

Infrared spectral characteristics of metal-support interactions in Ni-Silica catalysts†

G P Babu,* A G Basrur, A N Bhat & R S Murthy
Hindustan Lever Research Centre, Andheri (East), Bombay 400 099

The precipitation of nickel hydroxy carbonate on silica has been carried out using NiSO_4 and Na_2CO_3 under varying conditions of temperature and pH. Thermal and infrared studies show a shift of carbonate-rich to hydroxide-rich composition as the severity of precipitation medium increases. The doublet band at 1050 and 1000 cm^{-1} in the IR spectrum of silica-supported nickel catalyst is assigned to the silicate species bonded to Ni-O-C-O and Ni-O-H groups respectively. The IR spectra of samples with high $\text{CO}_3^{2-}/(\text{OH})_2^-$ ratio exhibit a strong band at 1050 cm^{-1} ; this disappears more rapidly compared to the band at 1000 cm^{-1} when the reduction temperature is increased from 200 to 450°C. Therefore, a strong interaction between $\text{Ni}(\text{OH})_2$ and silicate species is supported by infrared studies.

The metal support interaction between nickel metal and supports like Nb_2O_5 and TiO_2 has been claimed¹ to be only surface phenomenon, i.e., encapsulation of the metal.

The strong metal-support interaction has been suggested to result in the formation of nickel hydroxy-silicate layers on the surface of the silica matrix. Recently, Nitta *et al.*², reported that a metal-support interaction exists between nickel hydroxide and silica surface. The nature of such an interaction between nickel and silica support is yet to be made clear. The aim of this paper is to compare the results (both TGA and IR) with literature data to have a clear understanding of metal-support interaction in Ni-SiO₂ systems.

Materials & Methods

The catalyst precursors were prepared by precipitation method as described by Nitta *et al.*². The alkali solution and nickel solution were added to a vessel containing silica slurry. The precipitation temperature and alkalinities were varied to prepare precursors with different compositions.

Thermal analysis experiments were performed using Dupont 990 thermal analyzer. Infrared spectra of catalyst precursors were recorded on a Nicolet FTIR spectrophotometer 20 SXB with thin transparent disks containing 1 to 2 mg of sample and 10 to 20 mg of KBr powder.

Results and Discussion

Thermal studies

The TGA of nickel hydroxide (Fig. 1) shows two mass loss steps: (i) between 25 and 200°C (DTG peak

at 50°C) due to moisture loss; and (ii) between 200 and 450°C (DTG peak at 270°C) due to decomposition of nickel salt. Similarly basic nickel carbonate also shows two mass loss steps with DTG peaks at 50° and 285°C. Though the second step accounts for expulsion of CO_2 and H_2O from the basic carbonate a single DTG peak is observed due to the narrow gap between the temperatures at which NiCO_3 and $\text{Ni}(\text{OH})_2$ decompose.

The DTG peaks were recorded at very high attenuation for silica-supported nickel precursors and are shown in Fig. 2. The mass loss steps for the loss of moisture remain unaffected (DTG peak at 50°C) but the nickel salt decomposes at marginally delayed temperatures, the shift for hydroxide precursor showing from 270 to 290°C and that for basic carbonate from 285 to 300°C. Supported precursor precipitated at low severity (70°C) contains high concentration of carbonate species compared to the sample prepared at 90°C, the DTG position does not show any significant shift. Nitta *et al.*² and Blackmond and Ko³ during their thermal studies observed that decomposition of nickel salt takes place around 300°C. In their DTG profiles, the peaks were rather broad with nickel hydroxide rich samples. Low concentration of nickel loading and favoured conditions for nickel silicate formation could be responsible for the absence of sharp DTG peak of decomposition (between 200 and 450°C).

The DTG and TGA profiles of the catalyst precursors prepared at different pH values are shown in Fig. 3. Increase in alkalinity also shifted NiCO_3 to $\text{Ni}(\text{OH})_2$ species favouring nickel silicate formation resulting in decrease in mass loss between 200 and 450°C.

† Paper presented in the National Workshop on Spectroscopic Methods in Heterogeneous Catalysis held at Bombay during 20-22 December 1989.

IR spectral studies

More details concerning nickel precursors are provided by IR studies. The IR spectrum of the basic nickel carbonate exhibit characteristic bands at 835, 1380 and 1460 cm^{-1} and that of nickel hydroxide a few characteristic bands at 3648 and 530 cm^{-1} . The IR spectrum of silica support, before nickel precursor deposition, displays bands due to $\nu_{\text{as}}\text{Si-O}$ and $\nu_{\text{s}}\text{Si-O}$, respectively at 1097 and 800 cm^{-1} . These bands disappear completely after nickel precursor deposition and the IR spectrum of the metal-support catalyst exhibit a doublet at 1050 and 1000 cm^{-1} , in addition to the characteristic bands of basic nickel carbonate.

The IR spectrum of nickel precursor precipitated on silica at 70°C (less severity) rich in carbonate species exhibited a strong band at 1050 cm^{-1} , whereas that of the catalyst prepared at 90°C displayed comparatively a less intense band at 1050 and a more intense band at 1000 cm^{-1} . The $\text{CO}_3^{2-}/(\text{OH})_2^-$ mole ratio analysis of these samples also indicated a gradual fall in CO_3^{2-} concentration and increase in $(\text{OH})_2^-$ concentration (Table 1) as precipitation temperature rose from 70 to 90°C. Similarly, the IR spectra of nickel precursors precipitated on silica at pH values 8.8, 9.8 and 10.4 exhibited bands (Fig. 4) which appear to change the trend from relatively more intense 1050

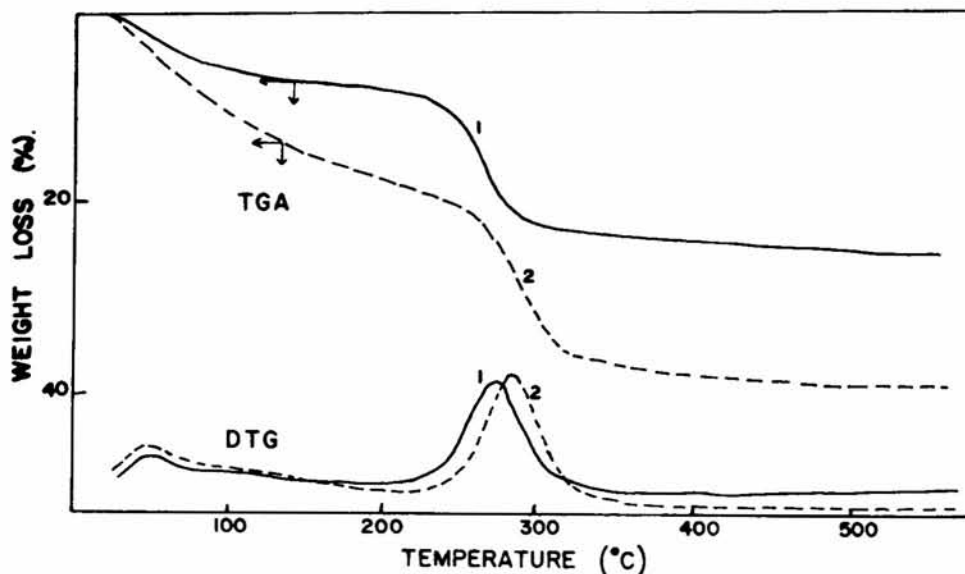


Fig. 1—TGA and DTG profiles of unsupported (1) nickel hydroxide and (2) basic nickel carbonate

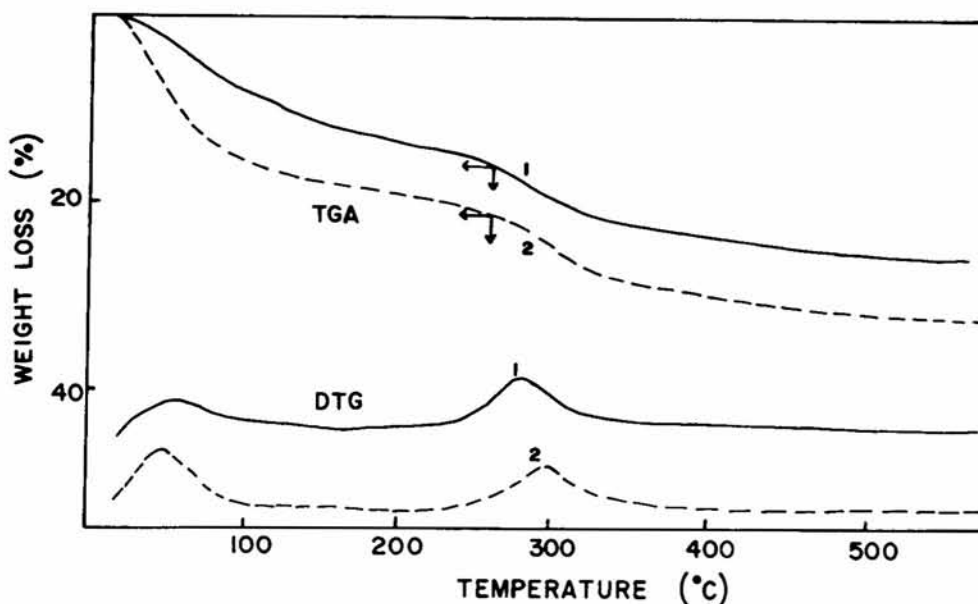


Fig. 2—TGA and DTG profiles of silica supported (1) nickel hydroxide and (2) basic nickel carbonate

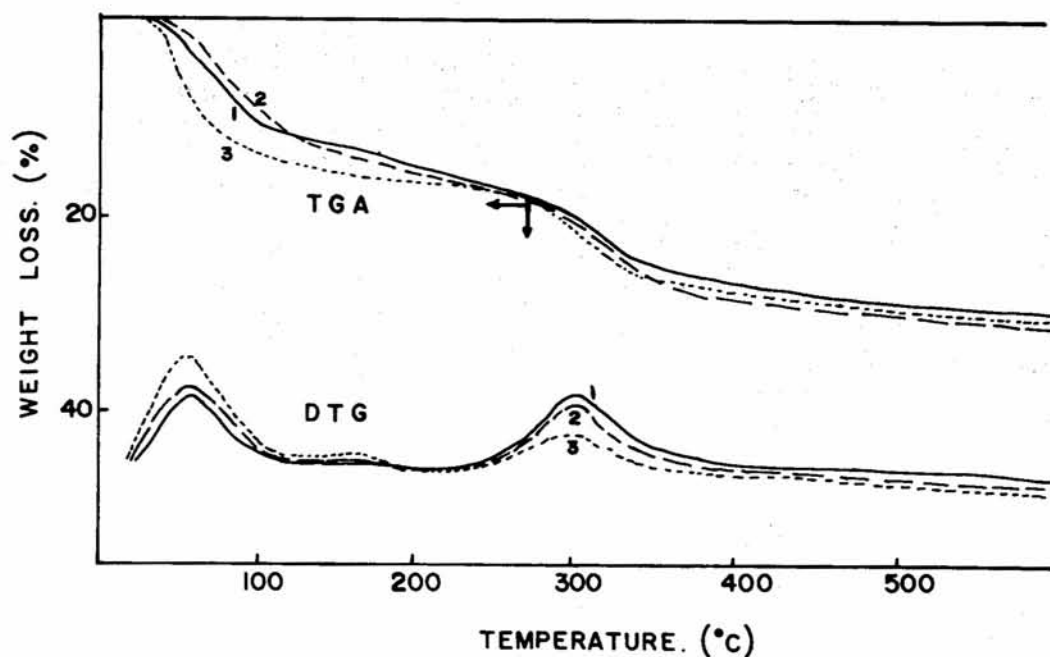


Fig. 3—TGA and DTG profiles of supported catalyst precursors prepared at different pH values (1) 8.8, (2) 9.8 and (3) 10.4

cm^{-1} band to more intense 1000 cm^{-1} band with the change in precursor composition from carbonate-rich to hydroxide-rich species.

The catalyst precursor with known $\text{CO}_3^{2-}/(\text{OH})_2^-$ mole ratio was reduced at different incremental temperatures viz., 200, 275, 310, 350, 400 and 450°C and the IR spectra of the reduced species then obtained were recorded (Fig. 5). Between 200 and 310°C the doublet band showed more rapid decrease in intensity of the band at 1050 cm^{-1} compared to the disappearance of the band at 1000 cm^{-1} . Analysis of the $\text{CO}_3^{2-}/(\text{OH})_2^-$ ratio also indicated that carbonate decomposed more rapidly than hydroxide in that temperature range. Finally, in the IR spectra of samples reduced between 310 and 450°C both the bands at 1050 and 1000 cm^{-1} disappeared leaving behind strong bands at 1022 and 672 cm^{-1} . All other bands due to basic nickel carbonate also completely disappeared for the sample reduced at 450°C . Though the high temperature (450°C) reduced sample has only Ni-SiO₂ species, surprisingly, the bands characteristic of silica vibrations (1097 and 800 cm^{-1}) were not observed. Instead, silicate vibrations appeared at 1022 and 672 cm^{-1} . From the above observation, it is concluded that the silica surface is coated or covered with nickel silicate layers. Similar observation was made on Ni-SiO₂ systems prepared by urea precipitation method³. Also, it has been reported³ that the tendency of silicate layer formation on the silica matrix was low on impregnated catalyst and it was more on precipitated catalysts. Van Dillen *et al.*⁴ have reported that during the precipi-

itation above 90°C the nickel hydroxide reacts more rapidly with silica support to give nickel silicate layers, over which the nickel precipitates as carbonate or as hydroxide depending on the severity of the precipitation. Therefore, the IR spectra of unreduced/reduced nickel-SiO₂ samples do not show the existence of free silica (bands at 1097 and 800 cm^{-1}). The silicate band 1022 cm^{-1} has split into doublet bands at 1050 and 1000 cm^{-1} were assigned to the silicate species

bonded to $-\text{Ni}-\text{O}-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{O}-$ and $-\text{Ni}-\text{O}-\text{H}$

Table 1—Characterization of catalyst precursors prepared and pretreated at various different conditions

Sample No.	Precipitation temp.	pH	Reduction temp. ($^\circ\text{C}$)	% mass loss between 200 and 450°C	$\text{CO}_3^{2-}/(\text{OH})_2^-$ mole ratio
1	70	10.4	NIL	14.18	0.67
2	90	10.4	NIL	10.99	0.44
3	90	8.8	NIL	14.20	0.73
4	90	9.8	NIL	13.12	0.67
5	90	10.4	NIL	11.02	0.44
6	90	8.5	250	12.08	0.74
7	90	8.5	275	12.10	0.59
8	90	8.5	310	9.90	0.49
9	90	8.5	350	3.99	0.35
10	90	8.5	400	3.50	0.14
11	90	8.5	450	<1.00	<0.10

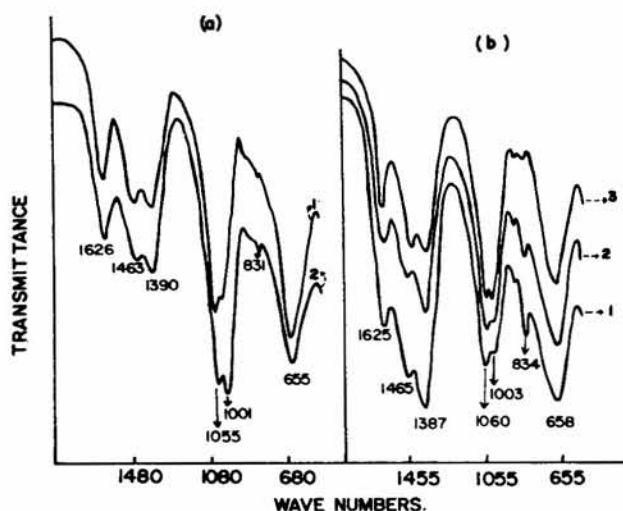


Fig. 4—Infrared spectra of supported catalyst precursors prepared: (a) at different temperatures (1) 70°C and (2) 90°C and: (b) at different pH values (1) 8.8 (2) 9.8 and (3) 10.4

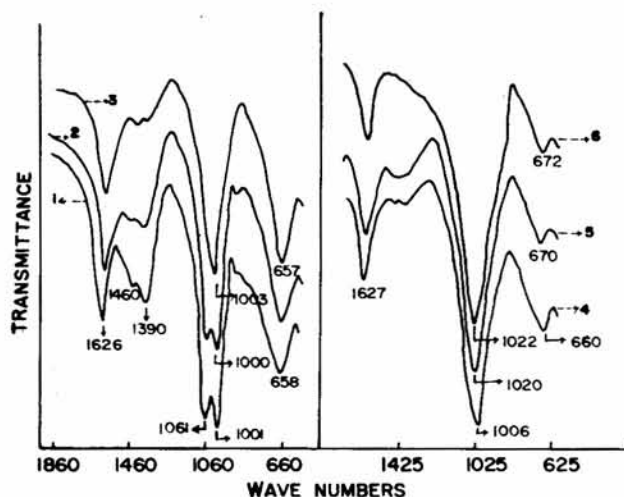


Fig. 5—Infrared spectra of supported catalyst precursors reduced at temperatures (1) 275°C, (2) 310°C, (3) 350°C, (4) 400°C and (5) 450°C and (6) commercial nickel silicate sample

groups respectively. Another important observation was that $-\text{Ni}-\text{O}-\overset{\text{I}}{\text{C}}-\text{O}-$ groups interact weakly with silicate and decomposes first compared to strongly interacted $-\text{Ni}-\text{O}-\text{H}$ groups which decomposes at higher temperature.

The results of IR studies reveal that the interaction exists between the nickel precursor and silicate layer (surface layer of silica). The strength of interaction is different for carbonate-rich and hydroxide-rich precursors with the support surface. There is no simple interaction between nickel hydroxide and silica surf-

ace, but a chemical reaction takes place during precipitation to give nickel silicate layers. On these layers, the basic carbonate deposits on continuation of precipitation. The nickel hydroxide has higher tendency to interact with silicate layer compared to nickel carboante.

References

- 1 Ko E I & Marcelin G, *J Catal*, 93 (1985) 201.
- 2 Nitta Y, Imanaka T & Teranishi S, *J Catal*, 96 (1985) 429.
- 3 Blackmond G & Ko E I, *Appl Catal*, 13 (1984) 49.
- 4 Van Dillen J A, Gues J W, Hermans L A & Meijden J V D, *Proc of 6th International Congress on Catalysis* edited by G C Bond, P D Wells, F C Tompkins (The Chemical Society) 1977, 471.