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Hydrogen sorption in transition metal modified NaETS-4

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ABSTRACT

Transition metals nickel (Ni), rhodium (Rh) and palladium (Pd) both exchanged and *in situ* loaded in NaETS-4 samples were synthesized and characterized. Hydrogen adsorption studies in the synthesized NaETS-4 samples were performed at 77.4 K up to 1 bar and at 303 K up to 40 bar pressure. The reversible adsorption isotherms at 77.4 K showed physisorption of hydrogen but at 303 K chemisorption was the major mechanism for hydrogen uptake, which is clear from the irreversible nature of adsorption isotherms at 303 K. Rhodium loaded NaETS-4 showed the highest hydrogen adsorption capacity of 66 cc/g at 77.4 K and 35 cc/g at 303 K. The hydrogen adsorption in transition metal modified NaETS-4 at 303 K is driven by the chemical interactions leading to the formation of transition metal hydrides inside the micropores of NaETS-4. The absorbed hydrogen at 303 K can be desorbed by heating the modified titanosilicates up to 423 K.

1. Introduction

Hydrogen is a promising alternative fuel since it is pollution free and can be readily produced from renewable energy resources, thus eliminating the net production of green house gases [1]. Studies have indicated that hydrogen fuel costs are reasonable and, therefore, hydrogen seems to be an ideal candidate to replace fossil fuels as an energy carrier [2]. Hydrogen contains more chemical energy per weight than any hydrocarbon fuel, but it is also the lightest existing substance and thus difficult to store in small containers. The lack of a convenient and cost effective method for hydrogen storage has limited its commercial application. Efficient storage of hydrogen is very important for the utilization of hydrogen especially for vehicles powered with fuel cells [3,4]. Among the various methods attempted for hydrogen storage, adsorption of hydrogen in various porous materials is promising due to their simplicity and safety. Porous materials such as aluminosilicate zeolites [5–11], carbons [12,13] and inorganic organic hybrid materials, such as metal-organic frameworks (MOFs) [14,15] have been studied as potential hydrogen sorbents. The highest hydrogen adsorption capacities for all these materials were reported at liquid nitrogen temperature.

Engelhard titanosilicate-4 (ETS-4) is a mixed oxide microporous molecular sieve material containing octahedral (six-coordinated) and square-pyramidal (five-coordinated) titanate structural unit, in addition to the tetrahedral silicate unit found in conventional zeolite materials. In 1989, Kuznicki reported the synthesis of NaETS-4 [16]. The presence of tetravalent titanium ion in octahedral coordination generates a formal negative charge of −2 in the framework of ETS-4 in the unit cell, which is balanced by the exchangeable cations Na^+. The effective pore size opening of this material is about 3–4 Å that can be tuned by systematic contraction through controlled dehydration [17,18]. The adjustable pore system of NaETS-4 offers various applications such as gas adsorption and separation [18–20]. Mitchel et al. have reported the Grand Canonical Monte Carlo simulation studies in titanosilicate molecular sieves ETS-4 and ETS-10 for separation of binary mixtures of hydrogen/methane and hydrogen/carbon dioxide at 298 K [21].

In the present study, we have synthesised transition metal nickel, palladium and rhodium both exchanged and *in situ* loaded NaETS-4 samples. The transition metals nickel, rhodium and palladium are known to form hydrides with hydrogen. Furthermore, these metals are also reported as catalysts for reactions such as hydrogenation and hydroformylation where interaction of these metals with hydrogen is demonstrated [22–24]. The hydrogen adsorption capacities of the synthesized samples were measured at 77.4 K up to 1 bar and at 303 K up to 40 bar pressure.

2. Experimental

2.1. Materials

Titanium (IV) butoxide (Aldrich, USA), sodium hydroxide, hydrogen peroxide (s.d. Fine Chemicals, India) and sodium silicate (Kadvani Chemicals Ltd., Jamnagar, India) were used for the synthesis of NaETS-4. Ultra high pure hydrogen (Inox Gas, India) was used for the adsorption isotherm measurements.

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2.2. Synthesis of NaETS-4 and transition metals modified NaETS-4

The initial chemical composition of the solution used for the synthesis of NaETS-4 was Ti:Si:Na:H_2O_2:H_2O = 0.9:10:14:8:675 on a molar basis. The details of the preparation of this solution are described elsewhere [25]. The hydrothermal synthesis was performed at 453 K for 72 h in an autoclave. The powder obtained was filtered, washed with distilled water, and dried at room temperature.

Nickel, rhodium and palladium cations were exchanged into the sodium form of ETS-4 by the conventional cation exchange method from the aqueous solution. Typically, NaETS-4 was treated with 0.05 M aqueous solution of nickel nitrate, rhodium chloride or tetra amine palladium (II) chloride with a solid to liquid ratio of 1:80 at 353 K for 4 h. The residue was filtered, washed with hot distilled water, until the washings were free from nitrate/chloride ions and dried in air at room temperature. Nickel, rhodium and palladium loaded NaETS-4 samples were prepared by the addition of nickel nitrate, rhodium chloride or tetra amine palladium (II) chloride salt solutions during the synthesis of NaETS-4. The extent of nickel, rhodium or palladium exchanged/loaded in NaETS-4 was determined by inductively coupled plasma (ICP) and energy dispersive X-ray (EDX) analyses. The following terminologies are used to describe the ion exchanged and *in situ* loaded samples: In case of ion exchanged samples the first two letters show the exchanged cation and for *in situ* loaded samples the last two letters in bracket show the cation loaded into NaETS-4.

2.3. X-ray powder diffraction

The X-ray powder diffraction studies at ambient temperature were carried out using a PHILIPS X'pert MPD system in the 2θ range of 5–65° using Cu Kα_1 (λ = 1.54056 Å). The diffraction patterns of the synthesized NaETS-4 samples show high crystallinity with reflections in the range 5–65° typically of NaETS-4 as reported in literature. The percentage crystallinity of the NaETS-4 samples was determined from the X-ray diffraction pattern by summation of the intensities of 10 major peaks at 2θ values 7.5, 12.7, 16.7, 19.9, 26.7, 30.0, 34.0, 52.1, 54.1 and 60.2. The as synthesized NaETS-4 sample was taken as an arbitrary standard for comparison.

2.4. Thermo-gravimetric analysis (TGA)

Thermo gravimetric analysis of the samples was carried out from room temperature to 873 K in a TGA/DTA analyzer (Mettler Toledo) at a heating rate of 10 K/min under nitrogen atmosphere.

2.5. Diffuse reflectance infrared fourier transform (DRIFT) spectroscopy

DRIFT spectroscopic studies of adsorbed hydrogen at 303 K in nickel, rhodium and palladium exchanged and *in situ* loaded NaETS-4 samples were carried out in a thermo electron corporation NICOLET 6700 FT-IR instrument equipped with the selector DRIFT accessory incorporating an environmental chamber (EC) assembly (Madison WI USA, P/N 0030-090 series). The titanosilicate samples were activated *in situ* at 393 K under a vacuum of 5×10^{-3} mm Hg at a heating rate of 10 K min^{-1} using an automatic temperature controller (Madison WI USA, P/N 0019-022e) connected with the EC. The sample was kept at 393 K for 60 min, then cooled to 303 K and the IR spectra was collected under vacuum, following this H_2 was purged on the sample at 1 atm pressure for 60 min and the IR spectra was collected.

2.6. Transmission electron microscope (TEM) analysis

The TEM analysis of the ETS-4 samples was performed on HRTEM JEOL, JEM-2100 electron microscope.

2.7. Adsorption isotherm measurements

Hydrogen adsorption measurements at 77.4 K were carried out in a static volumetric system (Micromeritics Instrument Corporation, USA, model ASAP 2010) up to 1 bar pressure. The samples were activated by heating at a rate of 1 K min^{-1}, to 393 K under vacuum (5×10^{-3} mmHg) and the temperature and vacuum was maintained for about 8 h prior to the adsorption measurements. The amount of activated sample was determined from the weight of the samples before as well after activation. The errors in the measurements of hydrogen uptake values were within the range of ±0.5%.

The high pressure hydrogen adsorption isotherm measurements at 303 K up to 40 bar were performed on an automatic high pressure gas adsorption system BELSORP-HP, BEL Japan, Inc. Prior to the adsorption isotherm measurements, the sample was first dried at 383 K, followed by treatment under hydrogen flow at 423 K to reduce nickel, rhodium and palladium cations to zerovalent state. The reduced sample was again activated thermally up to 423 K under high vacuum (6.7×10^{-2} Pa) for 8 h before the sorption measurements. After activation, the samples were allowed to cool down to the desired adsorption measurement temperature of 303 K and the temperature was maintained during the analysis using an external water circulator (PolyScience, USA). Desorption studies of hydrogen on heating from NaETS-4 samples were also performed in the adsorption system. The samples were heated at a rate of 1 K min^{-1} up to 473 K after the adsorption analysis, without removing the samples from the sample cell.

2.8. Surface area measurements

The Langmuir surface areas of the synthesized NaETS-4 samples were calculated by fitting the hydrogen adsorption isotherm data at 77.4 K into Langmuir isotherm model. The cross-sectional area of one hydrogen molecule is taken as 0.142 nm^2 [26] and the dry weight of the adsorbent samples were used for the surface area calculations.

3. Results and discussion

The powder X-ray diffraction patterns of NaETS-4 samples modified with transition metal ions both exchanged and *in situ* loaded are shown in Fig. 1. The X-ray diffraction pattern of the synthesized NaETS-4 sample is in good agreement with the reported data in literature [27]. The X-ray diffraction patterns of all the modified ETS-4 samples showed diffraction peaks at 2θ values similar to synthesized NaETS-4 sample. The percentage crystallinity of the modified NaETS-4 samples was determined from XRD data. A small decrease in the crystallinity of the ETS-4 samples was observed on transition metal exchange/loading into the NaETS-4 framework. Nickel exchanged NaETS-4 showed the maximum crystallinity loss. Similar loss of crystallinity during the transition metal exchange was observed for aluminosilicate zeolites [10,11]. The decrease in crystallinity during the transition metal exchange is mainly due to the hydrated transition metal ions, which hydrolyze within the ETS-4 channels leading to structural breakage of the framework. The decrease in diffraction intensity could also be due to presence of transition metal cations impregnated on the surface of ETS-4. The percentage of cation exchanged/loaded, percentage crystallinity and Langmuir surface area of ETS-4 samples are shown in Table 1.

The Langmuir surface areas of the transition metal exchanged/loaded ETS-4 samples were decreased as compared to bare NaETS-4 sample. The decrease in the Langmuir surface area was high in the case of nickel exchanged NaETS-4. The loss of crystallinity and the pore blocking by the transition metal cations on the surface of ETS-4 could be the reason for the decrease in the Langmuir surface area of the modified ETS-4 samples.

Thermo gravimetric analyses results of NaETS-4 and transition metal modified NaETS-4 samples are shown in Fig. 2. The thermograms show that the thermal stability of ETS-4 samples was greatly enhanced by the transition metal modification. The initial weight loss starting around 373 K in all the samples is due to the loss of loosely bound moisture from the pores of the samples. All the modified NaETS-4 samples showed higher thermal stability compared

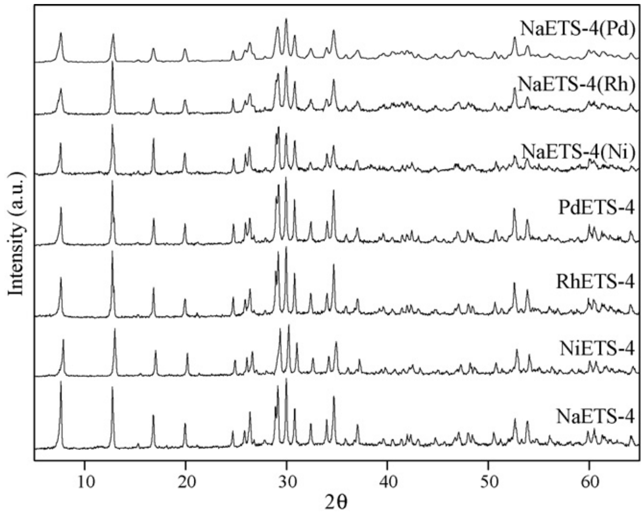

Fig. 1. XRD Patterns of NaETS-4 and transition metals exchanged and *in situ* loaded ETS-4 samples.

Table 1
Percentage of cation exchanged/loaded, percentage crystallinity, Langmuir surface area of NaETS-4 and modified NaETS-4 materials.

Sample name	Weight percentage of cation exchanged/loaded	Percentage crystallinity	Langmuir surface area ($m^2\,g^{-1}$)
NaETS-4	–	100	247 ± 2.35
NiETS-4	4.6%	72	80 ± 2.44
RhETS-4	2.8%	81	207 ± 2.23
PdETS-4	2.2%	86	145 ± 1.80
ETS-4(Ni)	10.4%	74	167 ± 1.67
ETS-4(Rh)	6.4%	84	225 ± 1.85
ETS-4(Pd)	6.8%	88	203 ± 1.92

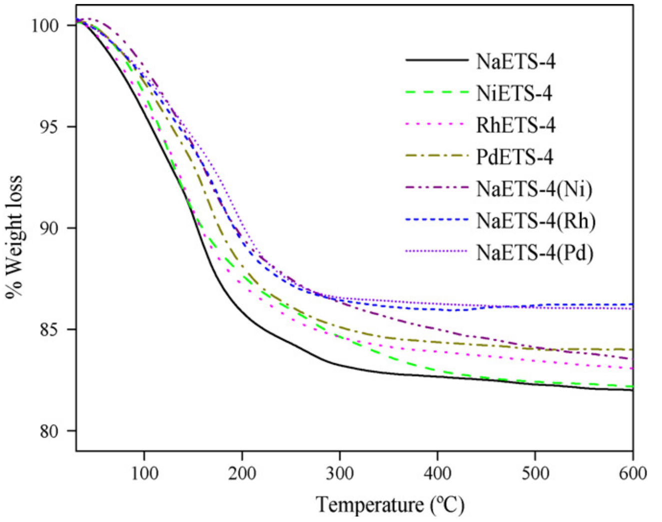

Fig. 2. TGA analysis plots for NaETS-4 and nickel, rhodium and palladium exchanged/loaded ETS-4 samples.

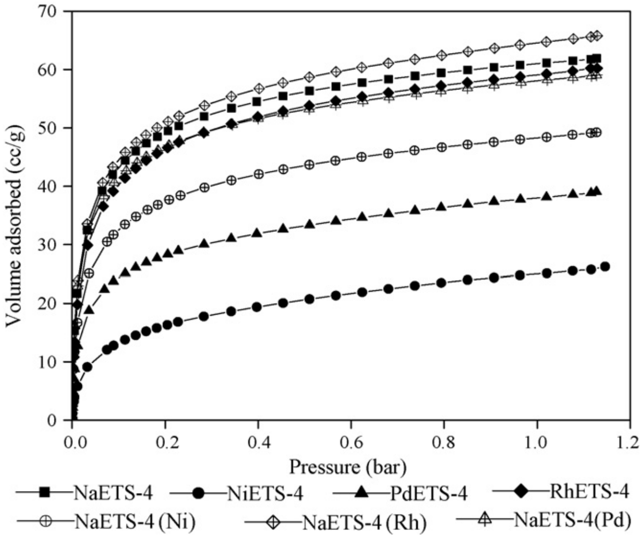

Fig. 4. Hydrogen adsorption isotherms of transition metal exchanged and substituted NaETS-4 samples at 77.4 K up to 1.2 bar pressure.

to bare NaETS-4. Among the transition metal modified NaETS-4 samples rhodium and palladium loaded NaETS-4 showed higher thermal stability compared to all other samples.

The unit cell structure of NaETS-4 is shown in Fig. 3. It has an orthorhombic crystal structure with space group symmetry of *Cmmm* (cell parameters $a = 23.2272$ Å, $b = 7.1751$ Å, $c = 6.9727$ Å and $\alpha = \beta = \gamma = 90^{\circ}$) [28]. The framework of NaETS-4 contains octahedral (six-coordinated) and square-pyramidal (five-coordinated) titanate structural units along with tetrahedral silicates units found in conventional zeolite materials. The NaETS-4 framework can be considered as being built from titania chains propagating in the [0 1 0] direction in which the titanium is octahedrally coordinated, and bridged by titanosilicate units connecting the chains in the [1 0 0] direction. These titania chains are connected in [0 0 1] direction by means of silicate tetrahedra. The titanosilicate bridging unit consists of a five coordinated titanium atom which is bonded to four silicate tetrahedra and to an apical oxygen atom [28,29]. The location and distribution of water molecules and Na^+ cations inside the pores of NaETS-4, greatly affect the diffusion and adsorption of sorbate molecules in it. There are two Na^+ cation sites in NaETS-4 [28,29]; one site (Na1) is in a D6MR titanosilicate ring and the other (Na2) in a 7MR formed by the titania chains and the bridging titanosilicate unit. Water molecules occupy four sites namely Ow1, Ow2, Ow3 and Ow4 in the 8MR [28]. Framework oxygen atoms occupy seven sites from O1 to O7. The Na^+ cation in site Na1 is coordinated to four framework oxygen atoms (O3 × 4) and two water molecules (Ow1 × 2). The cation in Na2 site is coordinated to three oxygen atoms of the titania chain, two oxygen atoms of titanosilicate unit and two water molecules (Ow1, Ow2). The water molecule satisfies its coordination requirements by contact with Na1 as well as hydrogen bonding with O3 atoms in the framework. The Ow2 molecule also coordinates with Na1 as well as hydrogen bond-

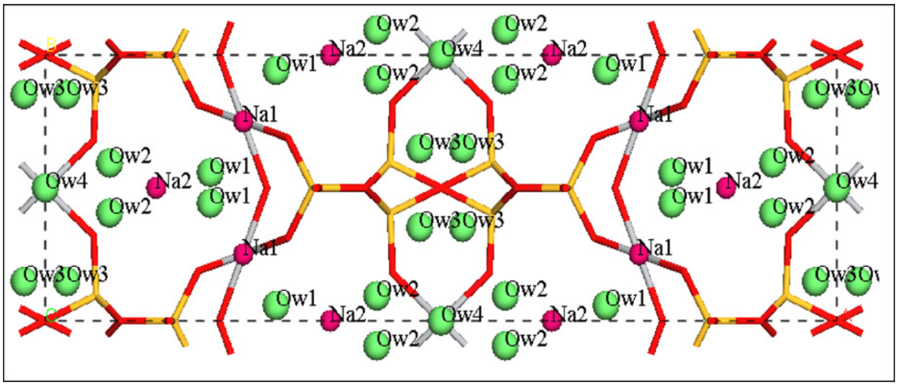

Fig. 3. Unit cell structure of NaETS-4.

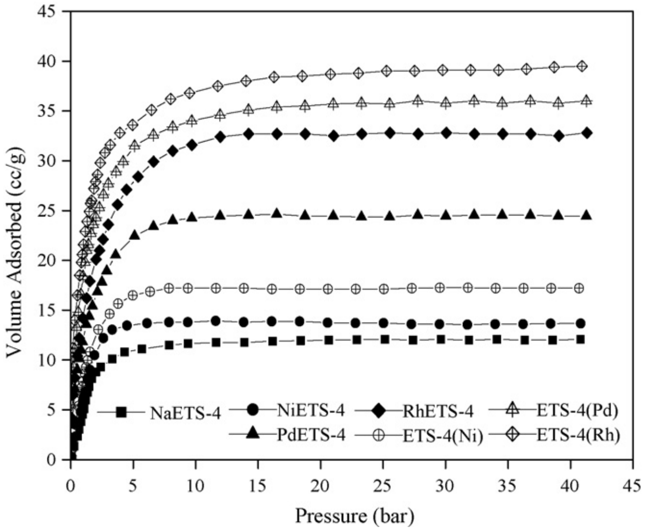

Fig. 5. Hydrogen adsorption isotherms of transition metal exchanged and *in situ* loaded ETS-4 samples at 303 K up to 40 bar pressure.

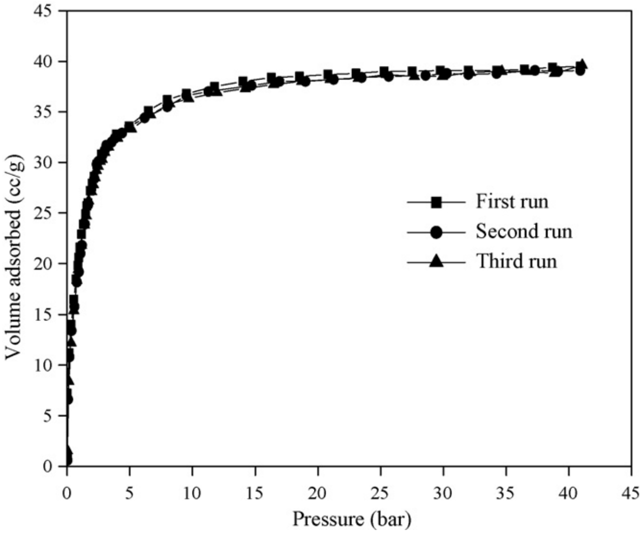

Fig. 6. Repeated hydrogen adsorption isotherms of ETS-4(Rh) sample at 303 K up to 40 bar.

ing with O7 apical atom. The water molecules Ow3 and Ow4 have very low occupancies and are weekly bound in the water sites of 8MR through hydrogen bonding with the framework oxygen atoms. The high tendency for hydrogen bonding between the extra framework water molecules and framework oxygen in NaETS-4 makes the structure thermally less stable. The possibility of 8MRs containing no water molecules will be extremely low and, therefore, the 8MR is either fully or partially blocked. There is no cation in the 8MR.

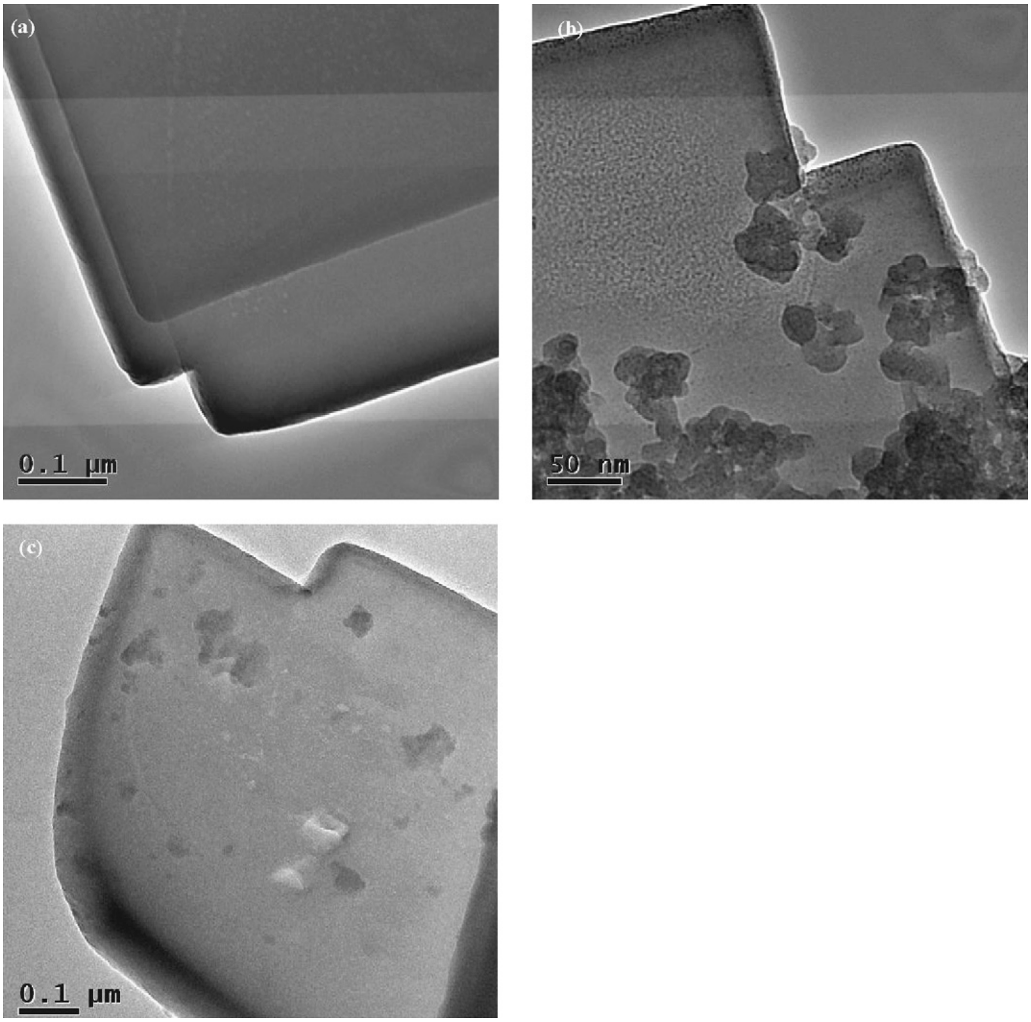

Fig. 7. TEM images of (a) NaETS-4, (b) ETS-4(Rh) and (c) RhETS-4.

Table 2
Hydrogen uptake values of NaETS-4 and modified NaETS-4 materials.

Sample name	Maximum hydrogen uptake values (cc/g)	
	77.4 K, 1 bar	303 K, 40 bar
NaETS-4	62.2	12.2
NiETS-4	26.3	13.8
PdETS-4	39.4	24.3
RhETS-4	60.0	32.8
ETS-4(Ni)	49.5	17.2
ETS-4(Pd)	59.1	36.0
ETS-4(Rh)	66.4	39.6

Hydrogen adsorption isotherms at 77.4 K in as synthesized NaETS-4 and modified with nickel, rhodium and palladium cations both by cation exchange and by *in situ* loading are shown in Fig. 4. From the figure, it is clear that the adsorption isotherms of NaETS-4 samples at 77.4 K are all of Type I in nature typical for adsorption in microporous frameworks. All the hydrogen adsorption isotherms of NaETS-4 samples at 77.4 K were highly reversible that is the adsorbed hydrogen at 77.4 K can be desorbed by decreasing the pressure. The transition metals nickel and palladium loaded NaETS-4 samples and nickel, palladium and rhodium exchanged NaETS-4 samples showed a decrease in hydrogen adsorption capacity, where as rhodium loaded NaETS-4 sample showed an increase in hydrogen adsorption capacity compared to bare NaETS-4. This decrease in hydrogen adsorption capacity in the case of transition metal modified samples, except for rhodium loaded NaETS-4 were probably

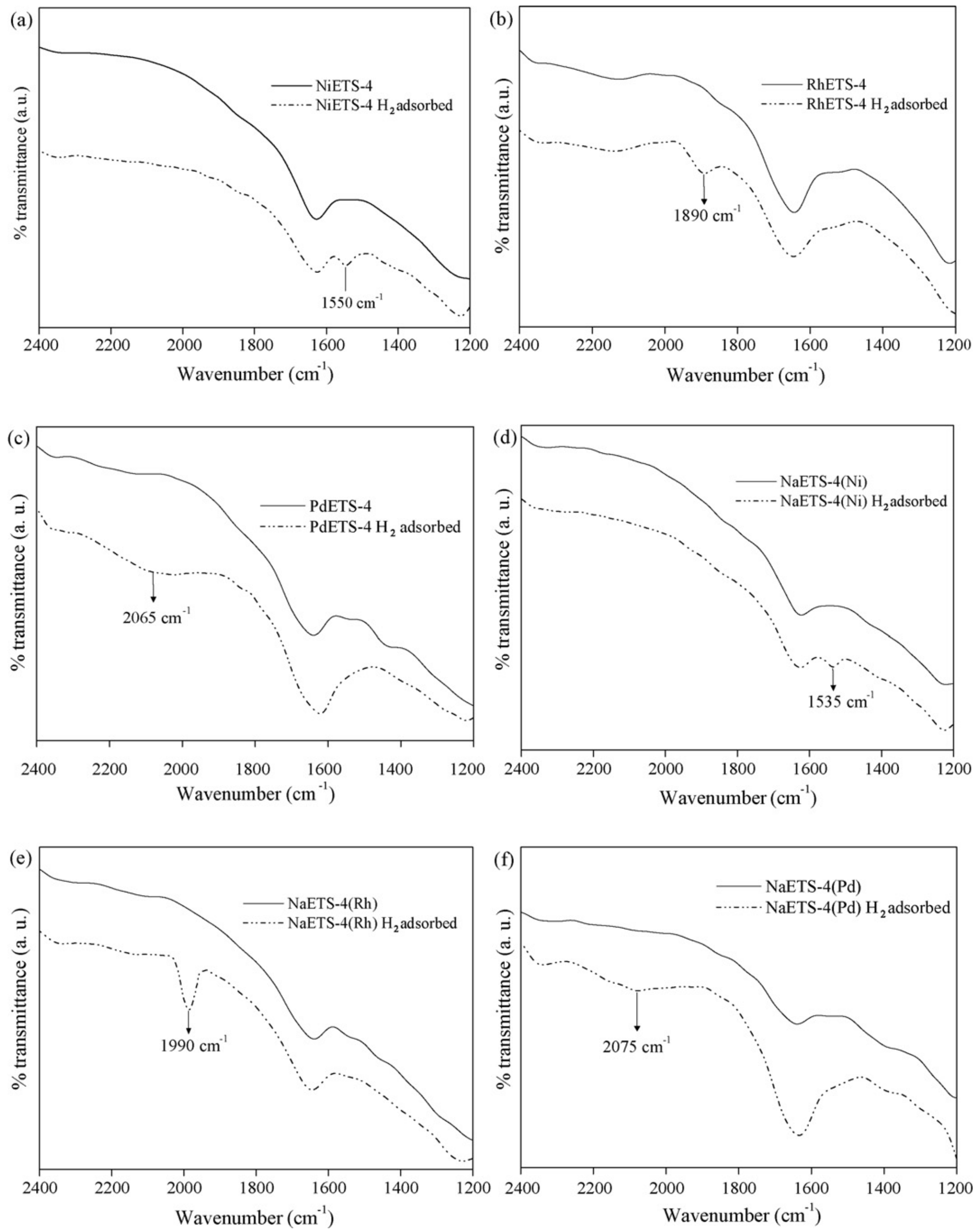

Fig. 8. DRIFT spectra of ETS-4 samples recorded at 303 K. (a) Nickel exchanged NaETS-4, (b) rhodium exchanged ETS-4, (c) palladium exchanged ETS-4, (d) nickel loaded ETS-4, (e) rhodium loaded ETS-4 and (f) palladium loaded ETS-4 samples.

due to the loss in crystallinity, and also the pore blocking by the transition metal cations sitting closer to the channels as reflected in surface area values and X-ray diffraction. The higher adsorption capacity of rhodium loaded NaETS-4 at 77.4 K could be due to the formation of $Rh^{3+}(H_2)$ adducts inside the ETS-4 channels [30].

Fig. 5 shows the hydrogen adsorption isotherms at 303 K in bare and modified NaETS-4 samples with nickel, rhodium and palladium both by *in situ* loading during synthesis and cation exchange, up to 40 bar pressure. All the samples were pre-reduced under hydrogen flow before the high pressure hydrogen adsorption isotherm analysis at 40 bar. As synthesized NaETS-4 sample showed a hydrogen adsorption capacity of 12.2 cc/g at 303 K and 40 bar pressure. Rhodium loaded NaETS-4 sample showed the maximum hydrogen uptake capacity of 39.6 cc/g at 303 K and 40 bar pressure. The number of transition metal cations introduced into the framework is much higher by *in situ* loading than by exchanging which could be done only by stoichiometric amounts. This may be the reason for higher hydrogen uptake capacity observed in transition metal loaded samples compared to metal exchanged samples.

The hydrogen adsorption isotherms at 303 K up to 40 bar were not reversible which show the chemisorption of hydrogen in the transition metal modified NaETS-4 samples. Transition metal loaded NaETS-4 samples showed higher hydrogen uptake capacities compared to transition metal exchanged samples. At higher temperatures the major interactions between the ETS-4 framework and the hydrogen molecules are the chemical interaction between the transition metal cations and hydrogen molecules. In other words, the hydrogen uptake in transition metal modified ETS-4 samples are due to the chemisorption of hydrogen in the form of transition metal hydrides of nickel, rhodium and palladium metals which were formed by the reduction of the corresponding cations by hydrogen inside the titanosilicate framework. The hydrogen uptake values of NaETS-4 and transition metal modified ETS-4 samples at 77.4 K up to 1 bar and 303 K up to 40 bar pressure are given in Table 2.

The repeated hydrogen adsorption measurements at 303 K up to 40 bar has been done in the pre-reduced rhodium loaded NaETS-4 sample. After the first hydrogen adsorption measurements, the sample was reactivated at 393 K for 6 h under vacuum and the second hydrogen adsorption run was carried out. This was followed by third hydrogen adsorption run after activating the sample as done in the second adsorption run. The hydrogen adsorption isotherm data obtained in the first, second and third runs were comparable and are shown in Fig. 6.

The TEM analysis of bare NaETS-4, ETS-4(Rh) and RhETS-4 after reduction under hydrogen was performed and is shown in Fig. 7. The plate like structure of NaETS-4 was clearly visible in the TEM image. The TEM image of rhodium loaded and rhodium exchanged ETS-4 samples show some aggregation/cluster formation of rhodium atoms after reduction under hydrogen.

The DRIFT spectra analyses of the transition metal modified NaETS-4 samples before and after hydrogen adsorption are shown in Fig. 8. The formation of transition metal hydrides inside the ETS-4 framework was confirmed by the DRIFT analysis. The M–H stretching (M = Ni, Pd, or Rh) frequencies observed in the range 1600–2200 cm^{-1} confirmed the formation of transition metal hydride [31]. In our previous studies, we have reported the mechanism for the hydride formation inside aluminosilicate zeolite framework [10,11]. The same mechanism could be applicable here for titanosilicate materials.

$$M^{n+} + nH_2 \rightleftarrows M\text{-}H_n + nH^+ \qquad (1)$$

Based on this mechanism, metal hydride species and H^+ ions are formed following the dissociation of hydrogen molecule inside the titanosilicate channels. A similar mechanism was proposed by Baba et al. [32] for dissociative adsorption of hydrogen on silver exchanged zeolites. Serykh et al. also proposed similar mechanism for the formation of Cd–H species inside ZSM-5 zeolites [31]. The H^+ ions formed during the dissociation of hydrogen molecule balance the framework neutrality of the titanosilicate material. The reversibility of hydrogen adsorption in modified NaETS-4 samples were also studied by heating the previously hydrogen adsorbed samples. Desorption studies were done by heating all the samples up to 473 K. The desorption plot of hydrogen from rhodium loaded NaETS-4 sample, which is having the highest hydrogen uptake capacity at 303 K has been shown in Fig. 9. From the figure it is clear that desorption of hydrogen was observed to start at around 403 K.

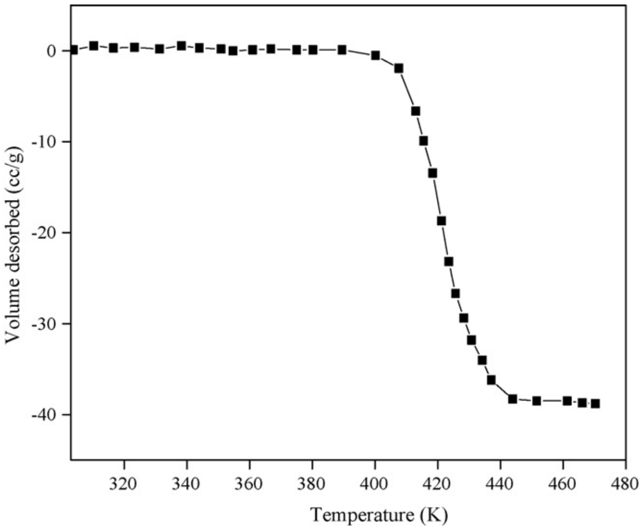

Fig. 9. Desorption of hydrogen by heating up to 473 K from NaETS-4(Rh) sample, previously hydrogen adsorbed at 303 K and 5 bar.

4. Conclusions

Hydrogen adsorption isotherm measurements were carried out at 77.4 K up to 1 bar and 303 K up to 5 bar pressures in NaETS-4 and transition metals nickel, rhodium and palladium exchanged and *in situ* loaded ETS-4 samples using volumetric and gravimetric adsorption systems, respectively. Physisorption of hydrogen was observed at 77.4 K and rhodium loaded ETS-4 sample showed maximum hydrogen adsorption capacity. Chemisorption of hydrogen was observed at 303 K up to 5 bar pressure; here also rhodium loaded ETS-4 showed highest hydrogen up take capacity. The transition metals were shown to increase the hydrogen adsorption capacity of NaETS-4 at 303 K by forming chemical interaction in the form of hydrides with hydrogen molecule. The chemisorbed hydrogen inside the titanosilicate channels could be easily desorbed by heating the titanosilicate up to 423 K. Transition metal modified NaETS-4 materials are a promising candidates for room temperature hydrogen storage if we can incorporate more transition metals into the micropore without any further loss of crystallinity.

Acknowledgements

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