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Rapid Microwaves Synthesis of $CoSi_x$/CNTs as Novel Catalytic Materials for Hydrogenation of Phthalic Anhydride

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Abstract

$CoSi_x$/CNTs catalysts with different $CoSi_x$ phases ($CoSi_2$, CoSi) have been rapidly synthesized via a microwave-assisted route and applied for the liquid phase hydrogenation of phthalic anhydride. The synthesized catalysts were analyzed and characterized by X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy-energy dispersive X-ray spectroscopy, thermogravimetric/derivative thermogravimetric analysis. The reaction progress of cobalt silicides and the ratio of Co:Si were monitored at different microwave irradiation times by XRD, giving insight into the formation mechanism.

Compared to the Co/CNTs catalyst, all the prepared $CoSi_x$/CNTs catalysts exhibited excellent activity and good selectivity to phthalide under mild reaction conditions (180-220 °C and 4.0 MPa H_2). This novel methodology can be applied to the synthesis of other transition metal silicides such as Cu_4Si, Ni_2Si, and FeSi.

Keywords: Microwave-assisted preparation, Cobalt silicides, Hydrogenation, Phthalic anhydride

1. Introduction

Metal silicides, the family of refractory intermetallic compounds between metals and silicon, have various excellent physical and chemical properties, which are useful for the applications including electronics and silicon-based devices [1]. Cobalt silicides have been shown to be high-melting point materials with very low resistivity and good chemical stability, offering the possibility for use as nanoscale electrical interconnections [2]. As novel catalytic materials, only a few reports have been published on cobalt silicide. It has recently been investigated for use as a solid catalyst for the formation of carbon nanotubes [3], and in silicon carbide composites for structural application [4]. In our early research, CoSi/SiO_2 synthesized by metal organic chemical vapor deposition of $Co(SiCl_3)(CO)_4$ showed high catalytic activity and selectivity for naphthalene hydrogenation [5].

During the recent years, cobalt silicides have been synthesized by various methods, such as spontaneous chemical vapour transport reaction, metal organic chemical vapour deposition, and focused electron beam-induced deposition [2,6-10]. Although these methods are very useful for preparing cobalt silicide samples, several shortcomings have restricted their

application in catalysis, including the high cost of devices used for synthesis, and the large consumption of energy and time due to the large energy barrier for the diffusion of solids [11]. These drawbacks motivate the development of new synthesis methods that can overcome these problems and facilitate the formation of well-dispersed metal silicides for catalytic applications under controllable conditions.

Microwave-assisted solid-state synthesis is a simple, fast, energy-efficient, and environmentally friendly technique. The fast synthesis is attributed to the nature of the microwave volumetric heating and to the associated thermal runaway effect [12]. This method has been reviewed extensively in the literature [13-15], and a number of intermetallic compounds have been produced with the aid of microwaves [11]. The rapid synthesis may lead to smaller grain size and to consequently better mechanical properties, and improve product uniformity. This is very interesting from an application point of view. Vaidhyanathan et al. prepared $CoSi_2$ samples by using high purity cobalt (particle size, 270 μm) and silicon (particle size, 37 μm) as starting materials, with high purity amorphous carbon powder as a microwave absorbing material [16]. Jokisaari et al. put a mixture of elemental cobalt (99.9 wt.%, <5 μm) and silicon (99.5 wt.%, -325 mesh) into an industrial microwave furnace and used SiC as the microwave absorbing material, synthesizing bulk cobalt silicides [17]. Compared with amorphous carbon and SiC, carbon nanotubes (CNTs) had been used as catalyst supports and showed an enhancement effect on the catalytic activity due to their unique mechanical, chemical and electrochemical properties [18-19]. In our previous research, carbides have been synthesized by microwave-assisted solid-state reaction, which can be used as efficient electrocatalyst supports for the oxygen reduction reaction [20-22]. Therefore,

microwave-assisted solid-state synthesis is a very useful technology to design cobalt silicides as catalytic materials.

In the present study, cobalt silicides supported on CNTs ($CoSi_x$/CNTs) catalysts have been synthesized through a microwave-assisted route, in which the CNTs act as both absorbing material and support. The as-prepared cobalt silicides supported on CNTs have been used in the hydrogenation of phthalic anhydride, and afford good activity and high selectivity to phthalide.

2. Experimental

Reagents and Equipment

The applied reagents included powders of CNTs (purity: 97.0 wt.%, diameter: 20-40 nm, producer: Shenzhen Nanotech Port Co. Ltd.), silicon (99.9 wt.%, -200 mesh), ferric chloride (97.0 wt.%), cobalt chloride (98.0 wt.%), nickel chloride (98.0 wt.%) and cupric chloride (99.0 wt.%). Silicon powder was directly used without further treatment. The CNTs powders and metal chloride powders were dried at 130 ^{o}C to remove the adsorbed water before use. A domestic microwave oven (WBFY-201) operated at 2.45 GHz with a power of 800 W was used for synthesis.

Catalyst Preparation

The $CoSi_x$/CNTs catalysts were synthesized via microwave-assisted route. Typically, 0.3 g of CNTs, 0.0757 g of cobalt chloride ($CoCl_2$), and a certain amount of silicon powder were put in an agate mortar, and mixed for 20 min. The completely homogeneous precursor mixture was put in a quartz-tube reactor and fluidized with argon for1 h to remove oxygen in

the reactor. Then, the reactor was placed in a domestic microwave oven operating at 2.45 GHz with a power of 800 W. Finally, the resulting products were cooled down naturally to room temperature under argon. The microwave irradiation time varied from 10 to 30 min and Co:Si ratios from 1:1 to 1:5 were investigated on the formation mechanism of the products.

Catalyst Characterization

Thermogravimetric/derivative thermogravimetric (TG/DTG) experiments were performed on a Mettler Toledo TGA/SDTA851^e thermogravimetric analyser. The samples were placed in an atmosphere of Ar and heated at 5 ^oC /min to the final temperature of 800 ^oC.

X-ray diffraction (XRD) analyses of the samples were carried out using a Rigaku D/Max-RB diffractometer with Cu Kα monochromatized radiation source, operated at 40 kV and 100 mA. The average size of cobalt silicide particles was evaluated by the Scherrer formula as:

$$L = \frac{0.9\lambda_{K\alpha_1}}{B_{(2\theta)}\cos\theta_{\max}} \quad (1)$$

where $\lambda_{K\alpha 1}$ is 1.54178 Å, and $B_{(2\theta)}$ is the full width at half-maximum of the diffraction peak in radian.

High-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectroscopy (EDX) were performed by using a T2-Tecnai F30 transmission electron microscope, operated at 200 KV.

H_2-temperature-programmed-reduction (H_2-TPR) analysis was carried out using a Quantachrome ChemBET TPR/TPD system. About 10 mg of sample was placed in a quartz

reactor and was reduced in a stream of Ar gas with a flow rate of 50 mL/min. The sample was heated from room temperature to 900 °C at 10 °C /min. The amount of the hydrogen consumption during the reduction was estimated with a thermal conductivity detector.

Surface compositions of the samples were characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo VG). The XPS measurements were performed using an X-ray source of Al Kα (1486.6 eV) with a powder of 150 W. The individual high-resolution spectra were recorded with a pass energy of 50 eV. Co 2p, Si 2p, and C1s lines were monitored. All the core-level spectra were corrected by referencing to the binding energy of the C1s neutral carbon peak at 284.6 eV, and were deconvoluted into Gaussian component peaks.

Catalyst Activity Evaluation

The catalytic activity of cobalt silicides supported on CNTs has been evaluated in the hydrogenation of phthalic anhydride. Before the reaction, the catalyst was activated in hydrogen at 400 °C for 2 h. Liquid-phase hydrogenation of phthalic anhydride was carried out in a 50 mL stainless steel autoclave. The catalyst (0.3 g) was mixed with 20 g 4-hydroxybutanoic acid lactone solution containing a 5 wt.% phthalic anhydride, followed by H_2 pressurization to 4 MPa. The reaction was carried out at 180~220 °C for 6 h under stirring. The products of hydrogenation were analysed by gas chromatography using a FID with a OV-101 capillary column. A known amount of cyclohexane was used as an internal standard in the analysis.

3. Results and Discussion

The XRD patterns of $CoSi_x$/CNTs prepared by microwave pyrolysis with different Co:Si

ratios are shown in Figure 1a. The diffraction peaks at 26.5, 43.8, and 54.0° observed in the patterns could be attributed to the hexagonal graphite structure of CNTs. During the microwave-assisted pyrolysis process, the CNTs played roles as both absorbing material and supporter. The XRD pattern of Co/CNTs sample showed three typical diffraction peaks at 44.2, 51.5, and 75.8°, which were assigned to the (111), (200) and (220) crystal faces of Co (JCPDS 15-0806), respectively. After silicon was put in the precursor, the XRD patterns of $CoSi_x$/CNTs showed no diffraction peaks that could be assigned to Co, indicating that cobalt chloride has reacted with silicon thoroughly. The XRD pattern of the sample prepared with a Co:Si ratio of 1:1 presented four typical diffraction peaks at 34.9, 40.5, 45.6 and 50.2°, which were, respectively, assigned to the (111), (200), (210) and (211) crystal faces of CoSi (JCPDS 50-1337). The formation mechanism of the cobalt silicide nanoparticles could be expressed by the following reaction equation.

$$2\ CoCl_2\,(s) + (2x+1)\ Si\,(s) \rightarrow 2\ CoSi_x\,(s) + SiCl_4\,(g)$$

With further decrease of the Co:Si ratio to 1:3, the (111), (220), (311) and (400) planes appeared at 2θ=28.8, 47.9, 56.9 and 70.1°, respectively, indicating the presence of $CoSi_2$ phase (JCPDS 38-1449). Upon decreasing the Co:Si ratio from 1:3 to 1:5, the diffraction peaks of the CoSi phase became weaker, and those of $CoSi_2$ phase became sharper. Since CoSi is a metastable phase, it will further react with silicon powder to form the $CoSi_2$ phase when the Co:Si ratio decreased.

To further study the formation process of cobalt silicide, the XRD patterns of the $CoSi_x$/CNTs prepared for different microwave times were recorded, as shown in Figure 1b. When the microwave time was extended from 10 to 30 min, the phase of the cobalt silicide

also transformed from CoSi to $CoSi_2$. Based on the (210) peak at 50.2°, the average crystallite size of the $CoSi_x$ samples were calculated to be ca. 37 nm using the Scherrer formula. The particle size did not apparently change with the transformation of the cobalt silicide phase, because the variation of peak width is inconspicuous.

Traditionally, the formation of metal silicides through the reaction between metal chloride and silicon powder requires high temperature (1200 ^{o}C) and long sintering time, which leads to the aggregation of particles. To obtain a good understanding of the as-prepared precursor reaction process in the synthesis of cobalt silicides, the thermal decomposition process of the precursor was characterized by TG/DTG (Figure 2). The mass loss at about 100 ^{o}C is attributed to the elimination of molecular water, and those at about 550 and 700 ^{o}C are only owing to the elimination of molecular chlorine. No cobalt silicide nanoparticles were synthesised, which further confirmed that the microwave-assisted thermolytic precursor method was an efficient way for the synthesis of evenly dispersed cobalt silicides.

Solid-state microwave synthesis of cobalt silicide is not an isolated phenomenon for a few selected substances. So the reaction between metal and the added material as an absorber of the microwave radiation may be proceed to form alloys or intermetallic compounds. According to this hypothesis, other transition metal silicides were attempted to be synthesized using this novel methodology. As shown in Figure 3, the (110), (111), (200), (210) and (211) planes appeared at 2θ=28.1, 34.6, 40.2, 45.1 and 49.7°, respectively, indicating the presence of FeSi phase. The (211), (021), (220), (121) and (002) planes appeared at 2θ=39.4, 43.5, 44.3, 45.5 and 48.8°, respectively, indicating the presence of Ni_2Si phase. And the planes appeared at 2θ=43.0, 43.5, 46.0, and 47.8°, respectively, indicating the presence of Cu_4Si phase.

Therefore, FeSi, Ni_2Si and Cu_4Si supported on CNTs can also be synthesized by these microwave-assisted solid-state reactions.

The TEM image in Figure 4a shows uniformly and highly dispersed cobalt silicide nanoparticles on the CNTs. The microwaves coupled with the absorption band of the materials, which heated the materials uniformly in a short time, avoiding the aggregation of cobalt silicide nanoparticles. The inset in Figure 4a displays a typical TEM image of the nanoparticles decorated on the CNTs, indicating that its size was approximately 40 nm, which is basically consistent with the calculated particle size value from XRD results by Scherrer formula. The high-magnification TEM image (Figure 4b) could be used to further probe the cobalt silicide nanoparticles. Based on two-dimensional fast Fourier transform (FFT), the observed lattice spacing of 0.182 nm matched well with the reported value of the (211) plane in the CoSi structure (JCPDS 50-1337) [7]. The EDX spectrum in Figure 4c from a single cobalt silicide nanoparticle indicated that Co and Si atoms were the only elements presenting in the nanoparticles with an atomic ratio of approximately 1:1, which was also in good agreement with the value from XRD. This data confirms that the prepared cobalt silicide particles have a composition of CoSi.

In order to investigate the catalytically active sites and surface chemical structure relationships, the surfaces of $CoSi_x$/CNTs catalysts have been probed by XPS. Figure 5a shows the XPS profiles, revealing that Co, C, Si, Cl and O elements were detected in the samples. From the Co 2p spectra shown in Figure 5b, the peak at about 785 eV can be attributed to the metallic cobalt phase for the Co/CNTs sample. With the decrease of the Co:Si ratio to 1:2, one peak at 782.5 eV was observed, which can be assigned to the CoSi

phase. With further decrease of the Co:Si ratio to 1:3, the peak at 778.2 eV due to the $CoSi_2$ phase can be observed in the Co-3Si/CNTs sample [23]. This result is consistent with the XRD results. The analytical result on Si 2p signal is shown in Figure 5c. The peak in the Si 2p region at 99 eV corresponding to silicon in cobalt silicide would shift to the higher binding energy due to the electron shift from cobalt to silicon atoms with the increased content of Si, which further confirmed the interaction between Co and Si [24]. Meanwhile, there is an extra broad peak at 101-104 eV in the Si 2p spectra attributed to Si-O_x, which is owing to the formation of passivated layers on the cobalt silicides [25].

TPR is a powerful tool for characterizing supported catalysts. Figure 6a shows the H_2-TPR profiles of cobalt silicide samples with different Co:Si ratios. Only one peak was observed at about 500 ^oC for Co/CNTs, which could be tentatively assigned to the reaction of cobalt oxide with H_2. When silicon was mixed in the precursor, two peaks were observed at about 470 and 530 °C, which could be tentatively assigned to the reaction of cobalt and cobalt silicide with H_2. In addition, the peak for the $CoSi_x$/CNTs is higher than that of Co/CNTs, indicating that $CoSi_x$/CNTs catalysts have higher activation temperature. However, the peak shifts to lower temperature for the samples with Co:Si ratio decreasing from 1:1 to 1:3, which can be attributed to the phase of cobalt silicides transforming from CoSi to $CoSi_2$. Because the Si content in $CoSi_2$ phase is significantly higher than that in CoSi, so more silicon oxides passivation layer attached on the $CoSi_2$/CNTs catalyst, which would lead to a lower activation temperature of $CoSi_2$ [5]. In addition, the silicides can react with H_2 at relatively high temperature (ca. 500 °C) as $CoSi_x + 2xH_2 \rightarrow Co + xSiH_4$ [26]. As shown in Figure 5b, the Co binding energy of $CoSi_2$ phase was lower than that of CoSi phase. Therefore, the $CoSi_2$ phase

can react with hydrogen easier than CoSi, indicating $CoSi_2$ has a lower activation temperature than CoSi.

The H_2-TPR profiles of cobalt silicide samples with different microwave times were also detected as shown in Figure 6b. For the samples prepared by increasing the microwave time from 10 to 20 min, the TPR peak became sharper. However, when increasing the microwave time to 30 min, the peak became weaker. The reason is also that the phase of cobalt silicides transformed from CoSi to $CoSi_2$ by increasing the microwave time to 30 min, which is in good agreement with the result from XRD.

The scheme of hydrogenation of phthalic anhydride is shown in Scheme 1 [27-28]. The results for hydrogenation of phthalic anhydride over Co/CNTs and $CoSi_x$/CNTs catalysts at 190 and 200 ^oC are shown in Table 1. It is clear that $CoSi_x$/CNTs catalyst could catalyze about 100% conversion of phthalic anhydride at 200 ^oC, while Co/CNTs catalyst only catalyzed about 80% conversion. Obviously, the addition of Si to Co/CNTs significantly promoted the rate of hydrogenation of phthalic anhydride. It is possible that the interaction between Co and Si atoms tuned the geometry and electronic structure, further effecting the catalytic activity and selectivity to phthalide. However, at the same time, the Co/CNTs catalyst has about 80% selectivity to phthalide. The as-prepared $CoSi_x$/CNTs catalysts have lower selectivity than the Co/CNTs catalyst. The as-prepared $CoSi_x$/CNTs are more stable than the corresponding metal catalyst in the acidic environment caused by the substrate, which is due to the higher chemical and thermal stability of cobalt silicides. With increasing Si powder concentration from Co:Si ratio 1:1 to 1:3, the phase of cobalt silicide samples transformed from CoSi to $CoSi_2$, which caused the conversion of phthalic anhydride to decrease from 98.8% to 44.4% at 190 ^oC. The

corresponding selectivity to phthalide increased from 72.7% to 77.7%. Increasing the hydrogenation reaction temperature from 190 to 200 ^{o}C, the conversion of phthalic anhydride increased.

Figure 7 shows the conversion of phthalic anhydride and selectivity to phthalide over Co/CNTs and $CoSi_x$/CNTs catalysts at 190 ^{o}C with different reaction times. The Co/CNTs catalyst showed only 70% conversion of phthalic anhydride in 9 h reaction time, lower than the conversion for the $CoSi_x$/CNTs catalysts, which is in good agreement with the result in Table 1. When increasing the Si powder concentration from Co:Si ratio 1:1 to 1:3, the prepared Co-3Si/CNTs had low conversion, because the phase of cobalt silicide transformed from CoSi to $CoSi_2$ phases. This result indicated that CoSi had higher catalytic activity than $CoSi_2$. When the catalytic reaction time is 7.5 h, the conversion of phthalic anhydride is about 100% by using the prepared Co-Si/CNTs as catalysts and the phthalide content is almost 80%. With further increase in reaction time, a part of phthalide was further hydrogenated to benzoic acid and o-toluic acid. So, it can be concluded that the catalyst activity of Co-Si/CNTs is apparently higher than those of Co-2Si/CNTs and Co-3Si/CNTs.

To probe the effect of microwave time on catalytic activity, the catalyst with a Co:Si ratio of 1:3 was treated at 10, 20 and 30 min. As shown in Figure 8, an optimum activity was found by increasing the microwave time. When increasing the time from 10 to 20 min, the conversion increased, but the selectivity to phthalide was almost invariant (about 75~80%). When further increasing the microwave time from 20 to 30 min, the conversion and the selectivity decreased. As shown in the results of XRD analysis (See in Figure 1b), cobalt silicide phases transformed from CoSi to $CoSi_2$ with increasing microwave time. However,

the particle size presented no significant change, keeping about 30-40 nm based on the calculation by the Scherrer formula. Therefore, the change of catalytic activity is mainly correlated to the phase composition, apparently indicating that CoSi phase have better catalytic activity than $CoSi_2$ phase.

4. Conclusions

Cobalt silicides with different phases (CoSi or $CoSi_2$) supported on CNTs catalysts have been successfully synthesized by a rapid microwave-assisted route. This novel methodology can also be applied to synthesize other transition metal silicides, such as FeSi, Ni_2Si and Cu_4Si. The as-prepared $CoSi_x$/CNTs can be employed in hydrogenation of phthalic anhydride. Due to the improved chemical and thermal stability of cobalt silicide, $CoSi_x$/CNTs catalysts, compared to their corresponding metal catalyst counterpart, presented high catalytic stability in the hydrogenation of phthalic anhydride. Si atoms reside into the interstitial sites between Co atoms and change the cobalt unit cell lattice, further effecting the catalytic activity and selectivity to phthalide.

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Scheme and figure captions

Scheme 1 The scheme of hydrogenation of phthalic anhydride over $CoSi_x$/CNTs catalysts.

Figure 1 (a) XRD patterns of the $CoSi_x$/CNTs with 20 min microwave irradiation time and different Co:Si ratios prepared by microwave pyrolysis, and the corresponding standard XRD patterns (Co JCPDS 15-0806, CoSi JCPDS 38-1337, and $CoSi_2$ JCPDS 38-1449). (b) XRD patterns of the $CoSi_x$/CNTs with different microwave times prepared by microwave pyrolysis.

Figure 2 TG-DTG profile of the as-prepared $CoSi_x$/CNTs precursor.

Figure 3 XRD patterns of the metal silicide phases supported on CNTs: (a) FeSi, (b) CoSi, (c) Ni_2Si and (d) Cu_4Si with 20 min microwave time prepared by microwave pyrolysis and the corresponding standard XRD patterns (FeSi JCPDS 38-1397, CoSi JCPDS 38-1337, Ni_2Si JCPDS 50-0779, and Cu_4Si JCPDS 03-0990).

Figure 4 TEM results of $CoSi_x$/CNTs prepared with Co:Si ratio 1:1: (a) low-magnification TEM image of the $CoSi_x$/CNTs and typical image of the nanoparticles decorated on the CNTs (the inset); (b) high-magnification TEM image and corresponding fast Fourier transforms of the lattice-resolved images (the inset), and (c) TEM-EDX spectrum from Figure 4(b).

Figure 5 XPS profiles of (a) all elements in sample and regions: (b) Co 2p and (c) Si 2p of $CoSi_x$/CNTs.

Figure 6 H_2-TPR profiles of the cobalt silicides supported on CNTs (a) with different Co:Si ratios and (b) with different microwave times.

Figure 7 Conversion of phthalic anhydride and selectivity to phthalide over Co/CNTs and $CoSi_x$/CNTs with different Co:Si ratios and reaction times.

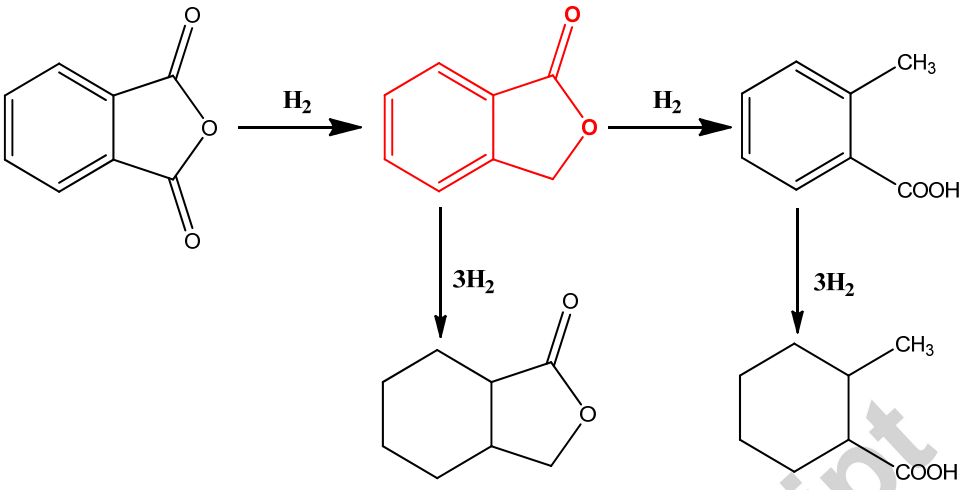
Figure 8 Conversion of phthalic anhydride and selectivity to phthalide over Co-3Si/CNTs with different microwave times and temperatures.

Table 1. Conversion of phthalic anhydride and selectivity to phthalide over $CoSi_x$/CNTs with the different Co/Si ratios

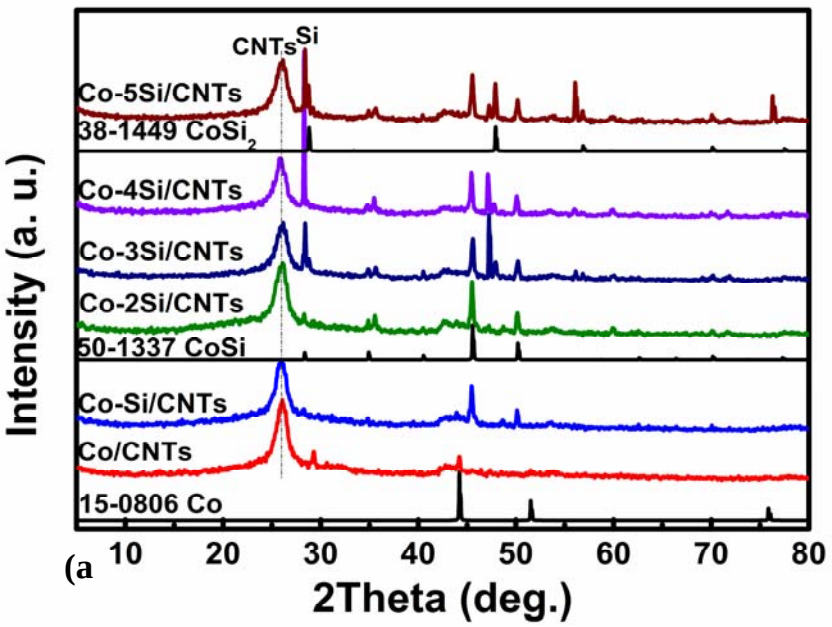
Catalyst (Co/Si ratio)	Temperature (^oC)	Conversion (%)	Selectivity to phthalide (%)
1:1	190	98.8	72.7
	200	99.7	57.8
1:2	190	71.0	72.5
	200	96.1	67.5
1:3	190	44.4	77.7
	200	97.8	60.3
Co/CNTs	190	49.2	82.8
	200	83.7	80.1

Graphical Legend

$CoSi_x$/CNTs catalysts with different $CoSi_x$ phases ($CoSi_2$, CoSi) have been rapidly synthesized via microwave-assisted route, which involves the vaporization of $CoCl_2$ and subsequent reaction of $CoCl_2$ with Si.



Scheme 1 The scheme of hydrogenation of phthalic anhydride over $CoSi_x$/CNTs catalysts.



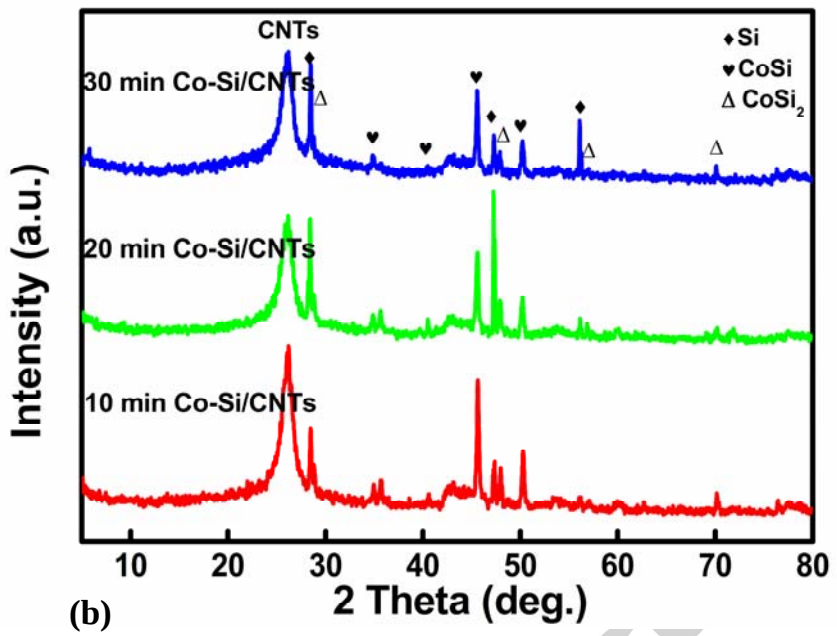


Figure 1 (a) XRD patterns of the $CoSi_x$/CNTs with 20 min microwave irradiation time and different Co:Si ratios prepared by microwave pyrolysis, and the corresponding standard XRD patterns (Co JCPDS 15-0806, CoSi JCPDS 38-1337, and $CoSi_2$ JCPDS 38-1449). (b) XRD patterns of the $CoSi_x$/CNTs with different microwave times prepared by microwave pyrolysis.

Figure 2

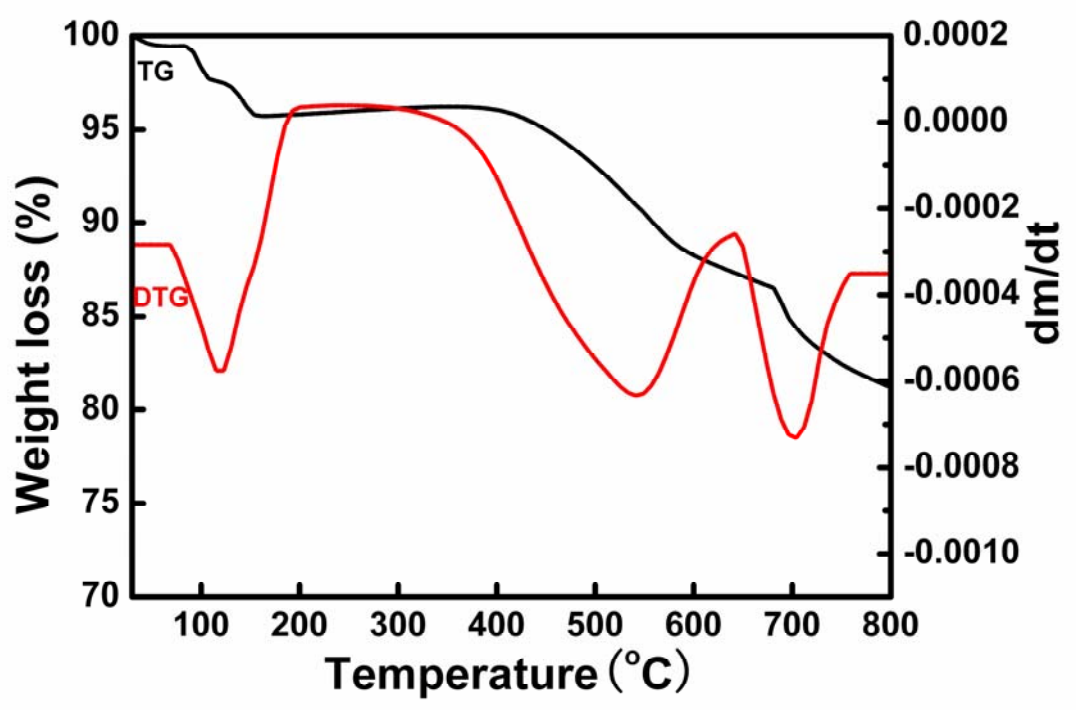


Figure 2 TG-DTG profile of the as-prepared $CoSi_x$/CNTs precursor.

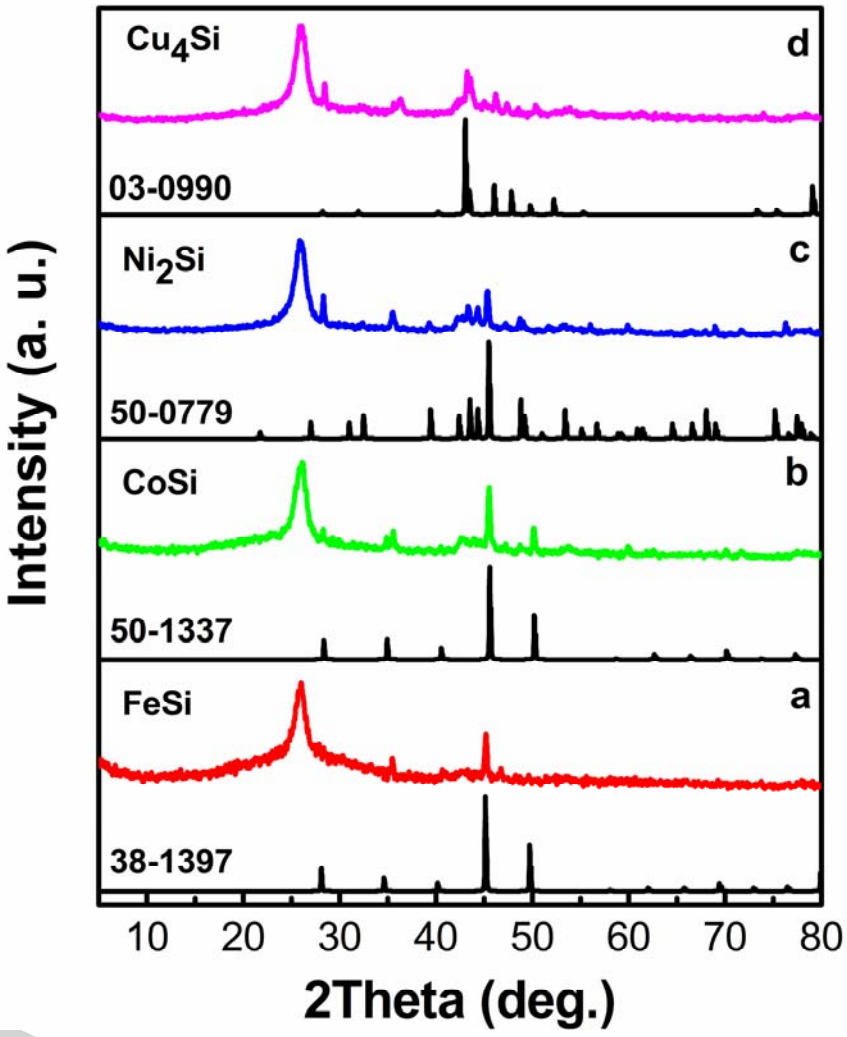


Figure 3 XRD patterns of the metal silicide phases supported on CNTs: (a) FeSi, (b) CoSi, (c) Ni_2Si and (d) Cu_4Si with 20 min microwave time prepared by microwave pyrolysis and the corresponding standard XRD patterns (FeSi JCPDS 38-1397, CoSi JCPDS 38-1337, Ni_2Si JCPDS 50-0779, and Cu_4Si JCPDS 03-0990).

Liangliang Zhang, et al., ***Journal of Solid State Chemistry***, Figure 4

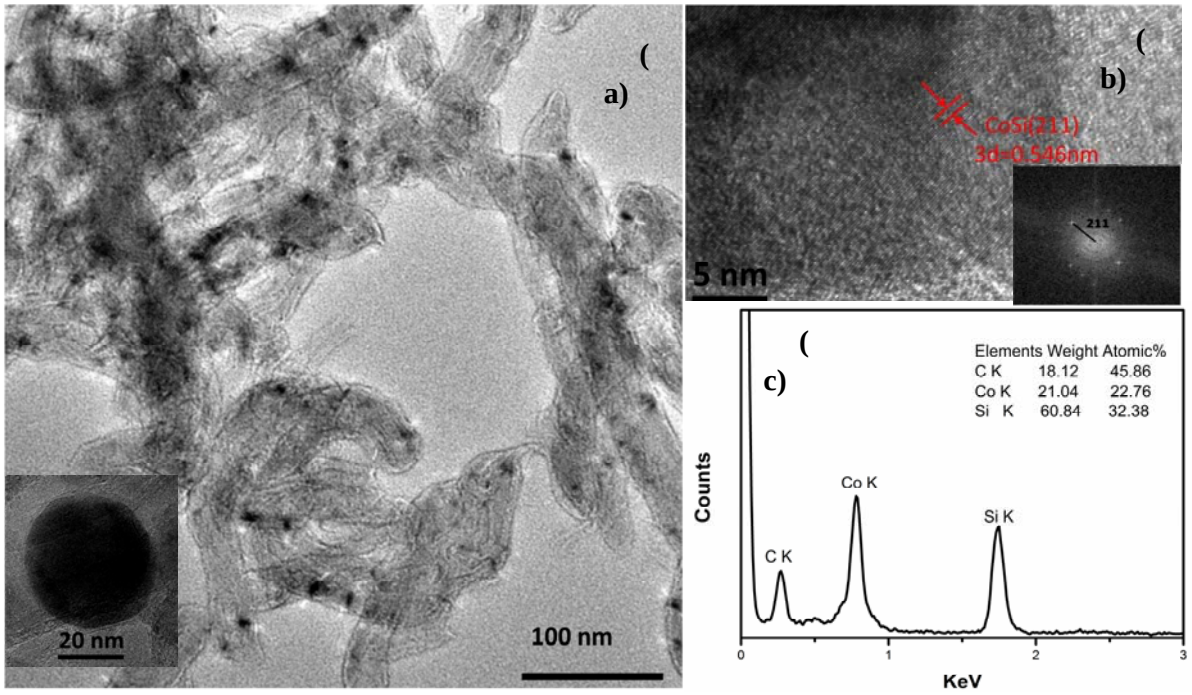


Figure 4 TEM results of $CoSi_x$/CNTs prepared with Co:Si ratio 1:1: (a) low-magnification TEM image of the $CoSi_x$/CNTs and typical image of the nanoparticles decorated on the CNTs (the inset); (b) high-magnification TEM image and corresponding fast Fourier transforms of the lattice-resolved images (the inset), and (c) TEM-EDX spectrum from Figure 4(b).

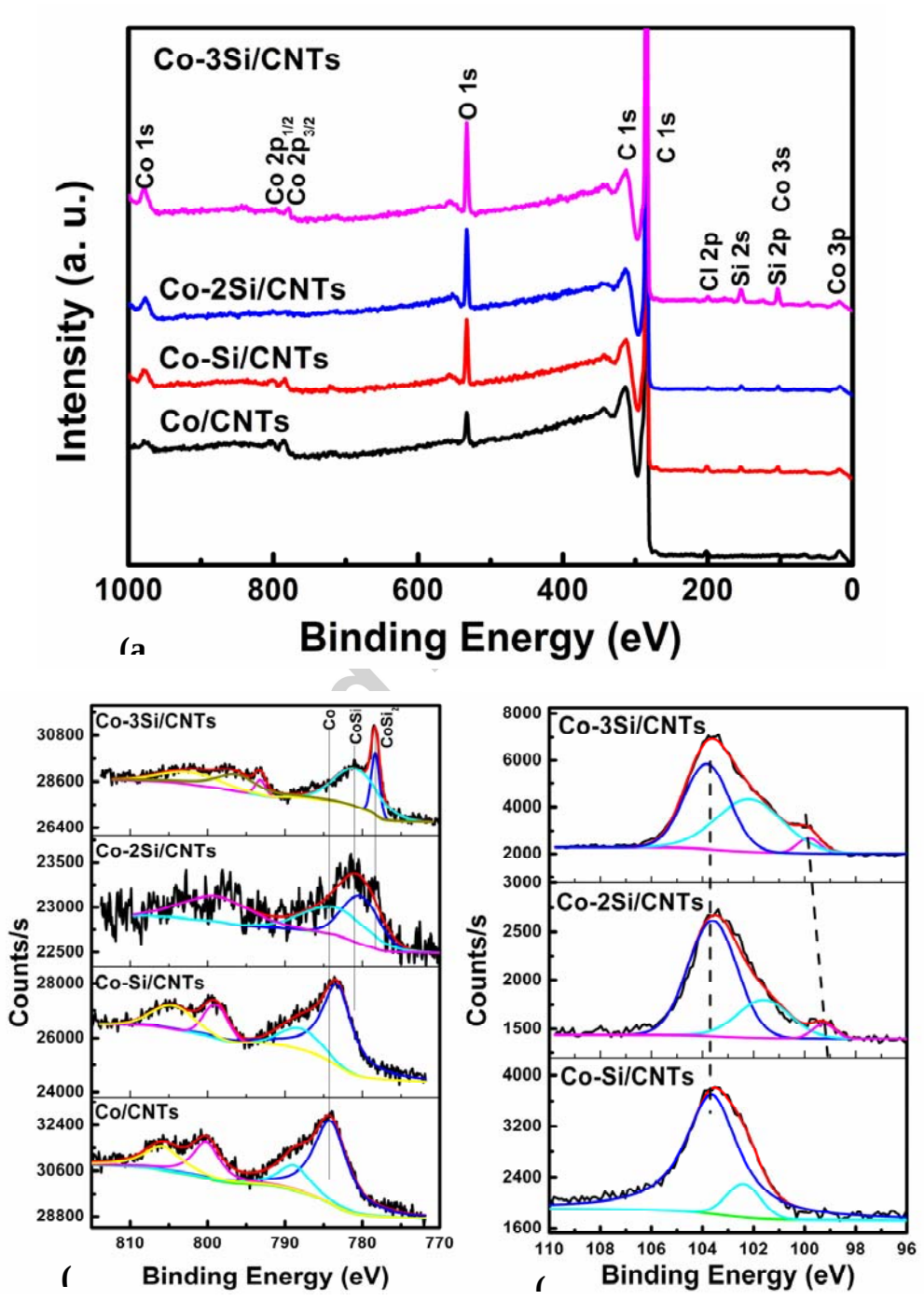


Figure 5 XPS profiles of (a) all elements in sample and regions: (b) Co 2p and (c) Si 2p of $CoSi_x$/CNTs.

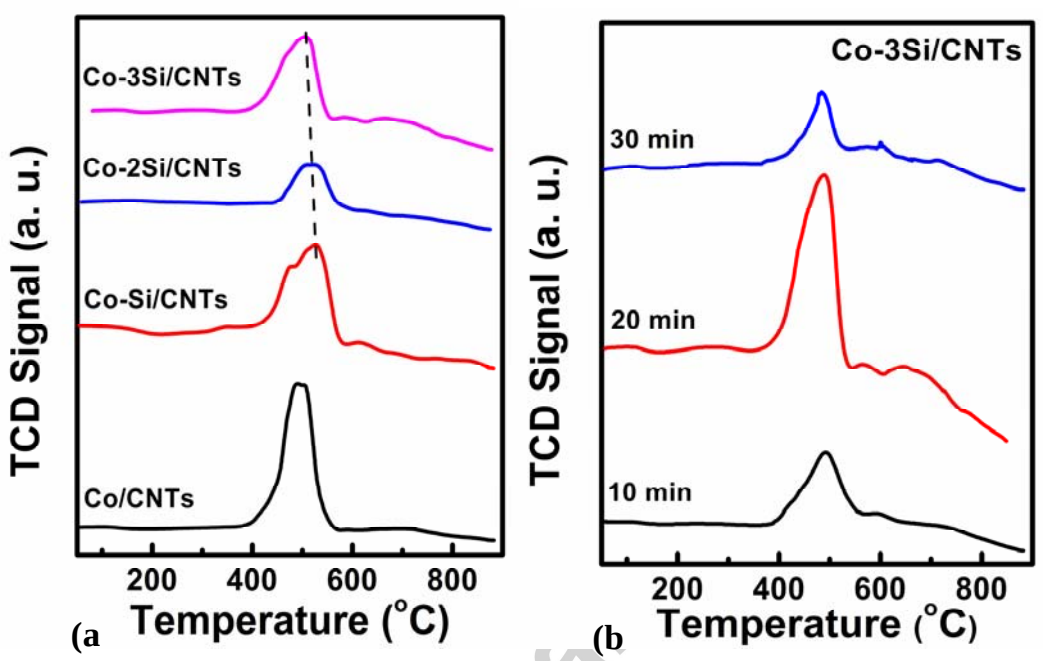
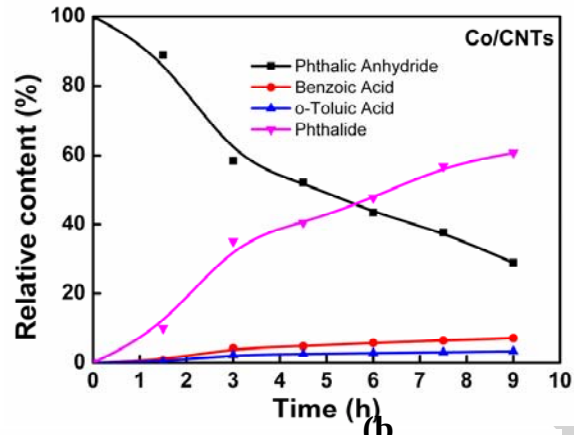
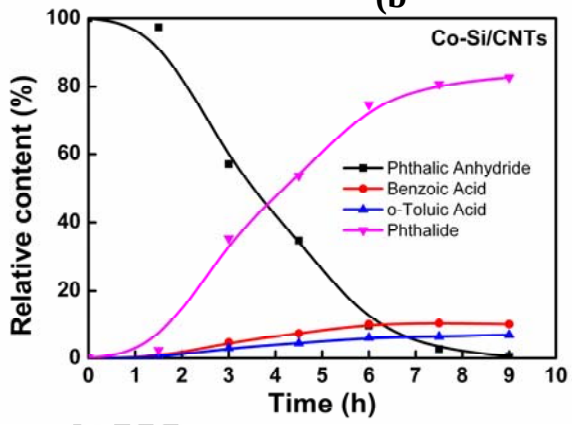


Figure 6 H_2-TPR profiles of the cobalt silicides supported on CNTs (a) with different Co:Si ratios and (b) with different microwave times.



(a **(b**



(c **(d**

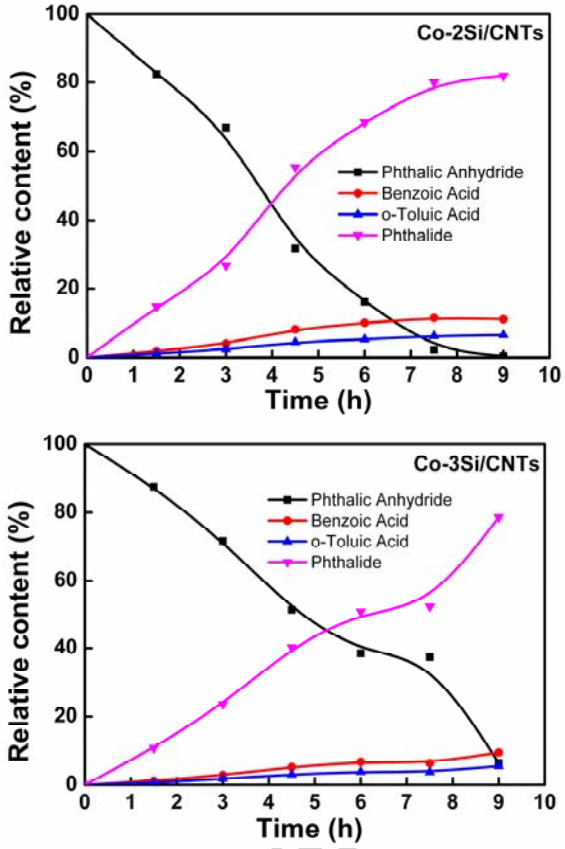


Figure 7 Conversion of phthalic anhydride and selectivity to phthalide over Co/CNTs and $CoSi_x$/CNTs with different Co:Si ratios and reaction times.

Liangliang Zhang, et al., ***Journal of Solid State Chemistry***, Figure 8

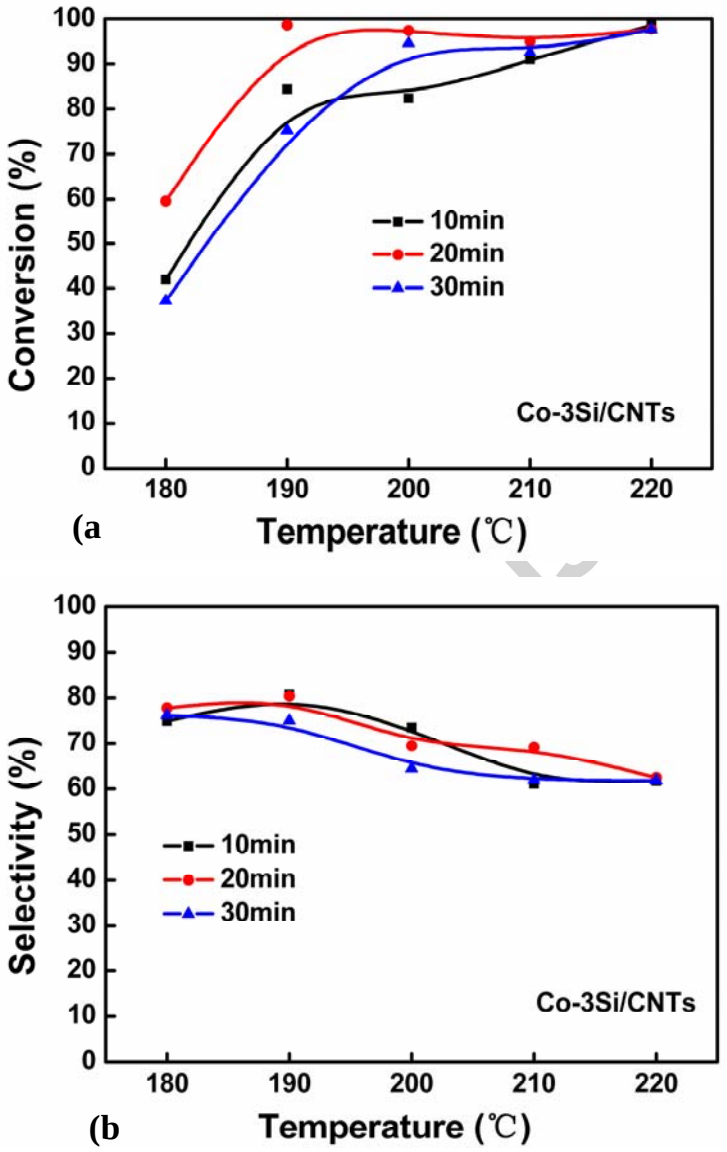


Figure 8 Conversion of phthalic anhydride and selectivity to phthalide over Co-3Si/CNTs with different microwave times and temperatures.

Highlights

- ✓ $CoSi_x$/CNTs catalysts have been rapid synthesized via microwave-assisted route.
- ✓ The phases of $CoSi_x$ were controlled by varying microwave time and Co:Si ratio.
- ✓ FeSi, Ni_2Si and Cu_4Si were also synthesized via microwave-assisted route.
- ✓ $CoSi_x$/CNTs catalysts can be applied in hydrogenation of phthalic anhydride.

Graphical Abstract