

Effect of nickel over the H₂ adsorption on Ni/MCM-41 materials

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Introduction

Repeated efforts have been made to introduce alternatives to petroleum. One of these alternatives is hydrogen, as it might be a clean and renewable energy vector. Ordered nanostructured materials such as MCM-41 mesoporous molecular sieves have been studied as promising candidates for hydrogen storage. There are several literature reports that concern the nickel loading on porous materials, which indicated that the hydrogen adsorption is maximum at a low metal content and it then decreases with increasing nickel loading on the support [1,2]. However, further investigations are necessary for a deeper understanding of the mechanism of hydrogen adsorption on nanoporous materials.

Therefore, in the present work the hydrogen storage capacity of Ni/MCM-41 materials was studied by means of experimental results and Density Functional Theory (DFT) calculations. The Ni/MCM-41 samples were reduced in order to analyze the metallic nickel contribution on the H₂ adsorption. Also, hydrogen adsorption isotherms at room temperature and high pressures for reduced and un-reduced samples were measured. The physicochemical properties of the samples, obtained by means of the characterizations performed (TPR, DRX, N₂ adsorption-desorption) were correlated with the information provided by the DFT calculations and used to interpret the behavior of the samples in hydrogen storage.

Results and Discussion

The reducibility of the samples was studied by means of Temperature-Programmed Reduction. These results were used for selecting the reductive conditions employed to reduce the Ni/MCM-41 materials. The structural regularity of the materials was corroborated by N₂ adsorption-desorption isotherms, DRX and transmission electron microscopy. The results show typical well defined mesoporous structures with uniform pore arrangement and high specific superficial area. Also, it was observed that the ordered pore structure of the samples was preserved both after the nickel loading as well as after the reduction treatment.

In order to analyze how the system behaves towards the adsorption of H₂, the hydrogen adsorption on SiO₂ and Ni/SiO₂ was studied by means of DFT calculations. On analyzing the values obtained, they indicated a low affinity of the silica surface towards hydrogen, but this affinity is enhanced with the presence of Ni on the surface of SiO₂. The adsorption energy of the first H₂ molecule adsorbed on a SiO₂ surface with low-coordinated Ni was high (-123.7 kJ/mol), indicating an enhancement in the surface-H₂ affinity due to the presence nickel in the surface.

The adsorption energies of the H₂ molecules adsorbed thereafter diminish with the increasing number of pre-adsorbed H₂, indicating that the presence of nickel favors the adsorption of H₂ molecules at the surroundings of nickel atoms dispersed on the surface of a silica material. Also, the adsorption of H₂ with Ni in its oxide state (bonded to oxygen atoms) was simulated,

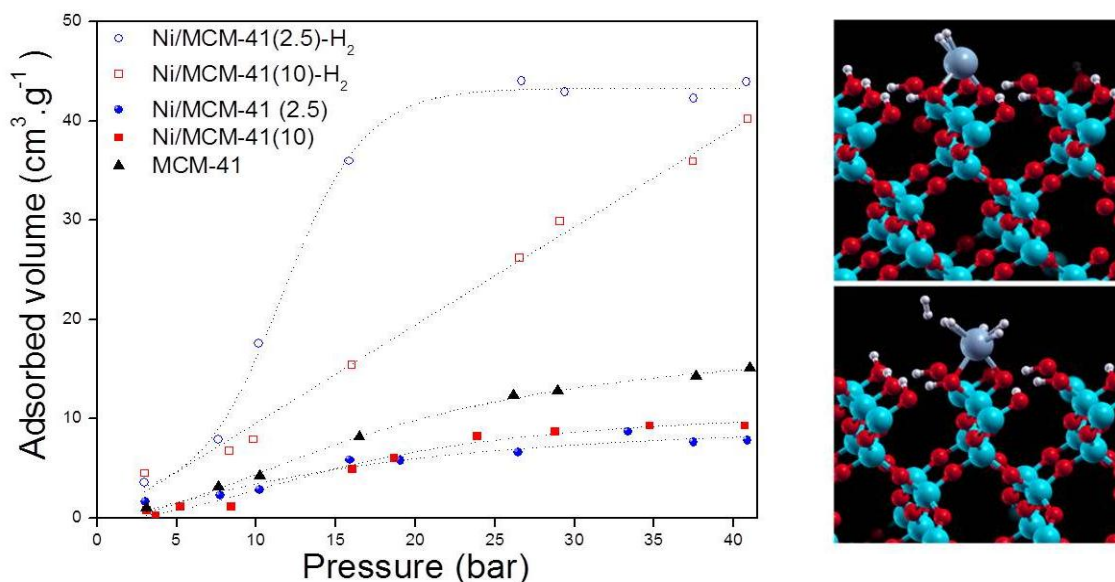


Figure 1: H₂ adsorption isotherms of the synthesized samples, measured at 293 K (left) and side views of the equilibrium structures of H₂ molecules adsorbed on SiO₂-Ni when one and five molecules adsorbed (right).

considering one or two oxygen atoms bonded to the Ni atom. These results showed that the presence of oxygen bonded to the nickel atom decreases the adsorption energy of hydrogen in a great extent. Thus, in order to increase the interaction, and consequently the adsorption capacity of hydrogen on a silica surface modified with Ni, it is important that the Ni atoms present low degrees of coordination. One of the possible routes for the increase of H₂ stored on Ni/MCM-41 materials is the spillover effect, so that DFT simulations were performed in order to analyse the energies involved in that process at the molecular level. These results showed that spillover in this system is energetically unfavourable.

In previous reports [2], we have shown the hydrogen adsorption behavior at 77 K of MCM-41 mesoporous materials modified with varying amounts of nickel. In those reports, an increase of the amount of hydrogen stored at 77 K was observed in samples with low nickel content. That behavior was assigned to a high interaction of hydrogen with some nickel clusters on the surface of the mesoporous material. When these samples were subjected to reductive treatments, they did not show any change in the H₂ adsorption at 77 K. These results suggest that the Ni species, which improve of H₂ adsorption, are perhaps not reducible. Therefore, maybe these species might be highly dispersed and stabilized by the high interaction between them and the SiO₂ surface.

The excess hydrogen isotherms at 293 K and up to 40 bar are represented in Figure 1. It can be observed that at these conditions the unreduced Ni/MCM-41 samples store less H₂ than the MCM-41; but an important increase in H₂ storage is observed for the reduced Ni/MCM-41 samples, indicating that Ni in its metallic phase favors the adsorption at 293 K.

An unusual isotherm shape was observed for the Ni/MCM-41(2.5)-H₂, which could be related to the possibility of hydrides formation instead of a spillover mechanism for hydrogen sorption.

Finally, we propose that nickel, a relatively inexpensive metal, at low loadings and high dispersions could be used to increase the hydrogen storage capacity of silica materials at 293 K.

References

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