Journal of Molecular Structure 1218 (2020) 128514



Contents lists available at ScienceDirect

Journal of Molecular Structure



journal homepage: http://www.elsevier.com/locate/molstruc

Novel monoanionic diphenate-nicotinamide/*N*,*N*-diethylnicotinamide complexes of Ni^{II}, Zn^{II}. Synthesis, structural investigations and hydrogen adsorption study



Ömer Yurdakul ^a, Zarife Sibel Şahin ^{b, *}, Dursun Ali Köse ^{a, **}, Onur Şahin ^c, Fatih Akkurt ^d

^a Department of Chemistry, Science and Art Faculty, Hitit University, 19100, Çorum, Turkey

^b Department of Energy Systems Engineering, Faculty of Engineering and Architecture, Sinop University, 57000, Sinop, Turkey

^c Department of Occupat Health & Safety, Faculty of Health Sciences, Sinop University, TR-57000, Sinop, Turkey

^d Gazi University, Engineering Faculty, Department of Chemical Engineering, Maltepe, Ankara, Turkey

ARTICLE INFO

Article history: Received 14 February 2020 Received in revised form 21 May 2020 Accepted 22 May 2020 Available online 25 May 2020

Keywords: Diphenic acid Nicotinamide Metal complexes Hydrogen adsorption Energy storage materials Metal-organic materials (MOMs)

ABSTRACT

Mixed ligand complexes containing monoanionic diphenate (*Hdiphen⁻*), dianionic diphenate (*diphen²*)nicotinamide (nic)/N,N-diethylnicotinamide (denic) ligands of Ni(II) and Zn(II) transition metal cations were synthesized, their structural characterizations and molecular simulation for hydrogen adsorption were performed. It is the salt type coordination compound of the Ni(II) complex, complementing the metal octahedral environment with 2 mol of nic and 4 mol of aqua ligands. Two moles of Hdiphen⁻ ligand is monoanionic located outside the coordination sphere and provides the charge equivalence of the complex. In the Zn(II) complex structure, denic and diphen²⁻ ligand is located within the coordination sphere. In the Zn(II) coordination compound structure, diphen²⁻ ligands, which are located in the structure of a bridge between two different metal centres, make the structure polymeric. The binding properties of complexes to metal cations are also elucidated by infrared spectra. It has also been clarified whether the diphenate ligand is bonded to monovalent or bivalent. The mixed ligand complexes of diphenate $[Ni(nic)(H_2O)_4]$.2(Hdiphen) (I) and $[Zn(denic)(diphen)(H_2O)] \cdot H_2O$ (II) distorted octahedral, and they have P-1 space group and triclinic crystal systems. The thermal decomposition of the complexes begins with dehydration steps and continues with the decomposition of organic ligands. As a result of the thermal analysis, it is determined that the oxides of the relevant metal cations remain as the final decomposition products of the molecules. The hydrogen storage of nickel complex is 0.153 wt% and the zinc complex is 0.289 wt% at 77 K and 10 bars.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

The coordination compounds and polymers in which the transition metals are taken centrally are of interest due to their very different properties. The studies on the synthesis and structural properties of these compounds due to their potential applications for nanotechnology, sensor applications, magnets, optoelectronics, energy conversation and storage, gas storage, separation, catalysis and similar industrial applications are of great interest [1–5]. The side ligands may also be positioned as bridges between the metal centres. In these structures, ligands such as salicylates, dicarboxylate succinate, maleate, terephthalate, polycarboxylate, coumarate, 1,3,5-benzenethicarboxylate, 1,2,4,5-benzenetetracarboxylate, benzene-1,3,5-tricarboxylate, diphenate, etc. are frequently used as linkers [6–12]. Such coordination compounds are also referred to as metal-organic frameworks. Studies on metal-organic frameworks (MOFs) structures (syntheses, characterizations and applications) have increased in recent years with a considerable acceleration. Because of their large surface areas and porosity, they find many uses, especially gas adsorption, separation and catalysis. Their structures are mainly based on the fact that an organic linker settles into a bridge between two metal centres and transforms the structure into a two-dimensional or three-dimensional framework. By changing the organic linker, the surface areas and porosities can be changed easily [13–18].

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: zarifesibel@sinop.edu.tr (Z.S. Şahin), dalikose@hitit.edu.tr (D.A. Köse).

Terephthalate, 2,6-naphthalene dicarboxylic and diphenic acid having dicarboxylic groups are amongst the aromatic ligand sources having two carboxylate groups capable of couple bonding for bridge ligands forming MOFs by settling in the bridge position. The diphenic acid (H₂diphen) contains two carboxylic acid groups bonded to the two phenyls, not co-planar rings. The protons of the carboxyl groups present in the structure can be partially or completely removed and ionized, making the metal ion more voluntary. It also makes it possible to form hydrogen bond interactions, thereby strengthening the molecular framework. Most of the structures of the frameworks constructed with a transition metal or rare earth metal cations of ionized dianionic ($diphen^{2-}$) or monoanionic (Hdiphen⁻) anions of diphenic acid have been reported using the synthetic hydrothermal method [19–28]. The coordination properties of the carboxyl group may vary depending on the reaction conditions such as temperature, solvent and auxiliary ligand. It has been shown that the pH value does not have a significant effect on the synthesized molecule and the conversion of the carboxyl group to the salt form with NaHCO₃ before the pH effect is eliminated [29–32]. The distortion of the space gap of the diphenyl group characterizes the formation of macrocyclic structures [33,34] or helical chains by locating the diphenic acid as a bridge between metal cations and metal clusters [35]. In the ligands such as 1,10-phenanthroline and 2,2-bipyridine, which exhibit double-thread binding, π - π may form interesting supramolecular structures with stacking interactions [36,37]. The ability of Bpyridine-like and dicarboxylate ligands to form MOFs constructs has also been studied [38].

Moreover, novel crystal structures had been used for many possible applications for the last decade, both theoretically and experimentally [39–41]. Hydrogen storage application which is the crucial part of the hydrogen energy system is compatible with the compounds that have metal centres with organic ligands. Thus the metal-organic compounds that are synthesized and characterized in this work were tested for hydrogen storage application. In other words, the hydrogen storage capacity of the compounds manufactured in this work was theoretically examined for hydrogen storage. Some of our previous works show that the theoretical calculations could be trustworthy for hydrogen storage capacity calculations [42,43]. A type of metal-organic compound, named Metal-Organic Framework (MOF) has great attention on it for hydrogen storage capacities. Siegel et al. reported that more than 500 000 different kinds of metal-organic compounds investigated and indexed for hydrogen storage and most effective of them have the hydrogen storage capability by 40 g hydrogen per litre storing material, approximately [44]. Department of Energy (DOE) (U.S.) targets for solid-state hydrogen storage have not been met yet thus the investigating storage capacities of novel metal-organic compounds have attention. Hydrogen storage by physical adsorption in hosting materials has better performance in low temperatures such as easily accessible lowest temperature, liquid nitrogen temperature, 77K (-196 °C). But the DOE focuses on room temperature storage which is shown on the targets [45]. This is why various temperatures, including room and liquid nitrogen temperatures, were calculated for the complexes in this work.

In this report, we synthesized and investigated structures and theoretical hydrogen storage capacity of two novel mixed ligand complexes of a flexible diphenic acid ligand. While one of them is salt type metal-organic materials (MOMs) complex containing diphenic acid/nicotinamide ligands [Ni(*nic*)₂(H₂O)₄].2*Hdphen*⁻ (*nic*:nicotinamide, *Hdphen*⁻:monoanionic diphenate), the other one is polymeric type metal-organic frameworks (MOFs) complex containing diphenic acid/*N*,*N*-diethylnicotinamide ligands, [Zn(*denic*)(*diphen*)(H₂O)]·H₂O (*denic*: *N*,*N*-diethylnicotinamide, *diphen*²⁻: monoanionic diphenate). The supramolecular structures

of the complexes are formed by $\pi - \pi$ stacking interactions and hydrogen bonds. Thermal decomposition parameters and analyzes of the complexes were investigated using TGA/DTA curves. The structural formulas of ligands used in the synthesis of complexes are given in Scheme 1.

2. Experimental

2.1. Materials and methods

The diphenic acid ([1,1'-biphenyl]-2,2'-dicarboxylic acid) and metal salts of (Ni(CH₃COO)₂·4H₂O, and Zn(CH₃COO)₂·2H₂O and nicotinamide (Vit. B3) and *N*,*N*-diethylnicotinamide (nikethamide) used in the synthesis of complexes were provided Sigma-Aldrich company.

2.2. Synthesis

Synthesis of metal-diphenate (Hdiphen⁻)/(diphen²⁻)-Nicotinamide (nic)/N,N-diethylnicotinamide (denic) Complexes.

In the initial step, sodium diphenate salt (Na-dphen) was prepared at room temperature in accordance with the reaction equation in eq. (1). Water was used as the solvent medium of the reactions.

$$C_{14}H_{10}O_4 + NaHCO_3 \rightarrow C_{14}H_9O_4Na + CO_2 + H_2O$$
 eq. 1

In the next step, the derivation of the dipenate salts of the transition metal cations was carried out by replacing the transition metal cation with the sodium metal cation. The transition metal salt solutions obtained according to the given reaction concentration below were stored for the next step.

$$\begin{array}{ll} 2C_{14}H_9O_4Na \,+\, M(CH_3COO)_2.nH_2O \,\rightarrow \\ M(C_{14}H_9O_4)_2.nH_2O \,+\, 2NaCH_3COO & eq.\,2 \end{array}$$

 $(M: Ni^{II}, Zn^{II}; n:3-6)$

For the synthesis of complex ligand complex structures, neutralized ligand solutions of nicotinamide or N,N-diethylnicotinamide were added at room temperature to the transition metal diphenate salt solutions prepared above. The resulting solution was allowed to crystallize at room temperature for 20-22 days. The crystals of salt-type complex ligand complexes $[C_{12}H_{20}N_4NiO_6 \cdot 2(C_{14}H_9O_4)$ (I) and $C_{24}H_{24}N_2O_6Zn \cdot H_2O$ (II)] where the difenate cation was located outside the coordination sphere as counter-ion were collected and washed with cold acetone and dried in vacuo. The equation for the synthesis reaction of the mixed ligand-containing complexes of transition metals is shown in eq. (3).

$$\begin{array}{l} M(C_{14}H_9O_4)_2.nH_2O \ + \ 2C_6H_6N_2O \ / \ C_{10}H_{14}N_2O \ \rightarrow \ C_{12}H_{20}N_4NiO_6\cdot 2(-C_{14}H_9O_4) \ / \ C_{24}H_{24}N_2O_6Zn\cdot H_2O \ \qquad eq. \ 3 \end{array}$$

(M: Co^{II}, Zn^{II}; n:3-6;)

The structural properties of non-metal cation pentaborate compounds were investigated with FT-IR (PerkinElmer Spectrum One B), elemental analysis (LECO, CHNS-932), magnetic measurements $M \times 1$ Sherwood Scientific model magnetic susceptibility balance and examined according to Gouy Method, TGA/DTA/DTG analysis (Shimadzu DTG60H) and P-XRD analysis (Rigaku Ultime-IV) using a copper target (Cu K α) forming an X-ray of the wavelength of 1.54 Å. The data were recorded from 20° to 100°.



Scheme 1. Structures of ligands. (a) diphenic acid, (b) nicotinamide, (c) N,N-diethylnicotinamide.

2.3. Crystallography

Table 2 Crystal data and structure refinement parameters for complexes I-II.

The H atoms of C atoms were treated as riding atoms with distances of 0.93–0.97 Å. We used these procedures for our analysis: solved by direct methods; SHELXS-2013 [46]; refined by full-matrix least-squares methods; SHELXL-2013 [47]; data collection: Bruker APEX2 [48]; molecular graphics: MERCURY [49]; solution: WinGX [50]. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC numbers 1853969 for I and 1853970 for II. Table 2 contains crystallographic data information of the structures.

2.4. Computational details

Adsorption isotherms calculated for 10-10000 kPa pressure range within 30 equilibration steps in logarithmic scale for different four temperatures which are 253K, 273K, 298K and 313K. Besides, low temperature (77K) adsorption isotherms calculated in 30 logarithmic equilibrium steps for both crystals in 0.01–10000 kPa pressure range. Materials Studio suite academic software collection used for computation. The sorption module of the software suite was the primary calculation tool for hydrogen adsorption calculations. Supercells created for calculation accuracy ($3 \times 3 \times 3$ for Zn complex and $4 \times 4 \times 4$ for Ni complex) by using *cif* (crystal information file) data to have geometrical coordinates and crystal parameters.

Hydrogen loading changes the electrostatic field of the host structure. Thus the Ewald summation method [51] used to calculate the electrostatic field for each equilibration step. And, Lennard Jones (LJ) 12-6 potentials that are explained by Rappe et al. [52] used for adsorbate-adsorbate and adsorbate-adsorbent interactions. A particular parameter set called "universal force field" consist of interaction parameters that responses accurately in comparison to experimental data [53,54].

3. Results and discussion

3.1. Elemental analysis

```
(see Table 1)
```

Table 1Analytical data of complexes.

Crystal data	Ni ^{II} complex	Zn ^{II} complex
Empirical formula	C40H38N4NiO14	C24H26N2O7Zn
Formula weight	857.45	519.84
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	8.3516 (14)	8.8027 (6)
b (Å)	10.656 (2)	10.9590 (9)
<i>c</i> (Å)	11.510 (2)	13.5806 (11)
α (°)	78.021 (6)	112.333 (3)
β(°)	88.738 (5)	97.703 (2)
γ (°)	78.971 (6)	96.774 (2)
V (Å ³)	983.3 (3)	1180.34 (16)
Z	1	2
Diffractometer	BRUKER D8-QUEST	
$\lambda(\mathbf{A})$	0.71073 (Mo Kα)	
Temperature (K)	296	
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.448	1.463
θ range (°)	3.0-28.4	3.1-28.3
Measured refls.	48447	55461
Independent refls.	4910	5879
R _{int}	0.044	0.036
S	1.13	1.18
R1/wR2	0.043/0.092	0.042/0.089
$\Delta \rho_{max} / \Delta \rho_{min} (e Å^{-3})$	0.35/-0.28	0.65/-0.54

3.2. Structural analysis

Complex (I): The molecular structure of complex **I**, with the atom numbering scheme, is shown in Fig. 1. The asymmetric unit of **I** contains one Ni(II) ion, one nicotinamide ligand, one non-coordinated diphenic acid ligand and two aqua ligands. The Ni(II) ion is located on a centre of symmetry and coordinated by two nitrogen atoms [Ni1–N1 = 2.1050(15) Å] of two different nicotinamide ligands and four oxygen atoms [Ni1–O2 = 2.0516(14) Å and Ni1–O3 = 2.0673(13) Å] from aqua ligands, thus showing a distorted octahedral coordination geometry. The selected bond parameters of the structures are given in Table 3. The crystal packing in **I** is provided by O–H···O, N–H···O and C–H···O hydrogen bonds The amino N2 atom acts as a hydrogen-bond donor to atom O1ⁱⁱ, so forming a centrosymmetric R²₂(8) ring centred at (n+1, n+1, 1/2) [n = zero or integer] [(ii) -x+2, -y+2, -z+1]. Similarly, aqua O3 atom acts as hydrogen-bond donor to atom O1ⁱⁱⁱ, so forming

Complex	MW g/mol	Yield	Contents % found(calcd.)			Colour	d.p.	μ _{eff.} BM
			С	Н	Ν		°C	
[Ni(<i>nic</i>)(H ₂ O) ₄].2(<i>Hdiphen</i>) C ₄₀ H ₃₈ N ₄ NiO ₁₄ (I)	857.45	92	55.88 (56.03)	4.65 (4.47)	6.49 (6.53)	green	112	2.63
[Zn(<i>denic</i>)(<i>diphen</i>)(H ₂ O)]·H ₂ O C ₂₄ H ₂₆ N ₂ O ₇ Zn (II)	519.84	89	55.69 (55.45)	4.82 (5.04)	5.35 (5.39)	pale white	123	diamag.

d.p: decomposition point.



Fig. 1. The molecular structure of complex I showing the atom numbering scheme. [(i) -x+1, -y+1, -z+1.].

Table 3Selected bond distances and angles for complexes I-II (Å, °).

Complex I			
Ni1–N1	2.1050(15)	Ni1-02	2.0516(14)
NII-03	2.0075(15)		
02-Ni1-03	90.29(6)	O2–Ni1–O3 ⁱ	89.71(6)
02-Ni1-N1	88.61(6)	O2-Ni1-N1 ⁱ	91.39(6)
O3-Ni1-N1	91.88(6)	O3–Ni1–N1 ⁱ	88.12(6)
Complex II			
Zn1–N1	2.098(2)	Zn1-02	2.2374(16)
Zn1-03	2.0959(19)	Zn1–O4 ⁱⁱ	2.1191(16)
Zn1–O5 ⁱⁱ	2.3281(19)	Zn1-06	1.9784(18)
06-Zn1-03	100.20(8)	06–Zn1–N1	102.90(8)
O3-Zn1-N1	145.48(7)	06–Zn1–O2	99.27(7)
O3-Zn1-O2	60.28(6)	N1-Zn1-O2	90.73(7)
O6-Zn1-O4 ⁱ	93.89(7)	03–Zn1–O4 ⁱ	108.68(7)
N1–Zn1–O4 ⁱ	95.02(7)	04 ⁱ -Zn1-02	164.09(6)
O6-Zn1-O5 ⁱ	152.31(7)	03–Zn1–O5 ⁱ	88.11(7)
N1-Zn1-O5 ⁱ	83.23(8)	O2–Zn1–O5 ⁱ	107.70(6)

Symmetry code: (i) -x+1, -y+1, -z+1 for I; (ii) x-1, y, z for II.

centrosymmetric $R_2^2(16)$ ring centred at (n+1, 1/2, 1/2) [n = zero or integer] [(iii) -x+2, -y+1, -z+1]. The combination of these hydrogen bonds produces edge-fused $R_2^2(8)R_4^2(20)R_2^2(16)$ rings which are running parallel to the *ab* plane (Fig. 2). In I, the O–H···O hydrogen bonds (Table 4) are observed between aqua ligands and carboxylate oxygen atoms, with the combination of these hydrogen bonds produces $R_2^2(8)R_4^6(16)$ rings which is running parallel to the [001] direction (Fig. 3). All of these intermolecular interactions give three-dimensional framework results.

Complex (II): The X-ray single-crystal study shows that complex **II** has 1D coordination polymer. The asymmetric unit of **II** contains one Zn(II) ion, one nikethamide ligand, one diphenic acid ligand, one aqua ligand and one non-coordinated aqua ligand (Fig. 4). The

Zn(II) ion is coordinated by one nitrogen atom [Zn1-N1 = 2.098(2)]Å] of nikethamide ligand, four oxygen atoms [range from 2.0959(19) to 2.3281(19) Å] of two different diphenic acid ligands and one oxygen atom [Zn1-O6 = 1.9784(18)]Å] from the aqua ligand, thus showing a distorted octahedral coordination geometry. For charge neutralization, the diphenic acid ligand is deprotonated. The Zn(II) ions are bridged by diphenic acid ligands to generate 1D coordination polymer which is running parallel to the [100] direction, with the Zn···Zn separation is 8.803 Å. The 1D polymers are further joined by O-H···O hydrogen bonds (Table 4), generating 2D supramolecular network, which is running parallel to the *ab* plane (Fig. 5).



Fig. 2. The formation of edge-fused $R_2^2(8)R_4^2(20)R_2^2(16)$ rings in I.



Fig. 3. The formation of edge-fused $R_2^2(8)$ and $R_6^4(16)$ rings in I.

3.3. Electronic spectra

The Bohr Magneton data of complexes (2.63 for I and diamagnetic for II) are an agreement with literature values for similar compounds [22,55–57]. According to elemental analysis results, the Ni(II) complex (I) contains 2 mol neutral *nic* ligand and 4 mol crystalline aqua inside of the coordination sphere and 2 mol

monoanionic *Hdiphen*⁻ ligand settle as a counter ion outside of the coordination sphere. The Zn(II) complex (**II**) includes 1-mol neutral *denic* ligand coordinated to metal cation as monodentate via pyridine nitrogen and 1-mol dianionic-bidentate *diphen*²⁻ bonded to metal cation and 1-mol coordination aqua and 1-mol aqua locate outside of the coordination sphere. The structure of the Zn(II) complex is thought to be polymeric, so the octahedral coordination



Fig. 4. The molecular structure of complex II showing the atom numbering scheme. [(i) x+1, y, z; (ii) x-1, y, z].

....

lable 4	
Hydrogen-bond para	ameters for complexes I-II (Å, °).

D-H···A	D-H	H···A	D···A	D-H···A
Complex I				
C5-H505	0.93	2.48	3.353 (2)	157
N2−H2A…01 ⁱⁱ	0.87(2)	2.13 (2)	2.992 (2)	175
N2-H2B…05	0.85(2)	2.48 (2)	3.227 (2)	146
O3−H3A…O5 ⁱ	0.83 (2)	1.86(2)	2.686 (2)	177
O3−H3B…O1 ⁱⁱⁱ	0.80(2)	2.00(2)	2.736 (2)	154
06-H6…04	0.84(2)	1.73 (2)	2.572 (2)	173
02-H2C…04	0.83 (2)	1.83 (2)	2.650 (2)	178
02–H2D···07 ^{iv}	0.82 (2)	1.94 (2)	2.739 (2)	163
Complex II				
O6−H6A···O2 ⁱⁱⁱ	0.90 (3)	1.75 (3)	2.651 (3)	178
O6−H6B…O4 ⁱⁱⁱ	0.83 (4)	1.83 (4)	2.658 (2)	178
07–H7C…05 ⁱⁱ	0.89 (4)	1.99 (4)	2.867 (3)	167
$07-H7D\cdots01^{iv}$	0.97 (5)	1.91 (5)	2.863 (3)	168
Symmetry codes: (iii) $-x+2$, $-y+1$, $-(iii)$ $x+1$ $y+1$ $z+1$	(i) $-x+1$, $-z+1$; (iv) -1 ; (iv) x y 1	-y+1, -z+1; x+1, -y+1, -	(ii) -x+2, - -z+2 for I ; (ii	-y+2, -z+1;) x-1, y, z;

of metal cation is complemented by the double-threaded bonding of the adjacent diphenic ligand. The coordination of the metal cations in both complexes is thought to be octahedral.

The electronic spectra showed three spin-allowed *d*-*d* transitions of complex (I) correspond to the wavelengths of 813 nm $(A_{2g} \rightarrow T_{1g})$, 611 nm $(A_{2g} \rightarrow T_{1g})$ and 366 nm $(A_{2g} \rightarrow T_{2g})$. These transition bands indicate that the *d* orbitals of the Ni¹¹ metal cation are supposed to support the octahedral geometry. The Zn^{II} complex (II) was expected to show no magnetic vibration due to full *d* orbitals. Since the complex did not show any vibration on the Gouy magnetic scale and was diamagnetic, no peaks were observed for *d*-*d* transitions in the UV–visible region spectrum. However,

Some inf	luential	FT-IR	bands	of	complexes.
----------	----------	-------	-------	----	------------

6	NI:II	7
Groups	NI	ZII
ν(OH) _{H2O}	3550-2950	3400-2900
$\nu(NH_2)$	3059	-
$\nu(C=0)_{amid}$	1601	1595
$\nu(C=0)_{anionic \ carbonyl}$	1624	1623
$\nu(C=0)_{neutral \ carbonyl}$	1683	_
v(COO-) _{sym}	1552	1546
$\nu(\text{COO-})_{asym}$	1396	1307
Δv_{as-s}	156	239
ν (C=C; C-C) _{ring}	1567; 1535	1560; 1531
$\nu(C_9 - O_1 - C_1)$	1243/1174	1242/1175
$\nu(CC) + \delta(CCH)_{ring}$	1297	1281
v(Ring)	1125-761	1133-751
$\nu(M - N)_{nic/denic}$	677	683
$\nu(M - O)_{carboxyl}$	441w	470s
$v(M - O)_{carbonyl}$	533w	540s
$\nu(M - O)_{H2O}$	595s	592s

high-intensity peaks were detected at 245 nm and 261 nm peaks in the spectrum. These peaks were interpreted to be the peaks in the assemblies, respectively, showing transitions due to metal-ligand and ligand-metal charge transfer. The results were consistent with the literature [22,56–58].

3.4. Infrared spectra

The infrared graphics of mixed ligands complexes were shown in Fig. 6 and some significant peaks of them were summarized in Table 5. The range of 3500-2650 cm⁻¹ stretching peaks can be attributed to -OH bands of coordinated aqua ligands. The stretching peak due to C=O group observed at 1753 cm⁻¹ for diphenic acid was shifted to the region at 1624 cm⁻¹ for (I) and 1645 cm⁻¹ for (II). The salt type ionic bonding in the complex (II)



Fig. 5. The 2D supramolecular network in II.



Fig. 6. FT-IR spectra of the metal complexes Ni(II) complex is (I), and Zn(II) complex is (II).

and the covalent bonding in the compound **(I)**. In the salt-type metal complex, electron transfer is carried out from the carbonyl group to the metal. At the same time, in the salt form (I) complex structure, the diphenic acid exhibits two types of carbonyl stretching. The first one is the carbonyl group of the ionic carboxylate group, which provides coordination of the metal by transferring electrons to the metal and provides a charge of the metal. This neutral stretching vibration carbonyl group occurs at 1683 cm⁻¹, which is a value close to the tensile wave of pure diphenic acid. The peak was observed at the 3059 cm⁻¹ belongs to stretching vibrations of $-NH_2$ group of nicotinamide ligand in the structure **(I)**. The carbonyl groups of *nic* and *denic* ligands (amide groups) stretching peaks were detected in the range of 1601 and 1595 cm⁻¹.

The numerical difference between *symmetrical* and *asymmetric* stretching vibrations $(COO^-_{sym}-COO^-_{asym})$ of the carboxylic group of the ligand is the most important indicator of whether the carboxyl group is bound to monodentate or bidentate. It can be observed that these differences are at 152 for the salt type *mono-anionic-monodentate* diphenate complex (I) and 239 for coordination type *dianionic-bidentate* diphenate complex (II).

The three type absorption bands were observed corresponding to M - O, and M - N bonding is the stretching vibrations in salt type complex (I). The absorption peak of $M-N_{nic-pyridine}$ bonding was obtained 677 cm⁻¹, and the $M-O_{H2O}$ was 595 cm⁻¹ (strong peak),



Fig. 7. TG-DrTG/DTA curves of complexes (a) Ni(II) complex (b) Zn(II) complex.



Fig. 8. The powder-XRD patterns of NiO (a) and ZnO (b).

and the M-O_{carboxyl} was 441 cm⁻¹ (weak peak). But for the complex (II) has four types M – O and M – N bonding peaks that are M-N_{denic-pyridine} at 683 cm⁻¹ and M-O_{H2O} at 592 cm⁻¹ (strong peak) and M-O_{carboxyl} at 540 cm⁻¹ (strong peak) and M-O_{carbonyl} at 470 cm⁻¹ (strong peak). The results obtained are sufficient to explain the coordination types and regions of ligands to metal, and they are compatible with the literature data [22,55–59].

3.5. Thermal analysis

 $[Ni(C_6H_6N_2O)_2(H_2O)_4] \cdot 2C_{14}H_8O_4$ (I): The thermal decomposition curves (TG-DTG/DTA) of complex I were showed Fig. 7a. The metal complex doesn't contain any hydrated water out of the coordination sphere. The four moles coordination agua remove with one step at the range of 101–156 °C (exp.8,75%; calc.8.40). Then in the field of 203–958 °C diphenate and nicotinamide ligands start to decompose. The decomposition of organic parts takes place in five steps, and the intermediate products are formed in each step. The decomposition proceeds with the output of CO/CO₂/NO₂/N₂O gases. The final decay product was determined by the powder XRD spectrum (Fig. 8) in which the black NiO residue was present in the reaction crucible. The black colour of the residual product is an indication that the combustion is not complete due to the low oxygen in the structure of the complex in degradation reactions in the inert nitrogen atmosphere. Accordingly, some carbon atoms remain carbonized carbon on the metal oxide surface. Theoretical and experimental data are compatible with each other (Table 6).

 $[Zn(C_{14}H_8O_4)(C_{10}H_{14}N_2O)(H_2O)] \cdot H_2O$ (**II**): The TG-DTG/DTA curves of mixed ligand complex II was given Fig. 7b. According to thermal analysis results, Zn^{II} coordination compound has five decomposition steps. Firstly, outside of the coordination sphere, hydrated aqua removes from the main structure by one step. Then one mole coordinated aqua ligand decomposes and leaves from the complex. The neutral ligand *N*,*N*-diethylnicotinamide ligand, starts to crumble from an anhydrous complex structure with one step at the 234 °C. Lastly, the diphenate ionic and bidentate ligand decomposes in the range of 382-893 °C by two steps. It was found that black ZnO residues remained in the reaction vessel as a thermal decomposition product. Experimental and computational per cent weight losses of all degradations are given in Table 6. It has been found that the details of the proposed degradation steps are consistent with the literature data [22,55-59].

Created supercells used for hydrogen adsorption calculations that are given in Fig. 9. It is seen in orthographic representation that the holes exist in the structures. That means the hydrogen could diffuse inner sites of the structure in this way. The phenomena were also discussed as an accessible solvent surface area previously in detail [60]. The supercells created because the adsorbate-adsorbate and adsorbate-adsorbent interactions get more realistic at the cells consist of more atoms; also, the electronic field makes sense while the electrostatic summation method ignores some of the interactions at small structures. The reason for creating small structures in comparison to much more significant supercells was the computation constraints.

Hydrogen adsorption capacities of the adsorbents collected in two temperature ranges which are low (77K) and relatively high (253K, 273K, 298K and 313K) temperatures. Because the calculated hydrogen capacities have meaningful differences to give the same plot, even each complex differs in hydrogen uptake capacities, so the following Figures (Fig. 10a and b) created. It is clear from the previous works [61,62] and the present work (Figs. 10 and 11) that the low-temperature hydrogen storage is more effective. But the main reason was to investigate if the complexes



Fig. 9. Created supercells for a) Zn complex and b) Ni complex.

work nicely in the room temperature region (253 K–313 K).

Both complexes had the highest hydrogen uptake at 253K for the room temperature region as it is expected. And the values are 0.0435 and 0.00254 wt % at 253K for the zinc and nickel complexes respectively. Also, the lowest hydrogen storage capacities calculated at 313K for both compounds. The capacities were 0.0200 and 0.0012 wt % at 313 K and 100 bars for complexes. Zinc complex had better uptake performance, so the calculated capacities were bigger than ten times in comparison to nickel complex at the same conditions (adsorption temperature and equilibrium pressure). There are two possible reasons which are two metal centres and aqua molecule existence in zinc complex. In the experimental measurements, degas procedure being applied to the host materials, by this way moist and free aqua molecules exhaust from the adsorbent. Thus the free aqua molecules that are existing in the zinc complex removed from the structure results in more surfaces that the hydrogen could be stored. Another possible reason for storing more hydrogen at the zinc complex is the two metal centre existence. Metal centres change the electrical charges of the molecule



Fig. 10. Hydrogen storage capacities of the complexes at the high-temperature region, a) Zn complex and b) Ni complex.

or crystal structures. So the charged structures allow to placing of hydrogen closer to the host material surfaces.

For better understanding, hydrogen molecules represented inside the host materials in Fig. 11. The positions of the hydrogen molecules were calculated by using simulated annealing algorithms that attend to the lowest total energy of the final structure. The positions of the hydrogens being change by the atomic coordinate shifting and rotating molecules. At last final locations being determined by the lowest total energy.

The highest storage capacities calculated for the compounds at 77 K as it is expected. Hydrogen uptake versus equilibrium pressure values given in Fig. 12. And the compounds had been storing hydrogen almost full capacity up to 2 bars for zinc complex and 10 bars for nickel complex. The differences between the complexes could be the same reasons, explained previously for hightemperature region calculations, which are the extra surfaces after molecular agua removal and two metal centre existence in zinc complex in comparison to nickel complex. Additional surfaces that the molecular hydrogen could be filled in the zinc complex could result from the two times more considerable hydrogen uptake at the maximum capacity (~10 bars for 77 K calculations). On the other side, two metal atom existence in the unit cell (the smallest unit of the crystal) could result in extra electrical charges which enable additional electrical attraction of molecular hydrogen. Thus the adsorbent could be filled relatively lower pressures (It is not meant fast filling because the time was not the parameter for calculations). Besides, a gap is also shown in Fig. 12.b. that the uptake trends differ for the complexes up to 10 bars.

The highest hydrogen uptake calculated for the zinc complex that is 0.289 wt % at 77 K and 10 bars. The other one, nickel complex, could uptake 0.153 wt % hydrogen at the same conditions. Calculated values are 0.0274 and 0.020 wt % at 77 K and 1 bar equilibrium pressure for the zinc and nickel complexes, respectively.

In consequence, the highest uptake capacities are shown that the complexes have mean and lower uptake capacities in comparison to previously examined calculations and experiments [44,62]. The hydrogen storage capacities of our complexes compared to the hydrogen storage values of the calculated MOF compounds studied in the literature can be evaluated as low [63–69]. But is not the concern that calculating hydrogen storage capacities such complexes is not meaningful. On the contrary, such complexes prove and show what kind of differences result in more hydrogen uptake.



Fig. 11. Molecular hydrogen adsorbed complexes (green ellipsoids are hydrogen molecule), a) Zn complex and b) Ni complex at 2 x 2 x 2 supercells.



Fig. 12. Hydrogen storage capacities of the complexes at 77 K and different pressures at logarithmic scale for the complexes.

4. Conclusions

In this study, two different metal cations and diphenic acid complexes were synthesized, and their structural characterizations were studied. The structures with neutral nicotinamide/*N*,*N*diethylnicotinmaid ligands were obtained as mixed ligand complexes. In structure, **I**, the 2 mol diphenic acids, was placed as a stabilizing ion outside the coordination sphere, while one of the two acidic carboxylate groups was ionized. Therefore, 2 mol of monoanionic diphenate ligand to balance the 2+ charge equivalence of the metal in the structure were included in the structure. The octahedral coordination of the metal is provided by 2 mol of nicotinamide and 4 mol of aqua ligands involved in the coordination sphere. In its complex structure **II**, it is involved in coordination

in both organic ligands and provides the octahedral coordination of the metal cation with 1-mol of *N*,*N*-diethylnicotinamide ligand, 1 mol of monoanionic-bidentate diphenate ligand, one mol of aqua ligand and the adjacent diphenate ligand that bind to the bidentate. In this structure, the diphenate ligand is located in the position of a bridge between two metal centres and transforms the structure into a polymeric coordinating compound. While structures I and II are considered as metal-organic materials (MOMs) growing with covalent and hydrogen bonds, structure II can be called metalorganic frameworks (MOFs) structure developed by coordinated covalent bonds. The binding properties of the molecules were supported by the infrared spectra, while the elemental analysis results explained the per cent compositions. The thermal decomposition steps of the structures were examined, and their thermal characterizations were explained. Thermal decomposition steps of coordination compounds begin with the degradation of the agua ligands. Both complexes in the final decomposition products were found in the reaction vessel as determined NiO and ZnO residue.

The highest hydrogen uptake calculated for the zinc complex that is 0.289 wt % at 77 K and 10 bars. The other one, nickel complex, could uptake 0.153 wt % hydrogen at the same conditions. Calculated values are 0.0274 and 0.020 wt % at 77 K and 1 bar equilibrium pressure for the zinc and nickel complexes, respectively.

In consequence, the highest uptake capacities are shown that the complexes have mean and lower uptake capacities in comparison to previously examined calculations and experiments. But is not the concern that calculating hydrogen storage capacities such compounds is not meaningful. On the contrary, such complexes prove and show what kind of differences result in more hydrogen uptake.

Thermal degradation is noticeable due to the different secondary ligands (*nicotinamide* and *N,N-diethylnicotinamide*) present in the complexes. Besides, depending on the complexes having a different metal centre, structural differences come to the fore. These differences are the most important reasons for the differences both in thermal analysis curves and in other spectroscopic analyzes. The salt type of the basic structure of the complex **I**, the crystallization of the compound **II** in the polymeric coordination compound structure was reflected in both thermal decomposition curves and FT-IR spectra. It is determined that the complex number **I** in the salt type structure shows low hydrogen storage capacity due to the lower molecular spaces due to more frequent stacking.

Declaration of competing interest

This study was financially supported by Hitit University Research Found (project No:FEF19001.16.004) and Sinop University Research Found (project No. MMF-1901-15-01).

CRediT authorship contribution statement

Ömer Yurdakul: Conceptualization, Methodology. Zarife Sibel Şahin: Writing - review & editing, Project administration. Dursun Ali Köse: Methodology, Software, Visualization, Investigation, Resources. Onur Şahin: Investigation, Visualization. Fatih Akkurt: Software, Visualization, Investigation.

Acknowledgements

This study was financially supported by Hitit University Research Found (project No:FEF19001.16.004) and Sinop University Research Found (project No. MMF-1901-15-01). The authors acknowledge to Scientific and Technological Research Application and Research Center, Sinop University, Turkey, for the use of the

Bruker D8 QUEST diffractometer.

References

- [1] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Nature 423 (6941) (2003) 705–714.
- [2] P.J. Hagrman, D. Hagrman, J. Zubieta, Angew. Chem. Int. Ed. 38 (18) (1999) 2638–2684.
- [3] A. Erxleben, Coord. Chem. Rev. 246 (1-2) (2003) 203-228.
- [4] C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. Chem. Int. Ed. 43 (12) (2004) 1466–1496.
- [5] J. Kim, U. Lee, B.K. Koo, Bull. Kor. Chem. Soc. 31 (2) (2010) 487–490.
- [6] J. Kim, U. Lee, B.K. Koo, Bull. Kor. Chem. Soc. 31 (6) (2010) 1743–1746.
- [7] B.K. Koo, J. Kim, U. Lee, Inorg. Chim. Acta. 363 (8) (2010) 1760–1766.
- [8] Y.B. Go, X. Wang, E.V. Anokhina, A.J. Jacobson, Inorg. Chem. 44 (23) (2005) 8265–8271.
- [9] H. Xu, R. Wang, Y. Li, J. Mol. Struct. 688 (1–3) (2004) 1–3.
- [10] O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy, Acc. Chem. Res. 31 (8) (1998) 474–484.
- [11] N. Hao, Y.G. Li, E.B. Wang, E.H. Shen, C.W. Hu, L. Xu, J. Mol. Struct. 697 (1–3) (2004) 1–8.
- [12] B.K. Koo, Bull. Kor. Chem. Soc. 33 (7) (2012) 2299–2304.
 [13] H.K. Chae, J. Kim, O.D. Friedrichs, M. O'Keeffe, O.M. Yaghi, Angew. Chem. Int.
- Ed. 42 (2003) 3907–3909.
- [14] H.C. Zhou, J.R. Long, O.M. Yaghi, Chem. Rev. 112 (2) (2012) 673-674.
- [15] U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastré, J. Mater. Chem. 16 (7) (2006) 626–636.
- [16] M. Jacoby, Chem. Eng. News 86 (34) (2008) 13–16.
- [17] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, Science 295 (5554) (2002) 469–472.
- [18] Z. Wang, S.M. Cohen, J. Am. Chem. Soc. 129 (41) (2007) 12368–12369.
- [19] I.L. Karle, P. Venkateshwarlu, R. Nagaraj, A.V.S. Sarma, D. Vijay, N.G. Sastry,
- S. Ranganathan, Chem. Eur J. 13 (15) (2007) 4253–4263. [20] X. Xu, Y. Lu, E. Wang, Y. Ma, X. Bai, J. Mol. Struct. 825 (1–3) (2006) 124–129.
- [21] J. Min, J. Li, W. Chen, F.X. Zhang, Struct. Chem. 17 (3) (2006) 327–331.
- [22] Z.S. Sahin, O. Sahin, Ö. Daglı, D.A. Köse, Polyhedron 117 (2016) 214–223.
- [23] J. Rueff, S. Pillet, G. Bonaventure, M. Souhassou, P. Rabu, Eur. J. Inorg. Chem. 23 (2003) 4173–4178.
- [24] Y. Wang, X. Zheng, W. Zhuang, L. Jin, Eur. J. Inorg. Chem. 7 (2003) 1355–1360.
- [25] J.Y. Lu, V. Schauss, Inorg. Chem. Commun. 6 (10) (2003) 1332–1334.
- [26] F. Guo, J. Xu, X. Zhang, B. Zhu, Inorg. Chim. Acta. 363 (2010) 3790–3797.
- [27] R. Wang, Y. Zhou, Y. Sun, D. Yuan, L. Han, B. Lou, B. Wu, M. Hong, Cryst.
- Growth Des. 5 (1) (2005) 251–256. [28] G.X. Liu, Y.Y. Xu, Y. Wang, S. Nishihara, X.M. Ren, Inorg. Chim. Acta. 363 (2010) 3932–3938.
- [29] P.X. Yin, J. Zhang, Z.J. Li, Y.Y. Qin, J.K. Cheng, L. Zhang, Q.P. Lin, Y.G. Yao, Cryst. Growth Des. 9 (11) (2009) 4884–4896.
- [30] M.T. Rispens, A. Meetsma, R. Rittberger, C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, Chem. Commun. (2003) 2116–2118, 0.
- [31] S.O. Ma, D.F. Sun, M. Ambrogio, J.A. Fillinger, S. Parkin, H.C. Zhou, J. Am. Chem. Soc. 129 (7) (2007) 1858–1859.
- [32] Q. Shi, Y. Sun, L. Sheng, K. Ma, M. Hu, X. Hu, S. Huang, Cryst. Growth Des. 8 (9) (2008) 3401–3407;

(b) R. Cao, Q. Shi, D. Sun, M. Hong, W. Bi, Y. Zhao, Inorg. Chem. 41 (23) (2002) 6161–8168;

(c) X.X. Xu, Y. Lu, E.B. Wang, Y. Ma, X.L. Bai, Cryst. Growth Des. 6 (9) (2006) 2029–2035;

(d) P.X. Yin, Z.J. Li, Y.Y. Qin, J.K. Cheng, L. Zhang, Y.G. Yao, Chin. J. Struct. Chem. 27 (8) (2008) 980–984

(e) L.E. Kreno, K. Leong, O.K. Farha, M. Allendorf, R.P. Van-Duyne, J.T. Hupp, Chem. Rev. 112 (2) (2012), 1105-1025.

 [33] I.A. Gural'skiy, D. Escudero, A. Frontera, P.V. Solntsev, E.B. Rusanov, A.N. Chernega, H. Krautscheid, K.V. Domasevitch, Dalton Trans. (2009) 2856–2864;
 (b) K.V. Domasevitch, P.V. Solntsev, I.A. Gural'skiy, H. Krautscheid,

E.B. Rusanov, A.N. Chernega, J.A.K. Howard, Dalton Trans. (2007) 3893–3905;
(c) B.L. Schottel, H.T. Chifotides, M. Shatruk, A. Chouai, L.M. Perez, J. Bacsa, K.R. Dunbar, J. Am. Chem. Soc. 128 (17) (2006) 5895–5912;
(d) M.H. Zeng, Q.T. Wang, Y.X. Tan, S. Hu, H.X. Zhao, L.S. Long, M. Kurmoo,

- J. Am. Chem. Soc. 132 (8) (2010) 2561–2563. [34] J.N. Tang, W.J. Xu, L.Y. Zhang, G.H. Pan, P. Liang, Z.J. Huang, Synth. React. Inorg.
- Metal-Org, Nano-Metal Chem. 44 (2014) 454–461. [35] J.M. Rueff, S. Pillet, N. Claiser, G. Bonaventure, M. Souhassou, P. Rabu, Eur. J.

Inorg. Chem. (2002) 895–900;
 (b) H. Kumagai, K. Inoue, M. Kurmoo, Bull. Chem. Soc. Jpn. 75 (6) (2002) 1283–1289

- [36] X.M. Chen, G.F. Liu, Chem. Eur J. 8 (20) (2002) 4811-4817.
- [37] G.F. Liu, B.H. Ye, Y.H. Ling, X.M. Chen, Chem. Commun. (14) (2002) 1442–1443.
- [38] B.H. Ye, M.L. Tong, X.M. Chen, Coord. Chem. Rev. 249 (5–6) (2005) 545–565.
 [39] M. Anis, M. Shkir, M.I. Baig, S.P. Ramteke, G.G. Muley, S. AlFaify, H.A. Ghramh,
- J. Mol. Struct. 1170 (2018) 151–159. [40] S.R. Maidur, J.R. Jahagirdar, P.S. Patil, T.S. Chia, C.K. Quah, Opt. Mater. 75 (2018)
- 40] S.R. Maidur, J.R. Jahagirdar, P.S. Patil, T.S. Chia, C.K. Quah, Opt. Mater. 75 (2018 580–594.

- [41] M.A. Bhat, S.H. Lone, M.A. Mir, S.A. Majid, H.M. Bhat, R.J. Butcher, S.K. Srivastava, J. Mol. Struct. 1164 (2018) 516–524.
- [42] Z. Ozturk, G. Ozkan, D.A. Kose, A. Asan, Int. J. Hydrogen Energy 41 (19) (2016) 8256–8263.
- [43] Z. Ozturk, G. Ozkan, A. Asan, D.A. Kose, Int. J. Hydrogen Energy 40 (17) (2015) 5907–5915.
- [44] A. Ahmed, S. Seth, J. Purewal, A.G. Wong-Foy, M. Veenstra, A.J. Matzger, D.J. Siegel, Nat. Commun. 10 (2019) 1568.
- [45] C. Jensen, S. McGrady, G. Severa, J. Eliseo, M. Chong, Final Report: DE- FC36-05G015063, Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides, Golden, CO (United States), 2015.
- [46] G.M. Sheldrick, Acta Crystallogr. E A64 (2008) 112-122.
- [47] G.M. Sheldrick, Acta Crystallogr. C71 (2015) 3–8.
- [48] Bruker-Axs, APEX2, SAINT and SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2013.
 [49] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock,
- [45] Ch. Marta, E. Bruho, J.A. Channon, F.K. Eugington, T. McCabe, E. Frickock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, J. Appl. Crystallogr. 41 (2) (2008) 466–470.
- [50] L.J. Farrugia, WinGX and ORTEP for windows: an update, J. Appl. Crystallogr. 45 (2012) 849–854.
- [51] P.P. Ewald, Ann. Phys. 64 (1921) 253-287.
- [52] A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. Goddard, W.M. Skiff, J. Am. Chem. Soc. 114 (1992) 10024–10035.
- [53] E. Poirier, RSC Adv. 4 (2014) 22848-22855.
- [54] M. Fischer, F. Hoffmann, M. Fröba, ChemPhysChem 10 (15) (2009) 2647–2657.
- [55] D.A. Köse, B. Öztürk, O. Şahin, O. Büyükgüngör, J. Therm. Anal. Calorim. 115 (2)

(2014) 1514-1524.

- [56] D.A. Köse, F. Akkurt, O. Şahin, O. Büyükgüngör, J. Chin. Chem. Soc. 61 (12) (2014) 1326–1332.
- [57] D.A. Köse, H. Necefoğlu, H. Icbudak, J. Coord. Chem. 61 (21) (2008) 3508–3515.
 [58] D.A. Köse, A.N. Ay, O. Şahin, O. Büyükgüngör, J. Iran. Chem. Soc. 9 (4) (2012)
- [58] D.A. Kose, A.N. Ay, O. şahih, O. Buyukgungor, J. Iran. Chem. Soc. 9 (4) (2012) 591–597.
 [50] H. Kose, A.N. Ay, O. Sahih, O. Buyukgungor, J. Iran. Chem. Soc. 9 (4) (2012)
- [59] H. Icbudak, Z. Heren, D.A. Köse, H. Necefoğlu, J. Therm. Anal. Calorim. 76 (3) (2004) 837–851.
- [60] Z. Ozturk, Int. J. Hydrogen Energy 43 (2018) 22365–22376.
- [61] R. Chahine, T.K. Bose, Int. J. Hydrogen Energy 19 (2) (1994) 161–164.
 [62] W.C. Xu, K. Takahashi, Y. Matsuo, Y. Hattori, M. Kumagai, S. Ishiyama,
- [02] W.C. Xu, K. Takanashi, T. Matsuo, T. Hattori, M. Kumagai, S. Isinyama, K. Kaneko, S. Ijima, Int. J. Hydrogen Energy 32 (13) (2007) 2504–2512.
- [63] K.S. Park, Z. Ni, A.P. Cote, J.Y. Choi, R. Huang, F.J. Uribe-Romo, H.K. Chae, M. O'Keeffe, O.M. Yaghi, Proc. Natl. Acad. Sci. Unit. States Am. 103 (27) (2006) 10186–10191.
- [64] M. Dinca, A.F. Yu, J.R. Long, J. Am. Chem. Soc. 128 (2006) 8904–8913.
 [65] Z. Ozturk, D.A. Kose, Z.S. Sahin, G. Ozkan, A. Asan, Int. J. Hydrogen Energy 41 (28) (2016) 12167–12174.
- [66] Y.S. Bae, R.O. Snurr, Microporous Mesoporous Mater, 132 (2010) 300–303.
- [67] W. Zhou, H. Wu, M.R. Hartman, T. Yildirim, J. Phys. Chem. C 111 (2007)
- 16131–16137. [68] W. Wei, S. Chen, Q. Wei, G. Xie, Q. Yang, S. Gao, Microporous Mesoporous
- Mater. 156 (2012) 202–208. [69] J.A. Villajos, G. Orcajo, C. Martos, J.A. Botas, J. Villacanas, C. Guillermo, Int. J.
- Hydrogen Energy 40 (2015) 5346–5352.