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RESEARCH ARTICLE

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Studies on high chemical reactivity of nano-NaH

Abstract A comparison between the initial reaction rates of nanometric and commercial NaH has been studied in four test reactions: 1) hydrogenolysis of chlorobenzene; 2) selective reduction of cinnamaldehyde to cinnamyl alcohol; 3) metallation of dimethyl sulfoxide; and 4) catalytic hydrogenation of olefins. The experimental results indicate that when NaH is used as a chemical reagent in the first three reactions, the initial reaction rates of nano-NaH is 230, 120 and 110 times higher than those of the commercial ones respectively, and it is in agreement with the difference in specific surface areas between these two forms of NaH. When NaH is used as a catalyst component together with Cp_2TiCl_2 in the fourth reaction, catalyst with nano-NaH gives extremely high activity in the hydrogenation of olefins, while the one with commercial NaH gives no activity at all even if a large amount of the commercial NaH is used to make the total surface area equivalent to that of nano-NaH. Thus, it is evident that although large specific surface area is important for nano-NaH to be used as a catalyst component, high surface energy with surface defects seems to be more important. The large specific surface and the activated surface of nano-NaH with high surface energy should be the main factors for their extremely high chemical reactivity, while whether the former or the latter one plays a leading role depends on the type of reactions involved.

Keywords nano-NaH, hydrogenolysis of chlorobenzene, selective reduction of cinnamaldehyde, metallation of dimethyl sulfoxide, catalytic hydrogenation of olefins

1 Introduction

In recent years, quite particular attention has been paid to the research field of nanochemistry [1–6]. With unique physiochemical properties, nanoparticles are found a significant foreground of application in many fields. Liao et al. [7] have prepared nanometric NaH powder by catalytic hydrogenation of the corresponding metal under mild conditions using $TiCl_4$-naphthalene as a catalyst. The prepared nano-NaH could be used as a reagent in some reactions, such as reductions of nitro, carbonyl, nitrile, thiophenols and hylohydrocarbon, etc. [8–11]. Nano-NaH was also used as co-catalysts with titanocene complexes in the hydrogenation of olefins [12–14]. When nano-NaH with a large specific surface area and high chemical reactivity was used, some reactions which were considered to be proceeded in thermodynamics but hardly proceeded in kinetics could be carried out efficiently [8,15–18]. The quantitative relationship among the chemical reactivity, particle size and specific surface area in the preparation of superfine magnesium powers was studied [17]. In this paper, a comparison of the difference in initial reaction rates between nanometric and commercial NaH, as well as the quantitative relationship of their chemical reactivities in four test reactions: 1) hydrogenolysis of chlorobenzene; 2) selective reduction of cinnamaldehyde to cinnamyl alcohol; 3) metallation of dimethyl sulfoxide; and 4) catalytic hydrogenation of olefins, was reported. The main factor of the high chemical reactivity of nano-NaH was also studied via the reaction rate.

2 Experimental

2.1 Reagents and apparatuses

Tetrahydrofuran (THF), toluene, chlorobenzene, cinnamaldehyde and dimethylsulfoxide are all in AR grade. The purity of 1-hexene is 98% and the 1-octene is in CP grade. The

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commercial NaH is from Serva Feinbiochemica and the Cp_2TiCl_2 is from Alfa. The purity of sodium metal is 98%.

Samples obtained in experiments were characterized and measured by JEM-1200EX electron microscope (Japan), Shimadzu GC-14 A gas chromatograph (Japan), 102G gas chromatograph (Shanghai) and AUTOSORB-IMP (the Quatachrome Company of America).

Nano-NaH powder was prepared according to the method reported by Liao et al. [7]. With regard to the comparability, nanometric and commercial NaH were both treaded by the same methods, such as washing with THF and centrifugalization, etc. Therefore, the oils on the surface of commercial NaH were removed. All reactions and operations were carried out under dry argon atmosphere using Schlenk technique.

2.2 Hydrodechlorination of chlorobenzene

NaH (13.5 mmol), THF (10 mL) and chlorobenzene (5 mmol) were added into a dry three-necked and jacketed flask, which had been evacuated and flushed with argon. The reaction mixture was stirred magnetically in refluxing THF solvent and the temperature was kept constant by a thermostat in oil. Samples were taken from the reaction mixture were analyzed by Shimadzu GC-14A gas chromatograph equipped with a 3-M DEGS (20%) column and a FID detector.

2.3 Selective reduction of cinnamaldehyde

NaH (3 mmol) and THF (15 mL) were placed in a three-necked, jacketed flask which was evacuated and filled with argon. The mixture was kept in agitation at 45°C. Cinnamaldehyde was then added after 15 min. Samples were taken from the reaction mixture at regular intervals and hydrolyzed by adding a drop of water. After centrifuging for 5 min, the hydrolysis was determined by Shimadzu GC-14A gas chromatograph with a PEG-20 M capillary column of 30 m and a FID detector.

2.4 Metallation of dimethyl sulfoxide

The reaction flask with a self-sealing silicon rubber septum and a sheath of constant temperature was evacuated and filled with argon. Quantitative NaH and 15 mL THF were then added. The temperature was maintained 45°C below zero by a thermostat (KRYOFLEX KF40). Agitation was provided by a magnetic stirrer. Dimethy sulfoxide was added in a ratio to the flask 15 min later. The hydrogen yielded in the reaction was measured with a constant-pressure gas burette.

2.5 Catalytic hydrogenation of olefins

The hydrogenation of olefins was carried out in a three-necked, jacketed flask closed with a self-sealing silicon rubber septum, and connected to the vacuum, argon and hydrogen lines, and to a constant-pressure gas burette. NaH weighted up exactly was added under argon. The argon was evacuated and hydrogen was passed into the reaction vessel. The 10 mL of toluene, 2 mL of 1-hexene or 2 mL of 1-octene were injected through the silicon rubber septum and stirred for 15 in at 20°C. Then, 0.2 μmol of Cp_2TiCl_2 already dissolved in toluene was injected and hydrogen uptakes were immediately followed by using a constant-pressure gas burette.

3 Results and discussion

3.1 Discussion of reaction activity in four test reactions

One of the special features of nanoparticles is their large specific surface area. In this paper, the specific surface areas of nanometric and commercial NaH were measured by BET measurements. The specific surface area of nanometric NaH is around 90 m^2/g, while that of the commercial NaH is too small to measure accurately (around 1.4 m^2/g).

Figure 1 shows the TEM images of nano-NaH. The average primary size of nanometric NaH is 23 μm [7], while that of the commercial NaH is 2.3 μm observed by optical microscope. With the analogous particle states, the specific surface area is in reversely proportional to the particle diameter [18]. As the specific surface area of nano-NaH and the difference of particle diameters between the two forms, the specific surface area of commercial NaH is around 0.9 m^2/g, which is a little different from the results of BET. The difference in specific surface areas between nanometric and commercial NaH is around two orders of magnitude. As NaH is insoluble in any organic solvent, the related reactions are gas-solid phase reactions, liquid-solid phase reactions and solid-solid phase reactions. It is clear that for a reaction involving gas-solid or liquid-solid phase, the reaction rate is usually directly proportional to the specific surface area of the solid phase. The larger the surface area of the solid phase is, the faster the rate of chemical reactions. In this paper, a comparison between

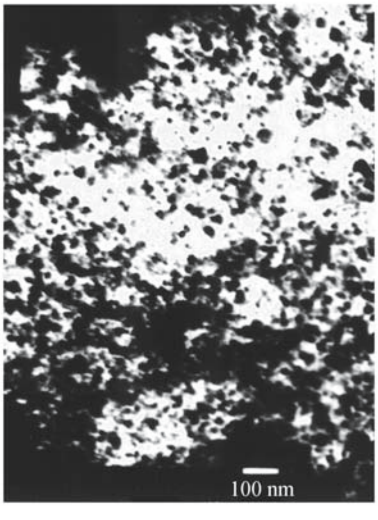

Fig. 1 Transmission electron microscopy (TEM) images of nanometric sodium hydrides

the initial reaction rates of nanometric and commercial NaH has been studied in four test reactions

$$C_6H_5Cl + NaH \rightarrow C_6H_6 + NaCl \qquad (1)$$

$$C_6H_5Cl = CHCH = O + NaH \rightarrow C_6H_5CH = CHCH_2ONa$$
$$\xrightarrow{H_2O} C_6H_5CH = CHCH_2OH \qquad (2)$$

$$CH_3SOCH_3 + NaH \rightarrow CH_3SOCH_2^-Na^+ + H_2 \qquad (3)$$

$$CH_2 = CH(CH_2)_x CH_3 + H_2 \xrightarrow{Cp_2TiCl_2/NaH}$$
$$CH_3(CH_2)_{x+1} CH_3 + H_2 \quad x = 3 \text{ or } 5 \qquad (4)$$

Equation (1) was employed as a typical reaction because nano-NaH is an effective reagent for dehalogenation of organic halogen compounds, which is a significant subject related to environmental protection [8,19]. In Eq. (2), nano-NaH was used as a reducing agent for the selective reduction of α,β-unsaturated aldehydes to the corresponding alcohols with high selectivity, in which the C=C was saved [15,20]. In Eq. (3), the metallation of dimethyl sulfoxide was carried out as well as the hydrogen was sent out from the methyl when nano-NaH was used. This reaction was carried out at 45°C below zero because of the extremely fast reaction rate which could not be measured at normal temperature. Equatino (4) was chosen as a typical reaction because the binary catalysts of Cp_2TiCl_2/NaH have specific selectivity to substrate and high chemical reactivity in catalytic hydrogenation of olefins, in which the terminal olefins were hydrogenated while internal and cyclic alkenes were not reacted and no isomerization. The former three of the four test reactions were stoichiometrical reactions, in which nano-NaH was used as a reducing agent. While the fourth reaction was a catalytic reaction, in which nano-NaH was used as a co-catalyst.

3.2 High reactivity of nanometric NaH

The comparison of chemical reactivities between commercial NaH and nano-NaH in the first three stoichiometrical reactions is showed in Table 1. It can be seen from Table 1 that the chemical reactivity of nano-NaH was much larger than that of the commercial one under the same reaction conditions. When commercial NaH was used, the conversions of reactions were low and the concentrations of substrates in the later period were still high. While the nano-NaH was used, the conversions were high and the concentrations of substrates in the later period were very low. Because of the difference of conversions, the difference of their reactivities could not be reflected truly. The remarkable difference of chemical reactivities leads to the different concentrations of substrates during the medium or later period. In order to avoid the influences above on the rate of chemical reactions, the differences of the initial reaction rates between nanometric and commercial NaH were quantitatively studied (Table 2). Table 2 shows that the difference in the reaction rates between nanometric and commercial NaH is around two orders of magnitude when NaH is used stoichiometrically as a reducing agent, which is in agreement with the difference of their specific surface areas. These results indicate that the large specific surface area of nano-NaH is the main factor for its extremely high chemical reactivity when it is used as a reducing agent.

Table 1 A comparison of chemical reactivities between commercial and nanometric sodium hydride

Test reactions	Commercial NaH	Nanometric NaH
Conversion of hydrogenolysis of chlorobenzene /%[a]	1.3	74.5
Conversion of selective reduction of cinnamaldehyde to cinnamyl alcohol /%[b]	1.4	95.2
Conversion of metallation of dimethylsulfoxide /%[c]	0.4	23.1

Note: NaH is used as a chemical reagent; reaction conditions: [a] hydrogenolysis of chlorobenzene: 5.4 mmol NaH, 2.0 mmol chlorobenzene, 10 mL THF, 8 h, normal pressure, in refluxing THF; [b] selective reduction of cinnamaldehyde to cinnamyl alcohol: 3 mmol NaH, 2.85 mmol cinnamaldehyde, 10 mL THF, 3 min, normal pressure, 45°C; [c] metallation of dimethyl sulfoxide: 15 mL THF, 4 mmol NaH, 4.8 mmol dimethyl sulfoxide, 10 s, –45°C, normal pressure.

Table 2 A comparison of initial reaction rates between commercial and nanometric sodium hydride

Test reactions	Commercial NaH	Nanometric NaH
Initial rate of hydrogenolysis of chlorobenzene/mmol/L·min	0.004 1	0.96
Initial rate of selective reduction of cinnamaldehyde to cinnamyl alcohol/mmol/L·min	0.121	14.3
Initial rate of metallation of dimethyl sulfoxide /mmol H_2/L·s[a]	0.112	12.3

Note: Reaction conditions are the same as those in Table 1 except reaction time, [a] the average value of the rate of releasing hydrogen in the first 5 s.

Table 3 shows the catalytic activities of nanometric and commercial sodium hydrides as cocatalysts in the hydrogenation of olefins catalyzed by Cp_2TiCl_2/NaH. When nano-NaH is used as a cocatalyst with Cp_2TiCl_2 in the hydrogenation of 1-hexene, this catalyst system gives very high catalytic activity (initial turnover frequency, TOF_{initial}), while the commercial NaH incorporated with the same Cp_2TiCl_2 does not show any activity at all. The TOF of nano-NaH reaches to 313 ($n(H_2)/n(\text{Ti}\cdot\text{s})$) and the catalyst efficiency (turnover, TO) is 25,000 ($n(H_2)/n(\text{Ti})$). In the hydrogenation of 1-octene, the TOF of nano-NaH reaches to 113 ($n(H_2)/n(\text{Ti}\cdot\text{s})$) and the TO is 17,000 ($n(H_2)/n(\text{Ti})$), while the commercial NaH incorporated with the same Cp_2TiCl_2 shows no activity at all even if a large amount of the former is used to make a total surface area equivalent to that of nano-NaH. The results above indicate that when nanometric and commercial NaH are used as a cocatalyst with Cp_2TiCl_2 respectively in catalytic hydrogenation of olefins, the former gives very high catalytic activity while the latter does not show any activity at all.

Table 3 A comparasion of anometric and commercial sodium hydride as cocatalyst in the hydrogenation of olefins catalyzed by Cp_2TiCl_2/NaH

Catalyst	Substrate	$TOF_{initial}$ /s^{-1} a)	TO b)
Cp_2TiCl_2/NaH (nanometric)	1-hexene	313	5300
Cp_2TiCl_2/NaH (commercial)	1-hexene	0	0
Cp_2TiCl_2/NaH (nanometric)	1-octene	113	17000
Cp_2TiCl_2/NaH (commercial)	1-octene	0	0
Cp_2TiCl_2/NaH (commercial)	1-octene c)	0	0

Note: Reaction conditions: 10 mL toluene; 2 mL 1-hexene or 1-octene, 0.2 μmol Cp_2TiCl_2, 0.5 mmol NaH, 2 h, 20°C, normal pressure; a) $TOF_{initial}$ (mol H_2/mol Ti · s) of the average value in the first 30 s; b) catalyst efficiency TO (mol H_2/mol Ti); c) using very large amount of commercial NaH (39 mmol) to make its total surface area equivalent to that of nano-NaH.

4 Conclusion

The experimental results indicate that large specific surface area of nano-NaH is the main factor for its extremely high chemical reactivity in comparison with commercial one when it is stoichiometrically used as a reducing agent. Although the large specific surface area is important, it is probably not the main factor when NaH is used as a catalyst component together with Cp_2TiCl_2 in the fourth reaction. As the particle size of NaH reduces to nanosacale, the ratio of surface molecules increases faster. Because the state of surface molecules and system molecules are different, the surface energy of nano-NaH increases due to the large ratio of surface molecules and surface defect, which is probably the key factor of its high catalytic activity as a catalyst component. The large specific surface and the activated surface of nano-NaH with high surface energy should be the main factors for their extremely high chemical reactivity, while whether the former or the latter one plays a leading role depends on the type of reactions involved.

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