Precursor-support interactions in the preparation of sepiolite-supported Ni and Pd catalysts

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ABSTRACT: Naturally occurring sepiolite has been used as a support in the preparation of Ni and Pd catalysts. A precipitation procedure has been applied for both metals to deposit the precursor on to the support surface. The interaction between the sepiolite and the metal precursor has been studied by use of IR and solid-state MAS-NMR. Results show that SiOH groups are consumed in forming the Ni precursor whereas no specific interactions occur in the case of the Pd. However, strong interactions between metal precursor and the tetrahedral sheet occur for both metals leading to precursors which show a high stability under reducing conditions.

Supported Ni catalysts have been studied widely because of their importance in catalytic hydrogenation reactions including hydrogenation of olefins (Ross *et al.*, 1975) and natural oils (Coenen *et al.*, 1964). It is known that following certain preparation procedures, strong interactions occur between the Ni precursor and the support surface (Coenen, 1986; Ghuge & Babu, 1995) which leads to formation of Ni species which are more difficult to reduce than NiO (Montes *et al.*, 1984; Zhang *et al.*, 1992; Zielinski, 1995). This is particularly the case where precipitation procedures are involved and Ni silicates and species comprising Ni−O−Si linkages are formed (van Dillen *et al.*, 1976; Ghuge & Babu, 1995; Montes *et al.*, 1984; Zielinski, 1995). These support-precursor interactions are advantageous in producing thermally stable catalysts which are resistant to sintering and which contain a distribution of uniformly-sized metal particles (Montes *et al.*, 1984; Richardson & Dubus, 1978). The strong support-precursor interactions often result in the formation of active catalysts which contain a proportion of unreduced Ni (Coenen, 1986; Richardson & Dubus, 1978).

Natural silicate materials such as sepiolite have been studied as supports for Pd (Martín *et al.*, 1985; Aramendia *et al.*, 1994) and Ni hydrogenation catalysts (Corma *et al.*, 1988; Anderson *et al.*, 1993a,b, 1994) and as in the case of Ni/silica, complete reduction to the metal is seldom achieved even for high reduction temperatures (Corma *et al.*, 1988; Anderson *et al.*, 1993a,b, 1994). The hydrogenation of benzene and styrene over Ni/sepiolite catalysts prepared by impregnation and precipitation procedures has previously been compared by Anderson *et al.* (1993b, 1994). Results for the two series of samples showed two distinct lines in plots of turn over frequency (TOF) against particle diameter over a range of dispersions. The most active catalyst for benzene hydrogenation (from the precipitated series) was one of the least active for styrene hydrogenation, and the most active catalyst for styrene hydrogenation (from the impregnation series) was among the poorest in the hydrogenation of benzene. Similarity in (i) the shapes of TOF/particle size and degree of reduction/particle size plots for benzene hydrogenation; and (ii) coincidence between the catalyst exhibiting maximum activity for styrene hydrogenation in each series and the maximum in the level of Ni^{2+} in these samples, led to the conclusion that the unreduced Ni species was detrimental for benzene hydrogenation by inhibiting planar adsorption of the ring but enhanced styrene hydrogenation

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by promoting adsorption of the molecule via the ethylene double bond (Anderson *et al*., 1993b, 1994).

The formation of layered Ni silicate precursors via the precipitation route may be significant in producing the high ratio of Ni (100) to (111) crystal planes for the reduced catalyst in contrast to the metal crystallite morphology obtained for catalysts with equivalent metal dispersions prepared by the impregnation route (Anderson *et al*., 1994, 1997).

The objective of this study was to examine the interactions between the precursor and the sepiolite surface using FTIR and ^{29}Si NMR to determine the nature of the Ni species formed and to extend our previous work by including the study of Pd catalysts.

MATERIALS AND METHODS

Catalyst preparation

The sepiolite (Yunclillos, Toledo, Spain) was supplied by Tolsa S.A. and used without further treatment. Chemical analysis of the material indicated SiO_2 (66.19%), MgO (13.16%), Na_2O (1.71%), Al_2O_3 (1.66%), CaO (0.56%), K_2O (0.41%) and Fe_2O_3 (0.36%) with the remainer being H_2O while XRD analysis indicated the material to be of high purity with small quantities of palygorskite, chlorite and vermiculite as indicated by characteristic diffraction lines at 0.650, 0.425 and 0.280 nm, respectively.

Samples were prepared by the precipitation method of van Dillen *et al*. (1977) by adding a 0.283 mol dm^{-3} solution of Ni nitrate or a 0.11 mol dm^{-3} solution of Pd acetate to a suspension of the support material and adjusting the pH to 3.5 by the addition of nitric acid. The quantities of solution and sepiolite were calculated to give nominal metal contents of 10% Ni and 1 and 5% Pd. This solution, in contact with the sepiolite, was heated at 363 K for 30 min before addition of a 0.42 mol dm^{-3} urea solution which resulted in the precipitation of hydroxide over the support. The suspension was filtered after 48 h, and the precipitate washed repeatedly with distilled water. Raising the pH of the liquid by addition of ammonia did not yield further precipitation indicating all of the metal had been deposited over the support. All samples were dried overnight in air at 383 K. Palladium catalysts were then calcined in a flow of air at 673 K for 1 h before storage, whereas all experiments

involving Ni catalysts were performed directly on the dried material.

FTIR

Diffuse reflectance infrared (DRIFT) spectra were recorded as an average of 100 scans (resolution of 4 cm^{-1}) using a Perkin Elmer 1720X Fourier Transform spectrometer fitted with a TGS detector and connected to a PC for data manipulation. Spectra of the OH-stretching region (3800−3400 cm^{-1}) were obtained in the Diffuse Reflectance mode with the sample presented as a loose powder contained within a Harrick DRIFT environmental chamber. Samples were heated under vacuum to 573 K and then held at this temperature for 1 h or heated in a flow of H_2 in Ar from ambient temperature up to 773 K, maintaining the temperature at each elevated value for sufficient time to allow recording of the spectrum.

MAS-NMR

The 59.6 MHz ^{29}Si MAS NMR spectra of the materials were obtained using a Chemagnetics multinuclear Fourier Transform spectrometer. Powdered samples were contained within 7.5 mm diameter zirconia rotors and spun at 5 kHz using compressed air. One-pulse experiments were conducted using a pulse width of 4 μs and a 10 s delay. Up to 3500 acquisitions were made. Instrument calibration was performed using 3(trimethylsilyl) 1-propanesulphonic acid sodium salt.

BET

The BET surface areas were measured using a Micromeritics Model 2205 High Speed Surface Area Analyser. Single point measurements were made at 77 K using Ar as adsorbate.

XRD

Powder X-ray diffraction (XRD) patterns were obtained using a Philips PW1060 diffractometer using Cu-$K\alpha$ radiation, scanning a range between 4 and 70° 2θ at 1° 2θ min^{-1}.

RESULTS AND DISCUSSION

The BET (Ar) surface area measurements for the untreated sepiolite following outgassing at 473 K

gave a value of 305 m^2 g^{-1}, consistent with earlier measurements (Vicente Rodriguez *et al*., 1994; Aramendía *et al*., 1994; Galán, 1996). The dried Ni precursor/sepiolite sample gave a value of 216 m^2 g^{-1} while the 1 and 5% Pd/sepiolite samples calcined at 673 K gave values of 167 and 215 m^2 g^{-1}, respectively. The latter values are in agreement with values reported for Pd/sepiolite catalysts prepared by cation exchange (Martín *et al*., 1985). A sample of 1% Pd/sepiolite prepared by an impregnation method gave an area of 175 m^2 g^{-1} after calcination at the same temperature indicating that the precipitation method did not lead to enhanced surface areas because of modification of the support morphology as often reported for silica supports (Coenen, 1986; Montes *et al*., 1984).

Powder XRD analyses were performed on samples at each stage of the preparation (i.e. after drying, calcination and/or reduction) and compared with patterns for similarly pre-treated sepiolite. The 110 reflection at 12.1 Å (7.3° 2θ) has previously been used as an indication of the state of crystallinity in the sepiolite after chemical treatment (Martinez-Ramirez *et al*., 1996). This line was the most intense feature in the diffraction pattern of sepiolite and the dried Ni precursor/sepiolite but following reduction at 773 K it became broader for Ni/sepiolite and relatively less intense compared to the 4.31 Å line (131 reflection) which was enhanced by this treatment. Sepiolite alone, following reduction under similar conditions, showed enhanced intensity in the 4.31 Å line but in contrast to the Ni containing sample, no loss in intensity or broadening of the 12.1 Å line was observed. The 12.1 Å line was intense and narrow for calcined samples of both the 1% Pd and 5% Pd/sepiolite samples and also for a 1% Pd/sepiolite sample prepared by impregnation. However reduction at 673 K led to the disappearance of this line for the 1% and 5% loaded samples and a corresponding enhancement in the 4.31 Å line although the former effect was not observed for similarly reduced catalysts which had been prepared by an impregnation route. It appears that unlike the impregnation route which leads to readily reducible Pd (Aramendía *et al*., 1994), precipitation of Pd and Ni leads to the formation of species which, upon reduction, results in modifications to the structure of the Mg silicate, which have also been observed, e.g. in the reduction of exchanged Ni in 2:1 phyllosilicates (Kermarec *et al*., 1983)

The DRIFT spectra of sepiolite and sepiolite containing Ni and Pd precursors were recorded at 573 K following outgassing at the same temperature to remove much of the sorbed water. The main features in the spectrum of sepiolite are bands at 3733, 3712, 3685, 3672, 3603, 3593 and 3528 cm^{-1} (Fig. 1a). The spectra obtained do not bear a direct resemblance to those reported by van der Marel & Beutelspacher (1976) for a Salinelles sepiolite but are in good agrement with those reported by Corma *et al*. (1985) for similarly pre-treated Vallecas sepiolite. They are also in general agreement with the four bands reported at 3740, 3674, 3599 and 3532 cm^{-1} by Cannings (1968) for an acid-washed Vallecas sepiolite with the additional features shown in this work present as shoulders or unresolved maxima in Cannings' spectra. The last two bands are assigned to the asymmetric and symmetric stretching modes of molecular water coordinated to Mg^{2+} at the edges of the channels (Cannings, 1968). The band at 3672 cm^{-1} observed for sepiolite (Cannings, 1968; Vicente Rodriguez *et al*., 1994; Martinez-Ramirez *et al*., 1996) is also observed for antigorite and talc (Farmer, 1974) and assigned to hydroxyls on Mg^{2+} ions. Under similar pre-treatment conditions, the Ni/sepiolite precursor spectrum (Fig. 1b) showed additional maxima in the 3650−3600 cm^{-1} range (3644 and 3634 cm^{-1}) and the high-frequency pair observed at 3733 and 3712 cm^{-1} for sepiolite alone were considerably suppressed.

Bands at *c*. 3740 cm^{-1} are a common feature of most silicon-containing oxide materials. For example, a band at 3747 cm^{-1} is present in all forms of dehydrated silicas, is observed at 3745 cm^{-1} for H-ZSM-5 and H-Y zeolites (Morrow, 1990) and bands in this region are also commonly observed for layered silicates (Farmer, 1974) including sepiolite (Cannings, 1968; Martinez-Ramirez *et al*., 1996). In all cases these bands are assigned to terminal, isolated SiOH groups. Adjacent, H-bonded hydroxyls are usually perturbed by ~25 cm^{-1} with respect to these free hydroxyls. The bands at 3733 and 3712 cm^{-1} for sepiolite are therefore attributed to free (Cannings, 1968) and adjacent hydroxyls on silicon atoms which are produced by breaking Si−O−Si bridges which link the silicate layers. Since these species are formed at terminations of the structure, their relative population will depend on fibre dimensions and crystal defects. These hydroxyls are clearly affected by the presence of the Ni precursor
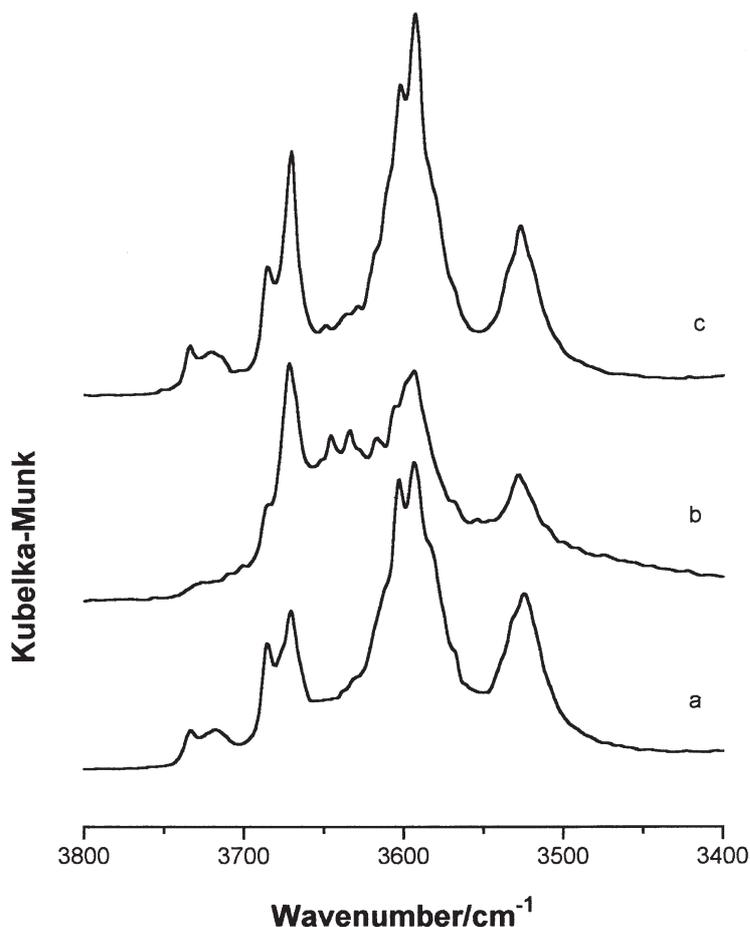
FIG. 1. DRIFT spectra recorded at 573 K of (a) sepiolite, (b) Ni precursor/sepiolite and (c) 5% Pd precursor/ sepiolite following *in situ* outgassing at 573 K for 1 h.

(Fig. 1b). This preferential reaction with, and the complete consumption of, these hydroxyls indicates that at least part, if not all, of the precursor nucleation occurs at these locations and hence that the Ni remains at the external surface of the fibres. The spectrum for the 5% loaded Pd precursor (Fig. 1c) showed relatively minor differences from the untreated sepiolite and these were restricted to differences in relative intensities rather than in band positions.

To determine how the hydroxyl species, and in particular those which might be related to the metal precursor, were affected by the reduction procedure, samples were heated in a flow of H_2/Ar and spectra collected at 100 K intervals up to 773 K. Spectra for Ni/sepiolite (Fig. 2B) are compared with those for a metal-free sepiolite sample (Fig. 2A) with spectra for 1% and 5% loaded Pd/sepiolite shown in Figs. 3A and B, respectively.

Spectra recorded at temperatures below 573 K were not well defined due to the high levels of retained molecular water probably located in the internal channels. However, on heating in a flow of H_2/Ar at temperatures above 573 K, the spectra (Fig. 2) begin to take on the appearance of the samples treated under vacuum at 573 K (Fig. 1) with bands due to the distinct hydroxyl species being resolved. After heating at 773 K, the main spectral features for sepiolite were bands at 3733/3712, 3685, 3672, 3593 and 3528 cm^{-1} (Fig. 2A) whereas at the same temperature the Ni/sepiolite showed maxima at 3672, 3644 and 3593 cm^{-1} (Fig. 2B).
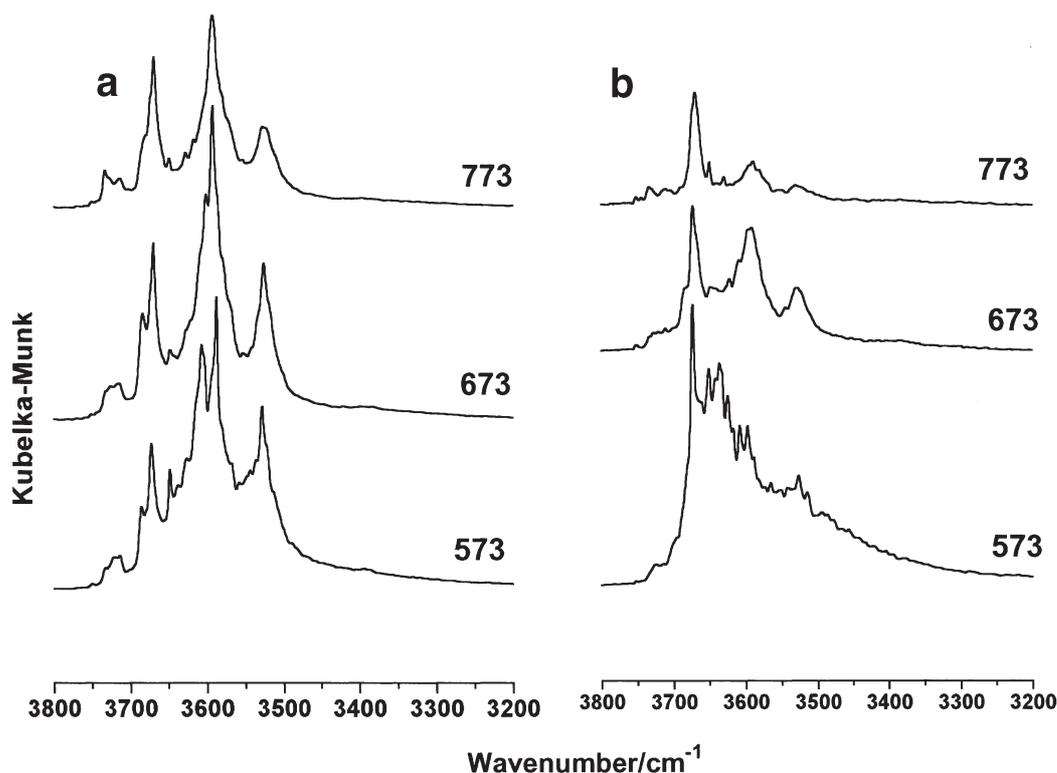
FIG. 2. DRIFT spectra of (a) sepiolite and (b) Ni precursor/sepiolite heated in H_2/Ar with spectra recorded at the temperatures (K) shown.

Bands at 3603 and 3528 cm^{-1} assigned to vOH modes of molecular water coordinated to Mg^{2+} at the edges of the channels disappeared on heating between 673 and 873 K (Cannings, 1968), consistent with the removal of water from these positions at *c*. 723 K (d'Espinose de la Caillerie & Fripiat, 1994). The progressive loss in intensity of these bands as a function of increasing temperature was concomitant with the reduced intensity of a maximum at 1622 cm^{-1} due to the deformation mode of adsorbed water, confirming the assignment of the 3603/3528 cm^{-1} pair to adsorbed H_2O rather than to surface hydroxyls. This water appeared to be more readily removed from the Ni/sepiolite (Fig. 2B) than from the Ni-free sample (Fig. 2A) under equivalent conditions. One explanation for this is that these edge Mg ions of the octahedral sheet are replaced by Ni ions which, as a result of their greater size, exhibit less polarizing power and subsequently weaker adsorption of the water molecules. Consistent with spectra obtained under

degassing conditions (Fig. 1), spectra recorded under a reducing atmosphere (Fig. 2) showed that bands at 3733 and 3712 cm^{-1} due to free and adjacent silanols observed for sepiolite alone were considerably suppressed for Ni/sepiolite.

Spectra for Pd catalysts at the lowest reduction temperatures (Fig. 3) revealed a better resolution of the hydroxyl bands than spectra at the equivalent temperatures for sepiolite or Ni/sepiolite (Fig. 2). This can be attributed to the removal of water during the pre-calcination treatment for these samples and is in agreement with a previous statement which attributed the poor signal in Fig. 2 to the high absorption by molecular water held within the layered structure. Palladium catalysts showed certain features common to the sepiolite alone, including bands at 3733, 3712, 3685 and 3672 cm^{-1} (Fig. 3). However, maxima in the range 3650−3450 cm^{-1} which are common to both sepiolite and the 5% Pd/sepiolite sample (Fig. 3B) were at best only very weak features for the 1% Pd
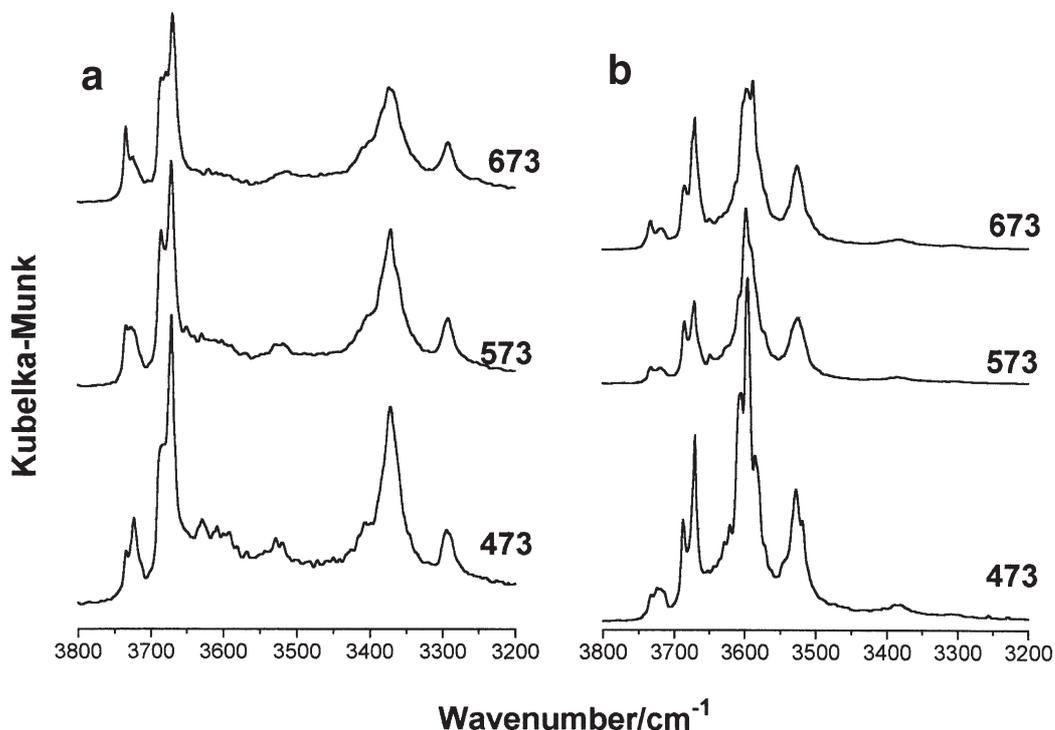
sample (Fig. 3A). Additional features for the 1% sample were bands at 3370 and 3293 cm^{-1} which were only very weak in the spectrum of the 5% Pd sample and absent for the Ni sample and for sepiolite alone. The appearance of a band at 1673 cm^{-1}, in addition to the 1622 cm^{-1} band in the case of the 1% Pd sample alone, indicates that bands at 3370 and 3293 cm^{-1} can be assigned to νNH modes of molecular ammonia produced by the preparation procedure involving decomposition of urea.

From a review of data for NH_3 coordinated to Lewis acidic sites on metal oxides (Kung & Kung, 1985) the $\nu_{as}NH$ and ν_sNH modes should fall within the range 3330−3380 and 3260−3280 cm^{-1}, respectively. This is consistent with observations made here and with bands at 3380 and 3275 cm^{-1} for ammonia adsorption on MgO (Coluccia *et al.*, 1983). The presence of these features due to adsorbed ammonia and the corresponding reduced intensities of bands at 3603 and 3528 cm^{-1}, previously assigned to νOH modes of molecular water coordinated to Mg^{2+} at the edges of the

channels, would suggest that this ammonia must be coordinated to the same sites having displaced some of the molecular water from the channels .

As indicated for the dried sample prior to reduction, the 5% Pd sample shows almost identical features to the support alone, and similarly, comparing spectra after reduction at 673 K (Figs. 2A,3B) reveals only minor differences.

The ^{29}Si MAS-NMR spectrum of sepiolite shows three main lines at −92, −95 and −98 ppm (Fig. 4a) due to the three different sites (near edge, centre and edge, respectively) of similar concentrations as expected for a structure in which the tetrahedral sheet exhibits inversion at every sixth Si. These results, and the detection of an additional, weaker line at −85 ppm are consistent with previous ^{29}Si NMR spectra of sepiolite (Barron & Frost, 1985; Komarneni *et al.*, 1986; d'Espinose de la Caillerie & Fripiat, 1994). From the chemical shift value observed (−85 ppm), it would appear that these are geminal (Q^2) rather than single (Q^3) silanols although the latter assignment would be the most logical in the case that
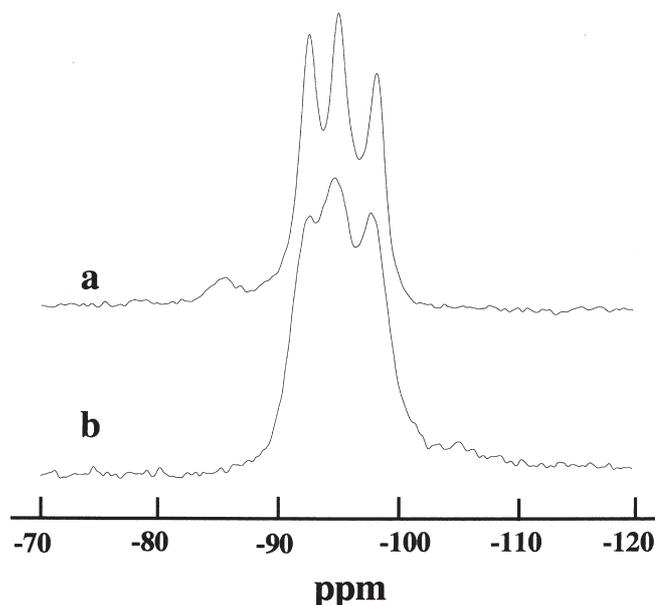
FIG. 4. One-pulse ^{29}Si MAS-NMR spectra of (a) sepiolite and (b) Ni precursor/sepiolite.

their origin is due to termination of the surface following rupture of Si−O−Si bridges between the silicate ribbons. Although there is some disagreement about the exact assignment (Barron & Frost, 1985, Komarneni *et al*., 1986), this line would appear to be due to an edge Si atom bonded to a hydroxyl (Barron & Frost, 1985; Komarneni *et al*., 1986) probably Q^2(Si−OH) (Barron & Frost, 1985; d'Espinose de la Caillerie & Fripiat, 1994). A reverse correlation between the −85 and the −98 ppm resonances, due to Si atoms at the edge of a silicate ribbon and bonded via a basal oxygen to an adjacent silicate layer (Barron & Frost, 1985) would confirm the assignment to an hydroxyl bound to an edge Si. The −85 ppm line was not observed under similar conditions for a sample of the Ni precursor/sepiolite (Fig. 4b). A ^{1}H to ^{29}Si cross polarization experiment at short contact time (1 ms) conducted with the same sample did not lead to the apperance of the −85 ppm line, hence confirming that removal of the hydroxyl group from this Si environment had occurred.

As in the case of Ni, the Pd precursor influences the ^{29}Si NMR spectrum, with some degree of sensitivity to the loading of the precursor (Fig. 5a,b). The lower loading gives Si lines at −85, −89, −92 and −96 ppm while the higher loading gives signals at −85, −88, −91, −95 and −97 ppm. The clear resolution between the signals of the sepiolite sample was lost following deposition of the Pd precursor. However, the −85 ppm line, although not well defined, remains, following addition of the Pd precursor, quite unlike the case for Ni (Fig. 4b). Single pulse experiments conducted with a 1% Pd/sepiolite sample prepared by an impregnation procedure produced a spectrum almost identical to that of the untreated sepiolite. This indicates that the impregnation route deposits a precursor with minimal interaction with the silicon environments whereas the Pd precursor formed by precipitation results in direct interaction with the silicons in the tetrahedral sheet.

The loss of the −85 ppm line in the NMR spectrum for Ni/sepiolite (Fig. 4), can be directly related to the loss of Si−OH groups (observed in IR spectra Figs. 1, 2) resulting from the interaction between the sepiolite and the Ni precursor. Precipitation-deposition of the Ni precursor appears to consume such hydroxyls. In contrast, Parkyns has commented (van Dillen *et al*., 1977) that the 3750 cm^{-1} band due to isolated silanols on silica is not affected during the preparation of catalysts containing 25% Ni using the same procedure although surface hydroxyl groups are known to play an important role in dispersing Ni precursors on silica supports (Guo *et al*., 1990). In
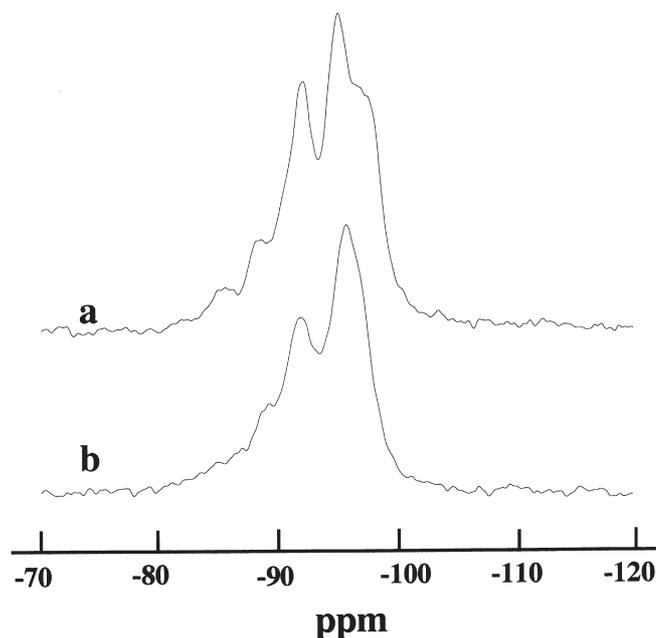
Fig. 5. One-pulse ^{29}Si MAS-NMR spectra of (a) 5% Pd precursor/sepiolite and (b) 1% Pd precursor/sepiolite.

contrast to the behaviour of Ni, neither the IR band pair at 3733/3712 cm^{-1}, due to surface silanols, nor the -85 ppm line are removed following precipitation of the Pd precursor, independent of the percentage loading. This indicates that the Pd precursor does not specifically interact with these surface sites.

The suppression of Si–OH species for the Ni/sepiolite precursor is compensated by additional IR bands at 3644 and 3634 cm^{-1} (Fig. 1b) which did not appear in the spectrum of the outgassed sepiolite alone. Similarly, although maxima appear in this region for sepiolite heated under reducing conditions (Fig. 2A), the relative intensities (e.g. compare spectra at 573 K in Fig. 2A and B) are considerably greater in this spectral region for the Ni containing sample, indicating additional types of hydroxyl to be present. Nickel talc and nepouite (Ni-antigorite) are known to give bands due to ν_{OH} at 3645 and 3625 cm^{-1}, respectively (Clause *et al*., 1992). However, partial replacement of Mg by Ni may give up to four stretching frequencies (3677, 3663, 3646 and 3627 cm^{-1}) corresponding to the possible combinations of the two different cations within the three octahedral sites which are directly linked to a hydroxyl group (Farmer, 1974). Large degrees of substitution give rise to a single

maximum at 3627 cm^{-1} consistent with the expected value for Ni talc (Clause *et al*., 1992). The band pair at 3644 and 3634 cm^{-1} observed for the Ni/sepiolite precursor may not be unambiguously assigned but probably indicates the presence of Ni substituted into the octahedral sheet near the edge and Ni–OH in a nepouite type layer, the latter being consistent with the band assignment at 670 cm^{-1} to δ_{OH}. in a nepouite structure (Clause *et al*., 1992) which we have also observed for these samples (Anderson *et al.,* 1997).

All samples produced by the precipitation procedures show a resistance to reduction, e.g. for the 10% Ni sample, only 54% of the total Ni was reduced at 773 K, while the 5% Pd sample was incompletely reduced at 573 K and could only be completely reduced above 673 K. This contrasts with published data for Pd/sepiolite samples prepared by impregnation where complete reduction is achieved below 493 K (Aramendía *et al*., 1994), and with the behaviour of other supported Pd catalysts in general where complete reduction is achieved below 523 K (Chang *et al*., 1985; Fagherazzi *et al*., 1995). In such cases, it can be assumed that the Pd precursor forms a phase which is chemically detached from the support, with the latter acting only as a physical matrix for the

precursor. In contrast, precursors formed by precipitation on sepiolite form a phase which exists as an integral part of the interface layer. This modifies the nature of the silica tetrahedral sheet as indicated by modifications to the ^{29}Si NMR spectrum, while removal of the metal ion by reduction leads to further structural modifications of the sepiolite as indicated in the diffraction patterns. The 4.6% unreduced Ni which remains following reduction at 773 K far exceeds the maximum quantity of Ni^{2+} which could be ion-exchanged into the sepiolite structure indicating the presence of an additional layer structure with high Ni concentration.

CONCLUSIONS

The nature of interaction between the sepiolite support and the metal precursor depends upon the method of preparation (comparing impregnation and precipitation), the metal ion involved, and the loading of precursor used. Precursors of both metals obtained by precipitation form an integral part of the interface layer leading to a high degree of resistance to reduction. Nickel precipitated onto the surface selectively reacts with Si−OH groups which may promote the onset of formation of Ni silicates while Pd shows no evidence of specific interactions, but again modifies the local Si environments of the tetrahedral sheets. Reduction of the metal precursors leads to modifications in the sepiolite structure resulting in alterations to some of the crystallographic parameters but without leading to collapse of the structure or significant loss of BET surface area. Ammonia produced by decomposition of the starting reagents may be retained within the sepiolite channels and may resist thermal treatments.

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