

Ni nanoparticles supported on mesoporous silica (2D, 3D) architectures: Highly efficient catalysts for the hydrocyclization of biomass derived levulinic acid

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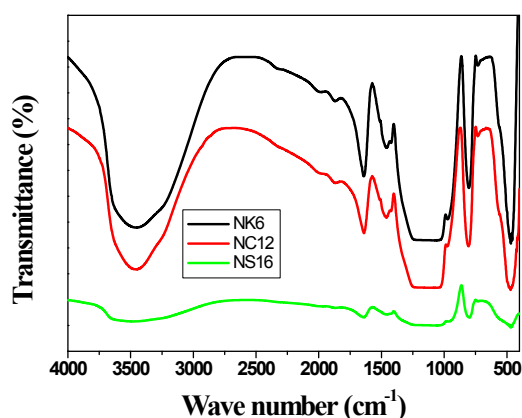


Figure – S1. FT-IR spectra of Ni incorporated mesoporous silicas.

The FT-IR spectra of Ni incorporated catalysts are shown in Figure – S1. For 30 wt% loading of Ni on various mesoporous supports like K6, C12 and S16 catalysts showed the bands at 3738, and 3600-3200 cm^{-1} are attributed to isolated, hydrogen-bonded and geminal types of the surface silanol groups, whereas 1632 cm^{-1} is ascribed to adsorbed water molecules¹. In addition to the bands as mentioned above, typical Si–O–Si bands are observed at around 1080, 814 and 459 cm^{-1} which are allied to the condensed silica network. The siloxane, $(\text{SiO})^n$ peak appears as a broad and a strong peak centered at 1100 cm^{-1} . Furthermore, the strong band at 1078 cm^{-1} can be ascribed to the Si–O–Ni². In the present case, these are not clearly visible most probably due to the merging with the broad signal appeared between 1000- 1300 cm^{-1} . Alternatively, a small intense peak at around 960 cm^{-1} could be due to Si–OH and/or Si–O–M stretching vibrations^{3,4}. It is reported that the slight shift in peak position in the region of 960 and 1080 cm^{-1} were observed through the modification of metal⁵.

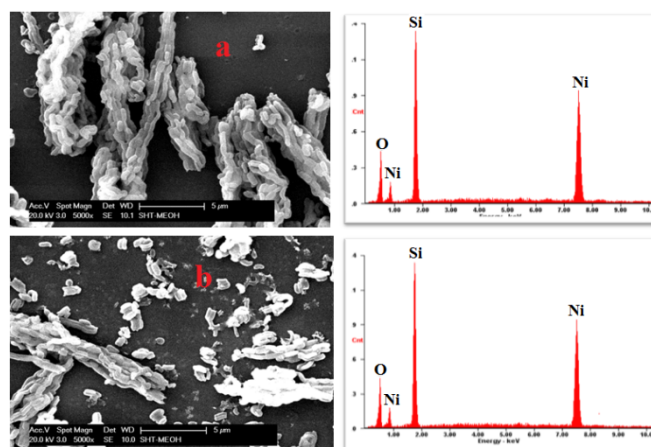


Figure – S2. SEM and EDAX images of NC12 (a) reduced (b) used.

Figure – S2 shows the SEM images of both reduced and used (collected after the levulinic acid hydrocyclization) NC12 catalysts with their corresponding EDAX profiles, which indicate the rod-like morphology and preserving hexagonal symmetry of the catalysts even after reaction. From the EDAX results, it is clear that the amount of Ni is almost same in fresh and used catalysts indicating no leaching of metal during the reaction.

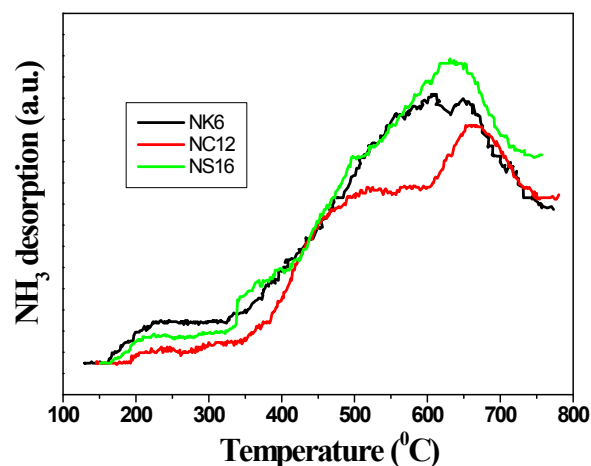


Figure-S3. NH₃-TPD profiles of Ni incorporated mesoporous silicas.

The NH₃-TPD profiles of the catalysts are displayed in Figure – S3 and the acidity values are shown in the Table-2. The acid site distributions are mainly classified by temperature range, which are < 250 °C (weak), 250-400 °C (medium) and > 400 °C (strong) acidic sites⁶. From these profiles, it is clear that all the catalysts predominantly showed strong acid sites which are due to the presence of Si-OH. As we know the presence of hydroxyl groups affects the surface acidic properties⁷. These results are in good agreement with the FTIR where we found the presence of Si-OH at 3600-3200 cm⁻¹ (Figure-S1). For the better understanding of the type of acid sites present in the catalysts, we recorded the FTIR spectra of the samples by adsorbing pyridine (Figure-S4). The spectra indicated the presence of Lewis acid sites (1445 , 1595 and 1612 cm⁻¹) and the combination of Lewis & Bronsted acid sites (1490 cm⁻¹)⁶. The peaks accessible at around 1545 and 1635 cm⁻¹ attributed to the Bronsted acid sites⁸. The existence of both Lewis and Bronsted acid sites plays a decisive role in the dehydration of intermediate (4-hydroxy valeric acid) which formed during the course of the reaction. Furthermore, the 2D mesoporous silica possesses high surface hydroxyl groups because of this one can see the significant difference in pyridine adsorbed FTIR patterns than the 3D mesoporous porous silica. This clearly indicates the acidity responsible for obtaining the gamma valerolactone while further hydrogenated products were noticed on 3D mesoporous silicas supported Ni catalysts attributed to the dominance of metallic nanoparticles.

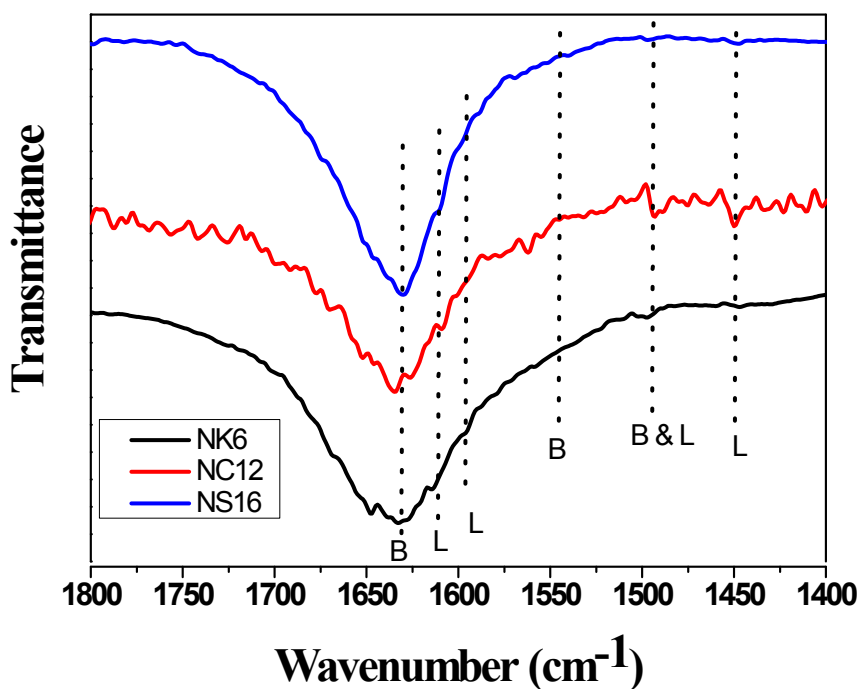


Figure – S4. FT-IR spectra of Pyridine adsorbed Ni incorporated mesoporous silicas (a) NK6 (b) NC12 (c) NS16.

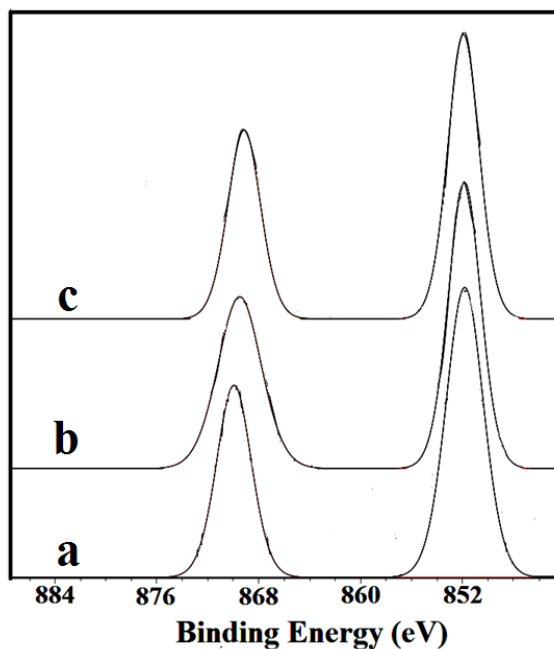


Figure – S5. XPS patterns of reduced Ni incorporated mesoporous silicas a) NK6 b) NC12 c) NS16.

The XPS spectra of all the reduced catalysts are shown in Figure – S5. It can be seen from the Figure – S5 that the two major peaks are observed with binding energies (BE) of 852.8 and 869.7 eV which corresponding to the core level Ni 2P_{3/2} and Ni 2P_{1/2} transitions of Ni metal.

The BE values are in line with the reported literature values^{6,8}. The separation between two peaks (≈ 17.2 eV) is very close to the reported values^{6,8}.

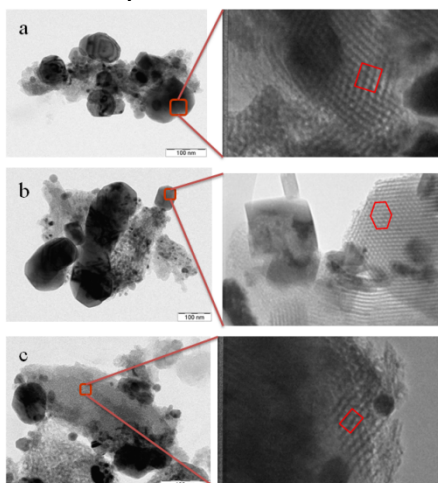


Figure – S6. TEM images of mesoporous silica's supported Ni catalysts a) NK6 b) NC12 c) NS16 (Cubic (NK6, NS16) and hexagonal (NC12) morphologies seen in alternate figures respectively).

References:

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