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Oxygen-vacancy-rich Ru-clusters decorated Co/Ce oxides modifying ZIF-67 nanocubes as a high-efficient catalyst for $NaBH_4$ hydrolysis

Luyan Shi [a], Ke Zhu [a], Yuting Yang [a], Yi Liu [a], Shoulei Xu [c,***], Tayirjan Taylor Isimjan [b,**], Xiulin Yang [a,*]

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

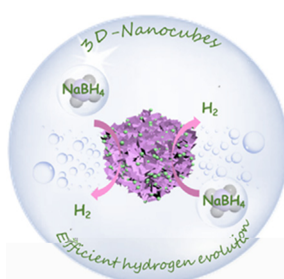
[b] Saudi Arabia Basic Industries Corporation (SABIC) at King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

[c] School of Physical Science and Technology, Guangxi University, 100 East Daxue Road, Nanning 530004, China

HIGHLIGHTS

- /C 6C 1@ IF-67
- HG OF (413.9 $^{-1}$)
- N BH_4
- O

GRAPHICAL ABSTRACT



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ABSTRACT

D N BH_4 . H IF-67 (/C 6C 1@ IF-67) N BH_4 (HG , 5726.1 L $^{-1}$ $^{-1}$), (OF, 413.9 $_{H2}$ $^{-1}$ $^{-1}_{Ru}$), (E , 53.0 J $^{-1}$), . F

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E- : @ ( ), @ (. I), @ ( ).

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P : L ., O C /C IF-67 N BH_4 , I J H E , :// /10.1016/ .2022.08.289

N BH_4 ... C /C ...
H ...
N BH_4

Introduction

E ... [1] ... [2,3] ...
H ... CO_2 ... [4,5]. H ...
... N BH_4 ...
... 10.6 %, ... [6,7]. N BH_4 ... H_2 ...
... [8]. M ... N BH_4 ...
... N BH_4–H_2-PEMFC ...
... [9]. N ...
... N BH_4 ... H_2 ...
... 7–8% ... [10,11].
C ...
P ...
... –C -PEDO [12] ... –F /G [13], ...
... N BH_4 ...
... [14]. H ...
... [15,16].
...
... N -,
F -, C - ... [17]. A ...
... [18] ... [19] ... C $_3O_4$ ...
... H ...
... [20]. M ...
... F ...
D ... [21] ...
C O @NPC ...
... M ... (MOF) ...
... [22,23]. IF-67 ... MOF ...

... [24,25]. M ... IF-67- ...
... N BH_4 ... P /
PD- IF-67 [15], / IF-67 [26] ... G ...
IF-67 ... N BH_4
... N ... , MOF ...
[27]. I ...
... [28]. I ... , C $^{3+}$ ... C $^{4+}$ ...
... C ...
... C $^{3+}$ ... C $^{4+}$, ...
... C -MOF ...
... [29,30]. B ...
... C ... C ...
H , ...
... /C $_6$C $_1$@ IF-67 ...
N BH_4 ...
(2.7) ...
C $_6$C $_1$@ IF-67 ...
... N BH_4 ... I
HG ... 5726.1 L ... $^{-1}$ $^{-1}$ ... OF ... 413.9
H2 ... $^{-1}$ ... $^{-1}$ Ru ...
IF-67 ...
... B–H ...
... C ...
... F ...
... M ...
M ... [31].

Experimental section

Materials

C ... (C ($NO_3)_2$·6H_2O, 99.0%, A ...),
... (C ($NO_3)_3$·6H_2O, 99.95%, M ...),
... (III) ... (C $_3$· H_2O, 99%, :37–40%,
I ...), 2- ... (2-MI, 98%, A ...), ...
... (C AB, 99.0%, A ...),
... (N BH_4 ≥ 98.0%, ... G ...),
... (N OH ≥96.0%, ...), ... (99.7%,
K ...). A ...

P ... : L ... O ... C /C ... IF-67 ...
... N BH_4 ... I ... J ... H ... E ... ://.../10.1016/ ... 2022.08.289

Synthesis of ZIF-67 nanocubes

C -. (IF-67) 32 . I , 580 C (NO3)2-·6H2O 20 L 10 C AB. 140 L 908 2- 20 , - 70 °C 12 .

Synthesis of Co_6Ce_1@ZIF-67

A 60 IF-67 40 L A. 160 C (NO3)2·6H2O 40 C (NO3)3·6H2O 10 L B. , B A 40 . F , , - 70 °C 12 . F , 0.2 , C C @ IF-67 C /C (1:1, 4:1, 6:1, 9:1, 12:1) C @ IF-67 C @ IF-67 C (NO3)3·6H2O C (NO3)2·6H2O.

Synthesis of Ru/Co_6Ce_1@ZIF-67

C 6C 1@ IF-67 (80) 50 L 20 L 15 C 3- · H2O. A 4 , 10 L 2.6 M N BH4 (2 % N OH) . A 0.5 , , , 70 °C 12 . I (ICP-AE) (1) 6.3 % 4.5 %. 10.6 % , C 3· H2O . A , 6.3 % /C @ IF-67 /C @ IF-67 C (NO3)3·6H2O C (NO3)2·6H2O. I , @ IF-67 C 3· H2O IF-67 ,

Synthesis of single Ru

200 C 3· H2O 40 L . A 30 , 10 L N BH4 .

F , , , .

Catalytic hydrolysis of $NaBH_4$ measurements

N BH4 . A 25 L, 150 L N BH4 0.4 % N OH, - - (100 L), - 25 °C A 0.5 , (10) , - . H N BH4 (298–318 K) . F , , 70

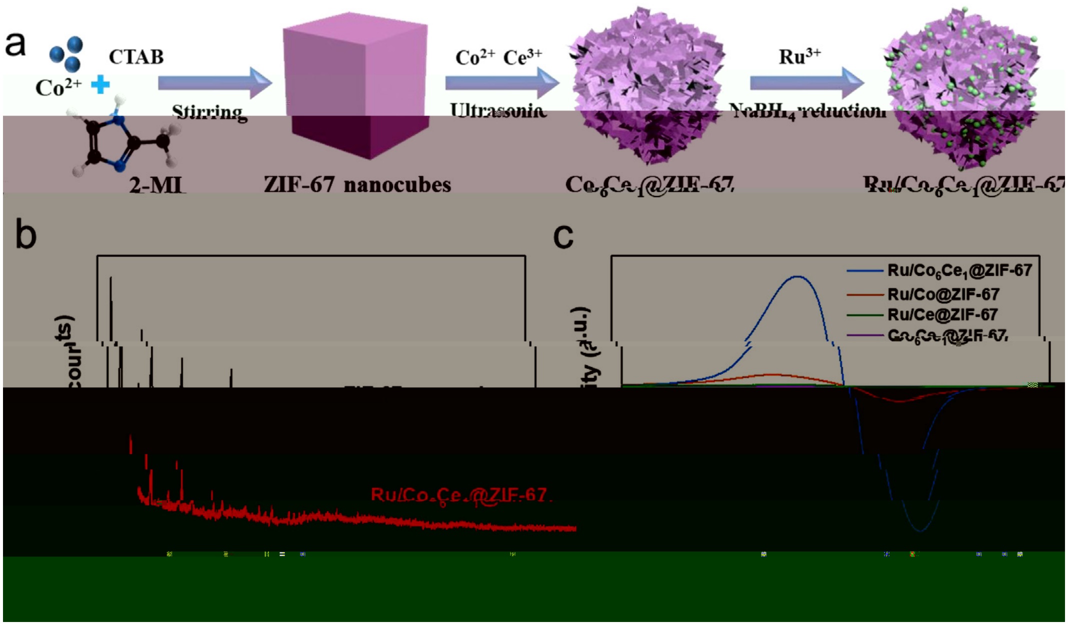

Fig. 1 — (a) Schematic diagram of the synthesis of Ru/Co_6Ce_1@ZIF-67. (b) XRD patterns of ZIF-67 nanocubes and Ru/Co_6Ce_1@ZIF-67. (c) EPR spectra of the synthesized Ru/Co_6Ce_1@ZIF-67, Ru/Co@ZIF-67, Ru/Ce@ZIF-67 and Co_6Ce_1@ZIF-67.

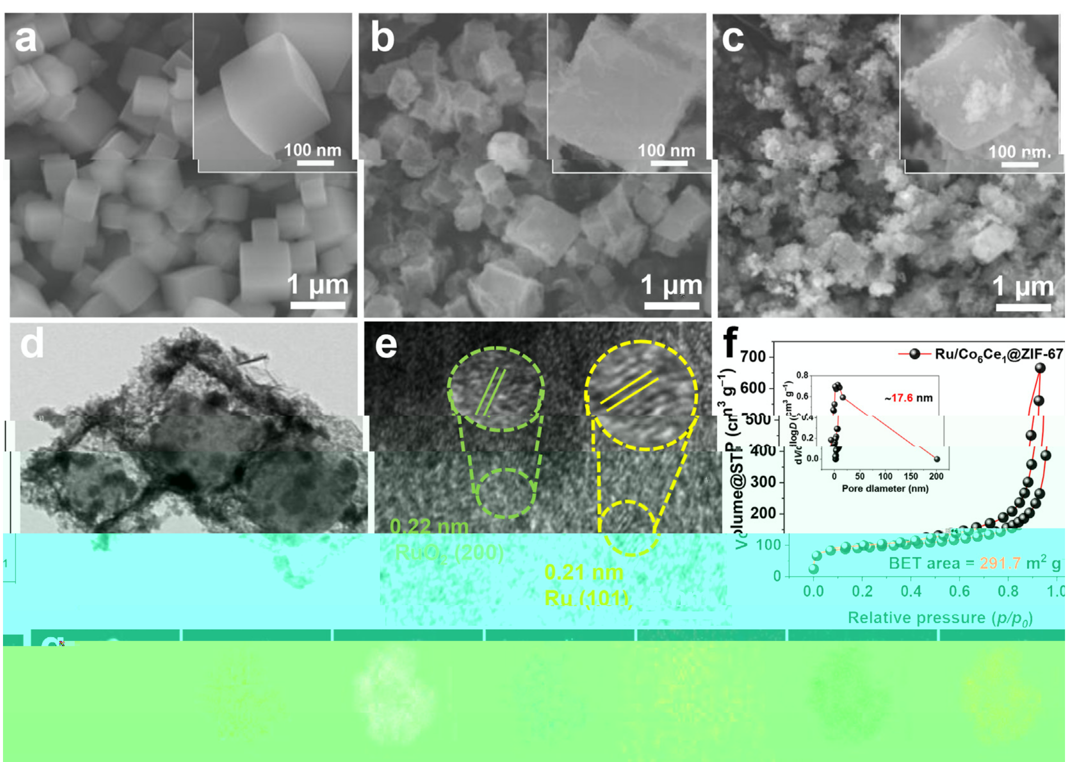

Fig. 2 — Scanning electron microscopy (SEM) of (a) ZIF-67 nanocubes, (b) Co_6Ce_1@ZIF-67 and (c) Ru/Co_6Ce_1@ZIF-67 (Insets are high-magnification SEM images). (d) Transmission electron microscopy (TEM) and (e) high-resolution TEM images of Ru/Co_6Ce_1@ZIF-67. (f) N_2 adsorption/desorption isotherms with pore-size distribution curve (inset) of Ru/Co_6Ce_1@ZIF-67. (g) HAADF-STEM image of Ru/Co_6Ce_1@ZIF-67 and corresponding elemental mappings of Co, Ce, Ru, C, N, and O.

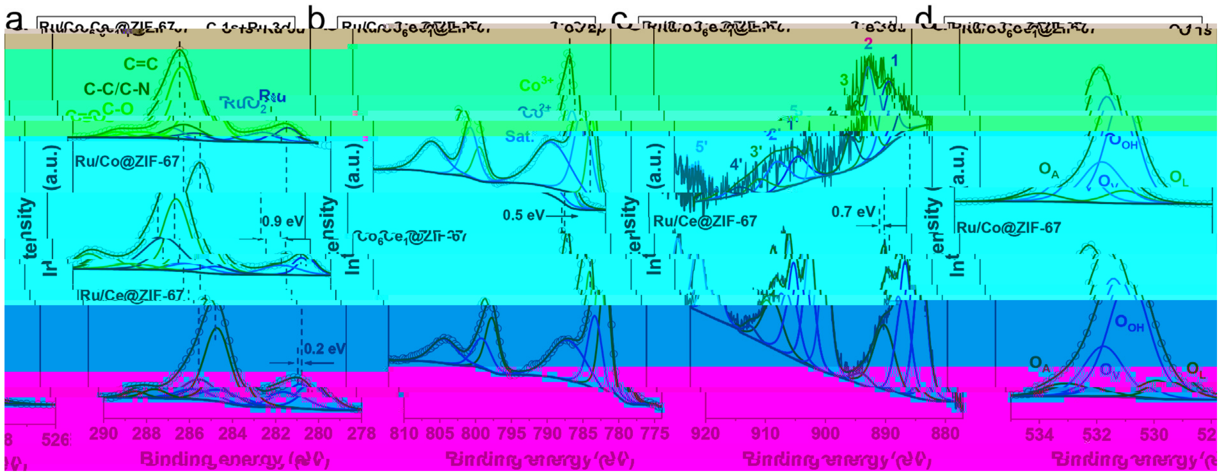

Fig. 3 – High-resolution XPS spectra of (a) C 1**s** + Ru 3**d**, (b) Co 2**p**, (c) Ce 3**d** and (d) O 1**s** regions of Ru/Co_6Ce_1@ZIF-67, Ru/Co@ZIF-67, Ru/Ce@ZIF-67 and Co_6Ce_1@ZIF-67, respectively.

Microstructure analysis

(EM) ... (EM). F . 2 ... IF-67 ... $C(NO_3)_2·6H_2O$ ... $C(NO_3)_3·6H_2O$ ... 40 ... C_6C_1@ IF-67 ... F . 2 ... EM ... C_6C_1@ IF-67 ... B ... C_6C_1 ... A ... (F . 2). ... C /C ... IF-67- ... A ... F . 2 ... EM ... /C_6C_1@ IF-67 ... IF-67 ... /C_6C_1 ... [37,38]. E ... 2.7 ... (F . 1). A ... EM ... /C_6C_1@-IF-67, F . 2 ... 0.21 ... (101) ... [39] ... 0.22 ... (200) ... O_2 [40]. ... N_2 ... – ... /C_6C_1@ IF-67 ... I ... [41]. ... B ... -E ... (BE) ... 291.7 ^{2} $^{-1}$ ... 17.6 ... (F . 2). ... 3D ... /C_6C_1@ IF-67 ... [42,43]. I ... ED ... (F . 2) ... , C , C , C, N, ... O, ... /C_6C_1@ IF-67 ... (F . 2).

X-ray photoelectron spectroscopy analysis

(P) ... A ... F . 3, ... P ... /C_6C_1@ IF-67 ... C, N, O, C , C ... HAADF- EM ... ED ... C 1s + 3d ... (F . 3) ... C=C (284.0), C–C (284.8) ... [44]. ... 280.0 ... 284.2 ... [21], ... 281.2 ... 285.4 ... O_2. ... C ... /C @ IF-67, ... 0.9 ... C ... /C_6C_1@ IF-67, [45]. C ... /C @ IF-67 ... 0.2 ... C ... [46]. F . 3 ... C 2p ... 779.5, 780.8 ... 785.3 [47]. ... C^{3+}, C^{2+}, ... C ... /C_6C_1@ IF-67 ... C_6C_1@ IF-67, ... C ... C^{2+}/C^{3+} ... /C_6C_1@ IF-67 ... C_6C_1@ IF-67, ... C^{3+} ... C^{2+} ... [48]. I ... [49,50]. ... C 3d ... /C_6C_1@ IF-67 ... (F . 3). ... 880.9 , 887.3 (1, 3) ... 899.5 , 905.9

P ... : L ., O ... C /C ... IF-67 ... N BH_4 ..., I ... J ... H ... E ... :// ... /10.1016/ 2022.08.289

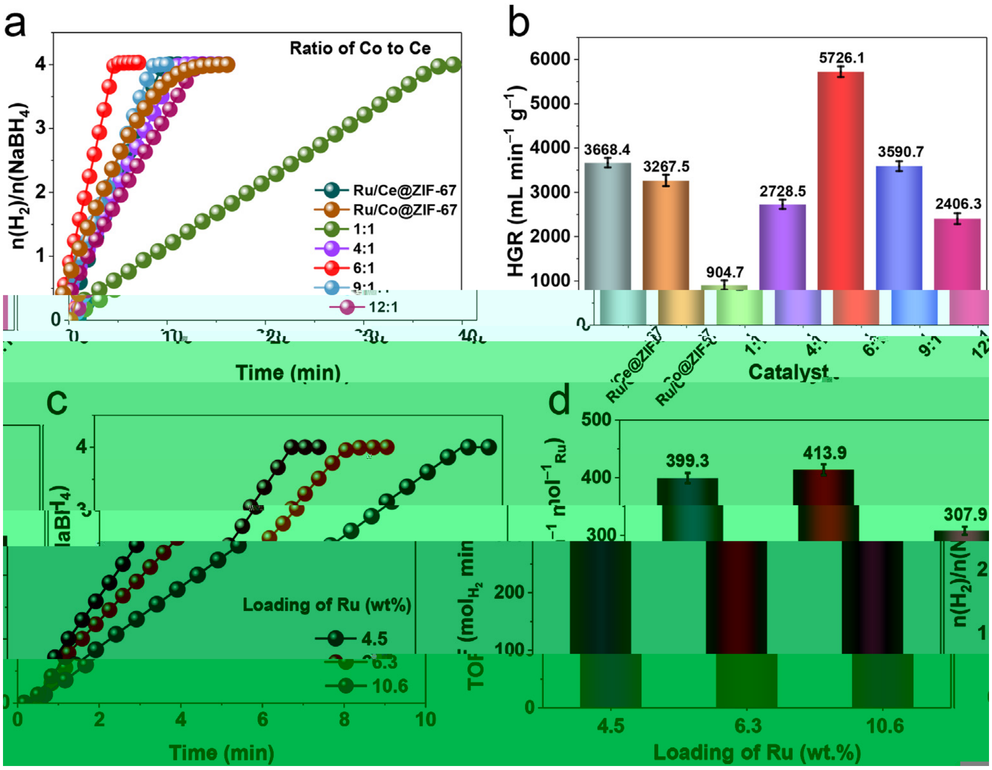

Fig. 4 — (a) Curves of hydrolysis of alkaline $NaBH_4$ solution with different rations of Co/Ce, and (b) the corresponding H_2 evolution rate values. (c) Curves of hydrolysis of alkaline $NaBH_4$ solution with different loadings of Ru species on Ru/Co_6Ce_1@ZIF-67 catalysts, and (d) the summarized TOF values.

(1′, 3′) C $^{3+}$ (3 ^{10}4 ^{1}), 884.4 , 890.6 , 897.4 (2, 4, 5) 903.0 , 909.2 , 916.0 (2′, 4′, 5′) C $^{4+}$ (3 ^{10}4 ^{0}) 51,52 . I C 3d , C $^{3+}$ C $^{4+}$ 53 . C , C $^{3+}$ /C $_6$C $_1$@ IF-67 0.7 /C @ IF-67, C C . I C $^{3+}$ C 4 ^{1} . I C $^{3+}$ 54 . C 55 . F O 1s P . F . 3 O 1s 529.1 , 530.0 , 530.7 , 532.0 (O$_L$), (O_{OH}), (O) (O_A), 56,57 . /C $_6$C $_1$@ IF-67 (26.3%) /C @ IF-67 (24.6%), C EP

Catalytic hydrolysis analysis

N BH$_4$ 25 °C, H_2

F . 4. N BH$_4$ (150 M) (F . 5), 150 M N BH$_4$ + 0.4 % N OH N BH$_4$ (F . 6). A F . 4 , C /C H_2 C /C 6:1, /C $_6$C $_1$@ IF-67 /C @ IF-67 /C @ IF-67. A HG (2). . A F . 4 — , H_2 OF 6.3 %, OF 413.9 $_{H2}$ $^{-1}$ $^{-1}$. A F . 5 /C $_6$C $_1$@ IF-67 6 . N / IF-67 35% 10% 6 , C $_6$C $_1$@ IF-67 IF-67 /C $_6$C $_1$@ IF-67 C $_6$C $_1$@ IF-67 58 . /C $_6$- C $_1$@ IF-67 N BH$_4$

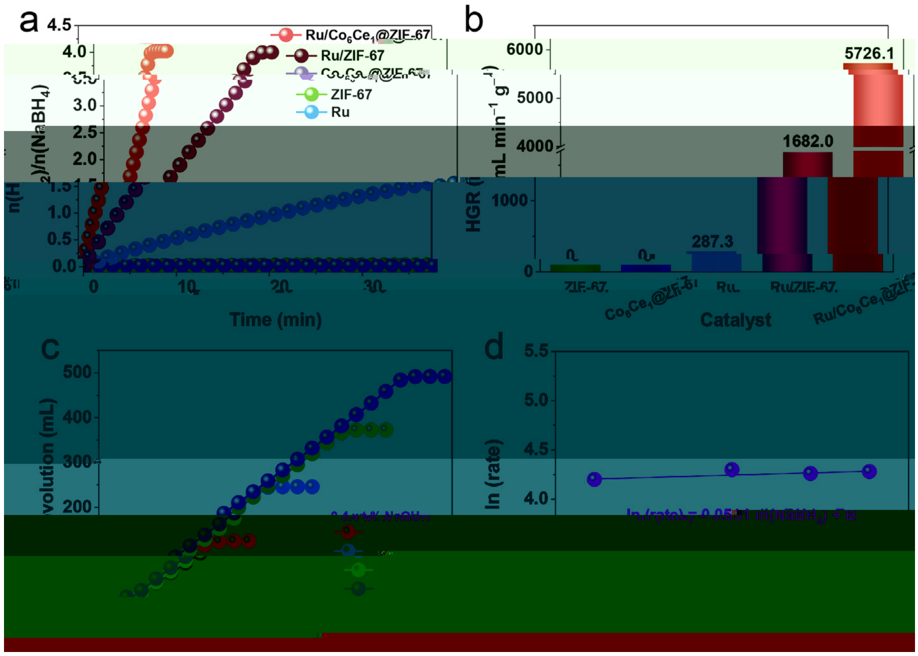

Fig. 5 — (a) Curves of hydrolysis of alkaline $NaBH_4$ solution with different kinds of catalysts, and (b) the corresponding H_2 evolution rate values. (c) The relationship between H_2 evolution and different $NaBH_4$ concentrations and (d) the corresponding plot of ln (rate) *vs* ln (concentration of $NaBH_4$).

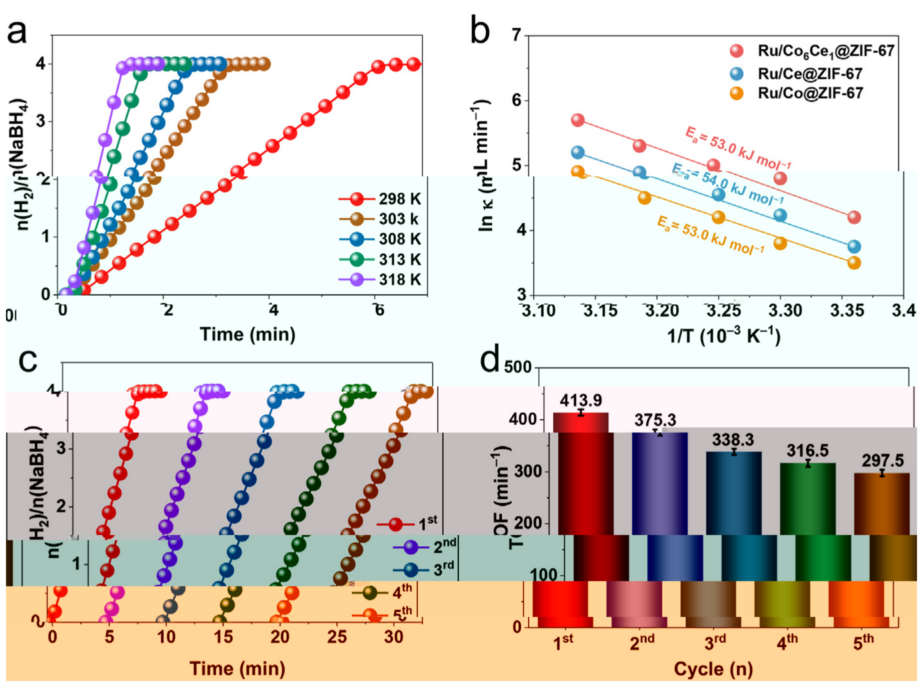

Fig. 6 — (a) Curves of hydrolysis of alkaline $NaBH_4$ solution with different reaction temperatures, and (b) the calculated activation energies of Ru/Co_6Ce_1@ZIF-67, Ru/Co@ZIF-67 and Ru/Ce@ZIF-67 catalysts. (c) Recycling stability test of Ru/Co_6Ce_1@ZIF-67 catalyst in alkaline $NaBH_4$ solution at 25 °C and (d) the corresponding TOF values in the different recycling test.

25 °C ... 10 ... /C $_6$C $_1$@ IF-67. ... 0.051, ... F . 5 ... 59 . N OH ... . M ... (.) ... N BH_4. ... (N BH_4) ... F . 5 , ... F . 7 ... N OH ...

P ... : L ., O ... C /C ... IF-67 ... N BH_4 ... , I ... J ... H ... E ... :// ... /10.1016/ 2022.08.289

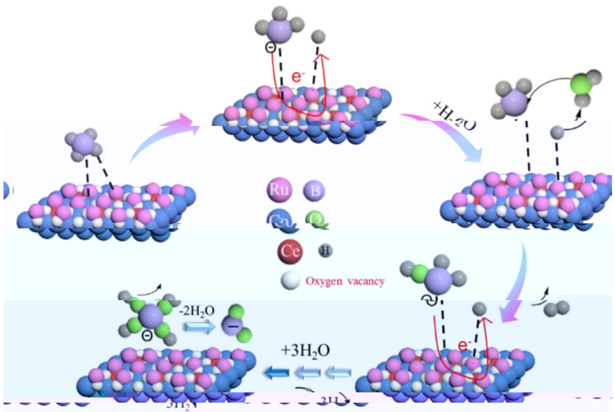

Fig. 7 — Proposed catalytic mechanism schematic of Ru/Co_6Ce_1@ZIF-67 catalyst for H_2 generation by hydrolysis of alkalized $NaBH_4$ solution.

N BH_4 ,
N OH
N BH_4. N , H_2
N OH
0.4 %. 10 %. 0.4 %
N OH ,

298 K–318 K (F . 6 F . 8).
HG
. A A
E /C $_6$C $_1$@ IF-67 /C @ IF-67 53.0 J $^{-1}$,
/C @ IF-67
(54.0 J $^{-1}$) (F . 6). /C $_6$C $_1$@ IF-67
N BH_4 25 °C
5 . A F . 6 — , H_2
(
6.2, 7.2, 8.5, 9.8 10.5 ,),
OF . A /
C $_6$C $_1$@ IF-67
,
(F . 9). A F . 10,
, C $^{2+}$, C $^{3+}$
O_2, C $^{3+}$ C $^{4+}$
. H ,
P O 1s
26.3% 17.0%. ,
,
60 .

Catalytic mechanism analysis

B ,
N BH_4 F . 7. F
P ,
/C $_6$C $_1$@ IF-67
/C @ IF-67, C
. C ,
C . H , BH_4^- .

C
, - BH_3^- C
, H
BH_3^- H
61 . H H
H_2. BH_3.
OH^- BH_3. F ,
$BH_2(OH)^-$
$B(OH)_4^-$ $4H_2$ 31 .

Conclusion

I ,
- - /C $_6$C $_1$@-
IF-67 N BH_4 . MOF
'
/C $_6$C $_1$@ IF-67 -
N BH_4
HG . C
, C , C
. I ,
. I ,
/C $_6$C $_1$@ IF-67
,
- /C $_6$C $_1$@ IF-67
,
. M - /C $_6$-
C $_1$@ IF-67 -
-
D , /C $_6$C $_1$@ IF-67 -
N BH_4 -
. O ,
/C $_6$C $_1$@ IF-67

Declaration of competing interest

fl .

Acknowledgements

N N
F C (. 21965005), N F -
G P (2018G N FAA294077, 2021G N F-
AA076001), P H -L G (F-
KA18015), G B
(G IKEAD18126001, G IKE 20297039 CE).

Appendix A. Supplementary data

://　/10.1016/　.2022.08.289.

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C -　M　N F
AC　C　E　2022;10:5683–92.

2 , L　P,　I
O　-　N-　B OC -
CN
. J C　I　2022;607:826–35.

3 F,　J,　, L　, M　J,　. I
A /N OOH/N 3 2
. AC　C　E
2022;10:5976–85.

4 P　Q,　, H　C, L　I　, D
C 4 3　1 -　2
. J C　I　2022;615:577–86.

5 H　F, H　M,　Q,　B,　. N F
@N-　-　N-
AC　C　E　2022;10:6094–105.

6 A　HN. A
. I　J H　E
2021;46:726–65.

7 O　L,　H, L　H-　M. A
N　BH4
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-
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E　2020;45:31952–62.

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N　BH4-H2
: . E　2021;14:3567.

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. J P
2004;135:36–41.

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P /C
. I　J E　2013;37:443–8.

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—C　-PEDO
. . C　E　J 2015;264:531–7.

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-F /GO

N BH_4 -
H_2 C C C 2021;13:3628–35.

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