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Ni-Silicides nanoparticles as substitute for noble metals for hydrogenation of nitrobenzene to *p*-Aminophenol in sulfuric acid

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ABSTRACT

The hydrogenation of nitrobenzene (NB) in acid medium is regarded as the most promising route to prepare *p*-aminophenol (PAP). The noble metals such as Pt have been reported as commercial catalysts but base metals are inactive due to strong acids needed in the reaction medium. Therefore, Ni-based catalyst has been attempted using solid acids, however, the results are not attractive. In this work, in order to improve the acid-resistance of Ni in sulfuric acid, we insert Si into the Ni crystal structure to form Ni-silicides. The as-prepared supported Ni-silicides nanoparticles exhibit excellent acid-resistance and perform high activity and selectivity of the entitled reaction. $NiSi_2$ nanoparticles supported on acid-treated active carbon are highly active and selective to convert NB to PAP in sulfuric acid. The XPS measurements show that the Ni in the Ni-silicides donates electrons to silicon, but the Ni valence is still far lower than nickel oxide, which causes its stability in acids and the activity to hydrogen activation is partially reserved. Thus, the catalysts exhibit excellent stability in alloy structure, morphology, and catalytic performance in reuses, suggesting the Ni-silicides nanoparticles as the promising substitute for precious metal for PAP manufactures.

1. Introduction

p-Aminophenol (PAP) is an important intermediate and being widely used in the manufacturers of medical drugs e.g. paracetamol and acetaminophen, anticorrosion agents, and dyeing agents [1–3]. Commonly, PAP is produced from phenol, *p*-chloronitrobenzene or *p*-nitrophenol, which has several drawbacks and suffers a poor overall yield [4,5]. The hydrogenation of nitrobenzene (NB) to PAP using Pt/C catalyst in acid medium is regarded as the most promising route owing to low economical feature and high quality product [6]. The reaction involves partially hydrogenation of NB to phenylhydroxylamine (PHA), followed by Bamberger's rearrangement in situ to PAP in the presence of mineral acid. Aniline becomes the main side product through the overhydrogenation of NB [2,3]. Carbon supported noble metal catalysts, especially Pt/C, are considered as the best catalyst for this reaction, whereas the high price and the inevitable loss of precious metal by corrosion limit its further application. Therefore, several attempts have been made to replace mineral aqueous acid by solid acid to eliminate the corrosion. However, the yield of PAP is not attractive [7,8]. In addition, noble metals suffering from low selectivity to PAP have been reported due to significant excessive hydrogenation of PHA to form aniline. Alternative of cheap and abundant base metals such as Ni to Pt or other noble metals was tried [9–11]. Considering transition metals always suffer from the acid corrosion, further modification to form novel materials with excellent acid-resistance is increasingly necessary. Binary alloys of Ni-silicides coating films was reported to have good corrosion resistance in the aqueous solutions of dilute acid solution [12,13]. To date, metal silicides have attracted grown attentions in many fields, including complementary metal-oxide-semiconductor devices [14,15], hydrogen evolution reaction [16], photoelectrochemical water splitting [17,18], thin film coatings [13,19], and especially some catalytic applications. For example, Nuzzo et al. reported the synthesis of metal silicides and their high activity and selectivity for the competitive dehydrogenation and hydrogenolysis of cyclohexane [20]. Recently, Baiker et al. revealed that amorphous $Pd_{81}Si_{19}$ exhibited a more than 50 times higher TOF than a conventional Pd/SiO_2 catalyst toward the semihydrogenation of a propargylic alcohol using "supercritical" CO_2 as solvent [21]. Liang et al. reported silicon modified Reney-Ni presented

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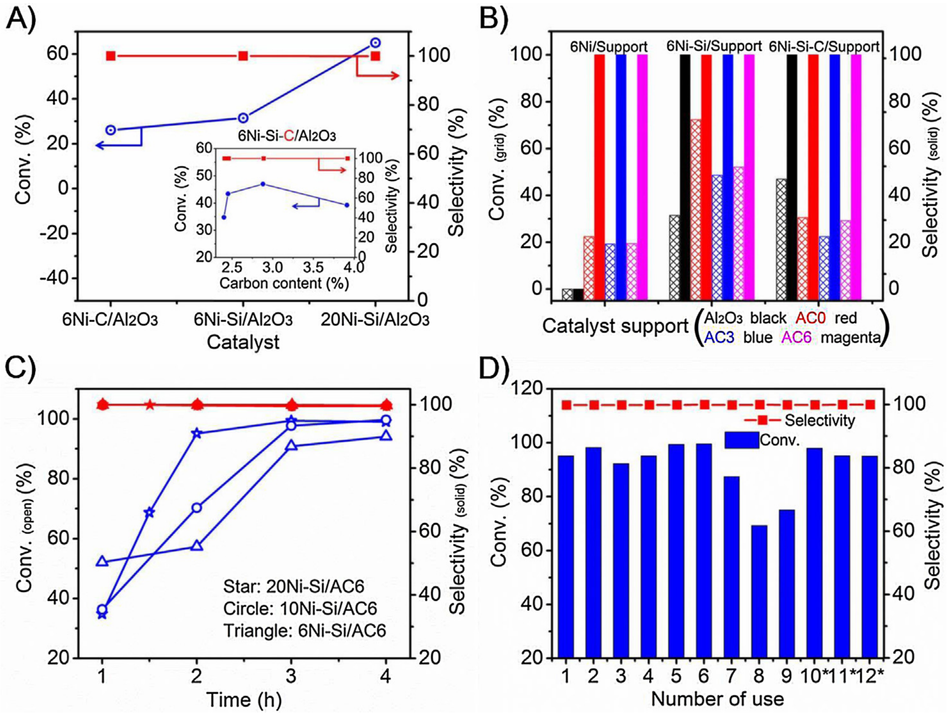

Fig. 1. Results of catalytic experiments. A) Catalyst supported on Al_2O_3, and the inset is Ni-Si-C/Al_2O_3 with different carbon contents. B) Support influences on catalytic performance of 6Ni/Support, 6Ni-Si/Support, and Ni-Si-C/Support. Reaction conditions: 60 mg catalyst, 80 mg nitrobenzene, 20 mL 1.5 mol/L H_2SO_4 solution, 1 MPa H_2, 393 K, 1 h C) Catalytic activity of yNi-Si/AC6 at various reaction time. D) The recycle experiment results of 20Ni-Si/AC6. The experiment was conducted at the conditions: 60 mg catalyst, 80 mg nitrobenzene, 20 mL 1.5 mol/L H_2SO_4 solution, 1 MPa H_2, 393 K, 2 h. Reaction 10* to 12* used 10 mL 3.0 mol/L H_2SO_4 solution and 10 mL ethanol as solvent. Catalyst was filtrated, washed, and dried at 353 K before next use.

Table 1
Comparison of catalysis performances on reported catalysts used for hydrogenation of NB to PAP.

			Reaction conditions						Catalysis performance		
	Catalyst	Loading (%)	Acid	Surfactant	T(K)	P(MPa)	Time(h)	n_{NB}/n_{metal}	Conv.(%)	PAP selectivity(%)	Ref.
1	20Ni-Si/AC6	20	H_2SO_4	×	393	1	3	3	99	100	This work
2	6Ni-Si/AC6	6	H_2SO_4	×	393	1	4	11	100	100	
3	Pt/C	3	H_2SO_4	×	353	0.7	8	15111	97	77	[4]
4	Pt/activated characol	5	H_2SO_4	√	358	0.5	1.5	25000	100	70	[29]
5	Pt/C	1.5	H_2SO_4	√	363	0.07	–	15115	100	85	[30]
6	PVP-$PdCl_2$-0.5$LaCl_3$	8×10^{-3} mol Pd/L	H_2SO_4	√	357	0.1	3	300	100	46	[31]
7	Au/TiO_2	0.9	H_2SO_4	×	373	1	4	1078	78	81	[32]
8	Pt/ZrO_2	2	Zirconium sulphate	×	353	2	8	38161	87	88	[33]
9	Pt-Sn/Al_2O_3	0.04Pt0.07Sn	CO_2	×	413	0.2	4	1000	20	85	[34]
10	Pb-Pt/MgAPO-5	0.015Pt	MgAPO-5	√	438	0.4	2	4200	100	76	[3]
11	Pt/C	3	carbon	√	383	0.4	10	10875	61	78	[1]
12	Pt/C	3	CF_3COOH	×	353	0.1	3	29870	41	26	[35]
13	Pt-$S_2O_8^{2-}$/ZrO_2	0.1	$S_2O_8^{2-}$/ZrO_2	√	423	0.4	2	1753	52	47	[7]
14	Pt/ZSM-5	1	ZSM-5	×	523	0.1	0.5	–	35	55	[36]
15	Pt/SiO_2	–	FSAPO-5	√	423	0.9	–	–	100	49	[37]
16	CN/Ni/Al_2O_3	4	H_2SO_4	×	393	1	2	12	80	100	[23]
17	Ni/SiO_2	20	SO_3H—C/SBA-15	√	393	0.8	3	9	85	24	[38]
18	NiCoB/SAPO-5		SAPO-5	√	383	0.4	3	5	90	50	[39]
19	Ni-Pt/ZSM-5	10Ni1Pt	H_2SO_4	×	353	2.8	–	50:1 w/w	93	63	[40]

high selectivity to semi-hydrogenated products (2-butene-1,4-diol) from hydrogenation of highly concentrated 2-butyne-1,4-diol [22]. These results documented have shown that the silicon added to form alloys with noble metals or transition metals modify the catalysts in both stability and products selectivity. But their catalytic property for hydrogenation under acid conditions has never been reported.

In this study, we report several Ni-silicides catalysts used for the entitled reaction with different supports, nickel loadings, and carbon coating contents via a very simple preparation route. According to characterizations, highly dispersed uniformly sized Ni-silicides nanoparticles exhibit superior acid-resistance under hydrothermally acid conditions with structural and catalytic stability in reuses and show excellent catalytic properties for producing PAP from hydrogenation of NB in harsh acidic medium.

2. Experimental

2.1. Support preparation

Rod-like γ-Al_2O_3 was synthesized by hydrothermal method [23]. Briefly, aluminum isopropoxide (Aladdin, 96 g) was added to