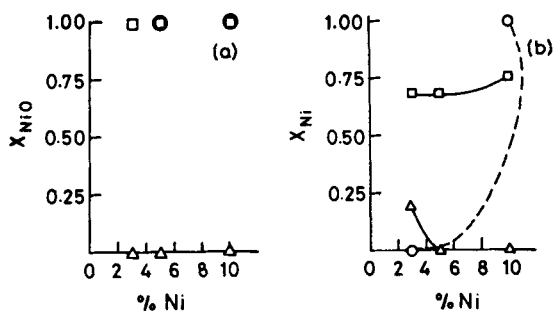


Figure 4. (a) Fraction of the NiO phase formed after calcination, with percentage loading of Ni, for three different precursors used. (b) Fraction of the bulk nickel metal formed after reduction, for the same precursors. □ - Ni(acac)₂/γ-Al₂O₃; ○ - Ni(NO₃)₂/γ-Al₂O₃; Δ - Ni-Al₂O₃.

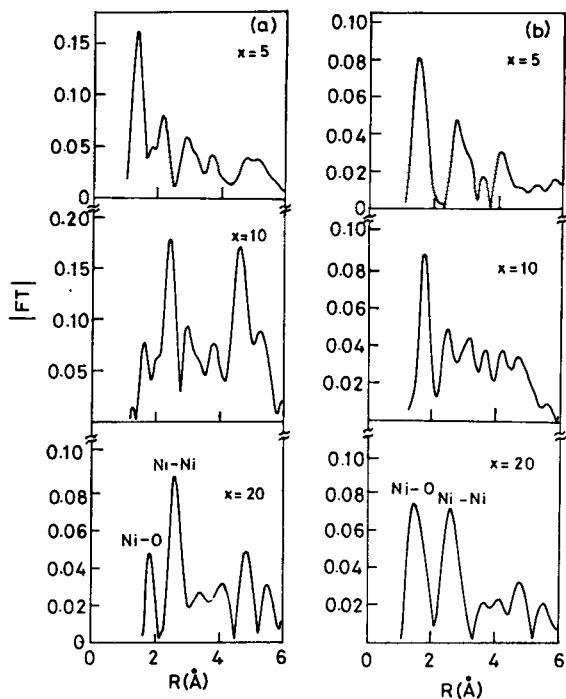


Figure 5. Fourier transforms (FT) of the Ni K-EXAFS of (a) Ni(x wt%)/AlPO₄ and (b) Ni(x wt%)/ γ -Al₂O₃ catalysts, after calcination at 873 K.

Table 5. Structural parameters of the Ni/AlPO₄ and Ni/ γ -Al₂O₃ catalysts after calcination at 873 K

x	Atom pair	Ni(x wt%)/AlPO ₄		Ni(x wt%)/ γ -Al ₂ O ₃	
		N	R(Å)	N	R(Å)
5	Ni-O	2	2.06	6	1.94
	Ni-Ni	—	—	2	2.08
10	Ni-O	4	2.06	4	1.94
	Ni-Ni	6	2.84	2	2.08
20	Ni-O	3	2.15	5	2.9
	Ni-Ni	—	—	4	2.09
		6	2.92	6	2.92

In figure 5 we compare the calcined catalyst precursors of Ni(x wt%)/AlPO₄ with the corresponding Ni(x wt%)/ γ -Al₂O₃ system (where x = 5, 10 and 20) prepared by wet-impregnation (the second procedure discussed earlier). All the three loadings of Ni/ γ -Al₂O₃ show the formation of fairly high amounts of NiAl₂O₄ along with NiO. This behaviour is to be compared with that of the Ni/AlPO₄ system, where we do not see the formation of the aluminate spinel. The 5 and 10 wt% nickel loaded precursors on AlPO₄ show the Ni-O bond length corresponding to that of NiO, whereas the

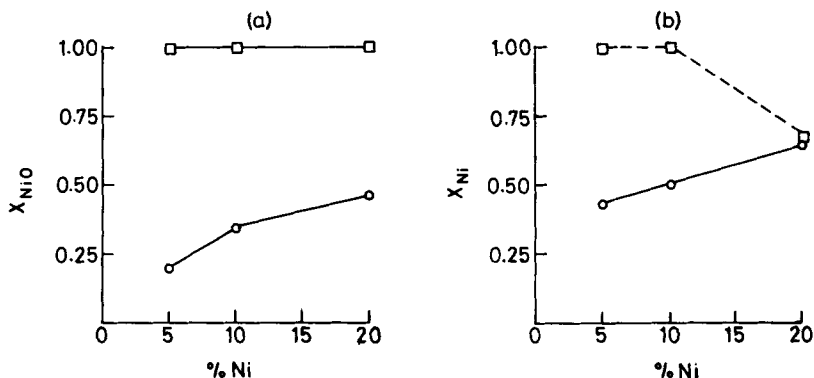


Figure 6. (a) Fraction of the NiO phase formed after calcination, for different loadings of nickel, in Ni/AlPO₄ and Ni/ γ -Al₂O₃ systems. (b) Fraction of the bulk nickel metal formed after hydrogen reduction, in the same systems. \square – Ni/AlPO₄, \circ – Ni/ γ -Al₂O₃.

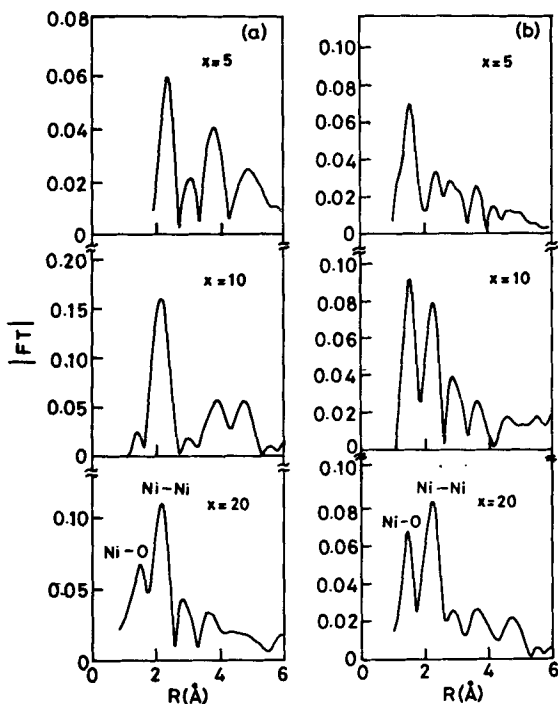


Figure 7. Fourier transforms (FT) of the Ni K-EXAFS of (a) Ni(x wt%)/AlPO₄ and (b) Ni(x wt%)/ γ -Al₂O₃ catalysts, after reduction in hydrogen at 773 K.

20 wt% catalyst shows an unusually long Ni–O distance of 2.15 Å with a coordination number of 3. The reason for this large distance is not clear to us at present. Structural parameters corresponding to both AlPO₄ and Al₂O₃ supported precursors are listed in table 5. In figure 6a, we plot the fraction of NiO phase varying with metal loading in these two precursors calcined at 825 K.

Table 6. Structural parameters of the Ni/AlPO₄ and Ni/γ-Al₂O₃ after reduction at 773 K

x	Atom pair	Ni(x wt%)/AlPO ₄		Ni(x wt%)/γ-Al ₂ O ₃	
		N	R(Å)	N	R(Å)
5	Ni-O	—	—	4	1.99
	Ni-Ni	4	2.56	3	2.7
10	Ni-O	—	—	5	1.96
	Ni-Ni	12	2.47	5	2.5
20	Ni-O	4	1.93	3	1.8
	Ni-Ni	8	2.46	6	2.5

In figure 7, we show the Ni/AlPO₄ and Ni/γ-Al₂O₃ catalysts obtained by reduction in hydrogen. The 5 and 10 wt% nickel-loaded catalysts on AlPO₄ show complete reduction to nickel metal. In the case of Ni/γ-Al₂O₃ catalysts, after reduction, the lowest loading of 5 wt% does not show any reduction at all while in the other loading with 10 wt% there is partial reduction to metallic nickel in the presence of unreduced NiAl₂O₄ species. Structural parameters of these reduced catalysts are listed in table 6 along with those of the calcined precursors. The variation in the fraction of the bulk nickel metal formed is shown in figure 6b.

4. Conclusions

The proportion of nickel metal obtained after reduction in hydrogen, in the case of Ni/Al₂O₃ catalysts, varies with the nature of the precursor. Nickel acetylacetonate gives the maximum proportion of metal irrespective of the metal loading while coprecipitated Ni-Al₂O₃ does not undergo any reduction. In the case of nitrate wet-impregnation, appreciable reduction to the metal occurs only if the metal loading is high (> 10%).

Ni/γ-Al₂O₃ catalysts do not undergo complete reduction to the metal and the proportion of metal formed increases with metal loading. In the case of Ni/AlPO₄ catalysts, however, complete reduction to the metal can be attained.

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