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Hydrolysis of ammonia-borane over Ni/ZIF-8 nanocatalyst: high efficiency, mechanism and controlled hydrogen release

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4 **Hydrolysis of ammonia-borane over Ni/ZIF-8 nanocatalyst:**
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6 **high efficiency, mechanism and controlled hydrogen release**
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41 **Abstract**
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46 Non-noble metal nanoparticles are notoriously difficult to prepare and stabilize with
47 appropriate dispersion, which in turn severely limits their catalytic functions. Here
48 using zeolitic imidazolate framework (ZIF-8) as MOF template, catalytically
49 remarkably efficient ligand-free first-row late transition-metal nanoparticles are
50 prepared and compared. Upon scrutiny of the catalytic principles in the hydrolysis of
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4 ammonia-borane, the highest total turnover frequency among these first-row late
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6 transition metals is achieved for the templated Ni nanoparticles with 85.7
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8 $\text{mol}_{\text{H}_2} \cdot \text{mol}_{\text{cat}}^{-1} \cdot \text{min}^{-1}$ at room temperature, which overtakes performances of previous
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10 non-noble metal nanoparticles systems, and is even better than some noble metal
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12 nanoparticles systems. Mechanistic studies especially using kinetic isotope effects
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14 show that cleavage by oxidative addition of an O–H bond in H_2O is the rate
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16 determining steps in this reaction. Inspired by these mechanistic studies, an attractive
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18 and effective “on-off” control of hydrogen production is further proposed.
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26 Introduction

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31 Catalytic hydrogen generation from hydrogen storage materials is considered as a
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33 convenient, inexpensive, and effective approach to address the energy and
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35 environmental concern.¹⁻⁴ Among various chemical hydrogen storage materials,
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37 ammonia-borane (AB) has a high hydrogen content (19.6 wt%), high stability in the
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39 solid state and solution under ambient conditions, nontoxicity, and high solubility.
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41 Therefore it is considered as one of the most leading contender in promising chemical
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43 hydrogen-storage materials for various applications.⁵⁻¹⁵
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49 Until now, effective catalysts for hydrolysis of AB are typically based on expensive
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51 and rare noble metal nanocatalysts (e.g., Rh, Pt, Ru). Considerable efforts have been
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53 devoted to the design of high-performance noble metal-free nanocatalysts,¹⁶⁻²⁵ On the
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55 other hand, the hydrolysis of AB under mild conditions by cheap and earth-abundant
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3 first row metal nanoparticles (Fe, Co, Ni and Cu, “BM”) with practical efficiency and
4 sustainability remains extremely challenging, largely due to their labile nature,
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6 complex mechanistic manifolds and low catalytic efficiencies.²⁶
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10 Supported nanoparticle (NP) catalysts have shown remarkable catalytic efficiencies. It
11 has also been found, however, that the activities were significantly influenced or/and
12 eventually determined by the NP supports.²⁷⁻³⁷ In this regard, metal organic
13 frameworks (MOFs) are outstanding emerging porous nanomaterials that are
14 advantageous compared to other conventional inorganic supports.³⁸⁻⁴³ MOFs allow
15 confining and stabilizing catalytically active metal NPs within their frameworks,
16 which controls the nucleation and growth of NPs, thus preventing their aggregation
17 and prolonging their stabilities.⁴⁴⁻⁵¹ Moreover, the high specific surface areas and
18 tunable pore sizes ensured good NP dispersion, which allows exposing active sites
19 and facilitates the accessibility of substrates to the active NP surface by reducing
20 diffusion resistance.⁴⁴⁻⁵¹ On the other hand, the direct use of nanoconfinement effect
21 by MOFs provides a facile method to prepare ligand-free and ultrafine NP/MOF
22 nanocatalysts, which is significant but also crucial for the design of highly efficient
23 heterogeneous catalysts. However, the comparison of the catalytic efficiencies of
24 BMNPs using the same MOF template have not yet been disclosed.
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48 In addition to the rational design of new nanocatalysts, insights to the mechanistic
49 aspects of the hydrolysis reaction would be essential for the enhancement of the
50 catalytic efficiencies of the BMNPs/MOFs nanocatalysts. The details of the reaction
51 process of AB hydrolysis over BMNPs/MOFs nanocatalysts again have rarely been
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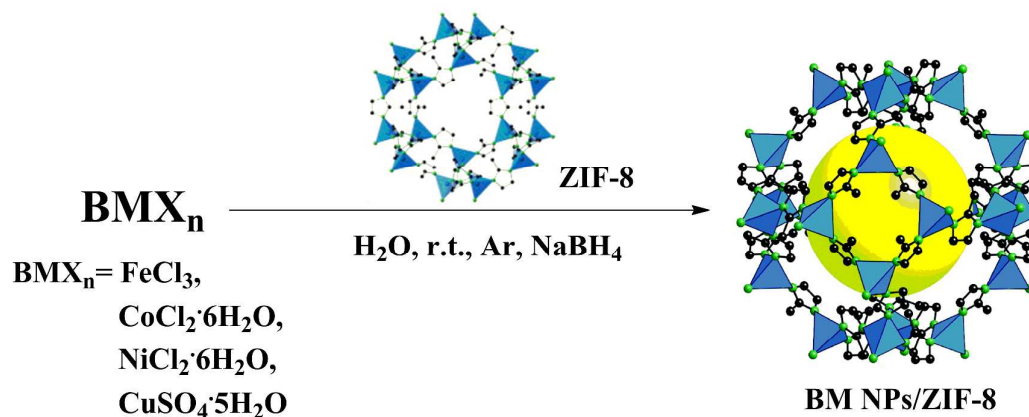
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4 experimentally examined, however. In order to address these challenging issues, we
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6 now report the synthesis, characterization and catalytic functions of the
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8 BMNPs/zeolitic imidazolate framework (ZIF-8; $[\text{Zn}(\text{MeIM})_2]_n$) nanocatalysts,
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10 especially with efforts to further improve the catalytic activity by understanding the
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12 mechanistic aspects of the hydrolysis reaction. First, the supporting nanomaterial of
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14 ZIF-8 is synthesized and characterized. Then we highlight the efficiency of
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16 Ni NPs/ZIF-8 nanocatalyst by comparing the catalytic activities of first-row late
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18 transition-metals NPs/ZIF-8 catalysts in the hydrolysis of AB in water under mild
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20 conditions. Subsequently we scrutinize the catalytic behavior of Ni NPs/ZIF-8
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22 nanocatalysts for the hydrolysis of AB in water, the mechanistic aspects of this
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24 reaction using kinetic isotope effects (KIEs), and an anion effect for the control of
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26 hydrogen release. The catalytic activity of the nanocatalyst Ni NPs/ZIF-8 surpassed
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28 all the non-noble metal NP systems for the hydrolysis of AB.
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39 **Result and discussion**

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43 **Synthesis and characterizations of the nanocatalysts:** The ZIF-8 nanoparticles⁵²
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45 are first rapidly synthesized in water using a modified method (SI).⁵³ Transmission
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47 electron microscope (TEM) image indicates that the ZIF-8 NPs are nanocrystals with
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49 sharp hexagonal facets, and the average size of ZIF-8 NPs is around 75 nm (Figure
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51 S1). Powder X-ray diffraction (PXRD) proves the pure phase of ZIF-8 nanomaterial
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53 (Figure S2). ZIF-8 NPs show a type I isotherm in the N_2 adsorption measurement. The
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4 presence of micropores results in volume increase adsorbed at very low relative
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6 pressures, whereas a second uptake at a high relative pressure indicates the existence
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8 of textural meso/macroporosity formed by the packing of NPs (Figure S3). The
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10 Brunauer-Emmett-Teller (BET) surface area of ZIF-8 NPs is $1663.3 \text{ m}^2 \text{ g}^{-1}$. Refluxing
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12 the ZIF-8 NPs in either methanol or water during one day does not change the
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14 framework structure, as evidenced from the unchanged PXRD patterns (Figure S2),
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16 showing the thermal and chemical stabilities of ZIF-8 NPs.^{52,53}

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21 The nanocatalysts BMNPs/ZIF-8 are prepared using the deposition-precipitation (DP)
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23 method with fast reduction by NaBH_4 , then collected by centrifugation followed by
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25 washing and drying *in vacuo* (Scheme 1 and SI). These nanomaterials are clearly
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27 distinguished by their colors (compare the photographs in Figure S4); for instance Ni
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29 NPs/ZIF-8 appears grey, whereas Cu NPs/ZIF-8 is completely black. No diffractions
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31 are detected for Ni NP species from PXRD patterns after reduction in Ni NPs/ZIF-8
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33 compared to ZIF-8 NPs, which indicates that Ni loadings are too low or Ni NPs are
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35 too small.^{49,54} The metal loading is determined by inductively coupled plasma-optical
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37 emission spectroscopy (ICP-AES); for instance the Ni loading in Ni NPs/ZIF-8 is 2.2
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39 wt%. The metal oxidation state is then identified by X-Ray photoelectron
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41 spectroscopy (XPS). Binding energies (B.E.) of 1021.4 and 1044.5 eV are observed
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43 for the $2p_{3/2}$ and $2p_{1/2}$ levels of the Zn^{2+} ion in the ZIF-8 framework, respectively
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45 (Figure S5). Moreover the well-defined peaks with B.E. of 852.2 and 870.1 eV are
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47 detected for the $2p_{3/2}$ and $2p_{1/2}$ levels (Figure S6), respectively, of metallic Ni^0 in the
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49 Ni NPs.^{17,21}



20 **Scheme 1.** Preparations of the nanocatalysts BMNP/ZIF-8.
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25 Interestingly, after the deposition of the BMNPs, the nanocatalysts BMNPs/ZIF-8
26 become more spherical, as exemplified by NiNPs/ZIF-8 (Figures 1a and 1b). The
27 measurements of the NP size by TEM encounters problems, however, probably due to
28 their small sizes and lack of contrast over ZIF-8 framework. In order to release the
29 BMNPs from the nanocatalysts BMNPs/ZIF-8 for direct TEM characterization, the
30 ZIF-8 framework was then digested using a solution of ethylenediaminetetraacetic
31 acid (EDTA)⁵⁵ in the presence of poly(vinylpyrrolidone) (PVP, Mw = 10,000) to
32 stabilize the ultras small NPs. In this way the sizes of the BMNPs are successfully
33 measured by TEM (Table 1). The size of the released NiNPs is 2.7 nm, and other size
34 distributions of FeNPs, CoNPs, and CuNPs are shown in Table 1 and in the SI
35 (Figures S7-S10). On the other hand, nitrogen sorption experiments of the
36 nanocatalysts show type I shape and considerable decrease of pore volume and BET
37 surface areas (Table 1 and Figure S3). This indicates blocking of the windows of the
38 ZIF-8 framework cavities by highly dispersed NPs within the locally distorted
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environment or/and the location of NPs at the surface; the latter was also shown by TEM in Figure 1b, for instance for NiNPs/ZIF-8.

Table 1. Physical properties and catalytic efficiencies of the nanocatalysts.

Sample	Size ^a (nm)	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	TOF ^b (mol _{H₂} · mol _{cat} ⁻¹ · min ⁻¹)
ZIF-8	75±3	1663.3	0.6614	--
FeNPs/ZIF-8	3.0±0.4	1313.3	0.4491	2.5
CoNPs/ZIF-8	2.9±0.3	1313.8	0.4539	19.4
NiNPs/ZIF-8	2.7±0.3	1324.3	0.4255	35.3/85.7 ^c
CuNPs/ZIF-8	3.2±0.4	1367.3	0.4110	5.6

^a TEM size. ^b Hydrolysis of AB in water at room temperature (25 ± 0.5°C), TOF = mol_{H₂} released / (mol_{catalyst} × reaction time_(min)). ^c TOF is obtained in the presence of 0.3M NaOH.

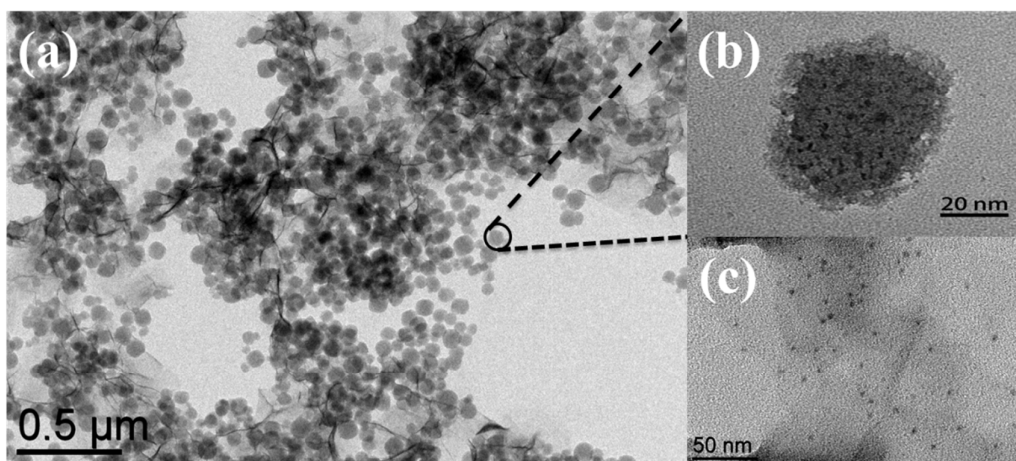
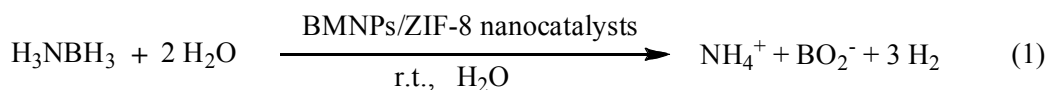


Figure 1. TEM images of NiNPs/ZIF-8: (a) at 500 nm scale. (b) at 20 nm scale. (c) NiNPs in NiNPs/ZIF-8 after digestion using EDTA and capping with PVP.

High efficiency of NiNPs/ZIF-8 in the hydrolysis of AB and mechanistic studies.

The catalytic performances of the BMNPs/ZIF-8 are evaluated for the hydrolysis of AB reaction in water. Hydrolysis of AB starts in water by employing 3 mol% of the various late transition metal nanocatalysts BMNPs/ZIF-8 (measured by ICP-AES). The reaction profile in the presence of the nanocatalysts BMNPs/ZIF-8 is shown in Figure S11. The volumes of gas collected represent nearly 3 equiv. H₂ per AB with no detectable NH₃ (SI),⁵⁶ indicating that hydrolysis of AB catalyzed by the nanocatalyst BMNPs/ZIF-8 proceeds according to Equation (1):



This comparison demonstrates the best activity of NiNPs/ZIF-8 in terms of turn over

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4 frequency (TOF) among the four nanocatalysts BMNPs/ZIF-8 (Table 1 and Figure
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6 S11). Therefore the catalytic system NiNPs/ZIF-8 was chosen for further studies.

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9 Figure S12 shows the logarithmic plot of the hydrogen generation rate vs.
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11 concentration of NiNPs/ZIF-8; the slope is 0.98, indicating that the hydrolysis of AB
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13 catalyzed by NiNPs/ZIF-8 is first-order with respect to the catalyst concentration. On
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15 the other hand hydrolysis of AB catalyzed by NiNPs/ZIF-8 is zero-order with respect
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17 to the AB concentration, as a nearly horizontal line (slope of 0.086) is observed
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19 (Figure S13). This implies that under the present reaction conditions, AB is easily
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21 activated, and thus the possibility of the activation of AB in the rate-determining step
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23 (RDS) is ruled out. This also is in accordance with the KIE results (*vide infra*). The
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25 activation energy (E_a) of AB hydrolysis, determined by measuring the time
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27 dependence of H₂ generation at various temperatures, is approximately 42.7 kJ/mol
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29 (Figure S14 and calculation). This value also is lower than those found for several
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31 known noble metal-based nanocatalysts (Table S1).
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39 Although the catalytic rates in the hydrolysis of AB catalyzed by NiNPs/ZIF-8 is
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41 independent of the AB concentration, the KIE⁵⁷⁻⁵⁹ was further investigated in order to
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43 shed light on the RDS of hydrolysis of AB catalyzed by NiNPs/ZIF-8. Indeed in this
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45 reaction the KIE value should tell if N-H or B-H or both bonds are broken during the
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47 RDS.^{16,60-63}
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51 The hydrolysis of the deuterated products of AB (for their synthesis, see S.I.) in the
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53 presence of NiNPs/ZIF-8 shows slower reaction rates (Figure S17). A KIE of 1.33 is
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55 determined for deuteration at the boron site (NH₃BD₃), indicating a similar
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4 dehydrogenation behavior to that of AB in H₂O. This indicates that the absence of
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6 large KIE for hydrolysis of AB deuterated at the boron site (NH₃BD₃). On the other
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8 hand, the KIE value of 2.49 is calculated according to the H₂ generation rates in
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10 ND₃BH₃ (NH₃BH₃-D₂O system), suggesting that the O-H bond cleavage of H₂O
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12 might be in the RDS. This would be similar to the metal-catalyzed borohydride
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14 hydrolysis, in which half of the hydrogen comes from water.⁶⁴ Previously, it has been
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16 suggested that the water activation by means of oxidative addition of a O-H bond on
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18 noble metal NP surfaces easily occurs, forming adsorbed -OH and -H species. For
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20 instance Pt NPs have been known as the redox catalyst for water photo-splitting.^{65,66}
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22 That Ni is the best metal found here for the hydrolysis reaction among those four
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24 first-row late transition metals is in accord with oxidative addition of water as the
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26 RDS, because Ni(0) is known by far the best first-row metal catalyst of reactions
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28 involving oxidative addition.⁶⁷ In addition the involvement of water activation in the
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30 RDS may be partially explained by the higher O-H bond energy ($\sim 493 \text{ kJ mol}^{-1}$)⁶⁸
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32 than that of B-N and B-H bond (~ 117 and $\sim 430 \text{ kJ mol}^{-1}$, respectively).⁶⁹ Thus it is
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34 mostly likely that the water molecule is activated by an indirect O-H bond cleavage to
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36 form -H and -OH species promoted by AB in the presence of the nanocatalyst
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38 NiNPs/ZIF-8. Since the NH₃ group does not participate in the hydrolysis, the B-N
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40 bond dissociates in AB, followed by H₂ release (Figure 2).
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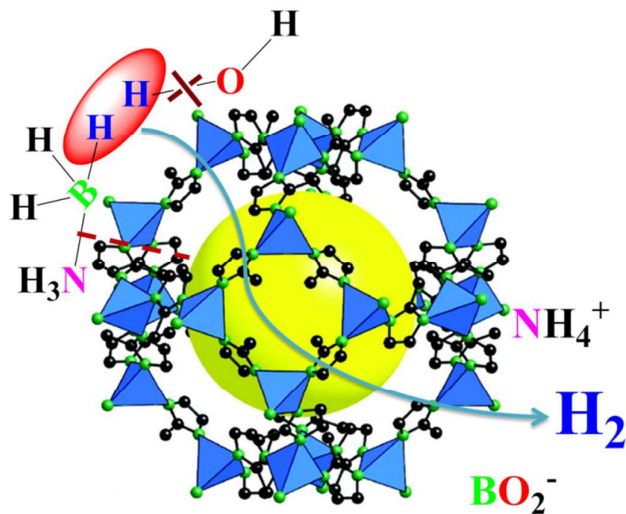


Figure 2. Proposed mechanism for the hydrolysis of AB catalyzed by NiNPs/ZIF-8.

Remarkable improvement of the catalytic performance by ion effect allowing the controlled release of hydrogen. From the mechanistic studies, it can be assumed that if OH^- is directly adsorbed on the surface of the Ni nanocatalyst, a bifunctional catalyst with both H and OH adsorptions should be highly expected to provoke the surface reaction. Thus the presence of surface OH^- should be of great value for the enhancement of the catalytic activity. To verify this hypothesis, various concentrations of NaOH (0.1-0.4 M), a conventional OH^- provider in aqueous solution, were separately added to the reaction media that only contained NiNPs/ZIF-8. After stirring for 30 min, the aqueous solution of AB was added, and the catalytic activities were examined. Surprisingly, as shown in Figure S18, the H_2 generation rates greatly improved as compared to the one in the absence of NaOH. The H_2 generation rates first increased with the increased NaOH concentrations (0.1-0.3 M), then decreased with higher NaOH concentration (0.4 M). It is suggested that the accumulation of too

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4 much OH⁻ beyond the optimum level (0.3 M) could significantly reduce the beneficial
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6 effect, resulting in the decrease of the H₂ generation rate. The highest reaction rate in
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8 term of TOF is 85.7 mol_{H₂}·mol_{cat}⁻¹·min⁻¹ with 0.3 M NaOH, showing the best activity
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10 among all the non-noble metal NP systems. This is even more efficient than noble
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12 metal NPs systems (Table S1); for instance the utilization of commercial 40 wt %
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14 Pt/C catalyst only had a TOF of 55.56 mol_{H₂}·mol_{cat}⁻¹·min⁻¹. Control experiment
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16 shows that the addition of NaOH has no effect on AB in aqueous solution in the
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18 absence of catalyst, as no H₂ release is observed, as also confirmed by the ¹H and ¹¹B
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20 NMR spectra.⁷⁰ On the other hand, other bases such as Na₂CO₃ and NaHCO₃ have no
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22 influence or slow down the H₂ generation rate (SI).
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29 In parallel the hydrolysis reaction was also conducted under identical conditions,
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31 except that NaOH was replaced by HCl (0.3 M solution for the final concentration),
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33 and it was surprisingly found that there was no hydrogen release. Thus in the present
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35 study, the contribution from OH⁻ predominated. The influence of OH⁻ and H⁺
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37 disclosed here is different from the very recent work involving AB hydrolysis by
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39 single Rh atoms/VO₂ nanorods, which showed positive correlation between the H⁺
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41 concentration and the reaction rate.⁷¹
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46 Density functional theory (DFT) calculations on the interaction of H and OH with
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48 (111) metal Ni surface suggested that H forms an essentially covalent bond with the
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50 metal, whereas OH forms a largely ionic bond.⁷² The weaker covalent interaction and
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52 a stronger Pauli repulsion of the OH with the metal *d* electrons result in the preference
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54 of binding molecular hydroxyl to Ni surface rather than H.^{73,74} Moreover, Ni is more
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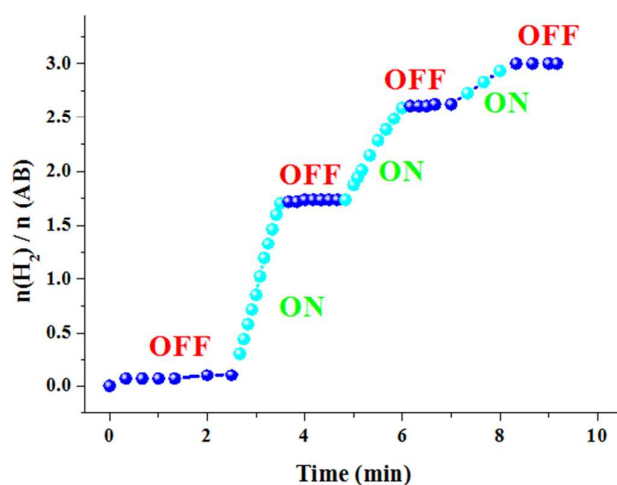
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4 oxophilic than Pt, so that it can better promote surface OH adsorption than Pt.⁷⁵ To
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6 confirm this, XPS is re-called to measure the surface binding energy of Ni 2p upon
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8 treatment with NaOH. As shown in Figure S23, upon treatment with NaOH, the
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10 binding energy at 855.6 eV that associates with Ni(OH)₂ species⁷⁶ becomes
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12 predominant, verifying the coordination of OH group to the Ni surface. On the other
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14 hand, a *ca.* 0.76 eV Ni 2p binding energy downshift was also observed. Thus upon
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16 coordination of OH group to the Ni surface, the OH adsorbates donate electrons to the
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18 Ni surface. This results in an increased electron density around the Ni surface, which
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20 facilitates the interaction with the reactant, AB. The E_a of AB hydrolysis in the
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22 presence 0.3 M NaOH was considerably decreased to 28.0 kJ/mol (Figure S24).
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24 Therefore the overall reaction activity is significantly improved.
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31 The reason for the switch off of hydrogen generation possibly comes from two
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33 aspects. One of them is the negative effect of H⁺ on the self-ionization of water that
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35 suppresses the OH⁻ formation and occupation of OH⁻ absorption sites on the NiNP
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37 surface. The other one is the ion effect, because Cl⁻ ligands are known to limit the
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39 catalytic activity of NPs by strongly bonding to NPs surface, which inhibits access to
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41 the surface active sites. We thus first conducted the initial reaction by adding NaCl
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43 solution (0.3 M), and found that the H₂ generation rate was slower than that without
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45 NaCl solution. H₂ was released smoothly, however, with a TOF of 16.67
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47 mol_{H₂}·mol_{cat}⁻¹·min⁻¹ (Figure S25). This result suggests the possible ion effect in the
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49 reaction. To confirm this ion effect, other aqueous solutions of for instance NaI,
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51 NaBF₄, NaBr, NaF, and Na₂SO₄ were then added to the reaction media with final
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4 concentration of 0.3 M (SI). The H₂ generation rates were considerably slowed down
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6 compared with the initial reaction performed with only NiNPs/ZIF-8, and the TOFs
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8 were 10.3, 13.7, 16.2, 18.5 and 21.4 mol_{H₂}·mol_{cat}⁻¹·min⁻¹ for NaI, NaBF₄, NaBr, NaF
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10 and Na₂SO₄, respectively. Interestingly, the catalytic activities follow the order: SO₄²⁻>
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12 F⁻> Cl⁻> Br⁻> I⁻, which also follows the direct Hofmeister series. Significant ion
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14 effects occurred and showed correlations with the catalytic activities obtained in the
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16 hydrolysis of AB reaction, a characteristic fingerprint of the Hofmeister effects. It is
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18 suggested that H⁺ plays a very negative effect in the hydrolysis reaction. On the other
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20 hand, ions such as Cl⁻, F⁻, Br⁻ et al present in the solution prefer to bind to the surface
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22 active sites of NiNPs, leaving less active surface sites available to OH⁻ generated from
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24 water activation in the RDS of hydrolysis. Thus the negative synergistic effects
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26 switched off the hydrogen release. Therefore here we establish for the first time that
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28 the anion effect tuned hydrolysis of AB catalyzed by the nanocatalyst NiNPs/ZIF-8 in
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30 water, allowing the hydrogen generation to reversibly turn “off” and “on”. This
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32 property is of great practical importance for on-board hydrogen applications under
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34 ambient conditions (*vide infra*).

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44 The “on-off” control of hydrogen generation is achieved by addition of an equimolar
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46 amount of aqueous solution of HCl and NaOH to the reaction media (Figure 3).
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49 Through the studies above, OH⁻ facilitates the hydrolysis reaction, while H⁺ and Cl⁻
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51 play negative roles in the hydrolysis of AB. At the beginning of the hydrolysis
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53 reaction, H₂ generation can be completely stopped by adding 0.3 M HCl solution, and
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56 the H₂ generation is released again by adding the same NaOH molarity. In this way,
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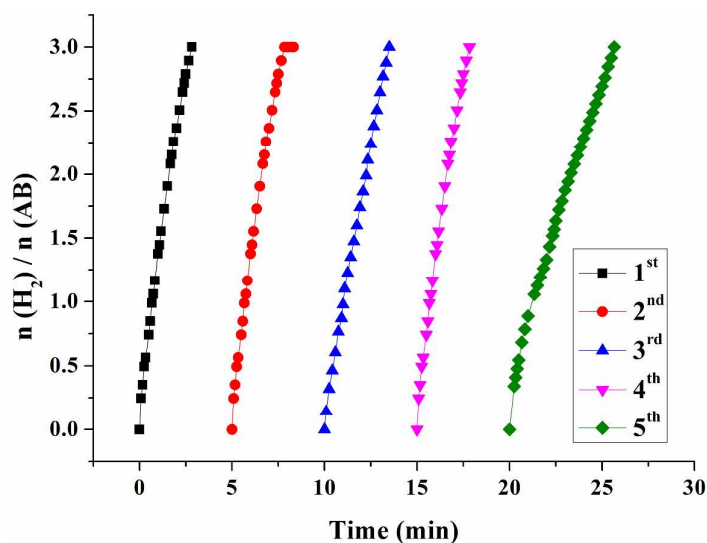
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4 the H₂ generation is controlled. In addition, in each “on-off” cycle, a gradual decrease
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6 in the H₂ generation is also observed. Indeed the poisoning effect of H⁺ dominates the
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8 switch off of the H₂ generation. The subsequent addition of NaOH neutralizes the HCl
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10 solution, however. The effect of NaCl production (from NaOH + HCl) was also
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12 observed in the medium, also considerably slowing down the H₂ generation (*vide*
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17 *supra*).



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39 **Figure 3.** “On-off” control of H₂ production in the AB hydrolysis in water.

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46 Finally, we examined the reusability of the nanocatalyst NiNPs/ZIF-8, which is a
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48 critical issue for further practical applications. The reusability tests were conducted
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50 under the present conditions by continuous addition of a new proportion of AB
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52 aqueous solution when the previous run was completed. As shown in Figure 4, the
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54 activity of NiNPs/ZIF-8 is essentially retained until the fifth runs, where a slight drop
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4 in reaction rate is observed. The nanocatalyst was then characterized after the fifth
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6 runs by PXRD and TEM techniques, PXRD showing the unchanged nanostructure
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8 (Figure S30), while TEM showed the increase of NiNP size (Figure S31). Thus the
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10 decrease in the activity is ascribed to the diluted reactant in water, the deactivation
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12 effect of the hydrolysis product metaborate,⁷⁷⁻⁷⁹ and to the increased NiNP size,
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14 especially for NPs at the surface of ZIF-8.
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39 **Figure 4.** Plots of volume of H₂ vs. time for the hydrolysis of AB catalyzed by the 3%
40 NiNPs/ZIF-8 during the reusability test.
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46 **Concluding remarks.** In summary, highly dispersed ligand-free Fe NPs, Co NPs, Ni
47 NPs and Cu NPs have been successfully synthesized using ZIF-8 as nanocatalyst
48 template, and the highest catalytic activity for hydrogen generation upon hydrolysis of
49 AB is shown to be that of NiNPs/ZIF-8 showing a TOF value of 85.7
50 mol_{H₂}·mol_{cat}⁻¹·min⁻¹. This represents the best TOF value ever reported for noble
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3 metal-free catalysts. Detailed mechanistic investigations, especially KIE
4 measurements, show that the RDS for AB hydrolysis is the cleavage of an O–H bond
5 in H₂O by means of oxidative addition of such a bond on Ni NP surfaces. Inspired by
6 this approach, we further disclosed the ion effect in this reaction, which allowed a
7 remarkable improvement of the catalytic performance and the controlled release of
8 hydrogen. The principles and results obtained here may not only provide insights into
9 the rational design of highly efficient non-noble metal-based nanocatalysts, but also
10 demonstrate a promising step towards the application of chemical hydrogen storage
11 materials in a fuel-cell-based hydrogen economy.
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28 ASSOCIATED CONTENT

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31 **Supporting Information.** Syntheses and characterization of the nanocatalysts. ¹H
32 NMR spectra of the products. Profiles of hydrolysis of the AB hydrolysis reactions.
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34 This material is available free of charge via the Internet at <http://pubs.acs.org>.
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51 **Notes**

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54 The authors declare no competing financial interest.
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