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NOTE

Infrared Investigations on Metal–Support Interactions in Ni–SiO_2 Catalyst Precursors: Role of Silica

In Ni–silica catalyst system prepared by precipitation/deposition method the silica is reported (1–3) to play a role in forming the "support" to nickel carbonate (or hydroxide) species. The support formed is identified as various types of nickel silicate species (4–8) and also as the species comprising -Ni–O–Si– linkages (9). Further, the support is shown to (i) provide the definite porous structure to the catalyst (10, 11) and (ii) influence the reducibility of nickel species (2). Also, in nickel catalyst system prepared by impregnation method, formation of silicate species on silica surface and its influence on reduction of nickel and restriction in metal sintering is well established (5, 12). However, the mechanism of silica conversion to support species and influence on metal dispersion, the formation of a definite porous network and catalytic activity in Ni–silica catalyst system prepared by precipitation is not well established.

In this paper Ni-silica catalyst precursors were prepared by adding separate solutions of nickel sulfate and sodium carbonate simultaneously to the precipitation vessel containing a silica slurry as described by Nitta *et al.* (2) and maintaining a SiO_2/Ni ratio of 0.5, precipitation temperature = 92°C, and pH = 8.5. During the precipitation reaction samples were collected from the precipitation vessel at different time intervals (0–40 min). The samples were washed free of sulfate, and dried and analysed for the type of nickel–silica interaction (by IR), porosity (by BET), and reducibility of nickel (by redox titration). For FTIR (Nicolet FTIR spectroscopy model 20 SXB) studies a thin transparent disk was prepared by homogenising and pressing 1–2 mg of sample with 10–20 mg of dry KBr powder. To measure the reducibility (% degree of reduction or % DR), the dried powder sample (0.2 g) was heated at 400°C for 30 min under hydrogen flow (15 liter/hr) and cooled. The reduced sample is transferred to conical flask using water (saturated with CO_2). By adding ferric ammonium sulfate the solution was boiled and then sulfuric acid and phosphoric acid were added. Titration was carried out using potassium permanganate at 50–60°C. Metal area was determined by the hydrogen chemisorption method by reducing the sample *in situ* and allowing hydrogen to chemisorb at 25°C. Hydrogenation of rice bran fatty acid (RBFA) was conducted in a 1-liter capacity autoclave by maintaining 200 psi pressure, 300 g RBFA, 0.05% Ni dosage (i.e., the dried precipitate sample equivalent of 0.15 g nickel is weighed and reduced in reduction tube and then added to 300 g RBFA), and 180°C as described in detail elsewhere (9). The reduced (at 400°C) and cooled (to ambient) sample was transferred to the autoclave by adding a small quantity from 300 g of hot (~60°C) RBFA to the reduction tube containing the sample (maintaining hydrogen flow). The remaining proportion of RBFA was used to rinse the reduction tube for effective transfer of the reduced sample. The air inside the autoclave was flushed with hydrogen gas and then heating was started. After attaining the temperature of 180°C the pressure was increased to 200 psi, and then after 1 hr of hydrogenation, the product sample was drawn out and measured for iodine value (IV) by standard iodimetric titration method.

The infrared spectrum of the sample collected at 0 min was analysed (Fig. 1); it was found that it matches closely with fresh parent silica which showed strong characteristic IR bands at 800 cm^{-1} (sym) and 1098 cm^{-1} (asym). The IR spectrum of the sample collected after 2 min was also found to be similar to that of pure silica with a shoulder at <1098 cm^{-1}. The intensity of this shoulder enhanced and appeared as a weak band around 1050 cm^{-1} in the sample collected after 5 min.

Very interesting observations were made with the sample collected at 10 min. Infrared bands of this sample appeared to be composed of multiple bands around 1098 cm^{-1}. Detailed and careful investigation showed the presence of three bands; i.e., (i) IR band characteristic of silica at 1098 cm^{-1} was reduced to a shoulder, (ii) strong IR band characteristic of silicate-type species connected/interacted with carbonate rich basic nickel carbonate species appeared at 1057 cm^{-1}, and (iii) a shoulder appeared around 1000 cm^{-1} which could be attributed to silicate-type species connected/interacted with hydroxide-rich basic nickel carbonate species (9, 13). At 50% addition of reactants (at 20 min) the precipitate sample showed a hardly noticeable IR band at 1098 cm^{-1}, indicating that most of the silica reacted to form silicate-type species.

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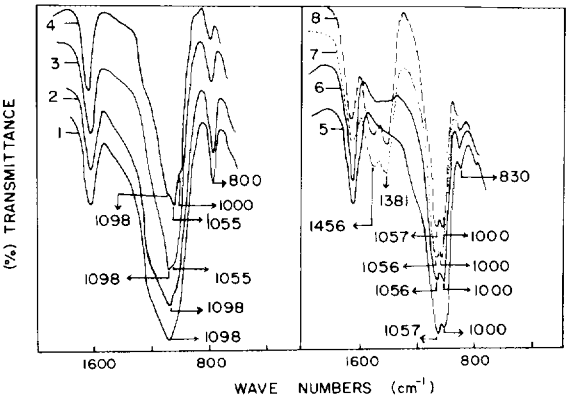

FIG. 1. Ir spectra of basic nickel carbonate precipitates collected from the precipitation vessel at different time intervals. (1) 0 min, (2) 2 min, (3) 5 min, (4) 10 min, (5) 20 min, (6) 30 min, (7) 35 min, and (8) 40 min during the precipitation reaction.

In addition the strong IR band appeared at 1057 cm^{-1}, and the shoulder in the previous sample at 1000 cm^{-1} was converted into a strong band in this sample. Further, the sample collected after 75% of reactants had been added (30 min) had no bands characteristic of silica. These observations confirm that silica conversion to silicate-type (Ni–O–Si) species was completed before the reactant addition was over. In support to the above assumption, the precipitate collected at 87 and 100% reactant addition showed further development in intensity of IR bands at 1381 and 1456 cm^{-1} which are characteristic of basic carbonate species and with no change in the intensities or shapes of the IR bands characteristic of nickel silicate-type species at 1057 and 1000 cm^{-1}.

The BET surface area measurements of the above samples collected during the precipitation were carried out after the reduction (at 400°C). The results indicate low surface areas for the samples collected at 0, 2, and 5 min, i.e., equivalent to the fresh parent silica sample (Table 1). A significant increase in surface area was observed with the sample collected between 10 and 30 min, i.e., from 78 to 200 m^2/g. With increase in precipitation time, the samples collected at 35 and 40 min have shown a marginal increase in surface area from 200 to 215 m^2/g. These results clearly indicate that during silica conversion to silicate-type species surface area increases significantly and after completion of the silica conversion, the increase in surface area is insignificant.

The degree of reduction (DR$^{400°C}$) of nickel in the dried precursor samples indicates low DR (26–35%) for the samples collected between 2 and 20 min as compared to the samples collected at 30, 35, and 40 min (DR = 55–68%). The presence of reactive OH groups in basic nickel carbonate is well established by Mallya (14); also it was described that the number of OH groups forming is dependent on pH and precipitation temperature. Echeverria and Andres (11) and Iler (15) have shown that siliceous matter forms Si–OH groups under alkaline conditions. Therefore, in our experimental studies, it is possible that the silica used in the precipitation reaction having low surface area reacts with basic nickel carbonate to form less easily reducible nickel silicate (Ni–O–Si) type species during the initial stage of precipitation which is responsible for low DR of nickel and also formation of porous network in the precipitate. The precipitate formed after the completion of the silica reaction comprises a high concentration of easily reducible basic nickel carbonate species. Therefore, comparatively high DR values are obtained for these precursor samples (55–68%).

Conclusive evidence on the role of silica is obtained by extracting the support species from the parent precursor and characterising it for textural properties. The support is extracted from the parent precursor as described by Coenen and Linsen (1); i.e., the precursor was treated with NH_4Cl/NH_4OH solution to convert the nickel species that is present as basic nickel carbonate into soluble nickel ammonium complex, leaving behind the nickel species associated with the support (as nickel silicate-type species) as "residue" in the ammoniacal solution. Surface area of the reduced (at 400°C) support (residue) species is measured and found to be comparable to that of reduced parent precursor (Table 1). It is therefore concluded that in Ni–silica system (prepared by precipitation method), during the initial stage of precipitation reaction the silica reacts with basic nickel carbonate to form a highly porous support species. On continuation of precipitation reaction, the fresh basic nickel carbonate species formed further reacts/interacts with the preformed support. During the reduction (at 400°C) stage the support species remain as unreduced and thermally stable species. On the other hand, the basic nickel carbonate species assumes the shape of metal crystallite and may not contribute to the porous structure in the final reduced precursor.

Further, the surface area measurement of silica samples treated with acid (0.1 *N* HCl or 0.1 *N* H_2SO_4) or alkali showed no significant change in surface area. These results indicate that in the absence of basic nickel carbonate precipitate, the silica with low surface area changing into highly porous support-type material is not envisaged under acid or alkaline (precipitation) conditions.

Nickel metal surface area and RBFA hydrogenation activities were measured on the reduced precipitate samples and results are listed in Table 1. The activity data are presented as IV drop and also as molecules converted/atom of nickel/second. From the data it is clear that for the precipitates collected between 5 and 20 min though the increase in DR was marginal (35.32 to 39.10%), the sharp rise in metal area, porosity, and activity indicates that performance of the catalyst is a function of accessibil-

TABLE 1

Properties of Ni–Silica Precursor Samples Collected from the Precipitation Vessel at Different Time Intervals

Sample number	Collected at (min)	Ni (%)	% DR of Ni at 400°C	Surface area (m^2/g)	Metal area (m^2/g Ni)	IV drop 1 hr	Conversion (mol/atom Ni/sec)
1	0	Nil	Nil	40.8	Nil	Nil	Nil
2	2	5.25	26.21	43.8	15.6	15.3	1.76×10^{-2}
3	5	11.58	35.32	46.9	18.6	23.4	2.72×10^{-2}
4	10	18.82	37.61	78.3	36.2	41.8	4.05×10^{-2}
5	20	28.77	39.10	114.3	55.8	52.3	6.08×10^{-2}
6	30	32.43	55.27	200.8	70.3	64.7	7.52×10^{-2}
7	35	34.01	68.28	208.1	80.7	69.2	8.05×10^{-2}
8	40	34.23	68.80	215.6	82.9	71.3	8.28×10^{-2}
9	Silica (fresh)	Nil	Nil	40.5	—	—	—
10	Silica (0.1 *N* HCl)	Nil	Nil	45.6	—	—	—
11	Silica (0.1 *N* H_2SO_4)	Nil	Nil	49.8	—	—	—
12	Silica (alkali)[a]	Nil	Nil	44.3	—	—	—
13	"Support" (extracted from sample No. 8)	24.7	2.90	210.5	1.0	1.8	0.21×10^{-2}

[a] Alkali, 15% sodium carbonate solution (w/v), initial iodine value (IV) of RBFA = 100, Ni dosage = 0.05%. IV drop = initial IV − IV after 1 hr.

ity of metal in suitable porous matrix to the reactant molecules.

From the above results and with the available information in the literature, it could be mentioned that during the intial stage of precipitation reaction (between 2 and 20 min), under alkaline (pH = 8–9) conditions the silica might react with basic nickel carbonate precipitate and generates the support (Si–O–Ni linkages). The above reaction further favours dissolution of silica in the precipitation vessel and therefore results in complete conversion of silica when around 75% of the reactants have been added into the precipitation vessel. The complex and highly disordered cross links of Ni–O–Si linkages could lead to formation of highly porous network. The high DR and no change in surface area for the samples collected at the end of the precipitation reaction (35 and 40 min) indicate that the proportion of basic nickel carbonate freshly precipitated might possibly react with the preformed cross-linked porous support material. Hydrogenation of RBFA over reduced precipitates depends on dispersion of nickel metal in highly porous matrix and accessibility of metal surface to the reactant molecules.

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