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# Hydrogen sorption in transition metal modified mesoporous materials

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## ABSTRACT

Ni, Rh and Pd incorporated mesoporous MCM-41, MCM-48, HMS and SBA-15 samples were synthesized and were characterized using XRD, ICP/EDX and N<sub>2</sub> adsorption–desorption at 77.4 K. The hydrogen adsorption studies in the synthesized materials were performed at 77.4 K (up to 112 kPa) and 303 K (up to 4000 kPa). The hydrogen adsorption isotherms of pristine and transition metals incorporated mesoporous materials at 77.4 K were completely reversible reflecting physisorption of hydrogen in these materials. The hydrogen adsorption isotherms at 303 K were not reversible showing the chemisorption of hydrogen in these materials at 303 K. Hydrogen sorption studies showed that transition metal modification improved the hydrogen storage capacity of mesoporous materials at 303 K. The desorption of the adsorbed hydrogen by heating up to 500 K from the mesoporous materials were also carried out for studying the recovery of adsorbed hydrogen from transition metal incorporated mesoporous materials.

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## 1. Introduction

Hydrogen production has increased significantly in recent years due to the potential use of hydrogen as a clean alternative fuel. In order to use hydrogen on demand for fuel cell and other applications it is imperative to have an efficient hydrogen storage and recovery system [26]. Several ways to store hydrogen such as in compressed or liquid forms and in solid-state hydrogen storage in sorbents are studied. Among these methods, solid-state hydrogen storage in sorbents is the most promising technology with respect to efficiency and safety [28,38]. Therefore, many studies are focused for storing hydrogen in complex hydrides and metal hydrides [8,9,25], zeolites [6,19,20], titanosilicates [21,22], carbon materials [5,16,34] and metal–organic frameworks [15,17,24]. There is

a family of mesoporous materials such as HMS, MCM-41, MCM-48, and SBA-15 which have potential to be used effectively as catalysts [2,4], catalyst supports and sorbents [3]. These materials have well defined pore structures, high surface area (ca. 900–1400 m<sup>2</sup>/g) and narrow pore size distribution which is controllable with average value in the range of 2–10 nm. These attributes make them potential candidates for hydrogen storage applications.

The first family of mesoporous molecular sieve (denoted M41S) using cationic surfactants to assemble silicate anions from solution was reported in 1992 [1,12]. For the M41S family of materials, the composition is restricted to silicate framework, including three main mesoporous silicate host structures, namely, hexagonal MCM-41, cubic MCM-48 and a lamellar MCM-50 silica phase. The mechanism of formation

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of M41S materials involve the charge matching between structure directing alkyl ammonium ion surfactants ( $S^+$ ) and the framework forming silicate oligomers ( $I^-$ ) present in the solution. Tanev and Pinnavaia, [31,32] and Zhang et al. [36] reported neutral ( $S^0I^0$ ) templating route, where uncharged silica precursors such as tetraethyl orthosilicate (TEOS) ( $I^0$ ) are assembled around neutral amine surfactant micelles ( $S^0$ ), producing a class of mesoporous molecular sieves, denoted as Hexagonal Mesoporous Silicas (HMS), with wormhole like frameworks. The triblock copolymers such as poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) ( $EO_mPO_nEO_m$ ) and some other were found to self-assemble with silicate species in acidic media to form periodic mesoporous silicas, including hexagonal structures referred to as Santa Barbara Amorphous silicas (SBA-15) with ordered pores as large as 30 nm and cubic structures [37].

Metal incorporation in the cavities of mesoporous silicates is one of the methods to stabilize highly dispersed metal particles and oxides in uniform porous matrices [10]. Such bifunctional materials are of interest in the nanotechnology, gas adsorption, separation, and catalysis as these combine unique physicochemical characteristics of nanoparticles with the well-ordered structure found in mesoporous molecular sieves [11]. The metal nanoparticles have been stabilized in mesoporous MCM-41, HMS, and SBA-15 materials [18,35].

The gas adsorption studies in the mesoporous silica matrices are scarce. Edler et al. [7] studied the hydrogen sorption characteristics of mesoporous silica MCM-41. Takei et al. [30] performed hydrogen adsorption studies in silylated mesoporous silica. Recently Wu et al. [33] studied hydrogen sorption properties of pure and metal ion doped MCM-41 at 77 K. Hydrogen sorption characteristics of the mesoporous materials can be improved by surface modification techniques such as incorporation of transition metals into the mesoporous structures. Palladium, rhodium and nickel are known for their affinity for hydrogen. It will be interesting to use these for modification of mesoporous materials to explore hydrogen storage applications of surface modified materials. In the present study, 3–5 wt% nickel, rhodium and palladium were incorporated into the mesoporous materials in situ during hydrothermal synthesis. Metal concentration was optimized because higher concentration of metals was observed to cause the structural collapse of the mesoporous silica framework as reported by Wu et al. [33]. Physical and chemical properties and surface morphology of the synthesized materials were characterized using XRD, nitrogen adsorption–desorption isotherms, ICP, EDX, TEM and DRIFT analysis.  $H_2$  adsorption isotherms were measured at 77.4 K up to 112 kPa and 303 K up to 4000 kPa. Adsorption–desorption properties of hydrogen in these metal modified mesoporous materials was discussed with a view to explore these for hydrogen storage applications.

## 2. Experimental

### 2.1. Materials

Sodium silicate (Kadvani Chemicals Ltd., Jamnagar, India, 7%  $Na_2O$ , 28%  $SiO_2$ ), cetyl trimethylammoniumbromide (CTAB),

tetraethoxysilane (TEOS), hexadecylamine (HDA) all from Aldrich,  $Ni(NO_3)_2 \cdot 6H_2O$ ,  $RhCl_3 \cdot nH_2O$ ,  $Pd(NH_3)_4Cl_2$ , sulphuric acid, ammonia, ethanol (s.d. Fine chemicals, India) were used for the synthesis of pure and modified mesoporous materials. Ultra high pure hydrogen, nitrogen and helium (Inox Gas, India) were used for the adsorption isotherm and surface area measurements.

### 2.2. Synthesis of HMS and transition metals modified HMS

10.7 ml TEOS was added slowly under vigorous stirring for 2 h to 3.13 g hexadecylamine dissolved in a mixture of deionized water (80.3 ml) and ethanol (15.3 ml). The molar concentration of the starting solution was:

1.0 TEOS : 0.27  $C_{16}H_{33}NH_2$  : 9.09 EtOH : 29.06  $H_2O$ .

The resultant solution was aged over night. The solid obtained was filtered, washed and dried at room temperature, calcined in air at 823 K for 6 h to remove template. To the starting HDA template solution appropriate amount of nickel, rhodium and palladium salt solutions were added to prepare transition metal modified HMS.

### 2.3. Synthesis of MCM-41 and transition metal modified MCM-41

CTAB was dissolved in warm (333 K) distilled water and sodium silicate solution was added to the surfactant solution under vigorous stirring. The pH of the reaction mixture was adjusted to 10 with dilute sulfuric acid. The reaction mixture obtained had the following molar composition:

1.0  $SiO_2$  : 0.5 CTAB : 0.31  $Na_2O$  : 0.13  $H_2SO_4$  : 64  $H_2O$

The resulting gel was then transferred to a Teflon-lined autoclave and heated at 383 K for 144 h. The solid product obtained was then filtered, washed thoroughly with deionized water and dried in air at room temperature. The template was removed by first heating at 573 K for 2 h and subsequent calcination in air at 823 K for 6 h at the heating rate of 2 °C/min. The procedure used is based as per reported method [32]. 3–5 wt% Ni, Rh and Pd incorporated MCM-41 samples were synthesized by adding the desired amount of  $Ni(NO_3)_2 \cdot 6H_2O$ ,  $RhCl_3 \cdot nH_2O$  and  $Pd(NH_3)_4Cl_2$  salt solutions to the starting CTAB solution under vigorous stirring until the solution became clear.

### 2.4. Synthesis of MCM-48 and transition metal modified MCM-48

CTAB (1.7 g) template was dissolved in deionized water (50 ml) and ethanol (50 ml). Aqueous ammonia (16 ml) was added to the surfactant solution followed by stirring for 30 min. TEOS (1.7 g) was added to the above solution that was stirred for 2 h at room temperature. The molar concentration of the starting gel was

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