Chemoselective syntheses of nitrogen-containing compounds from unsaturated nitro compounds by Ni-Sn alloy catalysts

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Abstract: Various supported Ni-Sn alloy catalysts were successfully prepared by hydrothermal method. When hydrogenation of 4-nitrostyrene was carried out by using the supported catalysts under 3 MPa H_2 pressure at 423 K in 1,4-dioxane, TiO_2 supported catalyst showed the highest catalytic performance, i.e., 100% 4-aminostyrene selectivity was obtained at full conversion after 1 h. Furthermore, the catalyst was applicable for chemoselective hydrogenation of other unsaturated nitro compounds to the corresponding unsaturated amines. To our knowledge, it is the first time to obtain significantly high catalytic activity and selectivity of nitro group with Ni-Sn alloy catalyst.

Keywords: Chemoselective hydrogenation, Unsaturated nitro compounds, Supported Ni-Sn alloy catalyst.

1. Introduction (11-point boldface)

Unsaturated amines are the important intermediates for the manufacture of fine chemicals, have been synthesized by the reduction of the corresponding unsaturated nitro compounds. Conventionally, Bechamp process (Fe/HCl) has been employed in the reduction of nitro group.[1] The drawbacks of this process have a large amount of wastes and poor reusability due to a stoichiometric reaction. In contrast, the catalytic hydrogenation of nitro group has overcome the disadvantages.[2] Recently, it has been demonstrated that novel metals, such as Au and Ag, showed significantly high selectivity of nitro group in the hydrogenation of various substituted nitroarenes, with low activity due to their intrinsically poor capability for H_2 activation.[3] On the other hands, a number of transition metals, such as Pt, Pd, Ru, and Ni, have been reported to be highly efficient for the hydrogenation of nitrobenzene.[3] However, it is well known that they show low selectivity of nitro group when one or more reducible groups are present in the same molecule. This unacceptable low selectivity of nitro group prevents the practical application of their catalysts. The most inexpensive Ni among these metals would be a good candidate from the economic and industrial points of view. On the previous work, we prepared various supported Ni-Sn alloy catalysts by hydrothermal method and applied for the hydrogenation of furfural to furfuryl alcohol with H_2 molecule as hydrogen donor, Ni-Sn/TiO_2 alloy catalyst leading to 100% chemoselectivity of carbonyl group at >99% conversion.[4] In continuous research of this catalyst, we found that Ni-Sn/TiO_2 alloy catalysts could be applied to the hydrogenation of unsaturated nitro compounds. Herein, the hydrogenation of 4-nitrostyrene as a model reaction was conducted under H_2 atmosphere over Ni-Sn/TiO_2 alloy catalysts. Additionally, various supported Ni-Sn alloy catalysts were applied to the same reaction to compare the catalytic performance with the above catalyst, and the substrate screening was also investigated.

2. Experimental (or Theoretical)

Ni(II) aqueous solution was added dropwise to Sn(IV) aqueous solution at room temperature, furthermore, support was added to the mixture to set the desired loading amount of Ni_3Sn_2. The pH of the mixture was adjusted to 12 with NaOH aqueous solution. After the hydrothermal reaction at 423 K for 24 h, the resulting precipitate was filtered, washed with distilled water, and dried under vacuum overnight. Finally, the obtained gray powder was treated under H_2 atmosphere at 673 K for 1 h.

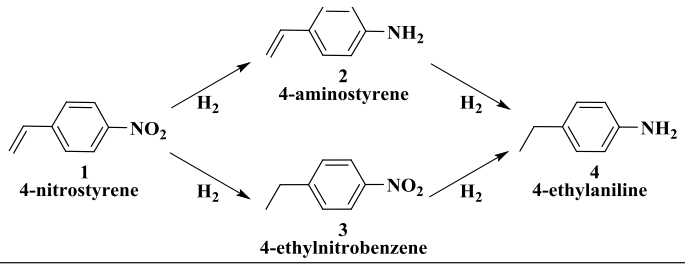
3. Results and discussion

In the XRD patterns of Ni-Sn/TiO_2 catalysts, the characteristic Ni_3Sn_2 peaks were observed in addition to TiO_2 (anatase) peaks, except for 10 wt%Ni-Sn/TiO_2 catalyst. Ni_3Sn_2 crystallinity became significant with

increasing Ni_3Sn_2 loading from 10 to 90 wt%. Distinct Ni_3Sn_2 alloy peaks were detected for other three types of supported catalysts (CeO_2, Al_2O_3, and SnO_2).

The hydrogenation results of 4-nitrostyrene are summarized in Table 1. To our pleasure, all catalysts contained Ni_3Sn_2 detected by XRD results didn't produce 4-ethylnitrobenzene**(3)**. As expected, the Ni_3Sn_2 crystallite sizes decreased remarkably after supported (entries 2-9). For Ni-Sn/TiO_2 catalysts, lower Ni_3Sn_2 loadings than 50 wt% showed tremendous lower catalytic performance (entries 2 and 3) than the bulk (entry 1), unlike smaller Ni_3Sn_2 crystallinity observed from XRD results. On the other hand, the catalytic performance increased with Ni_3Sn_2 crystalline sizes as well as Ni_3Sn_2 loadings (entries 4-6). Finally, 90 wt%Ni-Sn(1.5)/TiO_2 catalyst showed the best result, 100% 4-aminostyrene selectivity at full conversion after only 1 h (entry 6). In XRD patterns, other supported Ni-Sn alloy catalysts showed high 4-aminostyrene**(4)** selectivity because the transformation from 4-nitrostyrene to 4-aminostyrene proceeded with the presence of Ni_3Sn_2 alloy exclusively. From the above, it is demonstrated that Ni_3Sn_2 alloy plays an important role in the chemoselective hydrogenation of 4-nitrostyrene to 4-amonostyrene. However, 90 wt%Ni-Sn(1.5)/TiO_2 catalyst showed the extremely high catalytic performance compared to that of other supported catalysts so that it was regarded as the optimal catalyst.

Table 1. Hydrogenation of 4-nitrostyrene.



Entry	Catalyst	Time(h)	D(nm)[b]	Conv.(%)[c]	Yield(%)[c]			Sel.(%)[c]
					2	3	4	
1	Ni-Sn	11	27.3	100	87	0	13	87
2	10 wt%Ni-Sn/TiO_2	7.5	-	100	40	0	40	40
3	30 wt%Ni-Sn/TiO_2	24	12.4	42	14	0	0	33
4	50 wt%Ni-Sn/TiO_2	2	9.7	92	81	0	8	88
5	70 wt%Ni-Sn/TiO_2	9	11.0	100	90	0	7	90
6	90 wt%Ni-Sn/TiO_2	1	18.9	100	100	0	0	100
7	90 wt%Ni-Sn/CeO_2	4	15.9	100	88	0	12	88
8	90 wt%Ni-Sn/Al_2O_3	14	17.2	100	74	0	19	74
9	90 wt%Ni-Sn/SnO_2	19.5	15.9	97	76	0	4	78

[a]Reaction conditions: Substrate/Ni = 10; 1,4-dioxane, 5 mL; *n*-dodecane, 0.30 mmol; H_2, 3 MPa; 423 K.
[b]The average Ni_3Sn_2 crystalline size derived from the Scherrer's equation for $2\theta = 30.5^o$.
[c]Determined by GC using internal standard technique.

The hydrogenation of 3-nitrostyrene was also carried out with the optimal catalyst to disclose the industrial applicability. The same activity and selectivity of nitro group was obtained as the hydrogenation of 4-nitrostyrene. The catalyst gave 4-aminostilbene and 4-chloroaniline from the corresponding nitro compounds, respectively, with no any of byproduct.

4. Conclusions

Various supported Ni-Sn alloy catalysts were successfully synthesized by hydrothermal method. The catalytic performance increased with Ni_3Sn_2 alloy loadings, which depended on Ni_3Sn_2 crystallinity. Among them, 90wt%Ni-Sn(1.5)/TiO_2 catalyst showed 100% 4-aminostyrene selectivity at full conversion after 1 h. Other supported Ni-Sn catalysts also proceeded the transformation of 4-nitrostyrene to 4-aminostyrene smoothly. Finally, the applicability was investigated with various unsaturated nitro compounds. To our pleasure, the catalyst gave significantly high activity and selectivity toward the corresponding unsaturated amines.

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