

## ULTRASONICALLY SYNTHESIS OF NICKEL NANOPARTICLES IN 2D AND 3D HEXAGONAL MESOPOROUS SILICA

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### ABSTRACT

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Nickel catalyst supported on 2D and 3D hexagonal mesoporous silica was synthesized with ultrasonically incipient wet impregnation method. The catalysts prepared were characterized by HRTEM, XRD, and Nitrogen adsorption-desorption isotherm techniques. Nickel particles were finely dispersed on the surface of the mesoporous silica in case of 3D hexagonal morphology, and some particles were found to be aggregated on the outer wall of the support in the case of 2D hexagonal mesoporous silica.

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### 1.0 Introduction

Highly active heterogeneous catalysts often call for high surface area support materials onto which active phase(s) can be deposited. In this respect MCM-type [Kresge et al., 1992; Beck et al., 1992] and related mesoporous materials display interesting textural properties, combining high surface areas and porosities. Since the first discovery of MCM-41 efforts have been undertaken to apply metals inside the mesopores, to prepare silica-based heterogeneous catalysts with unprecedented high surface areas and unique structures. However, to exploit the favourable properties of MCM-41 and related mesoporous materials dedicated catalyst synthesis procedures need to be developed. The most frequently applied method to prepare nickel catalysts supported by mesoporous materials is incipient wetness impregnation with simple nickel precursor salts, such as nickel nitrate [Ziolek et al., 1998; Klimova et al., 1998] and nickel chloride [Junges et al., 1998]. Ziolek et al. showed that the hexagonal structure of

aluminum-containing MCM-41 was preserved upon impregnation with nickel nitrate (nickel loading was 5 wt %) [Ziolek et al., 1998]. Only catalyst preparation via impregnation with nickel nitrate has resulted in catalysts with nickel loadings exceeding 5 wt% [Cui et al., 1997; Yue et al., 1997]. Unfortunately, already at nickel oxide loadings as low as 6-10 wt % the use of this precursor results in intense NiO reflections in XRD after calcination, indicating the formation of large nickel oxide particles. Moreover, a rather large decrease in surface area and pore volume was observed, both with MCM-41 [Cui et al., 1997; Yue et al., 1997] and KIT-1 [Yue et al., 1997]. Here we used nickel nitrate solution, followed by addition to powder support with different morphology (2D and 3D hexagonal mesoporous silica) via ultrasonically incipient impregnation to understand the effect of mesoporous structure on the catalyst loading.

## 2. Experimental

### 2.1 Synthesis

#### 2.1.1 Support Synthesis

The mesophases were prepared in aqueous solution using EO106PO70EO106 (Pluronic F127, Sigma) as structural directing agent, and tetraethylorthosilicate (TEOS, Aldrich) as a silica precursor. High quality samples were obtained in the optimum conditions of synthesis. In a typical synthesis, for 2D-hexagonal (sample 1), 0.8 g and for 3D-hexagonal (sample 2), 1 g of F127 was dissolved in 4 g of acidified distilled water (pH =1.3) and 9 g EtOH, then reflux for 2h at 60 oC. To this mixture, 5 g of TEOS was added under stirring. The mixture still stirred at 60oC for 24h for the formation of mesostructured material. The solid product was then filtered and dried at 60oC without washing. To remove the template, the solid was slurried in an EtOH/HCl mixture, filtered, dried, and calcined in air at 450 oC with slow heating and cooling rates.

#### 2.1.2 Catalyst Preparation

For the 2 samples, nickel catalysts were prepared by incipient wetness impregnation of the powdered supports with solution of nickel nitrate under sonication for 4 hours. After impregnation the samples were dried for 8 hours at 100 oC and calcined for 6 hours at 450 oC in air.

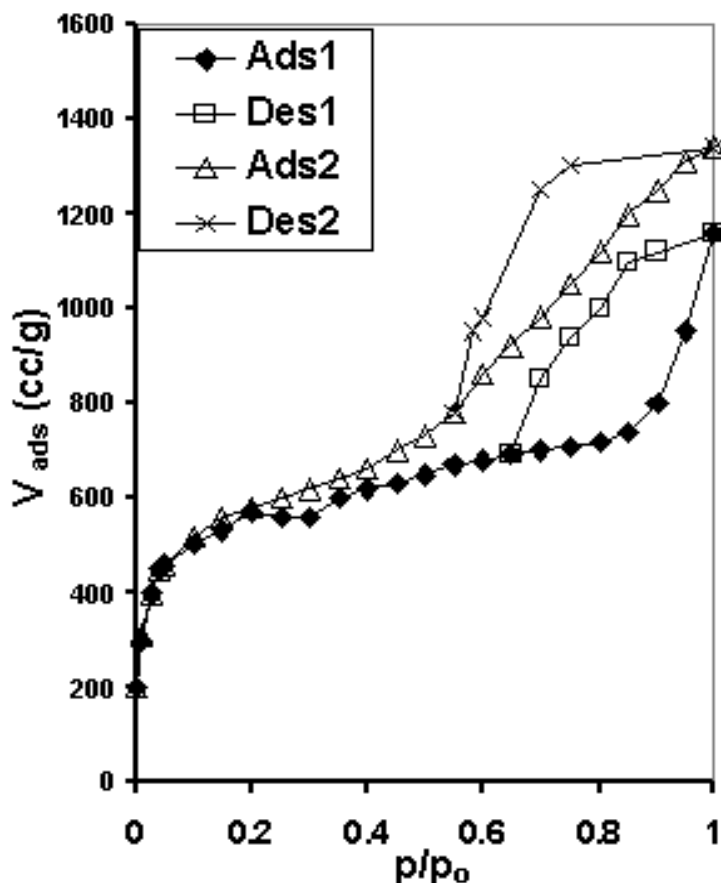
### 2.2 Characterization

The phase structure and pore size of mesoporous silica materials were evaluated by X-ray diffraction pattern obtained from Philip X-ray diffractometer equipped with a CuK $\alpha$  radiation source. High Resolution Transmission Electron Microscopy-Electron Diffraction (HRTEM-ED) Philips using an accelerating voltage of 200 kV and EMS software for electron diffraction analysis and TEM image simulation by using Bloch wave method was used to perform the morphology of the samples. The Brunauer–Emmett–Teller (BET) surface area was measured at 60 oC on Nitrogen adsorption isotherm apparatus USA. The samples were degassed for 12 hours at 300 oC.

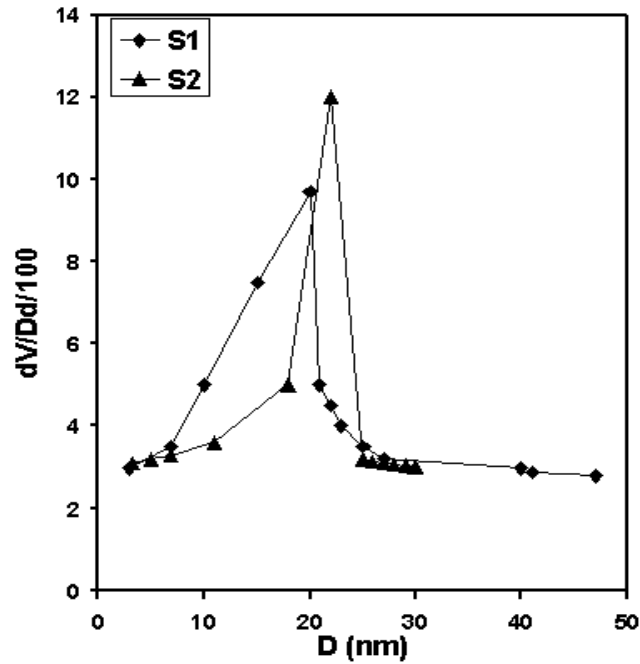
### 3. Results and Discussion

#### 3.1. Nitrogen Adsorption-Desorption Isotherm

The textural characteristics of the mesoporous support materials and the nickel catalysts were determined with nitrogen physisorption. Representative isotherms of the parent materials obtained are given in (Fig. 1). Sample 1 with 2D-hexagonal sample shows a hysteresis at a relative pressure 0.36, which indicates that the pores are mesoporous range. Sample 1 represents the parent sample (without loading catalyst) of mesoporous silica with pore size about 20 nm. Sample 2 which represents the parent sample of sample 2 (without loading catalyst) has 3D hexagonal structure with pore size about 25 nm. With 3D-hexagonal sample shows another hysteresis at partial pressure 0.37. The surface areas and pore volumes of the materials are reported in (Table 1). The 2 parent samples of mesoporous silica after loading with Ni oxide were difficult to be measured in details by using adsorption isotherms with respect to pore size, pore volume, and pore size distribution point of view, where pores become small enough to prevent isotherm from being completed easily. Approximate total surface area and total pore volume could be calculating after catalyst loading inside the mesoporous silica structures. Figure 2 represents the pore size distributions of the 2 parent samples, which indicate the narrow pore size distribution of the 2 parent samples with pore sizes 20 nm and 25 nm, respectively.



**Figure 1** N<sub>2</sub> adsorption-desorption isotherms of the two Mesoporous silica parent samples (2D, and 3D)



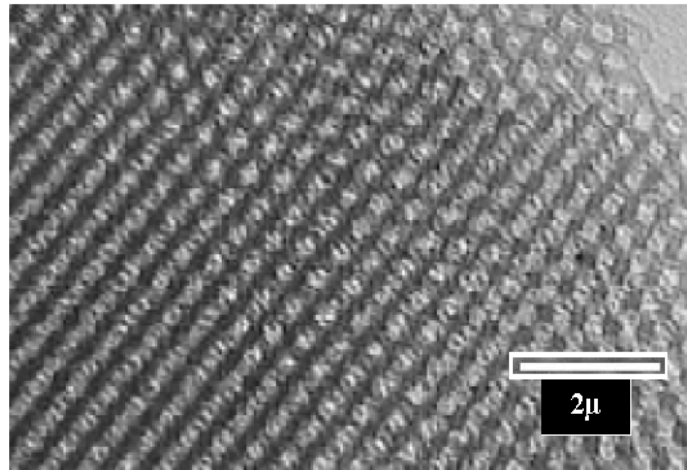
**Figure 2** Pore size distributions (PSD) of the two Mesoporous silica parent samples (2D, and 3D)

**Table 1** N<sub>2</sub> adsorption isotherms of two Mesoporous silica parent samples, and after Nickel oxide loading

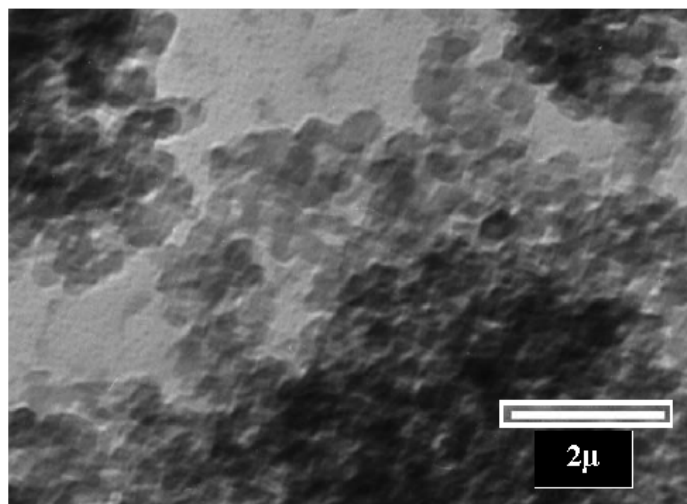
Sample	Total Surface Area ( $S_{BET}$ ) (m <sup>2</sup> /g)	Average Pore Diameter ( $D_p$ ) (nm)	Average Pore Volume ( $V_p$ ) (cc/g)
2D-Sample Parent	870	20	0.77
Ni-2D-sample	820	-----	-----
3D-Sample Parent	980	25	0.88
Ni-3D-sample	630	-----	-----

### 3.2 High Resolution Transmission Electron Microscopy (HRTEM)

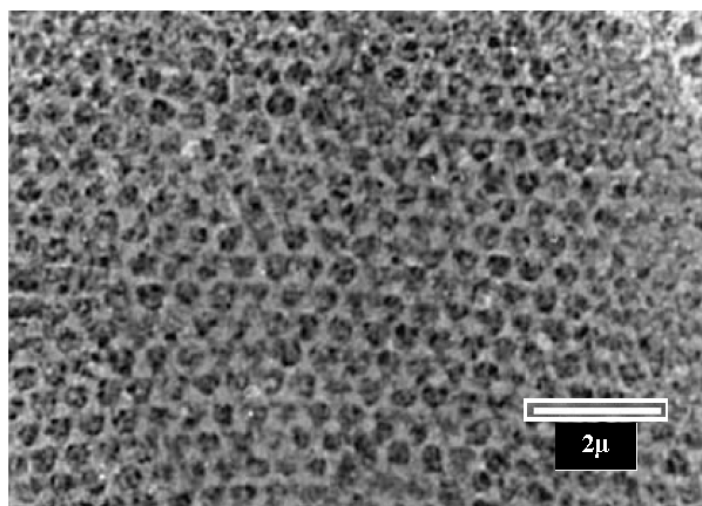
Figures 3 and 4 show 2D-mesoporous silica sample before and after nickel oxide loading, where pore size of the parent sample before loading is 20 nm. Figures 5 and 6 show 3D-mesoporous silica sample before and after nickel oxide loading, where pore size of the parent sample before loading is 25 nm. Pore sizes of two parent samples (2D and 3D) were difficult to measured, where nickel oxide particles penetrated the pores of the structures.



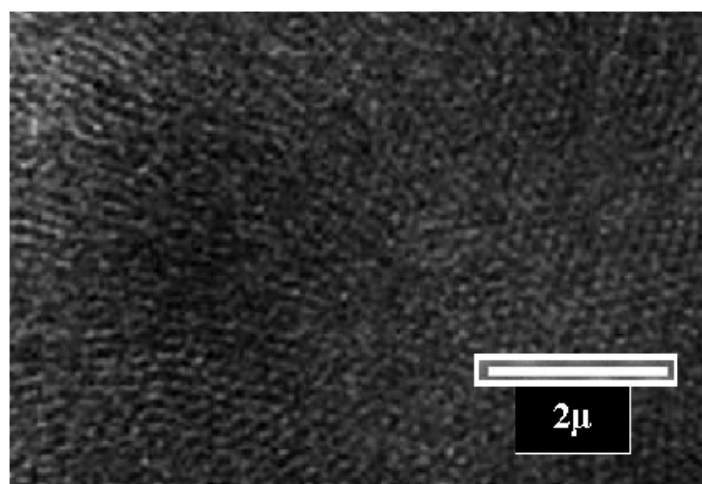
**Figure 3 HRTEM of parent 2D Hexagonal Mesoporous silica**



**Figure 4 HRTEM of 2D Hexagonal Ni-Mesoporous silica**



**Figure 5 HRTEM of parent 3D Hexagonal Mesoporous silica**

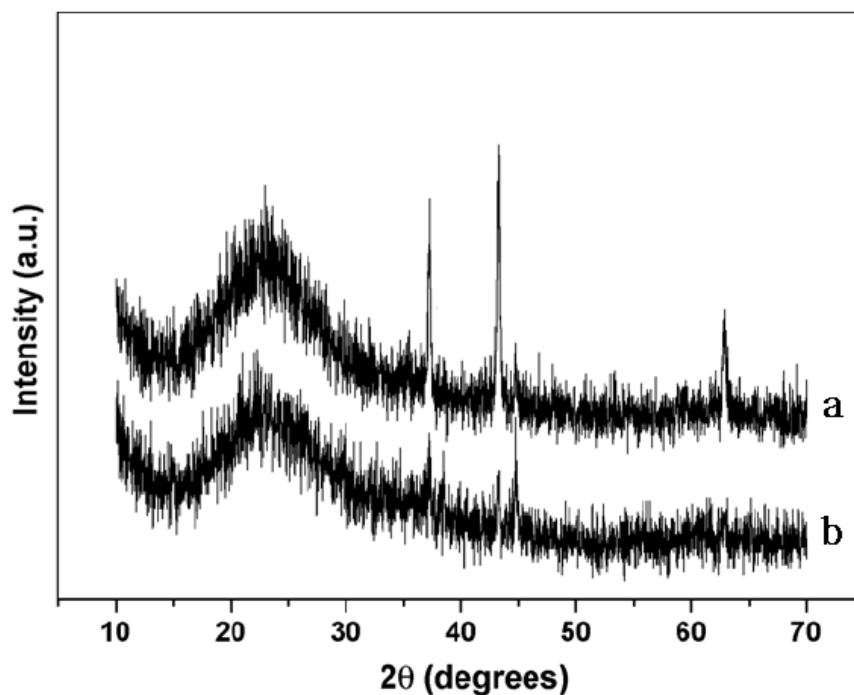


**Figure 6 HRTEM of 3D Hexagonal Ni-Mesoporous silica**

### 3.3 X-ray Diffraction (XRD)

Figure 7 shows X-ray diffraction patterns of the two loaded samples. X-ray of 2D-sample shows strong peaks (sharp reflection) of nickel oxide, which are stronger than the nickel oxide peaks appears in 3D-sample which also indicate that the nickel oxide in 2D-sample was large crystals and more on the outer walls of the mesoporous silica surface than that present in case of 3D-sample and at the same time agrees with the results coming from HRTEM. The most probable explanation is that in case of 2D-sample incipient wetness impregnation, a large amount of the nickel ions has been entrained out of the mesopores with the solvent flow during

the drying treatment. As a result, large nickel nitrate crystallines have precipitated at or next to the external surface during drying, thus giving rise to the formation of the very large nickel oxide crystallites of this catalyst during calcinations. In case of 3D-sample, we expect that this structure helps to avoid accumulation of nickel oxide particles on the outer walls of the mesoporous silica surfaces, so, the pores become always opened and the impregnation process still achieved.



**Figure 7** XRD of (a) 2D-Ni-Mesoporous silica sample; and (b) 3D-Ni-Mesoporous silica sample

#### 4.0 Conclusion

mesoporous silica synthesized by using TEOS as a silica source and F127 as a nonionic template. The powder produced characterized by Nitrogen adsorption-desorption isotherm, XRD, and HRTEM. Nickel catalyst supported on 2D and 3D hexagonal mesoporous silica prepared was synthesized with ultrasonically incipient wet impregnation method. In case of 2D-sample incipient wetness impregnation, a large amount of the nickel ions has been entrained out of the mesopores with the solvent flow during the drying treatment. As a result, large nickel nitrate crystalline have precipitated at or next to the external surface during drying, thus giving rise to the formation of the very large nickel oxide crystallites of this catalyst during calcinations. In case of 3D-sample, we expect that this structure helps to avoid accumulation of nickel oxide particles on the outer walls of the mesoporous silica surfaces, so, the pores become always opened and the impregnation process still achieved.

## 5.0 Acknowledgments

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