

Hydrogen storage investigation of fixed bed of nano-crystalline Mg-Ni-Cr mixed oxides

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Abstract. Nano-crystalline mixed oxides containing magnesium, nickel and chromium (MNCM) have been synthesized as an adsorbent using coprecipitation method and showed its reversible hydrogen storage capacity at ambient conditions using fixed bed. XRD and ICP-MS analyses ensured the adsorbent's phase and homogeneity. The microstructure of mixed oxide has been investigated using FESEM and BET and TEM technique respectively. The adsorbent consisted of mesoporous surface with a surface area of 254-370 m²gm⁻¹ and SAED pattern showed that the adsorbents are poly-crystalline. The mixed oxides exhibited a 3.2 wt% H₂ storage capacity and release 57% of adsorbed H₂. Adsorption enthalpy (ΔH) and entropy (ΔS) change of -27.58 kJ/mol and -70.21 J/mol.K are indicating favorable thermodynamics for reversible hydrogen storage material.

Introduction:

It is well known that hydrogen is a promising energy carrier for future. Hydrogen storage in solid state adsorbent for automotive application is one of the scientific targets. Several ways of H₂ storage have been investigated such as high pressure gas, liquid hydrogen, and adsorption on porous materials. None of these technologies satisfy all the criteria for effective hydrogen storage. It is believed that adsorption at near-ambient conditions on porous adsorbents with weak interaction can fulfill the criteria that has been set by the U.S. department of energy (DOE) [1-2].

Mixed oxides have recently emerged as promising candidates for hydrogen gas adsorbent [3-4]. They are also reported as a good adsorbents for carbon dioxide (CO₂) [5] nitrogen oxide (NO) and sulfur oxide [6-7] especially at high temperatures. Mixed oxides with a higher surface area can store hydrogen efficiently in different ways [8-10]. Metal oxides are surrounded by H₂ resulting in an instantaneous polarity on the atom. During this time, the polarized atom acts as a very weak dipole. The molecular form of H₂ binds with the oxide surface under ambient conditions induced by Van der Waals forces (meV range).

Fixed bed adsorption columns offer many advantages in simplicity, ease of operation and are economical for finding potential H₂ adsorbents. They have diversified applications such as in the petroleum industry, as in dehydration and purification of natural gases [11-12]. A fixed bed with a hydrogen analyzer has been used to investigate the hydrogen adsorption on mixed oxides that makes the bed more precise and effective.

The effort that was made by this investigation using the fixed bed is to explore the mixed oxides as a promising reversible H₂ adsorbent and to study its hydrogen adsorption capacity, kinetics and thermodynamics.

2. Materials and methods:

2.1. Mixed oxides synthesis as adsorbents

The mixed oxides containing magnesium, nickel and chromium were synthesized by using modified coprecipitation method from metal nitrate precursors and Na₂CO₃ as the precipitating agent. Three solutions, each containing appropriate quantities of the metal nitrate precursors of magnesium, nickel, and chromium were prepared [4]. Mixed nitrate solution was added drop wise into a 0.5M sodium carbonate solution maintained the temperature, 55°C with a vigorous stirring. The pH was varied initially from 12.5 to 9. The resulting precipitates were washed several times to remove the

excess Na^+ and NO_3^- ions then filtered and dried. The fresh dried material was calcined at 800°C for two hours to convert the mixed oxides. The mixed oxides samples were designated by MNMCM-xyz, respectively; MNMCM stands for Mg-Ni-Cr mixed oxides and xyz stands for the molar ratios of the Mg:Ni:Cr samples.

2.2. Fixed bed set up and theory

The fixed bed setup is shown in Fig. 1 which is consisting of a stainless steel (SS316L) tube column with internal diameter =11 mm and height=169mm. A furnace with an 800W/240VAC ceramic heater was used for heating the sample inside bed and a PID-type controller maintained the temperature of the adsorbent inside. A hydrogen gas analyzer (HY-OPTIMA-700, customized process parameters of analyzer: flow rate (20-80ml), gas temp.(20-80°C) and pressure (1-2 atm.) was used to measure the concentration of hydrogen gas. The system was calibrated without sample into the bed and using inert material as similar particle size (18-21nm) of mixed oxides. The sample (1 gm adsorbent) was placed on the sample holder/bed and heated to 150°C with a temperature ramp of $10^\circ\text{C}/\text{min}$ under a pure nitrogen gas atmosphere and continued with the same conditions for 2 hours to activate the adsorbent. Cooling down the adsorbent to room temperature (30°C) and different or required concentrated hydrogen gas (5%, volume percent and balance with N_2 gas and gas flow is 50ml/min) with a pressure (1 bar) was exposed to fixed bed in order to conduct H_2

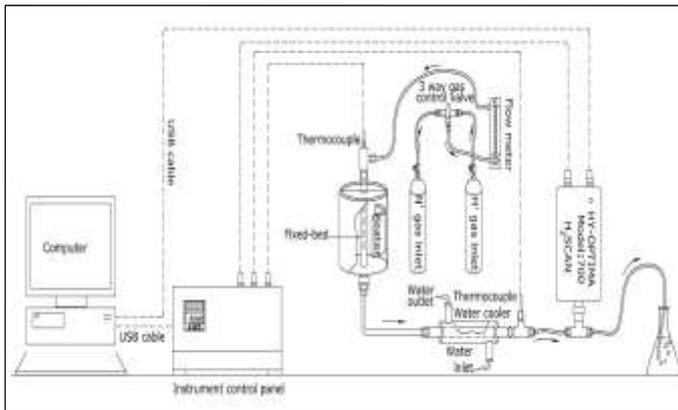


Fig.1: Diagram of the full fixed bed set up

adsorption on the adsorbent (1gm). The H_2 saturated adsorbent bed was used to release the H_2 gas under N_2 gas flow (50ml/min) with a temperature ramping $10^\circ\text{C}/\text{min}$ from 30°C to 150°C . Data have been collected using a USB6008 DAQ card and LABVIEW software. The hydrogen adsorption of the mixed oxide bed can be determined using the equation (1) for the adsorption breakthrough curve [13].

$$M_{ads} = \frac{Q_T(MW)}{(RT/P_A)} \cdot [\Delta t - \int_0^t \frac{y}{y_0} dt] \quad (1)$$

Where, t is the time equivalent to the total or stoichiometric capacity, M_{ads} = Adsorbed mass, Q_T = flow of gas, y_0 is inlet gas concentration and P_A is partial pressure of inlet H_2 gas. All unit are considered as SI unit for calculation and adsorption capacity of the bed determined as blow:

$$W = M_{ads}/M_{bed} \quad (2)$$

Where, M_{bed} = mass of the bed. The mass of the desorbed H_2 can be calculated by the numerical integration of the concentration profiles:

$$M_{des} = P \cdot Q_{N_2} \cdot (MW)/RT \int_0^t \frac{y_{out}}{1-y_{out}} \quad (3)$$

2.3. Experimentation

An elemental chemical analysis for magnesium, nickel and chromium has been performed using the ICP-MS, from Agilent 7500 series. Mixed oxides identification and its crystallinity were analyzed by powder X-ray diffraction (XRD) technique using a Bruker D8 advanced diffractometer

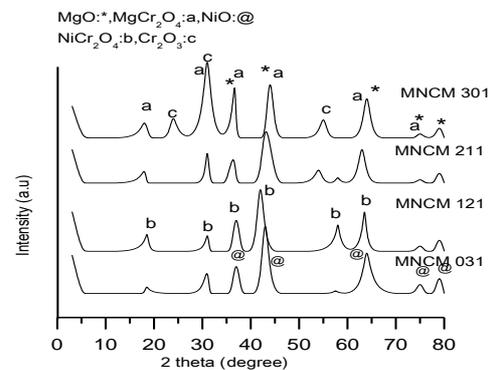


Fig.2: XRD pattern of MNMCM

with Cu-K α radiation. Surface morphology of the mixed oxides was studied by using a field-emission scanning electron microscope (FESEM) from CARLZEISS Supra 55VP instrument equipped with the Oxford INCA400 EDX microanalysis system. The Characterization of microstructure of mixed oxides has been carried out using a CARL Zeiss LIBRA^R 200FE transmission electron microscope (TEM) with an acceleration voltage of 200 kV on ultrasonically dispersed samples in isopropanol. Nitrogen gas adsorption-desorption isotherms of the samples were obtained using a Micromeritics ASAP 2020 Sorptometer. The total surface areas (S_{BET}) were calculated with the Brunauer-Emmet-Teller (BET) method.

Table 1: Compositional and textural properties of MNCM

3. Results and discussion:

The elemental chemical analysis results using ICP-MS is summarized in Table 1 where the results are shown in metal weight percent. The XRD patterns of the mixed oxides shown in Fig. 2 indicate that the precursor of the synthesized material has been decomposed fully at 800^oC and has led to the various oxide derivatives. Mg and Ni containing oxides are mainly of the spinel phases with the characteristic diffraction peaks of NiAl₂O₄ (JCPDS 10-0339), Mg₂NiO₄, (JCPDS 1-77-396) and magnesium chromites, MgCr₂O₄ (JCPDS- 10-0351) in addition to the individual spinels: nickel oxides, (JCPDS- 22-1189) and magnesium oxides MgO (JCPDS-4-829). The elemental analysis and XRD results clearly corresponds that the mixed oxides are homogenous and Nano-crystalline.

The FESEM image of MNCM 121 exhibits a mesoporous surface (Fig. 3) which can be ensured by BET nitrogen adsorption-desorption at -196^oC. The surface morphology of the mixed oxides depends on the synthesis condition (Temperature, pH) and chemical composition.

Adsorbent Name	M ^{II} /M ^{III} (EXPT.)	Elemental Composition			BET Surface area/ (m ² gm ⁻¹)
		Mg	Ni	Cr	
MNCM-031	3.04	---	18.77	5.83	254
MNCM-121	2.91	4.07	7.98	4.15	370
MNCM-211	3.14	8.18	4.32	3.98	285
MNCM-301	2.99	18.5	---	6.20	275

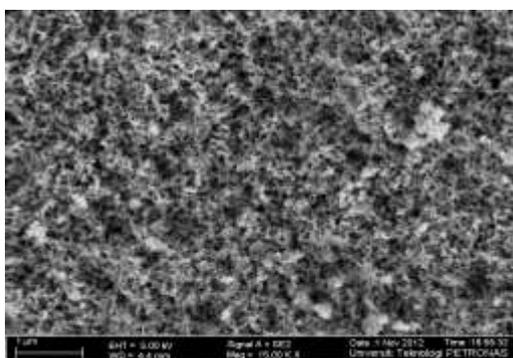


Fig.3: FESEM image of MNCM 121

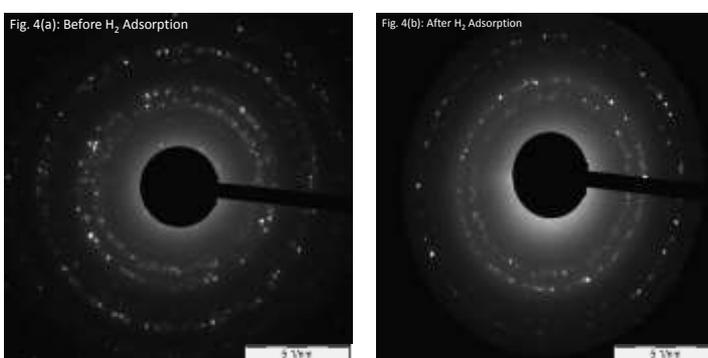


Fig.4: SAED Diffraction pattern of MNCM 121

The SAED (selected area diffraction pattern) pattern of Mg-Ni-Cr mixed oxide were collected using transmission electron microscopy (TEM). It can be observed that SAED pattern of mixed oxides before [Fig. 4a] and after hydrogen adsorption [Fig. 4b] consisted with few rings and dispersed bright spot. The micrograph correspond that the adsorbent are nano-level polycrystalline [14]. It has been observed that nano-crystalline powder show higher hydrogen adsorption capacity than amorphous powder samples which is agree with the work of Tanaka et al [15]. As a result, nano-crystalline material have well-established diffusion path for hydrogen atom along the numerous grain boundaries and slit shaped pore with opening geometry. The nominal differences have been observed between mixed oxides and hydrogen adsorbed mixed oxide is due to the physisorption and minor chemisorption that can realized from table 2.

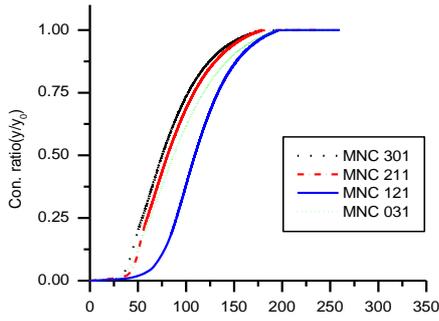


Fig.5: H₂ adsorption breakthrough curves

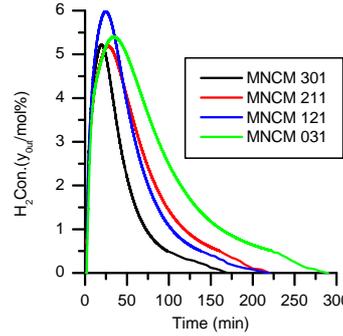


Fig.6: H₂ Desorption curve of MNMCM

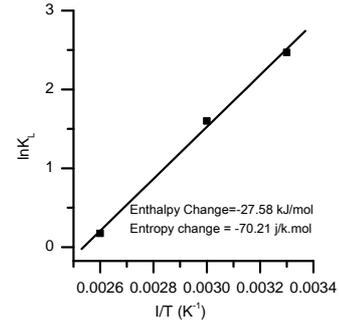


Fig.7: $\ln K_L$ vs. $1/T$ plot

The adsorbed mass of H₂ in the saturation condition ($y/y_0=1$) is determined for each experiment by using equation (2), a condition in which the bed and feeding of the gaseous mixture reached equilibrium. The breakthrough curves of the hydrogen adsorption on the mixed oxides with different molar ratios [Fig.5] at a 30°C temperature are steep and attribute that the porous adsorbent is medium dispersive and the breakthrough curves are symmetrical [16]. In mixed oxides, the binding energy of the metals is generally altered [17]. Any of them (Cr^{3+} or Ni^{2+}) might be more ionic and produce an electric field. So, the polarized hydrogen molecules by those ions can then bind to it in a quasi-molecular form which is intermediate interaction between physisorption and chemisorption. The adsorption capacity decreases with an increased temperature [not shown] but the adsorption rate is different at 60°C and 90°C which indicates that the adsorption is physisorption dominant.

TABLE 2: Adsorption and desorption capacity of MNMCM

Adsorbent	Ads. Capacity / (mg/g ads)	Des. Capacity/ (mg/g ads)	Desorption/ (in percent)
MNMCM 031	22.69	12.00	52.88
MNMCM 121	32.42	18.31	56.47
MNMCM 211	26.10	13.91	53.29
MNMCM 301	20.25	11.14	55.01

A desorption study has been carried out by ramping the temperature from room temperature to 150°C under 50 ml/min N₂ flow at 1 bar. Desorption curves of MCAM with different molar ratios are shown in Fig. 6; the desorbed amount of H₂ is calculated using equation (3), and summarized in Table 2. From the result (Table 2), it can be concluded that MNMCM 121 adsorbed the highest amount of H₂ (32.42 mg/g) and desorbed around 57% of that adsorbed H₂.

The hydrogen adsorption rate can be calculated by using a linear driving force model. The adsorption rate constant depends on the temperature that can be estimated by the Arrhenius equation [18].

$$\ln k = \ln k_0 - \frac{E_a}{RT} \quad (4)$$

Where, E_a is the activation energy and k_0 is the pre-exponential factor. The calculated activation energy from the linear plot of $\ln k$ versus $1/T$ is 8.31 kJ/mol. The Vant Hoff equation is an important tool to study the H₂ adsorption thermodynamics and can be defined in the form [19]:

$$\Delta G_{ads} = -RT \ln K_L = \Delta H_{ads} - T \Delta S_{ads} \quad (5)$$

Where, K_L is the standard equilibrium constant of the Langmuir type adsorption. The change of entropy (ΔS_{ads}) and enthalpy (ΔH_{ads}) of the hydrogen adsorption on the mixed oxides (MNMCM 121) can be determined from $\ln K_L$ versus $1/T$ plot (Fig.7). The values of ΔH_{ads} , ΔS_{ads} are calculated as -27.58 kJ/mol, -70.21 J/mol.K which attributed that the adsorption process is exothermic. The negative value of the entropy indicated the randomness of the hydrogen decreased from the molecular state to the adsorbed state and the regular ordering of the hydrogen on the mixed oxides surface. According to the Bhatia and Myers derived equation [20], optimum enthalpy of hydrogen adsorption on mixed oxide is -21kJ/mol at present experimental condition which is nearer to calculated value of this study. The thermodynamics and kinetics of hydrogen adsorption of different

hydrogen storage materials such as Mg-MOF-74 and cations exchange materials [21, 22] displayed almost similar trend. So, the predicted results attributed that the mixed oxides is a potential adsorbent for reversible hydrogen storage.

4. Conclusions

Mesoporous and homogenous nano-crystalline mixed oxides of Mg-Ni-Cr adsorb 3.2 wt% of hydrogen at near ambient conditions with promising adsorption kinetics and thermodynamics. The H₂ adsorption breakthrough curves and desorption curves showed sorption performance of the mixed oxides. The outcome of the investigation implies that adsorption capacity increases with the surface area and favorable electric field that produced by different oxides in spinels. To the best of the author's knowledge, this is one of the promising quantitative data concerning the kinetics and thermodynamics of H₂ adsorption on unreduced mixed oxides. The characterization results revealed the physio-chemical properties of mixed oxides that are clarifying the hydrogen adsorption phenomena. The material can be considered for different industrial uses as energy carrier.

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