



Promoted liquid-phase hydrodechlorination of chlorophenol over Raney Ni via controlling base: Performance, mechanism, and application

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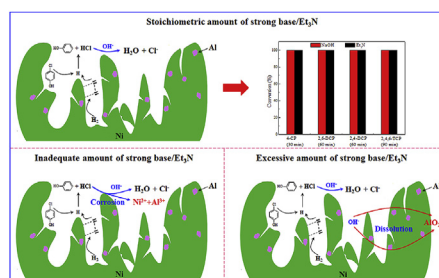
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HIGHLIGHTS

- Base and its addition amount influence the HDC reactivity of chlorophenol over Raney Ni.
- The mechanism for promoted effect of base is elucidated by characterization techniques.
- Promising bases and their optimal amount are developed for the excellent HDC of chlorophenols.
- The stoichiometric amount of NaOH enables Raney Ni to possess higher stability.

GRAPHICAL ABSTRACT



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ABSTRACT

The potential effect of base on Raney Ni-catalyzed hydrodechlorination (HDC) of chlorophenol was studied. Compared to weak inorganic bases, strong inorganic bases (NaOH and KOH) and triethylamine (Et₃N) were more favorable to promote Raney Ni-catalyzed HDC reaction. Moreover, a stoichiometric amount of NaOH/Et₃N was found to be optimal for the HDC reaction, and up to 100% conversion of 4-chlorophenol was achieved within 30 min. Catalyst characterization (SEM, EDXS, and XRD) combined with ICP-OES analysis were introduced to better understand the mechanism for the promoted effect of base on the HDC reaction. The results showed that the optimal amount of strong inorganic bases and Et₃N efficiently eliminated HCl corrosion to Raney Ni, greatly reduced the active phase Ni and Al leaching, and avoided collapse of the catalyst framework. Based on the mechanism, the best bases and their optimal amount were developed for further disposal of polychlorinated phenols, and excellently step-wise HDC of polychlorinated phenols was achieved. Recycling tests showed that Raney Ni could be reused at least 5 times for the HDC reaction with the stoichiometric amount of NaOH, which was a promising option for the HDC of wastewater containing chlorophenols over Raney Ni.

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1. Introduction

Chlorophenols (CPs) are a class of significant pollutants in wastewater effluents since they are used extensively in the manufacture of germicides, fungicides, herbicides, pesticide, and wood protectors (Ge et al., 2017). Owing to their wide application and physicochemical properties, chlorophenols have been detected in groundwater, sediments, soil, and organisms (Shu et al., 2019; Zhao et al., 2017). Some chlorophenols are now listed as priority pollutants due to their high toxicity, low biodegradability, potential carcinogenic, teratogenic, or mutagenic, and persistence in the environment (Liu et al., 2019). Therefore, it is a major environmental challenge to develop an effective technique for the abatement of chlorophenols, which must be treated before discharging into the environment.

At present, numerous methods like physical method (Madannejad et al., 2018), biological method (Song et al., 2019), incineration (Peng et al., 2016), advanced oxidation processes (Li et al., 2019; Luo et al., 2018; Zhou et al., 2018), zero-valent metal reduction (Duan et al., 2016; Yang et al., 2017; Zheng et al., 2019), catalytic hydrodechlorination (HDC) (Jadbabaei et al., 2017; Ma et al., 2015; Xiong et al., 2018), etc have been applied for the elimination of chlorophenols. However, harsh reaction conditions and/or special facilities are often required in these methods, many of which are high-cost and will generate even more toxic byproducts (Guan et al., 2019; Madannejad et al., 2018; Zhao et al., 2018). Among these methods, catalytic HDC is a more prospective detoxifying technologies due to low-energy demands and the fact that the highly toxic chlorophenols are effectively transformed into less harmful products, reducing dramatically their ecotoxicity (Pizarro et al., 2017; Wu et al., 2012; Xiong et al., 2018). Liquid-phase HDC of chlorophenols has been effectively catalyzed with supported noble metal (Rh, Au, Pt, Pd, etc.) catalysts (Descorme, 2017; Keane, 2011; Pizarro et al., 2015; Rong et al., 2013; Zhou et al., 2016). However, the high cost of these noble metal catalysts restricts their wide application in the HDC of chlorophenols (Xu et al., 2012). In this context, Raney Ni represent a promising option in catalytic HDC of chlorophenols due to its cost inexpensive and high resistance to halogen poisoning (Munoz et al., 2016). Moreover, Raney Ni possesses outstanding activity in catalytic HDC of chlorinated organic compounds under mild conditions (Ma et al., 2015; Zinovyev et al., 2007; Zinovyev and Tundo, 2007).

During liquid-phase HDC, HCl is produced and will poison the catalyst (Urbano and Marinas, 2001). Moreover, the poison of HCl to catalyst has been associated with active phase leaching, metal-Cl formation, support structural breakdown, and active phase oxidation (Cobo et al., 2008). Thus, various bases are usually introduced to minimize the catalyst deactivation and enhance stability (Ma et al., 2015). Yet, the addition of bases has showed both beneficial and negative effects on catalyst activity and/or stability (de Pedro et al., 2011). In Pd-catalyzed HDC of 2,4-dichlorophenol, the HDC activity and selectivity exhibited different pH dependent, which was attributed to the lessening of HCl inhibition (Yuan and Keane, 2004b). Cobo et al. (2008) suggested that optimal amount of NaOH was required to avoid the active metal leaching and to reduce solid residues deposition on catalyst surface. Gómez-Quero et al. (2008) found that solution pH values determined the reactant/catalyst interaction, and then impacted on the HDC pathway of 2,4-dichlorophenol over Pd/Al₂O₃. Ordóñez et al. (2010) studied Pd-catalyzed HDC of trichloroethylene in wastewaters, and found that Na₂CO₃ largely increased stability of the catalyst. In the HDC of 4-chlorophenol over Pd/Al₂O₃, de Pedro et al. (2011) attributed a stronger deactivation upon time on stream to the formation of palladium chloride complexes. We previously proposed that the

action and existing species of Et₃N in reaction medium determined Raney Ni catalyzed HDC reactivity/selectivity of chlorophenols (Ma et al., 2010). Noticeably, most of these studies focused on the influence of base on Pd-catalyzed HDC reactions. So far, research on the effect of bases on Raney Ni-catalyzed HDC reaction is limited. Moreover, the mechanism of base effect on Raney Ni-catalyzed HDC is still not well established.

Herein, we explore the potential effect of base on Raney Ni-catalyzed HDC of chlorophenol in aqueous solution. In this paper, 4-chlorophenol was selected as a representative pollutant to evaluate the influence of different bases and base amount on Raney Ni-catalyzed HDC reaction. With the aid of ICP-OES analysis and characterization techniques (SEM, EDXS, and XRD), the mechanism for the potential effect of base was elucidated. Moreover, the application on the HDC of polychlorinated phenols over Raney Ni were further investigated. Finally, this work is expected to offer useful information for the HDC of wastewater containing chlorophenols.

2. Experimental

2.1. Materials

Raney Ni was acquired from Dalian Tongyong Chemical Co., Ltd. The catalyst was used as received without pre-treated and was kept in water-sealing storage before each experiment (Physicochemical properties are provided in Table S1 of Supplementary Material). The chemicals were all listed in Supplementary Material (Text SM1).

2.2. General catalytic HDC procedure

Catalytic HDC reaction was operated in a 100 mL three-neck flask under a constant volumetric H₂ flow of 10 mL min⁻¹ as our previous report (Ma et al., 2018). The experimental processes and conditions were provided in Supplementary Material (Text SM2). The pH of initial and final solutions was measured using an FE28-standard pH meter (METTLER-TOLEDO). The inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 7000 DV, Perkin Elmer) was employed to test the active phase leaching of Raney Ni.

2.3. Analytical methods

The reaction intermediates of chlorophenols were identified by Thermo Fisher ITQ-900 GC-MS (Gas Chromatograph-Mass Spectrometry) with a 30 m TG-1701MS column (0.25 mm × 0.25 μm). The concentration of chlorophenols and their intermediate products were analyzed by Agilent-7890 A GC-FID (Gas Chromatograph-Flame Ionization Detector) equipped with a 30 m DB-1701 column (0.32 mm × 0.25 μm). The chromatographic conditions were given in Supplementary Material (Text SM3). The conversion was defined as Eq. (S1), while the HDC reactivity was evaluated using HDC rate, which was calculated as Eq. (S2).

2.4. Catalyst characterizations

The catalyst surface morphology and chemical elements were analyzed using Hitachi S-4800 FE-SEM (Field Emission Scanning Electron Microscope) and an attached HORIBA EMAX Energy EX-350 EDXS (Energy Dispersive X-ray Spectrometer) before and after the reaction. The X-ray diffraction (XRD) patterns were obtained by Shimadzu XRD-6100 (Cu Kα, 40 kV, and 30 mA), with 2θ ranged from 5° to 80°.

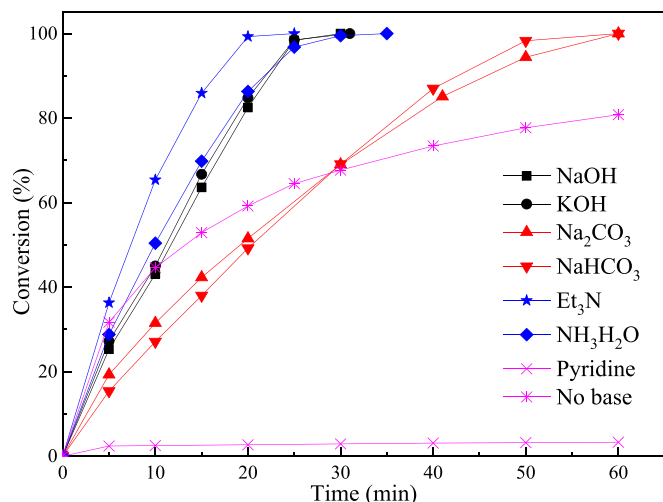


Fig. 1. The effect of various bases on Raney Ni-catalyzed HDC of 4-chlorophenol in aqueous medium. Reaction conditions: 4-chlorophenol (6.20 mmol), Raney Ni (0.12 g), NaOH (6.85 mmol), KOH (6.85 mmol), Na_2CO_3 (3.43 mmol), NaHCO_3 (6.85 mmol), $\text{NH}_3 \cdot \text{H}_2\text{O}$ (6.85 mmol), Et_3N (6.85 mmol), and pyridine (6.85 mmol), H_2 : 10 mL min^{-1} .

3. Results and discussion

3.1. Effect of various bases on Raney Ni-catalyzed HDC of 4-chlorophenol

Fig. 1 shows the conversion of 4-chlorophenol using Raney Ni versus reaction time in aqueous medium without base. As seen in Fig. 1, the conversion of 4-chlorophenol reached 80.8% without base. During the HDC reaction, a stoichiometric amount of HCl was generated, and thus caused a significantly negative effect to Raney Ni (Yuan and Keane, 2004a). As a result, Raney Ni exhibited rather low catalytic activity, and 4-chlorophenol could not be completely hydrodechlorinated within 60 min.

The time profiles for the HDC of 4-chlorophenol in aqueous medium of different bases are shown in Fig. 1. Notably, the HDC of 4-chlorophenol is promoted by base, and the HDC rate displays a strong correlation to bases in the following order: triethylamine (Et_3N) > sodium hydroxide (NaOH) \approx potassium hydroxide (KOH) > ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$) > sodium carbonate (Na_2CO_3) \approx sodium bicarbonate (NaHCO_3) > pyridine. It can be seen from Fig. 1 that the best catalytic activity of Raney Ni was observed with Et_3N . It is also noticed that Raney Ni possessed much stronger catalytic activities with strong inorganic bases than that with weak inorganic bases, which implied that strong inorganic bases were much better choices for the HDC reaction. Yet, the only negative effect on the HDC reaction occurred when pyridine was added, which should come from the catalyst poisoning caused by

pyridine (Xia et al., 2003). In addition, massive agglomerations of Raney Ni were observed during the HDC reaction with pyridine. These results showed that strong inorganic bases and Et_3N were better options which possessed much higher promoted effect on Raney Ni-catalyzed HDC reaction.

In order to clarify the promoted effect of base on liquid-phase HDC reaction, we compared the pH of initial and final solutions (Table 1). The results showed that the byproduct HCl produced an increasing acidity from initial pH 6.63 to final pH 2.30 when the HDC reaction was carried out without base. In the case of the HDC process conducted with NaOH, KOH, Na_2CO_3 , NaHCO_3 , $\text{NH}_3 \cdot \text{H}_2\text{O}$, Et_3N , and pyridine, the obvious decrease of pH was also observed, which could be attributed to the production of HCl. Nevertheless, the reaction solutions did not transform into the relatively strong acidic medium due to the base addition. This is in agreement with the observations reported by other scholars (Yuan and Keane, 2004b). Considering the HDC rate of 4-chlorophenol over Raney Ni with various bases (Table 1), a generally promoted effect on the HDC rate was obtained by adjusting the initial reaction medium pH from 7.62 to as high as 10.90. In a word, the addition of various bases, except for pyridine, adjusted reaction medium to alkaline condition, which served to limit HCl poisoning to Raney Ni. As a result, higher HDC rates of 4-chlorophenol over Raney Ni were achieved in alkaline medium provoked by the addition of various bases.

The active phase (Ni and Al) of Raney Ni are active metals and easy to be corroded, so the reaction medium pH has a considerable effect on the active phase leaching. To obtain further information about active phase leaching of Raney Ni, ICP-OES analysis was performed after the HDC reactions (Table 2). As expected, a large amount of Ni and Al leaching were observed, and their leaching amount were 72.76 mg and 3.85 mg when the HDC reaction was performed without base. The active phase Ni and Al leaching could be ascribed to the byproduct HCl and the subsequent corrosion effect. Similar results were found in the HDC of dioxins over Pd/ Al_2O_3 without base (Cobo et al., 2008). On the contrary, only a little amount of Ni and Al leaching were observed for the HDC reaction carried out in alkaline medium, as presented in Table 1. It would be reasonable to presume that the addition of bases suppressed the interaction of HCl with Raney Ni and largely reduced the active phase (Ni and Al) leaching.

To get more information on the promoted effect of bases, Raney Ni was characterized using SEM, EDXS, and XRD. Fig. 2 illustrates the SEM images of fresh and used catalysts. As shown in Fig. 2a, fresh Raney Ni possesses an obviously smooth surface morphology. Compared with the fresh catalyst, there are various thread-like structures appeared on surface morphology of the catalyst used in aqueous medium without base, which should be resulted from HCl corrosion. Fig. 2d-f show that surface morphologies of Raney Ni used in aqueous medium with NaOH, KOH, and Et_3N are almost the same as that of the fresh catalyst, revealing that the addition of

Table 1
The effect of various bases on Raney Ni-catalyzed HDC of 4-chlorophenol in aqueous medium.

Base	Addition (mmol)	pH ₀	pH _{1 h}	Ni leaching (mg)	Al leaching (mg) ^a	HDC rate (min^{-1})
No Base	0	6.63	2.30	72.76	3.85	0.51
NaOH	6.85	10.90	8.84	0.01	0.03	1.27
KOH	6.85	10.46	7.23	0.33	N.D.	1.27
Na_2CO_3	3.43	9.14	5.72	0.51	N.D.	0.63
NaHCO_3	6.85	7.62	5.71	0.80	N.D.	0.63
$\text{NH}_3 \cdot \text{H}_2\text{O}$	6.85	9.61	9.03	0.92	0.39	1.09
Et_3N	6.85	10.05	8.45	0.01	N.D.	1.52
pyridine	6.85	7.31	7.21	0.33	N.D.	0.02

^a N.D.: Not detected.

Table 2
The effect of NaOH/Et₃N amount on Raney Ni-catalyzed HDC of 4-chlorophenol in aqueous medium.

Base	Addition (mmol)	pH ₀	pH _{1 h}	Ni leaching (mg)	Al leaching (mg) ^a	HDC rate (min ⁻¹)
No Base	0	6.63	2.30	72.76	3.85	0.51
NaOH	3.12 (0.5NaOH)	9.16	3.27	31.88	0.70	0.55
	6.85 (1.1NaOH)	10.90	8.84	0.01	0.03	1.27
	13.70 (2.2NaOH)	12.54	11.77	3.20 × 10 ⁻³	4.02	0.53
	27.40 (4.4NaOH)	12.87	12.76	0.01	5.05	0.44
Et ₃ N	3.12 (0.5Et ₃ N)	9.11	2.87	33.84	0.48	0.55
	6.85 (1.1Et ₃ N)	10.05	8.44	0.01	N.D.	1.52
	13.70 (2.2Et ₃ N)	10.77	9.95	0.04	0.75	1.90
	27.40 (4.4Et ₃ N)	11.20	10.65	0.04	1.39	1.90

^a N.D.: Not detected.

NaOH, KOH, and Et₃N efficiently prevented HCl corrosion to the catalysts. Yet, surface morphology of the catalyst used in aqueous medium with NH₃·H₂O has a laminated structure (Fig. 2g). Moreover, there are also some thread-like structures dispersed on surface morphology of the catalysts used in aqueous medium with Na₂CO₃ and NaHCO₃ (Fig. 2h and i), which are similar to the observation without base. These results further suggested that the addition of NH₃·H₂O, Na₂CO₃, and NaHCO₃ could not avoid HCl corrosion to the catalysts. According to these SEM images, the addition of NaOH, KOH, and Et₃N effectively prevented HCl corrosion to surface morphology of the catalysts (Fig. 2d-f), yet the addition of NH₃·H₂O, Na₂CO₃, and NaHCO₃ could not (Fig. 2g-i).

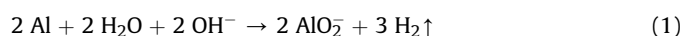
To get surface elemental composition of Raney Ni, EDXS analyses were carried out (Fig. S1). The EDXS patterns implied that the addition of bases reduced the accumulation of Cl⁻ on catalyst surface. Meanwhile, the elemental composition of catalyst surface changed after the HDC reaction. Further, XRD analysis of Raney Ni was performed (Fig. S2). The peaks at 2θ = 44.5°, 51.8°, and 76.3° are corresponding to (1 1 1), (2 0 0), and (2 2 0) planes of nickel, respectively (Cheng et al., 2010). Only Ni peaks were found in the XRD patterns of Raney Ni used in aqueous medium with or without base. These results confirmed that no other crystal appeared on catalyst surface after the HDC reaction.

According to the above discussion, a possible mechanism for promoted effect of base on Raney Ni-catalyzed HDC reaction is suggested (Scheme 1). When Raney Ni-catalyzed HDC reaction was carried out in aqueous medium without base, the byproduct HCl resulted in an increasing acidity from near-neutral pH to strong acidic pH, and the subsequent corrosion effect of HCl induced a large amount of Ni and Al leaching. As a result, catalytic activity of Raney Ni becomes lower and lower with the reaction time, and 4-chlorophenol could not be completely hydrodechlorinated within 60 min (Fig. 1). The addition of various bases enabled the HDC reaction to be carried out in alkaline medium, neutralizing the byproduct HCl (Descorme, 2017). As the HDC reaction medium, water could prevent inorganic salts, which were produced by neutralization of HCl and bases, from depositing on catalyst surface (Ma et al., 2015). Accordingly, the bases such as NaOH, KOH, and Et₃N efficiently prevented HCl corrosion to surface morphology of Raney Ni (Fig. 2d-f), and avoided the active phase Ni and Al leaching (Table 2), and thus enabled the HDC rate of 4-chlorophenol to be rather high. Weak inorganic bases such as NH₃·H₂O, Na₂CO₃, and NaHCO₃ could not efficiently avoid HCl corrosion to surface morphology of Raney Ni (Fig. 2g-i), but they greatly reduced the active phase Ni and Al leaching (Table 1), and thus led to relatively lower HDC rate of 4-chlorophenol. Therefore, strong inorganic bases (NaOH and KOH) and Et₃N were much better bases which possessed much higher promoted effect on Raney Ni-catalyzed HDC reaction.

3.2. Effect of NaOH and Et₃N amount on Raney Ni-catalyzed HDC of 4-chlorophenol

As mentioned above, the addition of various bases adjusted the reaction medium pH, and thus affected surface morphology and active phase of Raney Ni, and enhanced the HDC reactivity of 4-chlorophenol. Moreover, strong inorganic bases (NaOH and KOH) and Et₃N were much better choices for Raney Ni-catalyzed HDC reaction. Thus, effect of NaOH and Et₃N amount on Raney Ni-catalyzed HDC reaction was further studied to ascertain the optimal amount of base in the HDC reaction (Fig. 3).

Fig. 3A shows Raney Ni-catalyzed 4-chlorophenol conversion versus reaction time with different amount of NaOH. When the amount of NaOH were 0 mmol ([NaOH]₀/[organic-Cl]₀ = 0, 0 NaOH), 3.12 mmol (0.5 NaOH), 6.85 mmol (1.1 NaOH), 13.70 mmol (2.2 NaOH), and 27.40 mmol (4.4 NaOH), the HDC rates of 4-chlorophenol over Raney Ni are 0.51 min⁻¹, 0.55 min⁻¹, 1.27 min⁻¹, 0.53 min⁻¹, and 0.44 min⁻¹, respectively (Table 2). This confirmed that the HDC rate of 4-chlorophenol increased with NaOH amount at low concentration and then began to decrease after an excessive amount of NaOH was added. Notably, the optimal HDC rate of 4-chlorophenol shows up in the reaction medium with 1.1 NaOH. Furthermore, the initial and final reaction medium pH was compared (Table 2). When the reaction medium pH changed from 9.16 to 10.90, a promoted effect on the HDC rate of 4-chlorophenol was noticed. Yet, an opposite trend was observed when the reaction medium pH was higher than 10.90. Also, the obvious decrease of pH was seen resulted from the production of HCl when the HDC reaction was performed with different NaOH amount. Even after the HDC reaction, the pH of the reaction medium with 2.2 NaOH and 4.4 NaOH were 11.77 and 12.76. This implied that the low HDC rates of 4-chlorophenol with 2.2 NaOH and 4.4 NaOH could not be ascribed to the corrosion effect of HCl to Raney Ni. Subsequently, ICP-OES analysis was carried out to evaluate Ni and Al leaching of Raney Ni (Table 2). The amount of active phase Ni leaching of Raney Ni during the HDC reaction was greatly reduced due to NaOH addition. Yet, with the amount of NaOH increased, the amount of active phase Al leaching of Raney Ni decreased to minima and then increased. In other words, the excessive amount of NaOH avoided active phase Ni leaching of Raney Ni, but induced active phase Al leaching of the catalyst. During the HDC reaction, NaOH was used to neutralizing the byproduct HCl, and thus stoichiometric amount of NaOH or more prevented the active phase Ni leaching caused by the interaction of HCl with the catalyst. However, the excessive amount of NaOH would lead to the high pH, and thus induced dissolution of the active phase Al and could be expressed as follows.



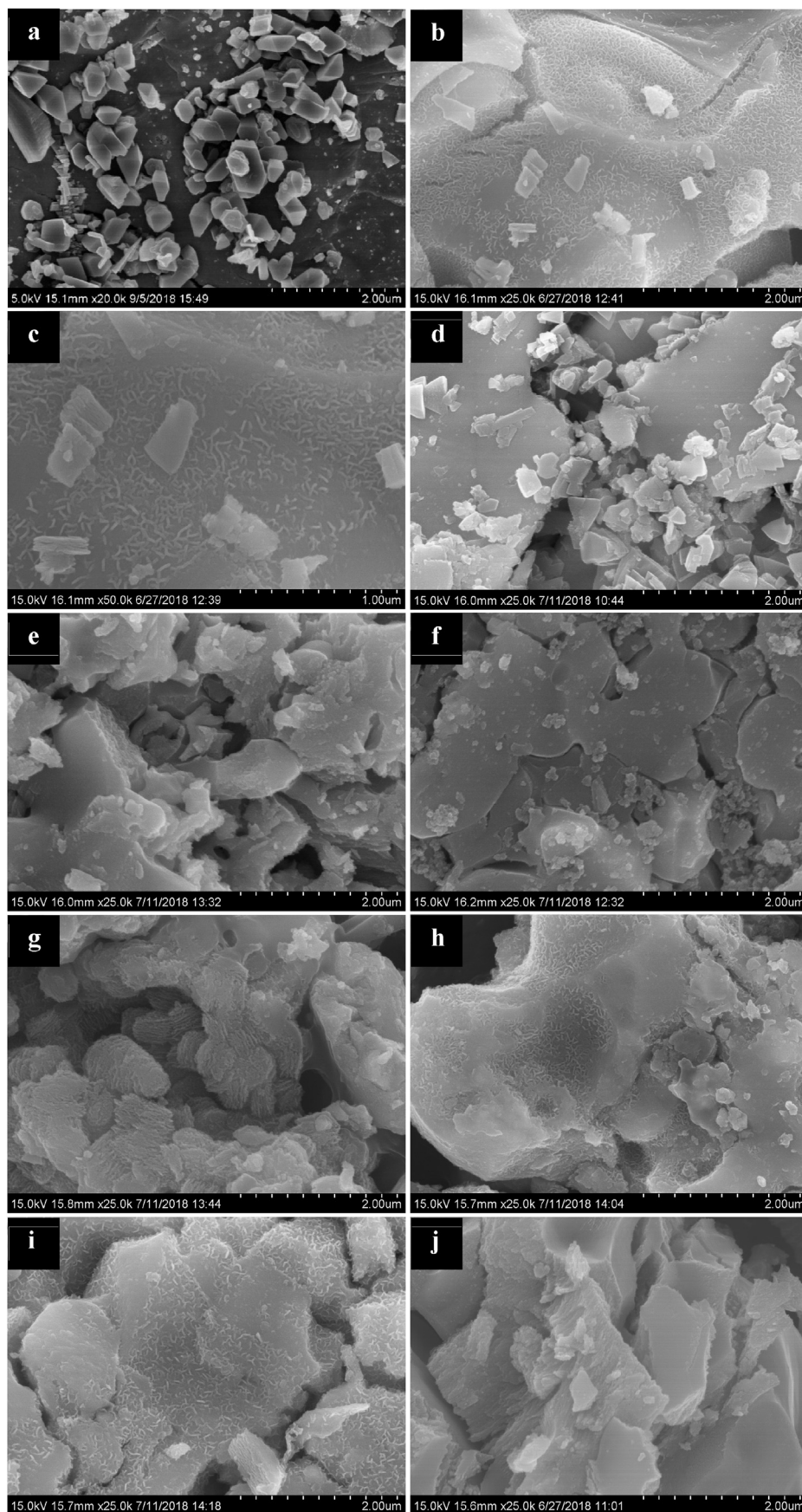


Fig. 2. Representative SEM images of (a) fresh Raney Ni, (b) Raney Ni used in aqueous medium without base, (c) is amplified image of b, (d) Raney Ni used in aqueous medium with NaOH, (e) Raney Ni used in aqueous medium with KOH, (f) Raney Ni used in aqueous medium with Et₃N, (g) Raney Ni used in aqueous medium with NH₃·H₂O, (h) Raney Ni used in aqueous medium with Na₂CO₃, (i) Raney Ni used in aqueous medium with NaHCO₃, and (j) Raney Ni used in aqueous medium with pyridine.

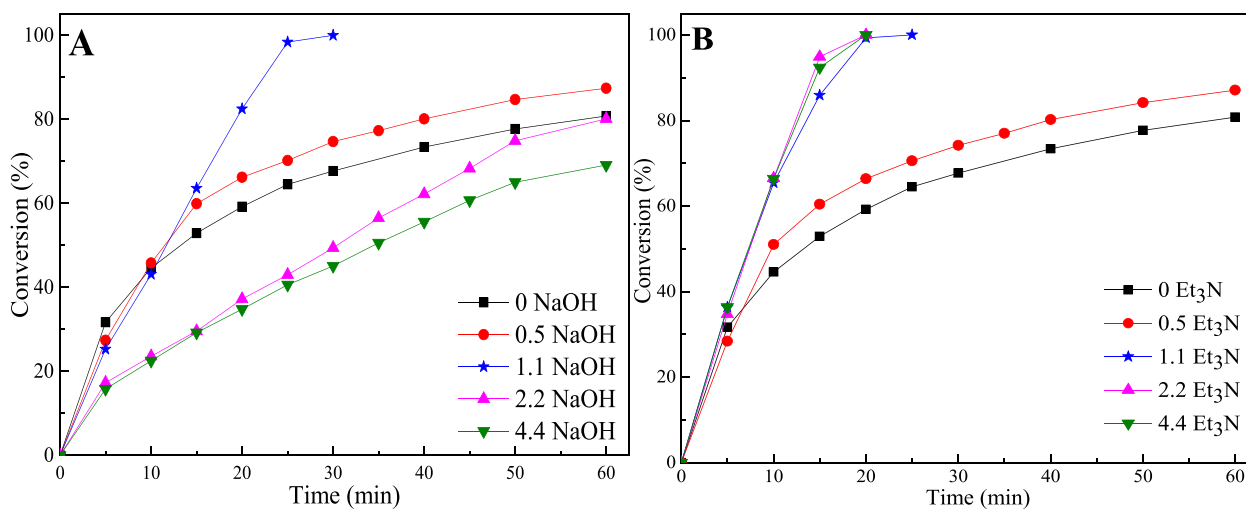
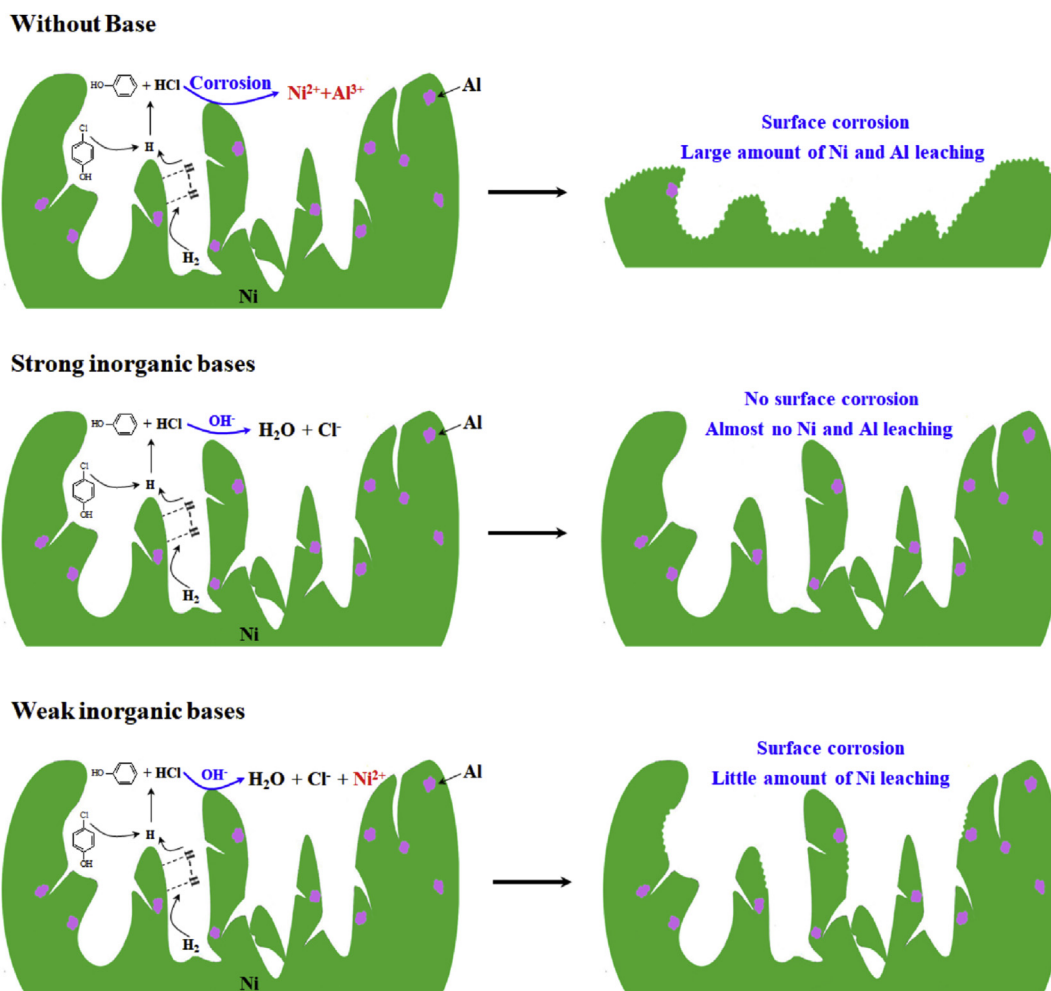
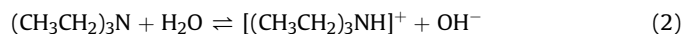


Fig. 3. The effect of NaOH (A) and Et₃N (B) amount on Raney Ni-catalyzed HDC of 4-chlorophenol in aqueous medium. Reaction conditions: 4-chlorophenol (6.20 mmol), Raney Ni (0.12 g), 0 NaOH/Et₃N (0 mmol), 0.5 NaOH/Et₃N (3.12 mmol), 1.1 NaOH/Et₃N (6.85 mmol), 2.2 NaOH/Et₃N (13.70 mmol), and 4.4 NaOH/Et₃N (27.40 mmol), H₂: 10 mL min⁻¹.

On the other hand, the HDC of 4-chlorophenol was carried out where Et₃N addition amount of the reaction medium spanned the range 0–27.40 mmol ([Et₃N]₀/[organic-Cl]₀ = 0–4.4) (Fig. 3B). As

illustrated in Fig. 3B, the HDC rate of 4-chlorophenol increased with the increased Et₃N amount, and the highest HDC rate was observed with 2.2 Et₃N and 4.4 Et₃N. After the HDC reaction, the pH of the

reaction medium with 0.5 Et₃N, 1.1 Et₃N, 2.2 Et₃N, and 4.4 Et₃N decreased to 2.87, 8.44, 9.95, and 10.65, respectively, with the initial pH 9.11, 10.05, 10.77, and 11.20. An obvious decrease of pH with different Et₃N amount was also noticed after HDC reaction. Meanwhile, the amount of active phase Ni and Al leaching are given in Table 2. In the reaction medium with 0.5 Et₃N, 1.1 Et₃N, 2.2 Et₃N, and 4.4 Et₃N, the amount of active phase Ni leaching was greatly reduced due to Et₃N addition. Yet, the amount of active phase Al leaching decreased to minima and then increased with the amount of Et₃N increased. Likewise, Et₃N was added to neutralizing HCl (listed as the following Eq. (2) and Eq. (3)), and thus the stoichiometric amount of Et₃N or more prevented the active phase Ni leaching.



However, the excessive amount of Et₃N also led to the high pH (Eq. (2)), and thus caused dissolution of active phase Al (Eq. (1)).

Further, characterization analyses (SEM, EDXS, and XRD) were carried out to evaluate the influence of NaOH/Et₃N amount. The representative SEM images of fresh and used Raney Ni are shown in Fig. 4. Compared with fresh Raney Ni (Fig. 4a), there are various thread-like structures appeared on surface morphology of the catalyst used in aqueous medium without base. Similar phenomenon was observed in the case of the catalyst used in aqueous medium with 0.5 NaOH (Fig. 4c). As mentioned above, surface morphology of Raney Ni used in aqueous medium with 1.1 NaOH (Fig. 4d) is almost unchanged after the HDC reaction. Yet, surface morphology of Raney Ni used in aqueous medium with 2.2 NaOH and 4.4 NaOH (Fig. 4e and f) are different from that of the fresh catalyst. Moreover, it is evident that the inherent framework of Raney Ni was breakdown, which was resulted from dissolution of Al. These results suggested that an inadequate amount of NaOH could not efficiently prevent HCl corrosion to Raney Ni, yet an excessive amount of NaOH would induce the dissolution of Al, and thus lead to collapse of the catalyst framework. The stoichiometric amount of NaOH could eliminate HCl corrosion to Raney Ni and prevent collapse of the catalyst framework. On the other hand, surface morphology of Raney Ni used in aqueous medium with 0.5 Et₃N and 1.1 Et₃N (Fig. 4g and h) are almost the same as those with 0.5 NaOH and 1.1 NaOH. For Raney Ni used in aqueous medium with 2.2 Et₃N and 4.4 Et₃N (Fig. 4i and j), surface morphology of the catalysts become much rougher than that of the fresh catalyst, which might provide more active sites for interfacial HDC reaction. These SEM images further indicated that a stoichiometric amount of Et₃N could efficiently eliminate the HCl corrosion to Raney Ni and prevent collapse of the catalyst framework.

Meanwhile, surface elemental composition of Raney Ni was analyzed using EDXS (Fig. S3). These EDXS results further confirmed that a stoichiometric amount of NaOH/Et₃N or more could inhibit the interaction of HCl with Raney Ni efficiently. Hence, the accumulation of Cl⁻ on the catalyst surface decreased obviously with NaOH/Et₃N amount increased. In addition, only Ni peaks were found in the XRD patterns of Raney Ni used in aqueous medium with different amount of NaOH/Et₃N (Fig. S4). This implied that no other crystal appeared on catalyst surface after the HDC reaction.

Combining analyses of ICP-OES, SEM, EDXS, and XRD, the mechanism for the potential effect of NaOH/Et₃N amount is proposed in Scheme 2. In aqueous medium with an inadequate amount of NaOH/Et₃N, the byproduct HCl caused significantly drop in the pH values as HCl could not be neutralized completely. The unreacted HCl would cause corrosion to Raney Ni and induced a large amount of Ni and Al leaching, and then led to deactivation of

the catalyst. As a result, the catalytic activity of Raney Ni decreased as the HDC reaction proceeding in aqueous medium with an inadequate amount of base (Fig. 4). In aqueous medium with an excessive amount of NaOH/Et₃N, the HDC of 4-chlorophenol was carried out in strong alkaline medium throughout the reaction time, which prevented HCl corrosion to Raney Ni and avoided the active phase Ni leaching. However, the strong alkaline pH induced dissolution of Al, leading to collapse of the catalyst framework. Moreover, the leaching amount of Al in aqueous medium with an excessive amount of NaOH was much more than that with Et₃N. Also, massive collapse of the catalyst framework could be observed in aqueous medium with an excessive amount of NaOH compared to rougher surface morphology of Raney Ni with the excessive amount of Et₃N (Fig. 4). Thus, an excessive amount of NaOH showed a negative effect on the HDC rate, while the excessive amount of Et₃N still exhibited a promoted effect on the HDC rate. In this sense, a stoichiometric amount of NaOH/Et₃N (1.1 NaOH/Et₃N) enabled the HDC reaction to be took place in the relatively mild alkaline medium, in which HCl corrosion to Raney Ni was eliminated and collapse of the catalysts framework was avoided. So, Raney Ni showed much stronger catalytic activity and accelerated the HDC of 4-chlorophenol when 1.1 NaOH/Et₃N was added. From a practical point of view, the catalytic activity of Raney Ni and the HDC reactivity of 4-chlorophenol can be efficiently regulated by means of adjusting the base and its amount.

3.3. The application of NaOH and Et₃N in Raney Ni-catalyzed HDC reaction

Based on the above discussion, the mechanism of base effect was demonstrated and the best bases and their optimal amount were developed for the further application. Firstly, Raney Ni catalyzed HDC of polychlorinated phenols was established in aqueous medium with 1.1 NaOH/Et₃N (Fig. 5A, see more details in the Supporting Information, Fig. S5). As observed, 2,6-dichlorophenol and 2,4-dichlorophenol are hydrodechlorinated over Raney Ni into monochlorophenols, which can be further transformed into phenol. Moreover, 2,6-dichlorophenol and 2,4-dichlorophenol are the HDC intermediate products of 2,4,6-trichlorophenol, and then they are further converted to monochlorophenol, and finally to phenol over Raney Ni. Therefore, the HDC of 2,6-dichlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol were stepwise processes (Scheme S1). Furthermore, it is important to remark that the excellent HDC of polychlorinated phenols over Raney Ni were achieved with 1.1 NaOH/Et₃N. This confirmed that 1.1 NaOH/Et₃N was promising for efficient HDC of polychlorinated phenols over Raney Ni.

Then, the stability of Raney Ni was evaluated in the HDC reaction with 1.1 NaOH/Et₃N. As shown in Fig. 5B, the conversion of 4-chlorophenol with 1.1 NaOH could reach 100% within 30 min after 5 cycles and gradually dropped to 73.9% in the 10th run. Yet, the conversion of 4-chlorophenol with 1.1 Et₃N was 100% at 30 min for the first 4 times but dropped to 56.3% in the 10th run. The phenomenon that the catalytic activity of Raney Ni gradually decreased when 1.1 Et₃N was used in the HDC reaction could be attributed to the poison effect of Et₃N·HCl (Kume et al., 2008). These results demonstrated that Raney Ni possessed higher stability when 1.1 NaOH was used as proton scavenger, and could be reused for at least 5 times with a complete conversion of 4-chlorophenol. Therefore, a stoichiometric amount of NaOH was a best option for Raney Ni-catalyzed HDC reaction.

4. Conclusions

In the present study, we evaluated the promoted effect of base

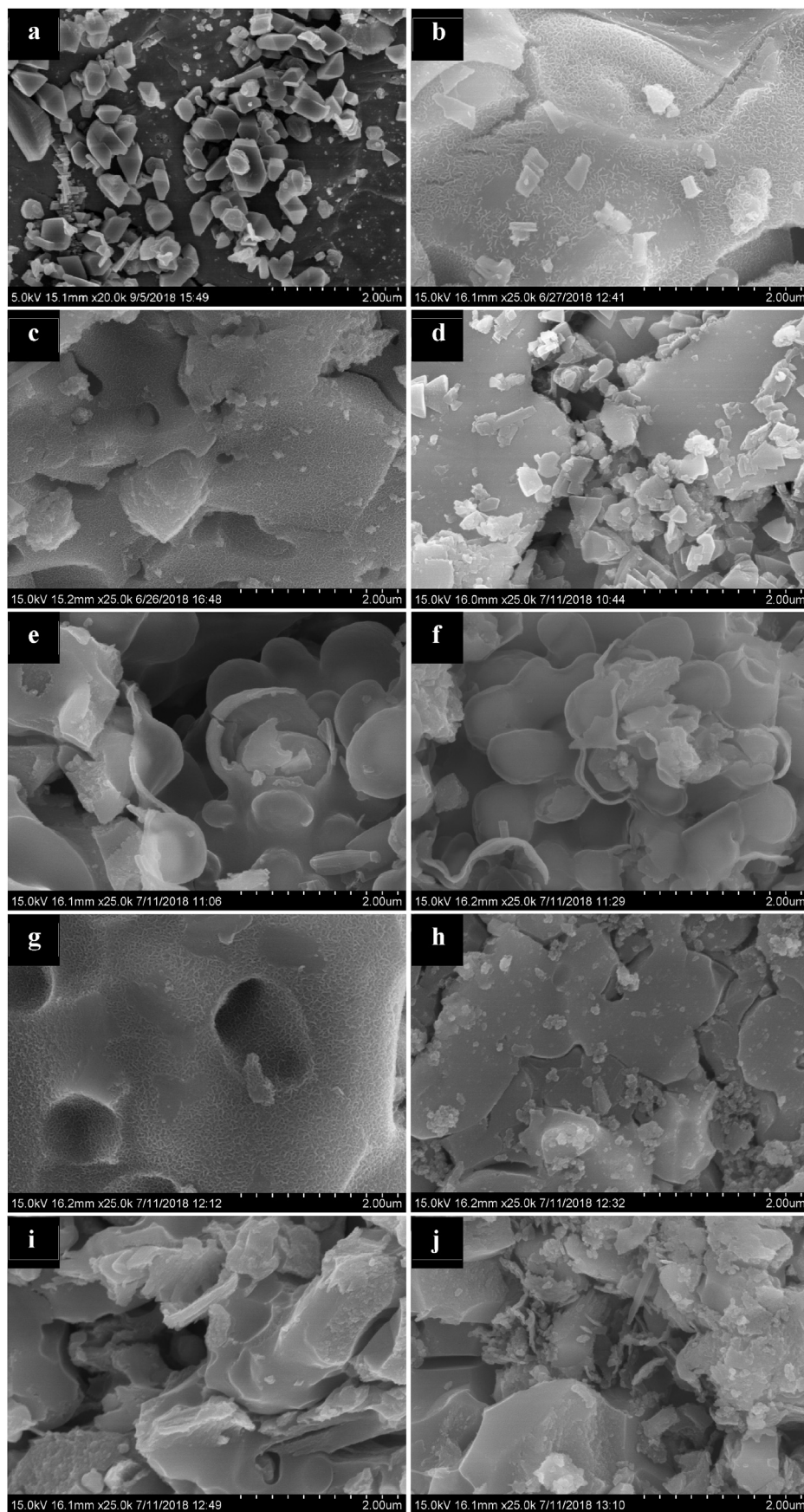
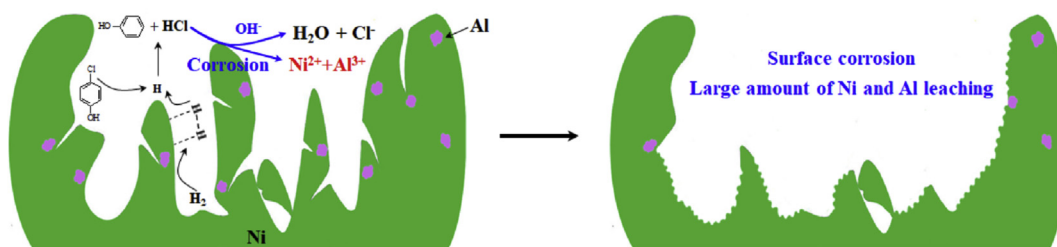
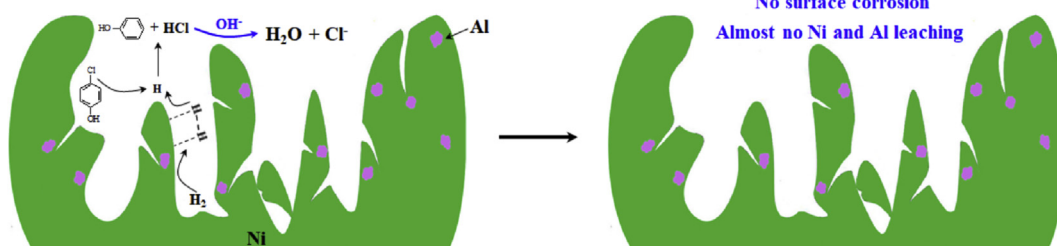
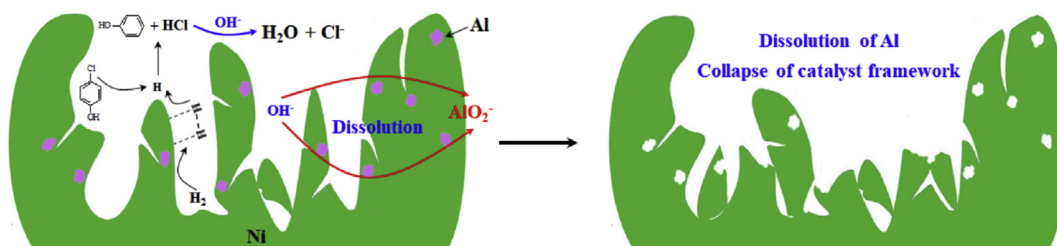
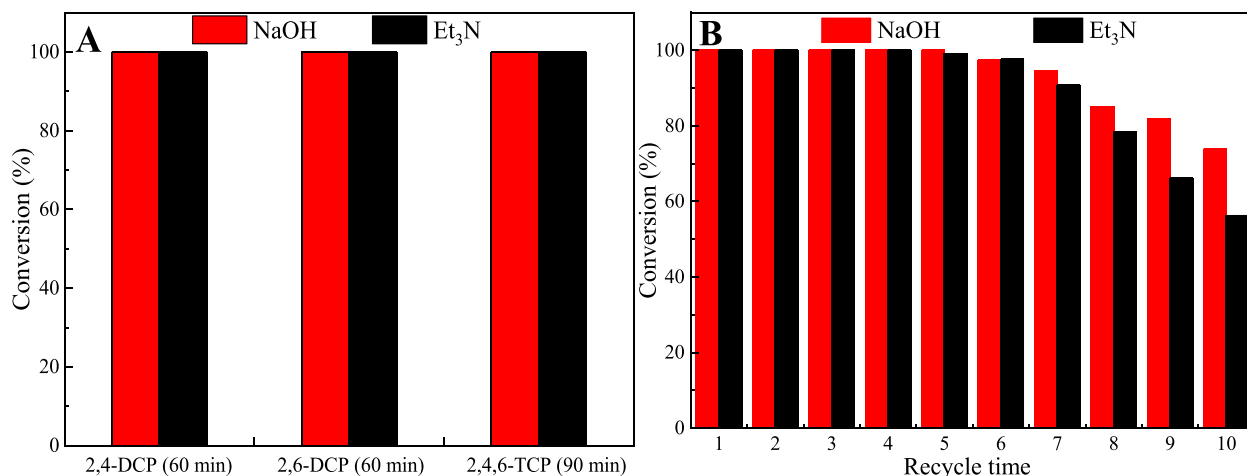


Fig. 4. Representative SEM images of (a) fresh Raney Ni, (b) Raney Ni used in aqueous medium without base, (c) Raney Ni used in aqueous medium with 0.5 NaOH, (d) Raney Ni used in aqueous medium with 1.1 NaOH, (e) Raney Ni used in aqueous medium with 2.2 NaOH, (f) Raney Ni used in aqueous medium with 4.4 NaOH, (g) Raney Ni used in aqueous medium with 0.5 Et₃N, (h) Raney Ni used in aqueous medium with 1.1 Et₃N, (i) Raney Ni used in aqueous medium with 2.2 Et₃N, and (j) Raney Ni used in aqueous medium with 4.4 Et₃N.

Inadequate amount of NaOH/Et₃N**Stoichiometric amount of NaOH/Et₃N****Excessive amount of NaOH/Et₃N****Scheme 2.** Proposed mechanism for the effect of NaOH/Et₃N amount on Raney Ni-catalyzed HDC of 4-chlorophenol.**Fig. 5.** Catalytic HDC of polychlorinated phenols (A) and repeated HDC of 4-chlorophenol (B) over Raney Ni with NaOH and Et₃N. Reaction conditions: chlorophenol (organic-Cl, 6.20 mmol), Raney Ni (0.12 g), NaOH/Et₃N (6.85 mmol), H₂: 10 mL min⁻¹.

on Raney Ni-catalyzed HDC reaction and clarified the mechanism of base promoted effect. It was found that bases significantly promoted Raney Ni-catalyzed HDC of chlorophenol, and strong inorganic bases (NaOH and KOH) and Et₃N were more effective for the

HDC reaction. Moreover, the amount of strong inorganic bases and Et₃N has significant effect on the HDC reaction. The addition of various bases suppressed HCl corrosion to Raney Ni, and decreased active phase Ni and Al leaching. Moreover, a stoichiometric amount

of NaOH/Et₃N could eliminated HCl corrosion to Raney Ni, and prevented collapse of the catalyst framework resulted from dissolution of Al. Furthermore, the stoichiometric amount of NaOH was applicable to the excellent HDC of polychlorinated phenols over Raney Ni, and the catalyst was stable after several recycles. From a practical viewpoint, the stoichiometric amount of NaOH is potentially available for the HDC of wastewater containing chlorophenols since it is cost efficiency and generally easy for practicality. Further investigation is in progress for the technical and economic feasibility of the base promoted HDC in wastewater containing chlorophenols, which is of environmental significance.

Declaration of competing interest

The authors declare no competing financial interest.

CRediT authorship contribution statement

Xuanxuan Ma: Investigation, Data curation, Formal analysis, Writing - original draft. **Sujing Liu:** Data curation, Formal analysis, Project administration. **Ying Liu:** Data curation, Supervision. **Xiaoqiang Li:** Formal analysis, Validation. **Qing Li:** Writing - review & editing. **Guodong Gu:** Writing - review & editing. **Chuanhai Xia:** Funding acquisition, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.125202>.

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