

A novel nickel trihydroxy isocyanate – preparation and characterisation

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Abstract. The preparation of a novel nickel trihydroxy isocyanate, along with its distinguishing physicochemical characteristics has been reported for the first time.

Keywords. Nickel; hydroxyisocyanate; PFHS.

1. Introduction

During efforts to prepare well-dispersed alumina-supported nickel catalysts, attempts were made (Maruthiprasad 1985) to deposit nickel on alumina via precipitation as nickel precursors. Three different methods of nickel precipitation from solutions of nickel nitrate were adopted. They were (i) homogeneous ammonia liberation (AL) via urea hydrolysis, (ii) homogeneous deposition of hydroxide by ammonia evaporation (AE) from hexamine nickel nitrate solution, and (iii) addition of aqueous ammonia (AA) solution. As a part of the study, detailed characterisation of the precursors formed in each of the three cases (without the alumina support) were also undertaken. Method AE yielded only Ni(OH)₂, AA resulted in a mixture of Ni(OH)₂ and NiOOH, while method AL gave a nickel compound hitherto unknown. The distinguishing features of the nickel precursor obtained by the AL method are described in this communication.

2. Experimental

Details of the preparation of precursors by AE and AA methods are discussed elsewhere (Maruthiprasad 1985). Preparation of the precursor by the AL method was carried out in the following manner. To 1.6 dm³ of deionised water, 20 g of urea and 0.06 dm³ of nickel nitrate solution containing 122.77 g Ni/dm³ were added with constant stirring at 363 K for 90 min. When the pH of the solution reached 7.0 a green precipitate formed which was filtered, washed and dried at 373 K, and its characteristics were determined.

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3. Results and discussion

The characteristics of the unsupported nickel precursors are summarised in table 1. The unique feature of the precursor AL-373 (373 denoted the Kelvin temperature at which the sample was dried) is revealed in the elemental analysis itself, as indicated by the carbon and nitrogen contents when compared to the other two. The presence of small amounts of carbon in AE-373 and AA-373 could be due to absorption of atmospheric carbon dioxide during preparation. In spite of the higher carbon content AL-373 does not exhibit any characteristic IR bands due to the

Table 1. Summary of characteristics of nickel oxide precursors.

Characteristics	AL-373	AE-373	AA-373
Elemental analysis (wt%)			
a) Carbon	5.68	0.48	0.20
b) Hydrogen	1.45	2.16	2.30
c) Nitrogen	6.63	0.00	0.00
d) Nickel	56.00	63.05	64.00
Phase identified (by XRD)	$\text{Ni}_2(\text{OH})_3(\text{NCO})^*$	$\text{Ni}(\text{OH})_2$	$\text{Ni}(\text{OH})_2 + \text{NiOOH}$
Crystallite size (nm)	—	21.2	17.7
Morphology	Spherical	Square platelets	Irregular
Decomposition temperature (K) (DTA)	614(EXO)	593(ENDO)	573(ENDO)

*On the basis of evidence from other experimental techniques.

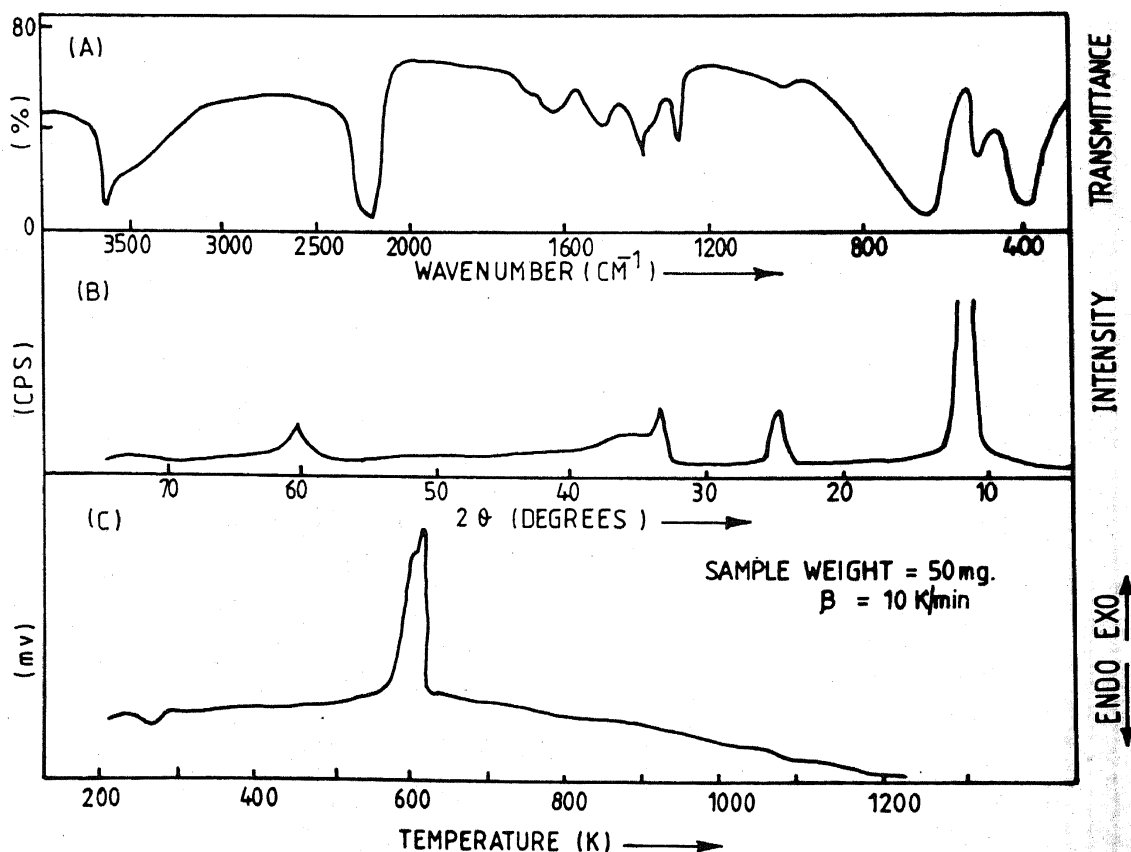


Figure 1. (A) IR spectrum, (B) X-ray diffractogram and (C) DTA curve for $\text{Ni}_2(\text{OH})_3(\text{NCO})$.

carbonate species (figure 1A). Instead, a very strong absorption band at 2200 cm^{-1} , characteristic of functional groups like $-\text{C}\equiv\text{N}$, $-\text{N}=\text{CO}$, or $\text{O}-\text{C}\equiv\text{N}$ is observed. XRD gave evidence of the presence of $\text{Ni}(\text{OH})_2$ in AE-373 and a mixture of $\text{Ni}(\text{OH})_2$ and NiOOH in AA-373 while the pattern for AL-373 (figure 1B) failed to conform to any known phases containing nickel, carbon and nitrogen. The XRD pattern also indicates that AL-373 is paracrystalline in nature and hence meaningful measurement of crystallite size by X-ray line broadening analysis was not possible. Neither XRD nor IR could provide any evidence for the presence of urea either free or bound in a complex.

The origin of the functional groups proposed above could be traced to the ability of urea to isomerise to form cyanic/isocyanic acids in weak acid media (Geus 1983). The transformations leading to isomerisation could be written as

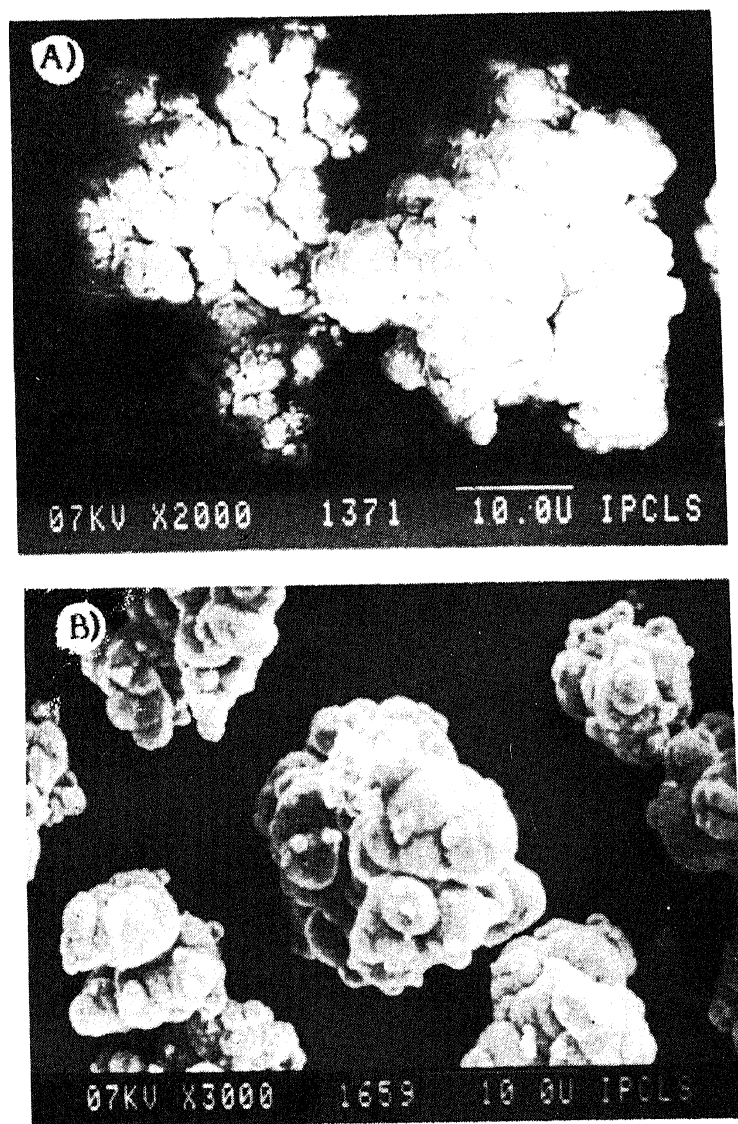
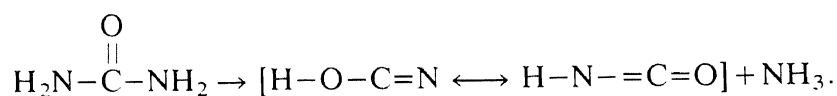
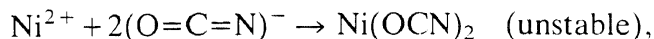
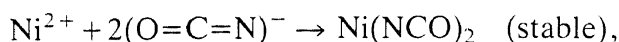


Figure 2. Morphology of $\text{Ni}_2(\text{OH})_3(\text{NCO})$, (A) dried at 373 K and (B) calcined at 673 K.

The presence of Ni^{2+} in the solution could lead to the following reactions



Though both cyanate and isocyanate ions are present in solution, Ni^{2+} species preferentially combine with the isocyanate ion since nitrogen bonding is favoured with nickel (Forster and Goodgame 1964, 1965). The elemental analysis data of AL-373 does not however correspond to a pure nickel isocyanate. Only an empirical formula of the type $\text{Ni}_2(\text{OH})_3(\text{NCO})$ could account for the C, H and N contents of AL-373. A compound of this type has not been reported so far, whose XRD pattern is unique and unindexed.

The most convincing evidence for the formula emerges from thermal analysis. The DTA curve of AL-373 (figure 1C) exhibits an exothermic peak at 610 K (in contrast to AE-373 and AA-373, which show endothermic peaks at 593 K and 573 K, respectively) due to decomposition of the isocyanate species. Weight loss measurements by TG also are in concurrence with the formula $\text{Ni}_2(\text{OH})_3(\text{NCO})$.

AL-373 also exhibits a unique morphology (figure 2), showing clusters of nearly spherical particles, which is retained even after calcination at 673 K. It would be appropriate to add here that Hermans and Geus (1979) obtained a nickel precursor by urea hydrolysis of nickel nitrate (in the absence of support) which also contained higher amounts (3.5%) of carbon. No further analysis data were reported by the authors. However, a detailed analysis of the precursor, as reported here has resulted in the identification of a unique compound $\text{Ni}_2(\text{OH})_3(\text{NCO})$.

Conclusions

Homogeneous precipitation of nickel from a solution of nickel nitrate by urea hydrolysis has resulted in the formation of a novel nickel trihydroxy isocyanate.

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References

- Forster D and Goodgame D M L 1964 *J. Chem. Soc.* 2790
- Forster D and Goodgame D M L 1965 *J. Chem. Soc.* 262
- Geus J W 1983 in *Preparation of catalysts* (eds) G Poncelet, P Grange and P A Jacobs (Amsterdam: Elsevier) vol. 3, p. 15
- Hermans L A M and Geus J W 1979 in *Preparation of catalysts* (eds) G Poncelet, P Grange and P A Jacobs (Amsterdam: Elsevier) vol. 2, p. 113
- Maruthiprasad B S 1985 *Studies on alumina and alumina-supported catalysts prepared by PFHS*, Ph.D. thesis, Andhra University, Waltair