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## COMMUNICATION

## Metal fluoride promoted catalytic hydrogenation of aromatic nitro compounds over Raney Ni

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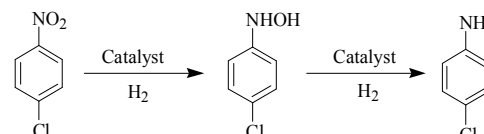
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**The catalytic hydrogenation reactivity of aromatic nitro compounds over Raney Ni was substantially improved when a moderate amount of metal fluoride (NaF, KF, MgF<sub>2</sub>, and CaF<sub>2</sub>) was added into the reaction system.**

Aromatic amines (ANs) are commercially important for the large scale production of many fine chemicals, such as dyes, herbicides, whiteners, pharmaceuticals, and agrochemicals.<sup>1-4</sup> Liquid-phase hydrogenation of nitro aromatic compounds (NBs) over metal catalyst is recognized as an efficient and environmentally friendly procedure to produce ANs as no other harmful effluents are produced except water. In catalytic reaction, the catalyst plays a very important part. Catalysts base on noble and non-noble metals, such as Pt,<sup>5-7</sup> Pd,<sup>8,9</sup> Rh,<sup>10-12</sup> Au,<sup>1-3,13</sup> Ni,<sup>14-18,21-28</sup> and Fe,<sup>19,20</sup> have been widely studied. Even though the noble metal catalysts show a good catalytic performance under mild conditions, their rather rare resource and high cost limit practical applications. Actually, in industrial production, Ni is usually chosen as catalyst rather than noble metals for the hydrogenation of NBs owing to its abundant resources and low price.<sup>14-18,21-28</sup> Therefore, the utilization of Ni catalyst has received considerable attention in the hydrogenation of NBs.

Recently, various types of Ni catalysts, including Raney Ni,<sup>21,22</sup> supported Ni catalysts,<sup>14,23</sup> amorphous alloy Ni,<sup>15,24</sup> and core-shell Ni,<sup>25</sup> have been intensively applied in catalytic hydrogenation of NBs. Moreover, many efforts have been made to improve the catalytic performance of Ni catalyst for hydrogenation of NBs, focusing on the catalyst structure<sup>23-25</sup>, the role of support (TiO<sub>2</sub>,<sup>23</sup> γ-Al<sub>2</sub>O<sub>3</sub>,<sup>26</sup> and SBA-15<sup>14</sup>), the effect of adding a second metal (Pt<sup>27</sup>, Pd<sup>28</sup>, and Rh<sup>12</sup>) or specific modifier (B and P<sup>15</sup>). In some other hydrogenation reactions, a special attention has been paid towards the use of inorganic fluoride as support or modifier for metal catalyst. For example, Coq et al. reported that the use of metal halides, especially inorganic metal fluorides, for supported metal catalysts could obtain more stable and selective materials for the catalytic transformation of chlorofluorocarbons.<sup>29</sup> Gao et al. also had similar report that fluorine-modified Cu/Zn/Al catalysts showed much better catalytic properties for CO<sub>2</sub> hydrogenation to methanol.<sup>30,31</sup> These two methods which introduced inorganic fluoride into metal catalysts obviously improved the catalytic performance. Whether

could it achieve the same promoting effect for catalytic hydrogenation of NBs over Raney Ni by adding a small amount of metal fluoride into the liquid phase reaction system? Herein, various metal fluorides (NaF, KF, CaF<sub>2</sub>, and MgF<sub>2</sub>) were explored to investigate the effect of these metal fluorides on the hydrogenation of NBs to ANs over Raney Ni catalyst.



**Scheme 1** Simplified reaction route of *p*-CNB hydrogenation to *p*-CAN

The simplified reaction route of *p*-chloronitrobenzene (*p*-CNB) hydrogenation to *p*-chloroaniline (*p*-CAN) is displayed in Scheme 1.<sup>2,32</sup> The target product is *p*-CAN and the main intermediate product is *p*-chlorophenylhydroxylamine (*p*-CHB). As shown in Scheme 1, the process involves two steps that *p*-CNB is hydrogenated to produce *p*-CHB, and then *p*-CHB is further hydrogenated to form *p*-CAN. Generally, the hydrogenation of *p*-CNB over Raney Ni catalyst is slowly under mild conditions. The hydrogenation of *p*-CNB over original Raney Ni was repeated three times to guarantee that every batch of Raney nickel could perform similarly (Table 1). To improve the catalytic activity of Raney Ni for the hydrogenation of *p*-CNB, a small amount of NaF was simply added into reaction system (Fig. 1). As illustrated in Fig. 1a, the yield of *p*-CAN reached the maximum within 2.5 h in hydrogenation of *p*-CNB over Raney Ni with a reaction rate of 9.71 mmol<sub>*p*-CNB</sub> g<sub>catal.</sub><sup>-1</sup> h<sup>-1</sup>. However, the yield of *p*-CAN in the hydrogenation with NaF addition could reach the maximum at 1.5 h, with a much higher reaction rate of 16.18 mmol<sub>*p*-CNB</sub> g<sub>catal.</sub><sup>-1</sup> h<sup>-1</sup> (Fig. 1b). These results implied that the small amount of NaF could enhance the catalytic activity of Raney Ni in catalytic hydrogenation of *p*-CNB to a certain degree.

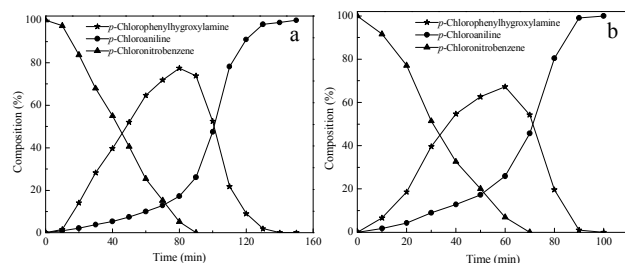
Further optimization was carried out to evaluate the influence of different amount of NaF (added respectively in 0, 1, 5, and 10 percent by weight of the catalyst) on hydrogenation of *p*-CNB over Raney Ni (Fig. 2a). Compared with the hydrogenation without NaF, the hydrogenation rates of *p*-CNB with different amount of NaF addition were all improved to some extent. Within the first 1.5 h, the

average reaction rates of hydrogenations with different amount of NaF were all higher than  $12.57 \text{ mmol}_{p\text{-CNB}} \cdot \text{g}_{\text{cat.}}^{-1} \cdot \text{h}^{-1}$ , while that without NaF was only  $6.28 \text{ mmol}_{p\text{-CNB}} \cdot \text{g}_{\text{cat.}}^{-1} \cdot \text{h}^{-1}$ . As shown in Fig. 2a, the average reaction rate in hydrogenations over Raney Ni with 0%, 1%, 5%, and 10% NaF were about  $9.71 \text{ mmol}_{p\text{-CNB}} \cdot \text{g}_{\text{cat.}}^{-1} \cdot \text{h}^{-1}$ ,  $13.71 \text{ mmol}_{p\text{-CNB}} \cdot \text{g}_{\text{cat.}}^{-1} \cdot \text{h}^{-1}$ ,  $16.18 \text{ mmol}_{p\text{-CNB}} \cdot \text{g}_{\text{cat.}}^{-1} \cdot \text{h}^{-1}$ , and  $13.90 \text{ mmol}_{p\text{-CNB}} \cdot \text{g}_{\text{cat.}}^{-1} \cdot \text{h}^{-1}$ , respectively. This suggested that the catalytic activity decreased in the order  $5\% \text{ NaF} > 10\% \text{ NaF} > 1\% \text{ NaF} > \text{No NaF}$ . The catalytic activity was best when 5% NaF was added.

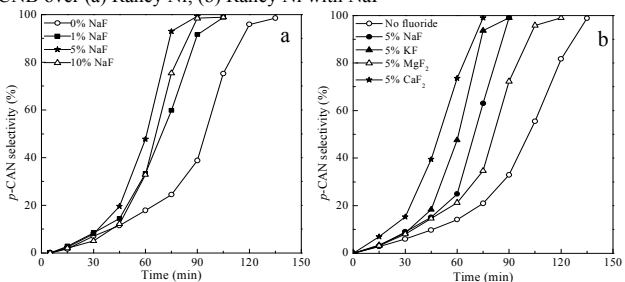
**Table 1** Repeatability of original Raney Ni in the hydrogenation of *p*-CNB

Parallel experiment	Conversion of <i>p</i> -CNB (%)		Yield of <i>p</i> -CAN (%)	
	1.0 h	2.5 h	1.0 h	2.5 h
1	75.6	100	8.2	99.0
2	73.1	100	6.8	98.1
3	75.0	100	7.2	98.5

Reaction conditions: 5.10 mmol substrate, 80 mL methanol,  $0.20 \pm 0.02 \text{ g}$  Raney Ni added NaF in 0 or 5 percent by weight of catalyst, 313 K reaction temperature,  $10 \text{ mL} \cdot \text{min}^{-1} \text{ H}_2$ , 500 rpm stirring speed.



**Fig. 1** Course of the reaction and product distribution for the hydrogenation of *p*-CNB over (a) Raney Ni, (b) Raney Ni with NaF



**Fig. 2** (a) Effect of different NaF amount on the hydrogenation of *p*-CNB over Raney Ni; (b) Effect of different inorganic fluorides on the hydrogenation of *p*-CNB over Raney Ni

Furthermore, in order to test whether other metal fluorides could also promote the hydrogenation of NBs into ANs over Raney Ni, the effect of another three metal fluorides (KF,  $\text{MgF}_2$ , and  $\text{CaF}_2$ ) was investigated. It turned out that the catalytic activity of Raney Ni in hydrogenation of *p*-CNB was also remarkably improved when KF,  $\text{MgF}_2$ , or  $\text{CaF}_2$  was added into the reaction system (Fig. 2b). As demonstrated in Fig. 2b, Raney Ni with 5%  $\text{CaF}_2$  showed the best catalytic activity. Moreover, the effect of KF and NaF on hydrogenation of *p*-CNB over Raney Ni was more or less the same. Yet, the effect of  $\text{MgF}_2$  on the hydrogenation of *p*-CNB over Raney Ni was not as good as  $\text{CaF}_2$ , NaF and KF, but it was still better than that without fluoride. In other words, the hydrogenation rate decreased in the order  $\text{CaF}_2 > \text{KF} > \text{NaF} > \text{MgF}_2 > \text{No fluoride}$ .

Subsequently, the effect of NaF on the hydrogenation of nitrobenzene, *p*-nitrobenzotrile, and *m*-dinitrobenzene over Raney Ni was investigated to explore whether NaF could promote the hydrogenation of other NBs (Table 1). It could be found from Table 1 that hydrogenation rates of the three NBs (nitrobenzene, *p*-nitrobenzotrile, and *m*-dinitrobenzene) were all obviously improved when 5% NaF was added. As shown in Table 1, the yields of ANs in the hydrogenation of NBs over Raney Ni with NaF were

all much higher than that without NaF within the same time. Therefore, it could be concluded that NaF can promote the hydrogenation of aromatic nitro compounds over Raney Ni.

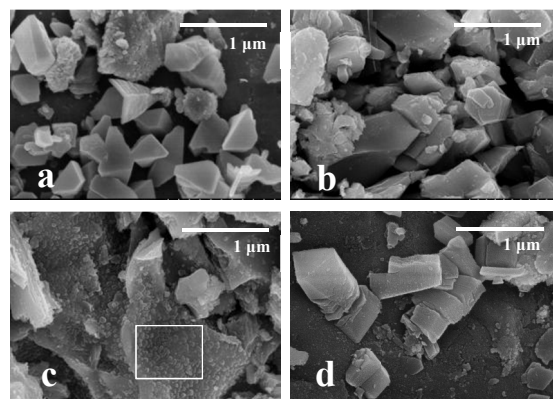
**Table 2** The effect of NaF on the hydrogenation of nitrobenzene, *p*-nitrobenzotrile, and *m*-dinitrobenzene over Raney Ni

Substrate	NaF (%)	Reaction time (h)	Conversion of NBs (%)	Yield of ANs (%)
nitrobenzene	0	1.25	89.8	35.3
nitrobenzene	5	1.25	100	98.9
<i>p</i> -nitrobenzotrile	0	3.00	98.4	67.4
<i>p</i> -nitrobenzotrile	5	3.00	100	99.6
<i>m</i> -dinitrobenzene	0	2.17	100	76.0
<i>m</i> -dinitrobenzene	5	2.17	100	100

Reaction conditions are similar to those in Table 1.

Subsequently, the effect of NaF on the hydrogenation of nitrobenzene, *p*-nitrobenzotrile, and *m*-dinitrobenzene over Raney Ni was investigated to explore whether NaF could promote the hydrogenation of other NBs (Table 2). It could be found from Table 1 that hydrogenation rates of the three NBs (nitrobenzene, *p*-nitrobenzotrile, and *m*-dinitrobenzene) were all obviously improved when 5% NaF was added. As shown in Table 1, the yields of ANs in the hydrogenation of NBs over Raney Ni with NaF were all much higher than that without NaF within the same time. Therefore, it could be concluded that NaF can promote the hydrogenation of aromatic nitro compounds over Raney Ni.

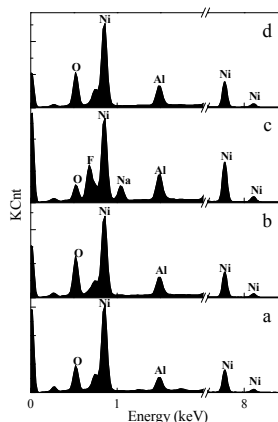
To clarify the mechanism of the promoting effect of metal fluorides on Raney Ni for hydrogenation of NBs, the catalysts were characterized by scanning electron microscopy (SEM), energy-dispersive spectrometer (EDS), and X-ray diffraction (XRD). Fig. 4 shows the representative SEM images of Raney Ni catalysts before and after hydrogenation. The surface morphology of Raney Ni after the hydrogenation was similar to that of original Raney Ni (Fig. 4a and 4b), and their surfaces were clean. Yet, there are some small particles depositing on the surface of Raney Ni after the hydrogenation added NaF (Fig. 4c). SEM-EDS data of the catalysts is given in Fig. 5. The characteristic peaks of O, Ni, and Al were present in all EDX spectra of Raney Ni catalyst before and after the hydrogenation, which revealed that elements of O, Ni, and Al existed in all the catalysts. No other peak was found in the sample of Raney Ni after the hydrogenation without NaF addition (Fig. 5b). However, there were additional peaks for elements of Na and F in the sample of Raney Ni after the hydrogenation added NaF (Fig. 5c), which indicated that the small particles appearing on the surface of Raney Ni after the hydrogenation added NaF were mainly composed of Na and F elements.



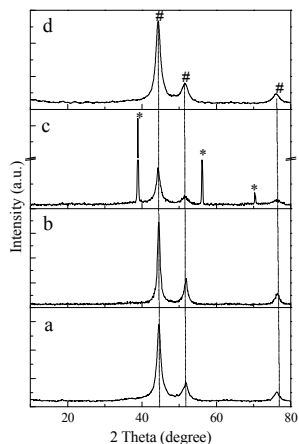
**Fig. 4** Representative SEM images of catalysts (a) original Raney Ni, (b) Raney Ni after hydrogenation, (c) Raney Ni added NaF after hydrogenation, (d) Raney Ni added NaF after hydrogenation and washed with water

Fig. 6 displays the XRD patterns of the four catalysts with different treatment. As shown by the arrows, there were three more intense peaks at  $2\theta=39.0^\circ$ ,  $56.1^\circ$ , and  $70.7^\circ$  in the XRD pattern of Raney Ni after the hydrogenation added NaF compared with that of fresh catalyst. According to JCPDS (Joint Committee on Powder Diffraction Standards) standard card, the extra three peaks at  $2\theta=39.0^\circ$ ,  $56.1^\circ$ , and  $70.7^\circ$  were respectively identified to (2 0 0), (2 2 0), and (2 2 2) NaF planes. Therefore, it would be reasonable to presume that the small particles appearing on the sample of Raney Ni added NaF after hydrogenation was NaF and its existing state was crystal. When the sample of Raney Ni after the hydrogenation added NaF was washed with water,<sup>33</sup> NaF was dissolved and would not be present on the surface of the catalyst (Fig. 4d, 5d, and 6d).

In order to investigate the content distribution of the added NaF in reaction solution and on catalyst surface, the concentrations of fluorine anions (F<sup>-</sup>) in the reaction solution and the water solution of washing the catalyst added NaF with water were measured by ion chromatography (IC). On the basis of IC analysis data, when 5% NaF (10.0 mg) was added, 4.5 mg NaF was found in the methanol solution and 5.3 mg NaF adsorbed on the surface of Raney Ni catalyst. In other words, when NaF was added into the catalytic system, a part of it was dissolved in the catalytic system and another part would absorb on the surface of Raney Ni, which was in accordance with the SEM, EDS, and XRD results (Fig. 4c, 5c, and 6c).



**Fig. 5** EDS Spectra of catalysts (a) original Raney Ni, (b) Raney Ni after hydrogenation, (c) Raney Ni added NaF after hydrogenation, (d) Raney Ni added NaF after hydrogenation and washed with water



**Fig. 6** XRD patterns of catalysts (a) original Raney Ni, (b) Raney Ni after hydrogenation, (c) Raney Ni added NaF after hydrogenation, (d) Raney Ni added NaF after hydrogenation and washed with water; (#) Raney Ni, (\*) NaF

BET measurement is reported in Table 3. The total surface area was found to be similar for all the samples studied, which meant that the introduction of NaF had hardly any influence on the surface area

of catalysts. Hence, the difference in catalytic activity could not be explained in terms of the difference in surface area.

**Table 3** BET data

Catalyst	BET ( $\text{m}^2 \cdot \text{g}^{-1}$ )
Original Raney Ni	62
Raney Ni after hydrogenation	68
Raney Ni added NaF after hydrogenation	65

As mentioned above, Raney Ni catalyst with addition of a moderate amount of metal fluorides exhibited much higher catalytic performance for the hydrogenation of NBs. Furthermore, the introduction of metal fluoride did not change the catalyst surface area. Therefore the difference in catalytic activity could not be explained by the difference in surface area. The possible reason of the promoting effect of these metal fluorides could be referred to the literature,<sup>29</sup> which proposed that the good hydrodechlorination performance of Pd/fluoride catalyst came from an electronic modification of Pd by fluoride species in decoration onto the metal particles. The electron withdrawing effect of these species favored the desorption of Pd-substrate to yield the target compounds. Similar research about the fluorine-modified metal catalysts was also reported by Gao et al.,<sup>30, 31</sup> who found that the introduction of fluorine showed a significant influence on the physicochemical and catalytic properties of the. **According to Coq's and Gao's points, we speculate that the promoting effect of metal fluorides in this work might be interpreted by a possible electronic interaction between the deposited fluoride and Raney Ni, which might be similar to the electron withdrawing effect between Pd and fluoride. The possible electronic interaction will be further investigated in following research.**

## Conclusions

In conclusion, this work presents a remarkably improvement of the catalytic performance of Raney Ni for NBs hydrogenation to ANs. By simply adding metal fluorides into the liquid reaction system, the hydrogenation reaction performed more excellently than that free of metal fluoride. The promoting effect of metal fluorides decreased as the order of  $\text{CaF}_2 > \text{NaF} \approx \text{KF} > \text{MgF}_2 > \text{No fluoride}$ . The added fluorides would deposit on catalyst surface, and thereby change the electronic property of Raney Ni as an electronic modification, consequently leading to a faster conversion of substrate to target compound.

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## Notes and references

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