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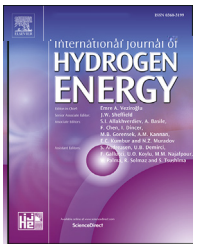


Shaggy-like Ru-clusters decorated core-shell metal-organic framework-derived CoO_x@NPC as high-efficiency catalyst for $NaBH_4$ hydrolysis

Sha ha D [a], Wa Zha g [a], Y i g Ya g [a], Sh i g Zh [a], Xia fa Ra [b], P a Ya [a], Ta i ja Ta l I i ja [c,**], Xi li Ya g [a,*]

[a] Guangxi Key Laboratory of Low Carbon Energy Materials, School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin, 541004, China

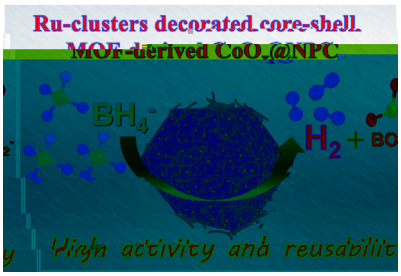
[b] School of Resources and Environmental Engineering, Jiangxi University of Science and Technology, Ganzhou, 341000, China

[c] Saudi Arabia Basic Industries Corporation (SABIC) at King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia

HIGHLIGHTS

- R /CoO @NPC i fab ica ed b a eed-media ed g o h pl p eci e calcina ion.
- The ca al e hibi high ac i i and e abili fo $NaBH_4$ h d ol i .
- Ca boni ed ZIF-8 and ZIF-67 p o- ide high cond c i i and ich ac i e i e .
- The pe io pe fo mance a ib- ed o he ne g of Co o ide and R cl e .

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Recei ed 16 A g 2020
Recei ed in e i ed fo m
16 No embe 2020
Accep ed 2 Decembe 2020
A ailable online

Keywords:
Me al-o ganic f ame o k
N-doped po o ca bon

ABSTRACT

Achie ing high ca al ic pe fo mance i h he lo e po ible amo n of noble me al i c i ical fo an ca al ic applica ion . He ein, e epo a con ollable me hod of p epa ing lo R loaded, N-doped po o ca bon embedded i h cobal o ide pecie (R /CoO @- NPC) ing co e- hell me al-o ganic f ame o k (MOF) a a empla e. The op imi ed ca a- l e hibi a highl po e f l e able pe fo mance of H_2 p od c ion h o gh odi m bo oh d ide ($NaBH_4$) h d ol i . The R /CoO @NPC ca al ho a fa H_2 gene a ion a e (8019.5 mL min^{-1} g_{ca}^{-1}), high no e f eq enc (1118.6 mol min^{-1} mol_R^{-1}), and e - abili . The ca boni ed ZIF-8 co e and he ZIF-67 o e hell pplie a po o ca bon moie ha no onl imp o e he cond c i i and b al o p o ide nifo m di ib ion of he ac i e i e . The XPS anal i indica e ha he e i a ong elec onic in e ac ion

* Corresponding author.
** Corresponding author.
E-mail add e : i imjan @ abic.com (T.T. I imjan), l ang@g n .ed .cn (X. Yang).

h p ://doi.o g/10.1016/j.ijh dene.2020.12.011

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S ne gi ic effec
NaBH4 h d ol i
H d ogen gene a ion

be een Co pecie and R pecie . The pe io ca al ic pe fo mance can be a ib able o he la ge peci c face a ea a ell a he ne g be een Co-o ide and R cl e .

Introduction

The g o ing demand fo fo il f el (*e.g.*, coal, oil and na al ga , *etc.*) i a igni can ca e of global a ming e l ed f om acce ed CO_2 emi ion [1,2]. The efo e, de eloping a - ainable ene g o ce and dec ea ing fo il f el dependenc i he cen al heme of clean ene g e ea ch [3]. A an al e - na i e ene g ca ie , h d ogen i becoming mo e and mo e iable d e o i high ene g den i and e o CO_2 emi ion [4]. The o main challenge in de eloping H_2 f el a e he co and afe- o age ince he adi ional H_2 o age in ol e high-ene g eq i emen and comple echnical i e . In gene al, he h d ogen o age me hod fo b eq en e can be di ided in o ph ical o age [5], ch a p e h d ogen o age ia comp e ion and liq efac ion, and chemical o age incl ding me al h d ide [6] and liq id o ganic h d ogen ca ie [7], *etc.* A a chemical o age app oach, he me al h d ide (*e.g.*, $NaBH_4$, $LiAlH_4$, MgH_2, *etc.*) ha e ecei ed mo e and mo e a en ion in ecen ea d e o hei afe , and adap abili o he mild eac ion condi ion [8,9]. Among hem, odi m bo oh d ide ($NaBH_4$) ha he ad an age of high h d ogen den i , non-flammabili , con ollable h d ogen p od c ion a e, mode a e ope a ing empe a e, e cellen abili in alkaline ol ion, non- o ic h d ol i b -p od c [10,11], *etc.* One of he idel belie ed challenge in ing $NaBH_4$ a he h d ogen o age ma e ial i egene a ion. Ho e e , ecen die ha e ho n ha $NaBH_4$ can be e- gene a ed b high-ene g ball milling of he h d ol a e in an a gon a mo phe e a oom empe a e. The ield can each p o 80%, and i i calable [12]. In addi ion, ome o he egene a ion me hod ha e epo ed egene a ion a e anging f om 60% o 90% [13–15].

Ho e e , he pon aneo h d ol i of $NaBH_4$ i a lo p oce he eof eq i e an ef cien ca al o dec ea e he ac i a ion ene g and inc ea e he eac ion a e [16,17]. The commonl ed ca al a e mainl noble me al , ch a P / CeO_2–Co_7Ni_2O [18], P –Co/ca bon nano phe e [19], Pd/PD- ZIF-67 [20], Ag–Ni nanopa icle [21], R –Co ca al [22], R /ZIF67 [23], *etc.* Same a o he noble me al ca al , he a e limi ed b co fo ind ial applica ion [9]. A a e l , man effo ha e been de o ed o de eloping Co-ba ed none noble me al ca al fo $NaBH_4$ h d ol i d e o he high ac i i and lo co [14,24,25]. Ne e hele , he a e f- fe ed f om apid deac i a ion [26,27]. Recen l , e epo ed a no el me hod of inco po a ing ela i el mall amo n of R P_3 on o hie a chicall c ed cobal pho phide a a on nickel foam. Thi app oach p od ced a highl ef cien and able ca al fo h d ogen gene a ion f om $NaBH_4$ h d ol - i in alkaline media [28].

A he con in a ion of hi o k, e aim o imp o e he ca al ic pe fo mance f he hile dec ea ing he R loading. Thi goal can be eali ed b adj ing he ppo p ope ie o a d be e cond c i i and accele a ed ma an fe . Recen l , Pan e al. epo ed a high-pe fo mance nano c ed ca al ba ed on ZIF-67@ZIF-8 co e- hell empla e [29]. Ba ed on he e l , he claim ha he e cellen ca al ic pe fo mance i he o come of he accel- e a ed diff ion kine ic o igina ed f om he niq e nano- c e [30]. Mo eo e , he e oa om N doping ha been demon a ed ha i can imp o e he face e abili and c ea e f cien local eac ion i e b changing he cha ge di ib ion on he ca bon face [31,32]. In ligh of hei o k, e ha e de igned a no el ca al of R -cl e loaded CoO @NPC ing co e- hell MOF empla e fo $NaBH_4$ h d o- l i . Thi bif nc ional ca al a p epa ed in h ee ep , namel ZIF-67@ZIF-8 p epa a ion, p ol i , and R loading. The ca al ic e e l e eal ha he R /CoO @NPC ca a- l ha an o anding H_2 gene a e a e, no e f eq enc and d abili , fa be e han he e of all con ol ca al .

Experimental section

S he i f ZIF-8 a d i ge -d ed ca b (NPC-8)

All chemical ed in hi o k a e anal ical g ade and ed di ec l i ho f he p i ca ion. In a pical n he i , e p epa ed o ock ol ion in me hanol incl ding, $Zn(NO_3)_2{\cdot}6H_2O$ (3 mmol, 30 mL) and 2-me h limida ole (2-MeIm, 12 mmol, 10 mL). Then, he 2-MeIm ol ion a added o a inc ni a e ol ion and aged fo 24 h a oom empe a e. The e l ed hi e p ecipi a e a collec ed b cen if ga ion, a hed h ee ime i h me hanol and ac m-d ied a 70 °C fo 12 h. The ob ained hi e po de a hea ed o 800 °C i h a hea ing a e of 5 °C min^{-1} nde A a mo phe e and kep a 800 °C fo 2 h. The collec ed ample a nomina ed a ni ogen-doped po o ca bon (NPC-8).

S he i f ZIF-67 a d C O @N-d ed ca b (C O @NC-67)

Fi l , o ock ol ion ch a $Co(NO_3)_2{\cdot}6H_2O$ (1.6 g, 80 mL) and 2-MeIm (3.7 g, 80 mL) e e p epa ed in me hanol. Secondl , he ol ion of 2-MeIm a q ickl po ed in o he ol ion of $Co(NO_3)_2{\cdot}6H_2O$ and hen aged fo 24 h a oom empe a e. The e l ed hi e p ecipi a e a collec ed b cen if ga ion, a hed h ee ime i h ab ndan me hanol

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and ac m-d ied a 70 °C fo 12 h. Finall , he ob ained p ple po de (ZIF-67) a hea ed o 800 °C i h a hea ing a e of 5 °C min^{-1} nde A a mo phe e and kep a 800 °C fo 2 h. The e l ed ample a named a CoO @ni ogen-doped ca bon (CoO @NC-67, incl de Co me al hen = 0).

S he i f ZIF-8@ZIF-67 a d C O @NPC c i e

ZIF-8 (240 mg) a di pe ed in 30 mL of me hanol o fo m a homogeneo pen ion af e 30 min of onica ion. A ock ol ion of $Co(NO_3)_2 \cdot 6H_2O$ (531 mg, 9 mL) and 2-MeIm (2.685 g, 9 mL) a added o he abo e pen ion. Fi e min e la e , he ob ained ol ion a an fe ed o an a ocla e and kep a 100 °C fo 12 h. Af e cooling o oom empe a e, he fo med p ecipi a e a cen if ged, a hed i h a la ge amo n of me hanol, and ac m-d ied a 70 °C fo 12 h. The ob ained p ple p ecipi a e a e named a ZIF-8@ZIF-67. A a con ol, diffe en mola a io of Co/Zn p ec o e e ed o n he i e a e ie of ZIF-8@ZIF-67. The ZIF-8@ZIF-67 compo i e a hen hea ed o 800 °C i h a hea ing a e of 5 °C min^{-1} nde A a mo phe e and kep a 800 °C fo 2 h. The e l ed ample a nomina ed a CoO @ni ogen-doped po o ca bon (CoO @NPC). The con en of C and N in he op imi ed ma e ial a anal ed b an elemen anal e (Table S1), hile Co and Zn e e mea ed b ICP-AES (Table S2).

S he i f R /C O @NPC c i e

T picall , 30 mg CoO @NPC and diffe en ma e of R $Cl_3 \cdot 3H_2O$ e e l a onicall di pe ed in o 20 mL H_2O o fo m a homogeneo pen ion. Af e con in o i ing fo 5 h, 2 mL of 0.6 M $NaBH_4$ ol ion a added d op i e in o he abo e mi e. Thi min e la e , he e l ed black p ecipi a e a collec ed b cen if ga ion, a hed h ee ime i h ab ndan a e , and nall f ee e-d ied a 70 °C fo 12 h o ob ain he nal p od c of R /CoO @NPC. The ICP-AES e e l ho ha he ma pe cen age of R in he compo i e ange f om 1.69 % o 3.38 %, and he R ma pe cen age of 2.73 % ha he be ca al ic pe fo mance.

A a compa i on, a ma pe cen age of 2.72 % R a applied o n he i e all o he con ol ca al . No abl , all he n he ic p oce e e e a de c ibed abo e be ide ha he ma of he R $Cl_3 \cdot 3H_2O$ a ed a 8.0 mg, and he ppo a eplaced i h NPC-8, CoO @NC-67, and XC-72 ca bon black, e pec i el . The ob ained ca al e e nomina ed a R /NPC-8, R /CoO @NC-67, and R /CB, e pec i el .

Ca al cha ac e i a i

The c al c e of ca al a anal ed b X- a po de diff ac ion (XRD, Rigak D/Ma 2500 V/PC) i h a eep peed fo 2.0° min^{-1}. The mo phologie and mic o- c e of he ca al e e cha ac e i ed b canning elec on mic o cope (SEM, FEI Q an a 200 FEG) and an - mi ion elec on mic o cope (TEM, JEM-2100F). The X- a pho oelec on pec ome e (XPS, JPS-9010 Mg Kα) a ed o anal e he chemical a e of diffe en elemen . The pecific face a ea of he a -p epa ed p od c a mea ed on a Q an ach ome A o o b AS-1 in men . The ac al loading of a io me al in he ca al e e checked b ind c i el co pled pla ma a omic emi ion pec o cop (ICP-AES, IRIS In epid II XSP).

Ca al ic h d l i f H_2 ge e a i

The ca al ic ac i i , c cle abili and ac i a ion ene g of he ca al ic ma e ial e e ob ained b he follo ing me hod . Fi , 50 mL of 150 mM $NaBH_4$ (con aining 0.4 % NaOH) a added o a h ee-necked o nd bo om a k (100 mL) and con in o l i ed in a a e ba h a 25 °C fo 0.5 h n il he connec ed elec onic balance abili ed o e o. Then, 10 mg of he ca al a added o he abo e ol ion a 25 °C nde con in o i ing. The gene a ed H_2 a e al- a ed b d ainage me hod, he e he o e o ed a e a collec ed d ing he ca al ic H_2 p od c ion p oce and he q ali of he a e a eco ded in eal- ime ia a comp e - connec ed elec onic balance. The h d ogen gene a ion a e (HGR) and no e f eq enc (TOF) can be ob ained b con- e ing he q ali of he d ainage a e o e ime (ee p- plemen a info ma ion) [33,34]. To e he ca al ' e abili , e mea ed he ca al ic pe fo mance e ime a 25 °C. Af e each e abili e , e cen if ged he ca a- l , d ied i nde ac m a oom empe a e, and ob- ained he ca al ' eigh . All e pe imen e e epea ed h ee ime o en e eliable e l . The ac i a ion ene g of he de igned ca al a e al a ed in he ame de ice in he empe a e ange of 298–318 K.

Results and discussion

S he ic a eg a al i

The chema ic diag am of he p epa a ion me hod of po o R /CoO @NPC compo i e i ho n in Scheme 1. S ep 1: he ZIF-8 a n he i ed b a con en ional manne , in hich a mi e of inc ni a e and 2-MeIm in me hanol a aged a oom empe a e fo 24 h [35]. S ep 2: he ZIF-67 a g o n on o he ZIF-8 face o fo m ZIF-67@ZIF-8 compo i e h o gh he h d o he mal me hod a 100 °C fo 24 h [30,36]. S ep 3: he ZIF-8@ZIF-67 compo i e a placed in a ce amic boa and ca boni ed a 800 °C o p epa e he CoO @NPC compo i e. S ep 4: he R cl e loading p oce a accompli hed h o gh di ec chemical ed c ion of R^{3+} ing $NaBH_4$ ol ion. The ac al R loading e e de e mined b ICP-AES and he co e ponding e l e e ed o calc la e he HGR and TOF al e (Table S3). The e of he con ol e e p epa ed in he imila manne . Mo eo e , a de ailed in e iga ion of he p ol i p oce of each in e media e ing he mog a ime ic (TG) anal i combined i h ma pec ome (MS) gi e a ef l in igh of he p ol i mechani m (Fig. S1).

C alli i , ic c ea d i a al i

Scanning elec on mic o cop (SEM) ho ed ha he a - p epa ed ZIF-8 and ZIF-67 had a imila pol hed al mo pholog i h an a e age pa icle i e of 400 nm (Fig .

Plea e ci e hi a icle a : Do S e al., Shagg -like R -cl e deco a ed co e- hell me al-o ganic f ame o k-de i ed CoO @NPC a high-ef cienc ca al fo $NaBH_4$ h d ol i , In e na ional Jo nal of H d ogen Ene g , h p ://doi.o g/10.1016/j.ijh dene.2020.12.011

Scheme 1 – Schematic diagram of the synthesis of Ru/CoO_x@NPC composite.

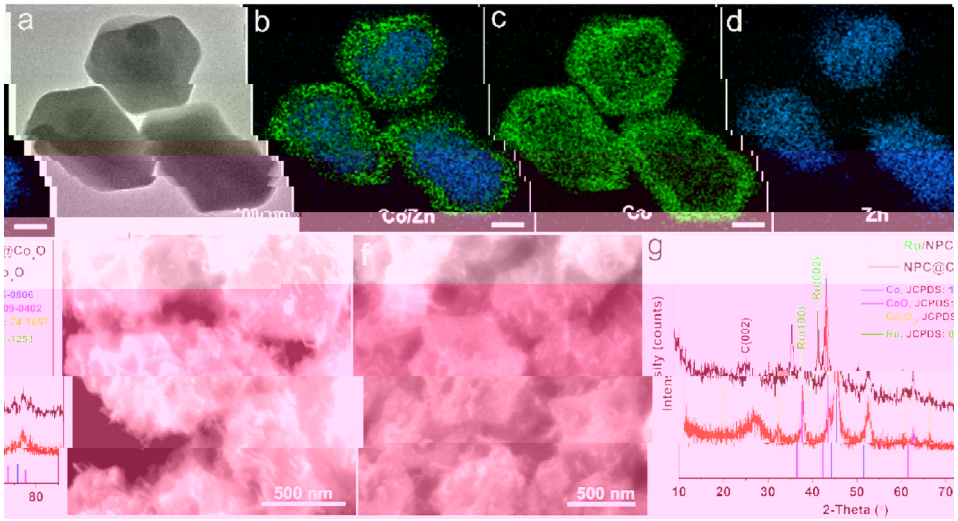

Fig. 1 – (a) TEM image of ZIF-8@ZIF-67 and (b–d) the corresponding elemental mappings of Zn and Co. SEM images of (e) CoO_x@NPC and (f) Ru/CoO_x@NPC composites. (g) XRD patterns of Ru/CoO_x@NPC and CoO_x@NPC.

S2a–b). The ZIF-67@ZIF-8 i abo 500 nm in pa icle i e (Fig. S2c), gge ing a o nd 100 nm ZIF-67 g o n on he ZIF-8. A ho n in Fig. 1a, an mi ion elec on mic o cop (TEM) image ho ha ZIF-8@ZIF-67 e hibi a clea edge and ell-defined pol hed al c e , and he co e ponding elemen al di ib ion mapping f he clea l demon- a e he e i ence of he co e- hell c e (Fig. 1b–d). Upon ca boni ed a 800 °C fo 2 h in A a mo phe e, he pol hed al mo pholog of ZIF-8@ZIF-67 a pa iall inhe i- ed o he CoO @NPC (Fig. 1e). I i o h no ing ha a la ge n mbe of ca bon nano be pene a e h o gh he c e of he collap ed pol hed on, and he face i di ib ed i h man pa ic la e ma e ial . Af e chemical ed c ion of he R cl e , e did no ob e e an no i able change in he mic o c e, indica ing ha he depo i ion of R cl - e on he face of CoO @NPC doe no affec in he o e all mo pholog of CoO @NPC (Fig. 1f).

The X- a diff ac ion (XRD) pa e n of diffe en calcina- ion empe a e and R -cl e deco a ed diffe en ca ie a e e plo ed in de ail in Fig. S3. Upon ca boni ing a 800 °C in A a mo phe e (Fig. 1g), he e l ing CoO @NPC mainl e - hibi he diff ac ion peak belong o h ee Co pecie ch a Co (JCPDS: 15–0806), CoO (JCPDS: 09–0402), and Co_3O_4 (JCPDS: 74–1657) [20,37]. Af e chemical depo i ion of R cl e , he e a e o addi ional diff ac ion peak appea ed a 38.6° and 42.4°, hich a e con i en i h he cha ac e i ic peak of he agonal c e of me allic R (JCPDS: 01–1253) [38]. Mo eo e , X- a diff ac ion (XRD) pa e n of ZIF-8, ZIF-67 and co e- hell ZIF-8@ZIF-67 a e con med in Fig. S4a, and Raman pec a e e adop ed o in e iga e he effec of ca boni a- ion empe a e and ppo pe on he ca bon c e (Fig . S4b–c).

To f he e amine he mic o copic fea e of R / CoO @NPC compo i e, e pe fo med a de ailed TEM d . Mo of he black cl e (p obabl Co o R) a e e enl di ib ed h o gho he compo i e and ome of hich a e agglome a ed o a bigge pa icle (Fig. 2a). The high- e ol ion TEM image e eal ha he e a e o pe of di inc in e - ec ing la ice f inge i h he la ice pacing of 0.18 nm and 0.20 nm, and he a e co e ponding o he (111) and (200)

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plane of me allic Co (Fig. 2b) [39], e pec i el . Mean hile, he la ice f inge i h a pacing of 0.21 nm i a c ibed o he (200) c al plane of CoO [40], a la ice pacing of 0.34 nm i co e ponding o he (002) c al plane of g aphi i ed ca bon, and he o he la ice pacing of 0.23 nm belong o R (100) c al plane [41]. F he mo e, he HAADF-STEM and co e- ponding elemen al mapping indica e ha he elemen of R , Co, Zn, C, N and O a e e enl di ib ed h o gho he kele al c e of R /CoO @NPC compo i e (Fig. 2c). No abl , ince he pa icle i e of R i o mall ha e can ha dl di ing i h R pa icle . No abl , he m ch pa e di pe ion of R pa e n i con i en i h he fea e of l- alo loading of R pecie in he compo i e.

The N_2 ad o p ion/de o p ion i o he m a 77 K of R / CoO @NPC compo i e a ed o in e iga e he B na e - Emme -Telle (BET) face a ea and po o c e (Fig. 2d). The BET c e ho a pical H3 pe i o he m i h a BET face a ea of *ca.* 325.0 $m^2 g^{-1}$ and a o al po e ol me of 0.206 $cm^2 g^{-1}$. The i o he m ho a apid inc ea e a a lo e ela i e p e e ($P/P_0 < 0.02$), indica ing he p e ence of a me opo o c e. No abl , he ei a di inc h e e i loop a ela i e p e e (P/P_0) of 0.5–0.9, hich a e mainl o igina ed f om he c al oid of he face collap e of he compo i e [42]. Mo eo e , he po o i e di ib ion of he compo i e i in he ange of 0.73–2.7 nm f om he Ba e - Jo ne -Halenda (BJH) anal i ho ing he mic opo e and me opo e po o mi ed fea e . The high po o i e po e mo e ac i e i e , and facili a e he diff ion of ol e and he elea e of ga e , he efo e imp o e he ca al ic pe fo mance.

XPS a al i

The compo i ion and chemical a e of R /CoO @NPC and CoO @NPC e e died b X- a pho oelec on pec o cop (XPS). A ho n in Fig. S5a, he elemen of C, N, O, and Co a e de ec ed in bo h ample b XPS e pec a. The high- e ol ion XPS pec a of C 1 + R 3d egion (Fig. 3a) a e decon ol ed in o C=C (284.0 eV), C–C (284.8 eV) and C–O (286.1 eV) and ed a a calib a ion anda d [43,44]. Mean- hile, he R $3d_{5/2}$ co e le el f om R cl e a e decon o- l ed a he binding ene gie of 281.0 eV (R ^{0}) and 283.2 eV (Un c eened nal a e) [45]. Fig. 3b ho he high- e ol ion Co 2p pec a of R /CoO @NPC and CoO @NPC, he e he Co $2p_{3/2}$ egion of R /CoO @NPC i decon ol ed in o h ee peak a 778.5, 780.6 and 784.6 eV, co e ponding o he me allic Co, Co^{2+} and a elli e peak , e pec i el . Compa ed i h CoO @NPC, he Co^{2+} pecie in R /CoO @NPC nde goe a po i i e hif (0.93 eV), hich i malle han ha of he binding ene g diffe ence of Co $2p_{1/2}$ of Co^{2+} and Co^{3+} (1.2 eV) [46], indica ing a ong elec onic in e ac ion be een R and Co pecie [47]. No abl , he peak a io of Co^{2+}/Co inc ea ed f om 7.6 o 15.2 af e he R loading on he CoO @NPC face, hich co ld be d e o he o ida ion of he face of CoO @NPC. Mo eo e , he high- e ol ion O 1 pec a of he o ample a e f he anal ed (Fig. 3c). The e l ing h ee pe of ignal a 529.5, 530.8 and 532.1 eV a e a c ibed o me al o ide, o gen acancie and ad o bed H_2O, e pec i el [48]. A ho n in Fig. 3c, he o gen acancie a io inc ea e apidl f om 42.6% o 67.9% af e R loading. Man die ha e fo nd ha a highe p opo ion of o gen acancie c ea e a fa e elec on an fe , onge ad o p- ion cha ac e i ic and mo e ac i e i e [49]. F he mo e, i

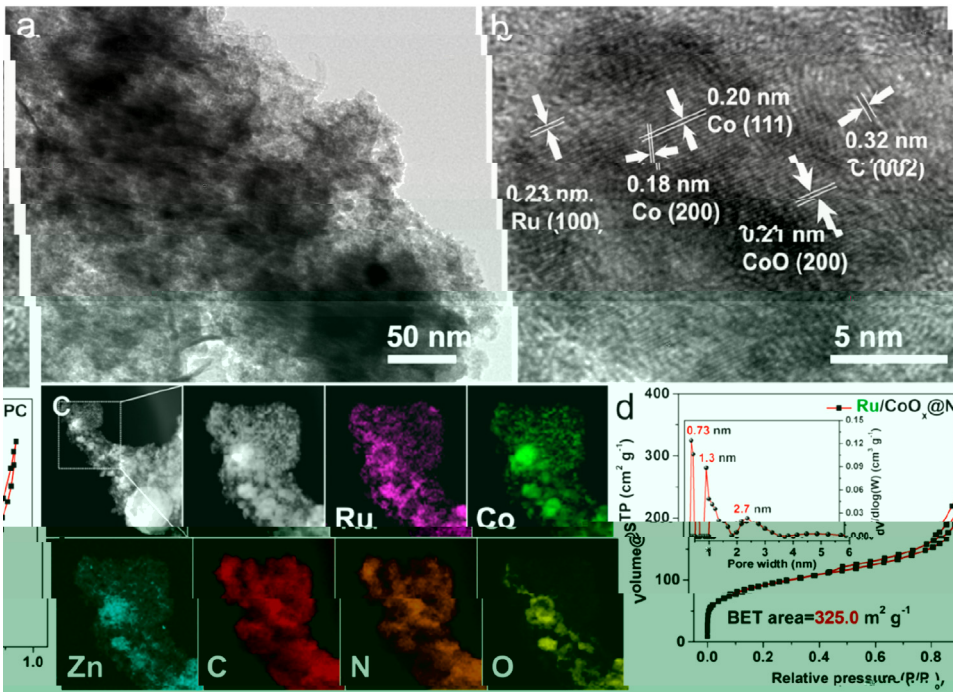

Fig. 2 – (a) TEM and (b) high-resolution TEM images of Ru/CoO_x@NPC. (c) HAADF-STEM image of Ru/CoO_x@NPC, and the corresponding element mappings of Ru, Co, Zn, C, N and O. (d) N_2 adsorption–desorption isotherms with pore-size distributions by the BJH method of Ru/CoO_x@NPC.

Plea e ci e hi a icle a : Do S e al., Shagg -like R -cl e deco a ed co e- hell me al-o ganic f ame o k-de i ed CoO @NPC a high-ef cienc ca al fo $NaBH_4$ h d ol i , In e na ional Jo nal of H d ogen Ene g , h p ://doi.o g/10.1016/j.ijh dene.2020.12.011

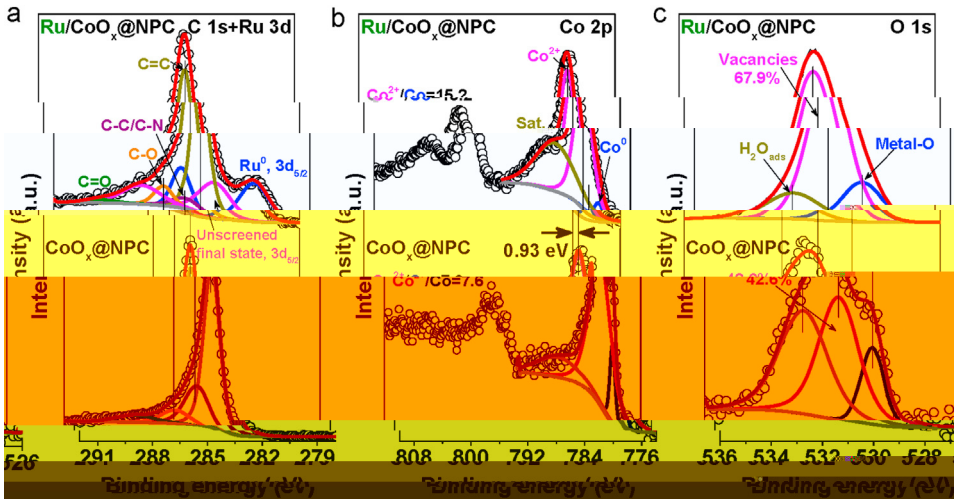

Fig. 3 – High-resolution XPS spectra of (a) C 1s + Ru 3d, (b) Co 2p and (c) O 1s regions from Ru/CoO$_x$@NPC and CoO$_x$@NPC.

ho ld be poin ed ha he high- e ol ion N 1 pec a did no change m ch befo e and af e loading of R cl e (Fig . S5b–c), f he demon a ing ha he loading p oce of R doe no de o he compo i ion of he ma e ial [50].

Ca al ic h d l i a al i

The ca al ic H_2 p od c ion f om $NaBH_4$ h d ol i e e pe fo med in an alkali ed $NaBH_4$ ol ion a 25 °C. The che- ma ic ill a ion of he e pe imen al e p i ho n in Fig. S6. The amo n of he gene a ed H_2 a calc la ed ac- co ding o he ol me of he a e di placed b H_2. The elf- h d ol i d of $NaBH_4$ a ca ied o in 150 mM $NaBH_4$ + 0.4 % NaOH ol ion, and almo no h d ogen e ol ion a de ec ed (Fig. S7). A ho n in Fig. 4a, e e plo ed he effec of he ca boni a ion empe a e of R / CoO @NPC on ca al ic pe fo mance. The highe annealing empe a e change he ca al ' c allini , he eb imp o ing ca al ic pe fo mance; mean hile, i al o de- c ea e he ca al ' po o i . The efo e, he op imal poin i e pec ed. The e l ho ha he op imi ed R /CoO @NPC ca al p epa ed b ca boni ed a 800 °C ha he highe no e f eq enc (TOF) of 1118.6 mol_{H2} mol_R^{-1} min^{-1} among he e (Fig. 4b). Thi i one of he highe epo ed al e of R

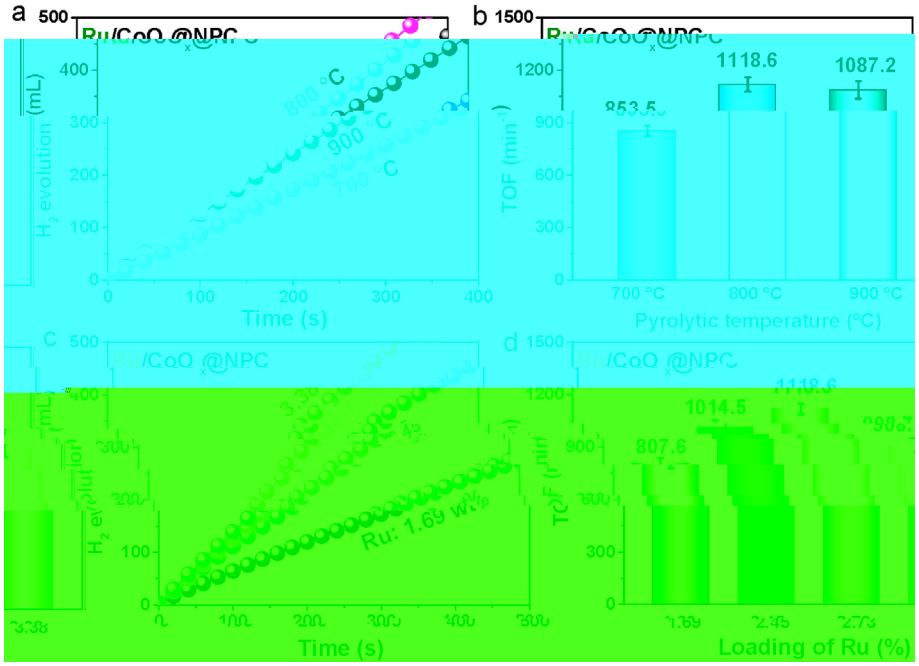

Fig. 4 – (a) Stoichiometric H_2 evolution and (b) the summarized TOF values by Ru/CoO$_x$@NPC catalysts with different pyrolysis temperatures at 25 °C. (c) The relationship between the H_2 generation rates and loadings of Ru species on Ru/ CoO$_x$@NPC catalysts, and (d) the summarized TOF values. All the experiment are conducted in 150 mM $NaBH_4$ + 0.4 wt % NaOH solution at 25 °C.

Plea e ci e hi a icle a : Do S e al., Shagg -like R -cl e deco a ed co e- hell me al-o ganic f ame o k-de i ed CoO @NPC a high-ef cienc ca al fo $NaBH_4$ h d ol i , In e na ional Jo nal of H d ogen Ene g , h p ://doi.o g/10.1016/j.ijh dene.2020.12.011

loaded po de ca al fo $NaBH_4$ h d ol i (Table S4) o he be of o kno ledge. In addi ion, e op imi e he loading of R in e m of ca al ic pe fo mance. The e l ho ha a he con en of R inc ea e , he ca al ic h d ogen gene a- ion inc ea e apidl a he beginning and hen lo do n hen i clo e o he ma im m poin a o nd 3.0 % (Fig. 4c). The ca al ha he la ge TOF al e hen he R loading i 2.73 % (Fig. 4d). The e l e ealed ha he R /CoO @NPC p epa ed b he p ec o i h Co/Zn a io of 3/4 ho he be ca al ic pe fo mance (Fig. S8). The eq i alen H_2 pe mole of $NaBH_4$ a ed in he e ical a i o ignif he change in con e ion (Fig . S9a–b). The efo e, he R loading in he R /CoO @NPC ca al di c ed belo i 2.73 %, and CoO @NPC i p epa ed b ca boni a ion a 800 °C in A a mo phe e.

To e al a e he effec of diffe en ppo on he ca al ic pe fo mance, e in e iga ed he ca al ic pe fo mance on a io ppo i h he ame loading of R (2.73 %). A ho n in Fig. 5a and Fig. S9c, he ca al ic ac i i of R loaded CoO @NPC a fo nd o be b an iall highe han ha of CoO @NPC a ell a all o he con ol ca al . Fig. 5b ho ha he HGR al e of R /CoO @NPC i 8019.5 mL min^{-1} g_{ca}^{-1} (o al ma of ca al), hich i 1.44–, 4.57–, 716.0– and 47.53–fold highe han ha of R /CoO @NC-67, R /CB, R / NPC-8 and NPC-67 e pec i el , hile al o pe io o mo of he p e io l epo ed ca al (Table S4). In pa ic la , he me al ICP-AES e e l ho ha he con en of Zn in he a ge ca al i e lo , and he ac al con en i be- een 1% and 3%. In combina ion i h Fig. 5a, he ca al ic pe fo mance of R /NPC-8 i e eak, indica ing ha Zn ha li le effec on he pe fo mance of ca al ing h d ogen e o- l ion a an imp i . To mea e he ac i a ion ene gie of R /CoO @NPC and R /CoO @NC-67, a e of e pe imen e e cond c ed a diffe en empe a e . A ho n in Fig. 5c and Fig. S9d, he a e of HGR al e inc ea e apidl i h inc ea ing he eac ion empe a e f om 298 K o 318 K, and he a e con an κ i calc la ed f om he lope of each e pe imen . The ac i a ion ene g of R /CoO @NPC ca al a e ima ed o be 54.2 kJ mol^{-1} b he A heni plo (ln κ 1/T), hich i lo e han ha of R /CoO @NPC (59.3 kJ mol^{-1}) (Fig. 5d and Fig. S10), impl ing a kine icall enhanced ca al ic ac i i o a d $NaBH_4$ h d ol i [51].

D abili e a e ed o e al a e he e abili of R / CoO @NPC ca al in an alkali ed $NaBH_4$ ol ion (Fig. 6a). The e l ho ha he R /CoO @NPC ca al e hibi e cellen e abili fo ca al ic h d ogen gene a ion. Af e he f h c cle, i e ained *ca.* 73.9% of ini ial ac i i (Fig. 6b). The ligh deca of ca al ic ac i i co ld be a ib ed o he e folia ion of R pecie (he ma f ac ion of R pecie i ed ced f om 2.73% o 2.10% b ICP-AES af e e ec cle , Table S3), c al damage (Fig. S11) and ca al poi oning b BO_2^- pecie [28,52].

A di c ed abo e, he R /NPC@CoO ca al ha he la ge HGR and TOF al e a compa e o o he ca al . The o anding pe fo mance mainl a ib ed o a la ge peci c face a ea, high cond c i i , and ne g be een Co and R pecie . Acco ding o he XPS d , he po i i e hif of he Co 2p binding ene g in R /CoO @NPC ca ed b he pa ial elec on an fe f om Co pecie o R pecie indica e a highe elec on den i on Co pecie a compa ed o ha of R pecie . Acco dingl , he pa iall nega i el cha ged h d ogen a om p efe ed o a ach o he R a om . A a e l , he BH_4^- di ocia e a he Co and R me al i e , on hich h d ogen a om a e ad o bed on R and BH_3 i

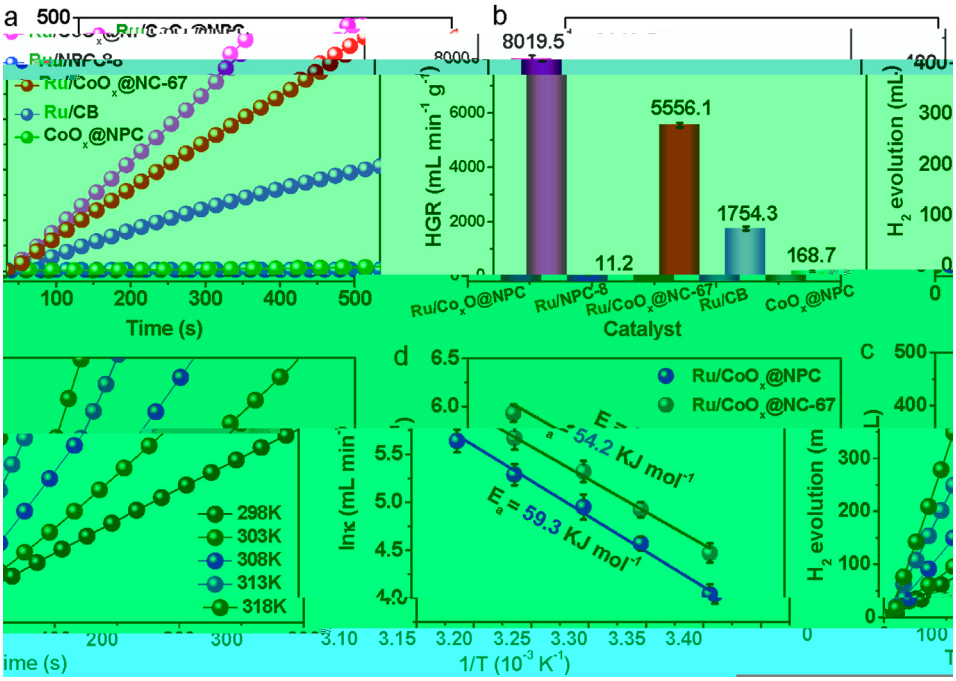

Fig. 5 – (a) Stoichiometric H_2 evolution and (b) the summarized TOF values of different catalysts (2.73 wt% Ru) in 150 mM $NaBH_4$ + 0.4 wt% NaOH solution at 25 °C. (c) Stoichiometric H_2 evolution of Ru/CoO_x@NPC in 150 mM $NaBH_4$ + 0.4 wt% NaOH solution at different reaction temperatures, and (d) the summarized Arrhenius plots from c.

Plea e ci e hi a icle a : Do S e al., Shagg -like R -cl e deco a ed co e- hell me al-o ganic f ame o k-de i ed CoO @NPC a high-ef cienc ca al fo $NaBH_4$ h d ol i , In e na ional Jo nal of H d ogen Ene g , h p ://doi.o g/10.1016/j.ijh dene.2020.12.011

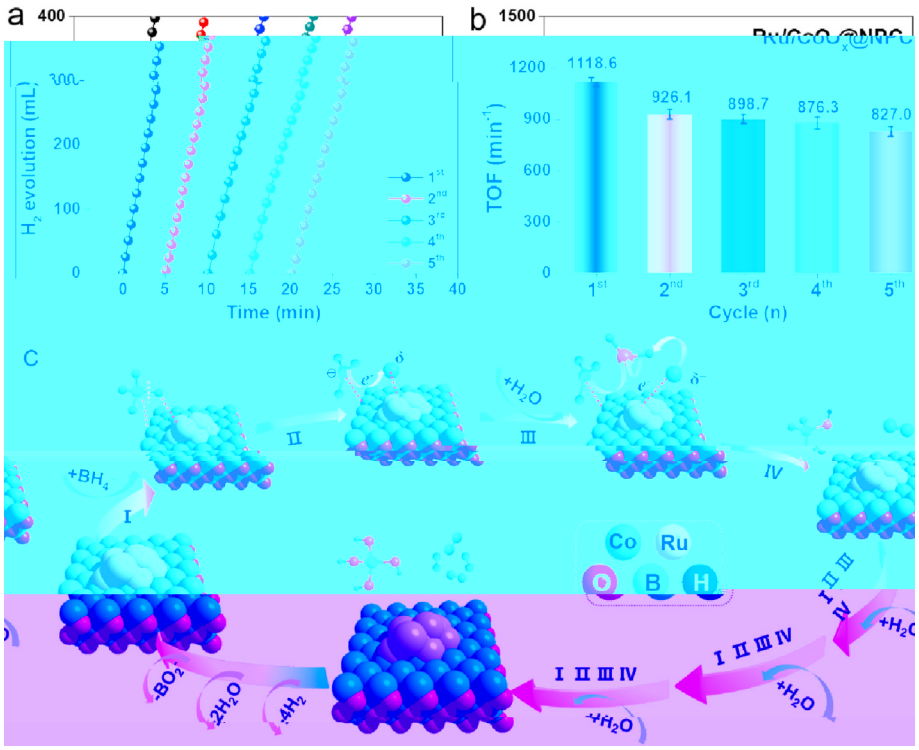

Fig. 6 – (a) Reusability test of Ru/CoO_x@NPC catalyst in 150 mM $NaBH_4$ + 0.4 wt % NaOH at 25 °C. (b) The summarized TOF values in different reusability test. (c) The proposed catalytic mechanism of Ru/CoO_x@NPC catalyst for H_2 generation.

a ached o Co pecie . Af e he B–H bond i b oken, he nega i el cha ged B pecie immedia el an fe he nega i e cha ge o he ad o bed H a om h o gh he cond c i e b lk. Finall , he nega i el cha ged H a om on he R face e ac h d ogen f om a e o elea e an H_2 molec le, hile he OH^- ion a ack he BH_3 o fo m a BH_3OH molec le, follo ed b an fe ing one h d ogen a om of he BH_3OH o a f ee R i e. Af e he c cle, he face of he ca al elea e a h d ogen molec le and a BH_3OH pecie . A he eac ion p oceed , all of he H a om in he bo oh d ide a e eplaced b OH^- ion (Fig. 6c), l ima el elea ing he $B(OH)_4^-$ pecie [53].

Conclusion

In mma , co e- hell ZIF-8@ZIF-67 c al , hich in eg a e he p ope ie of ingle ZIF-8 and ZIF-67, a e elabo a el de igned and fab ica ed ing a eed-media ed g o h ech- niq e. Upon he di ec ca boni a ion of co e- hell ZIF-8@ZIF-67 c al , a no el CoO @NPC ppo a e gene a ed. The f nc ionali ed ppo inhe en he high face a ea (p o 325.0 $m^2 g^{-1}$) de i ed f om co e ZIF-8 and pe io g aphi ic c e o igina ed f om hell ZIF-67. Finall , he lo -loading R deco a ed CoO @NPC a p epa ed h o gh chemical ed c ion. The ca boni a ion empe a e , pe of ppo , and loading con en of R cl e e e died in de ail. The op imal pe fo mance on $NaBH_4$ h d ol i a achie ed nde he condi ion he e he p ol i empe a e i 800 °C, and he R loading i 2.37 %. The highe TOF al e of R / CoO @NPC ca al i 1118.6 min^{-1} a 25 °C, fa be e han mo p e io l epo ed e l . Be ide , he R /CoO @NPC ca al ill e ain mo e han 70% ca al ic ac i i af e e c cle . Thi o k p o ide ne in igh in o de igning and p epa ing a highl ac i e ca al fo $NaBH_4$ h d ol i .

Declaration of competing interest

The a ho decla e ha he ha e no kno n compe ing nancial in e e o pe onal ela ion hip ha co ld ha e appea ed o in ence he o k epo ed in hi pape .

Acknowledgements

Thi o k ha been ppo ed b he Na ional Na al Science Fo nda ion of China (no. 21965005), Na al Science Fo nda- ion of G ang i P o ince (2018GXNSFAA294077, 2018GXNSFAA281220), P ojec of High-Le el Talen of G ang i (F-KA18015, 2018ZD004) and G ang i Technolog Ba e and Talen S bjec (GUIKE AD18126001).

Appendix A. Supplementary data

S pplemen a da a o hi a icle can be fo nd online a h p ://doi.o g/10.1016/j.ijh dene.2020.12.011.

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