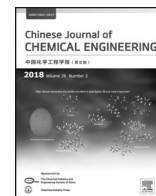




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## Article

## Ni nanoparticles supported on carbon as efficient catalysts for steam reforming of toluene (model tar)☆

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## ABSTRACT

This paper investigated the influences of surface properties of carbon support and nickel precursors (nickel nitrate, nickel chloride and nickel acetate) on Ni nanoparticle sizes and catalytic performances for steam reforming of toluene. Treatment with nitric acid helped to increase the amount of functional groups on the surface and hydrophilic nature of carbon support, leading to a homogeneous distribution of Ni nanoparticles. The thermal decomposition products of nickel precursor also played an important role. Ni nanoparticles supported on carbon treated with acid using nickel nitrate as the precursor exhibited the smallest mean diameter of 4.5 nm. With the loading amount increased from 6 wt% to 18 wt%, the mean particle size of Ni nanoparticles varied from 4.5 nm to 9.1 nm. The as-prepared catalyst showed a high catalytic activity and a good stability for toluene steam reforming: 98.1% conversion of toluene was obtained with the Ni content of 12 wt% and the S/C ratio of 3, and the conversion only decreased to 92.0% after 700 min. Because of the high activity, good stability, and low cost, the as-prepared catalyst opens up new opportunities for tar removing.

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## 1. Introduction

Compared with fossil fuels, biomass exhibits significant advantages: abundance, inexhaustibility, renewability, carbon-neutrality, and low sulfur content as well. Therefore, biomass utilization has received increasing attention [1,2]. Gasification for producing syngas is one of the most important technologies for biomass utilization [3–5]. However, tar impurity, which would contaminate the downstream equipment, block system pipeline, and pollute the environment, is usually generated during the gasification process [6–9]. Therefore, tar removing has become one of the major concerns in recent years.

Catalytic reforming is considered as the most potential method for removing tar [10–14]. Nickel nanoparticles have been widely used as the active component for the removal and transformation of tar because of their high activity and low cost [15–20]. Compared with homogeneous catalysts, Ni-based catalysts in the immobilization mode are more popular because of the good stability, easy separation and feasibility for continuous operation. Gong and coworkers [21–25] have devoted great efforts in catalytic reforming of oxygenates using Ni-based heterogeneous catalysts, providing deep insight into the structure–activity

relationship and strategies for improving the catalytic performance. It is well demonstrated that decreasing the mean particle size of Ni nanoparticles and increasing the surface oxygen mobility would be benefit for improvement of catalytic activity and stability.

Because of the high specific surface area, developed pore structure and low cost, activated carbon (AC) are extensively explored as the supporting material for metal nanoparticles [26–32]. However, control over the mean diameter of Ni nanoparticles supported on carbon material remains a serious challenge until today. Hou *et al.* [30] prepared Ni-carbon nanotubes through homogeneous deposition–precipitation method. The average particle sizes of nickel nanoparticles are 6.1, 11.2 and 19.4 nm, respectively for the catalyst with the Ni loading amount of 5, 15 and 35 wt%. In the work of Rashidi [31], the mean particle size of Ni nanoparticles (loading amount is 5 wt%) is 11.3 nm. It is reported that the particle size of Ni nanoparticles has great effect both on the catalytic activity and stability [33,34]. Therefore, how to prepare Ni nanoparticles supported on AC with small particle size and narrow distribution has become a hot topic in this field.

It has been well established that the nature of nickel precursors used during the catalyst preparation process and surface property of the supporting material are important parameters affecting the catalytic performance [1,35]. However, there have been few studies discussing influences of precursors and surface properties of carbon material on nanoparticle morphology and catalytic activity until now.

Herein, in this work, we attempted to investigate effects of surface properties of the support and nickel precursors on morphology of Ni nanoparticles, and their catalytic performances for steam reforming of

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toluene. A series of Ni–AC catalysts were prepared using nickel nitrate, nickel chloride, and nickel acetate as the precursors, which were characterized by Fourier-transform infrared (FTIR), transmission electron microscopy (TEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), and temperature programmed reduction (TPR) under hydrogen flow. The catalytic activities for steam reforming of toluene were investigated as well as the changes in morphologies of Ni nanoparticles. Effects of residence time, S/C ratio (molar ratio of steam to carbon in toluene), and nickel loading amount on conversion have been systematically investigated. The stability test of the catalyst was carried out as well.

## 2. Experimental

### 2.1. Materials and chemicals

Nickel nitrate hexahydrate, nickel chloride hexahydrate and nickel acetate tetrahydrate were purchased from Fuchen Chemical Plant in Tianjin, China. AC support was obtained from the pretreatment of charcoal active granular. The charcoal active granular was purchased from Xilong Chemical Industry Incorporated Co., Ltd. Analytical toluene was purchased from Beijing Chemical Plant. Nickel nitrate hexahydrate and toluene were used as received without further treatment and the charcoal active granular needed further preprocessing.

### 2.2. Preparation and characteristic of AC supported with Ni nanoparticles

Charcoal active granular pretreated with concentrated  $\text{HNO}_3$  was selected as the support. The char particles were sieved before pretreatment, and char particles with the size ranged from 590 to 840  $\mu\text{m}$  were treated with concentrated  $\text{HNO}_3$  for 2 h at room temperature. Then they were washed with deionized water for several times to remove the remaining nitric acid and dried at 378 K overnight before use.

A series of Ni–AC is synthesized using three different precursors, nickel nitrate, nickel chloride and nickel acetate by impregnation method and they are labeled as Ni–AC(N), Ni–AC(C) and Ni–AC(AC), respectively. A certain amount of precursors was dissolved in deionized water, followed by addition of the acid-treated char particles. After 5 h mixing at room temperature, the mixture was heated to evaporate the solution. The obtained solid was dried at 373 K for 12 h, and reduced by  $\text{H}_2$  at 923 K.

The prepared catalysts were characterized by XRD on a Rigaku D/max-2500 diffractometer, using the  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) over the  $2\theta$  range from  $10^\circ$  to  $90^\circ$ . The microstructure of the catalyst was examined with transmission electron microscopy (TEM, JEOL JEM-2011, JEOL Ltd., Japan). Analysis of BET surface area and pore diameter and volume was done using a surface area analyzer (Quantachrome model 1-C, Boynton Beach, FL). The Fourier transformed infrared spectrums in the range  $4000\text{--}400 \text{ cm}^{-1}$  were recorded using a Thermo Nicolet FTIR spectrophotometer.  $\text{H}_2$  temperature-programmed reduction (TPR) measurements for fresh catalysts were performed on a Micromeritics Autochem II equipped with a thermal conductivity detector (TCD). The temperature increased to 1050 K with a speed of  $10 \text{ K}\cdot\text{min}^{-1}$ .

### 2.3. Steam reforming of toluene

Catalytic tests were carried out in a continuous flow system, using a quartz fixed-bed reactor under atmospheric pressure. The internal diameter and length of the reactor were 8 and 550 mm, respectively. The temperature of the bed was monitored using a K-type thermocouple. 0.2 g of catalyst was used in each test and held by the quartz wool placed in the middle of the reactor. Toluene and water were fed into the reactor using micro-injection pumps (Model: TS2-60, Longer Precision Pump) at a specific S/C ratio. They were firstly vaporized and then mixed with  $\text{N}_2$  with the flow rate of  $30 \text{ ml}\cdot\text{min}^{-1}$  before entering the

catalyst bed. The reaction products flowed through a cold trap maintaining 268 K to condense the unreacted toluene and water. Liquid product was analyzed using a gas chromatograph (GC) equipped with a flame ionization detector (FID) with a Porapak-Q column and the gas product was analyzed using a gas chromatograph (HP 6890) equipped with a thermal conductivity detector. The total flow rate of the produced gases was measured by a wet gas flow meter. Conversion of toluene was defined as Eq. (1), where  $C_{\text{toluene}}^{\text{in}}$  and  $C_{\text{toluene}}^{\text{out}}$  were molar flow rates of toluene at the inlet and outlet, respectively. Gas product composition was calculated using Eq. (2).

$$X = \frac{C_{\text{toluene}}^{\text{in}} - C_{\text{toluene}}^{\text{out}}}{C_{\text{toluene}}^{\text{in}}} \times 100\% \quad (1)$$

Product composition

$$= \frac{\text{mole of each gas product}}{\text{total moles of gas products}(\text{H}_2 + \text{CO} + \text{CO}_2 + \text{CH}_4)} \times 100\% \quad (2)$$

## 3. Results and Discussion

### 3.1. Characteristics of AC supported with Ni nanoparticles

In order to obtain Ni nanoparticles highly dispersed on AC, two groups of experiments were carried out.

In the first group of experiment, effect of the surface property was investigated, and AC before and after the treatment with nitric acid were used as the support for Ni nanoparticles (the loading amount of Ni was kept as 10 wt%). Because of the hydrophobic nature of carbon materials and their poor wettability in aqueous solutions, the adsorption and transportation of metal ions along the channel of carbon material are difficult [36–41]. As a result, the target metal ions which are just adsorbed on the outer surface of carbon material would be impregnated onto carbon support via drying and reduction steps, resulting in poor dispersion and severe aggregation of metal species. In order to get the carbon material hydrophilic, pretreatment with concentrated  $\text{HNO}_3$  ( $16 \text{ mol}\cdot\text{L}^{-1}$ ) was carried out. The acid treatment would increase the amount of oxygen-containing functional groups on the surface of the carbon material (such as  $\text{C}=\text{O}$ ,  $\text{COOH}$  and  $\text{OH}$ ) [36,38], and it has also been proved by FTIR characterization. As shown in Fig. 1, peaks at  $1711 \text{ cm}^{-1}$  and  $1529 \text{ cm}^{-1}$  assigned to the  $\text{C}=\text{O}$  stretching vibration and lactone structure, respectively were detected in AC support treated with nitric acid. The presence of the functional groups could help to get the metal ions adsorbed on the surface more homogeneously by making the support more hydrophilic [26]. TEM images of Ni nanoparticles supported on AC before and after the treatment are shown in

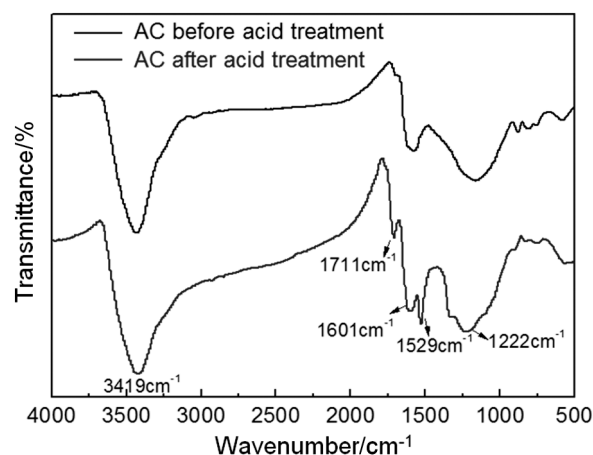


Fig. 1. FTIR spectra of raw and nitric acid treated AC.

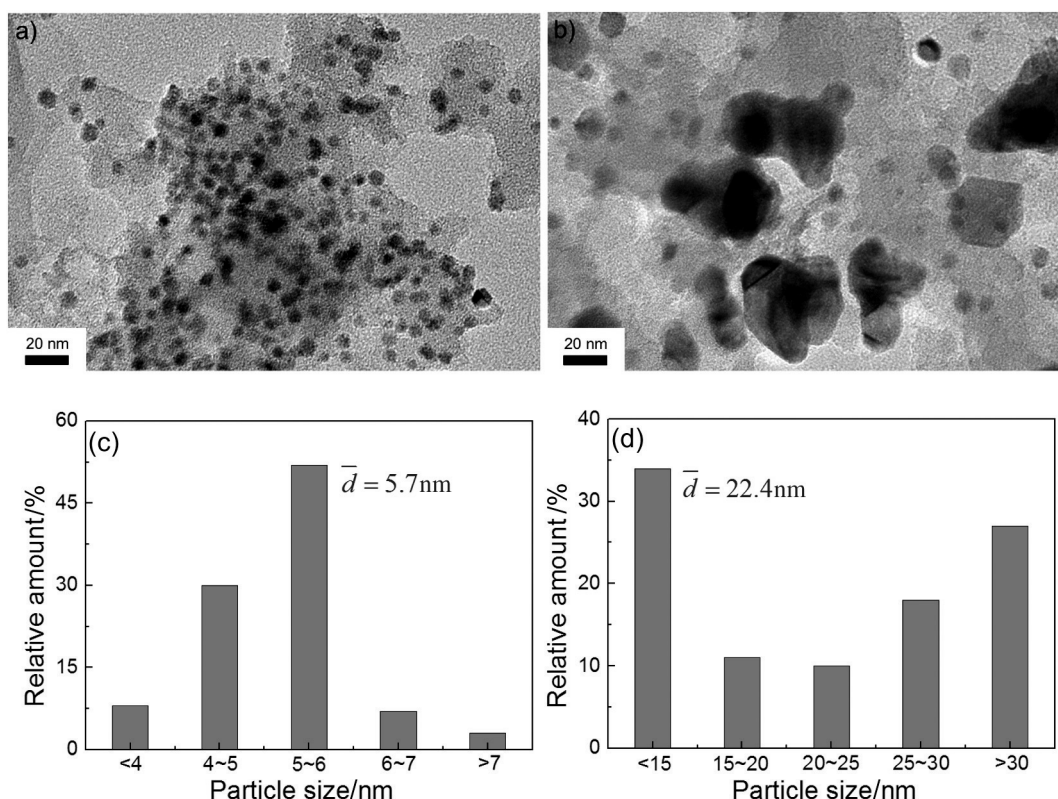


**Fig. 2.** (a) and (b): TEM images of Ni nanoparticles supported on raw AC and acid treated AC, respectively; (c) and (d): histograms of particle size distribution for Ni nanoparticles supported on raw AC and acid treated AC, respectively. (Ni loading amount: 10 wt%).

Fig. 2(a) and (b), respectively. And the corresponding histograms of particle size distribution are given in Fig. 2(c) and (d), respectively. The average Ni particle size was quantified based on a number-weighted diameter ( $\bar{d} = \sum n_i d_i / \sum n_i$ ,  $n_i$  is the number of counted Ni particles with a diameter of  $d_i$ ). As expected, Ni nanoparticles supported on raw AC exhibited poor dispersion and severe aggregation of metal species. While Ni nanoparticles showed much smaller mean particle size and narrow distribution if the support was treated with concentrated nitric acid.

In the second group of experiment, the effect of nickel precursors was investigated. TEM images of immobilized Ni nanoparticles synthesized with different precursors (the loading amount of Ni was kept as 6 wt%) are presented in Fig. 3(a) to (c), and the corresponding particle size distributions are shown as Fig. 3(d) to (f), respectively. As for the Ni-AC(N) catalyst, Ni nanoparticles were uniformly dispersed with a narrow size distribution. While Ni-AC(AC) and Ni-AC(C) catalysts showed much larger mean particle sizes of Ni nanoparticles. The mean diameter of Ni nanoparticles followed the order Ni-AC(N) (4.5 nm) < Ni-AC(AC) (36.5 nm) < Ni-AC(C) (41.5 nm). When nickel acetate was used,  $\text{CH}_4$  was formed during the thermal decomposition. As reported by Helveg [42],  $\text{CH}_4$  decomposed over Ni nanocrystals forming carbon nanofibers. It suggested that Ni nanoparticles would sinter due to the cracking of  $\text{CH}_4$ . This explained the larger mean diameter of Ni nanoparticles using nickel acetate as the precursor. Similar results were also reported by Sietsma *et al.* and Ren *et al.* [43–45]. When nickel chloride was used, hydrogen chloride was one of the products during the reduction of  $\text{Ni}^{2+}$  ions; furthermore, nickel chloride was appreciable volatile in the presence of hydrogen and hydrogen chloride [46]. As the reaction proceeded, nickel chloride crystals vaporized and tended to deposit on the formed Ni nanocrystals. It promoted the growth of Ni nanoparticles and resulted in the largest mean particle size as shown in Fig. 3c. Therefore, nickel nitrate was chosen as the optimized precursor for the preparation of catalysts.

A series of Ni-AC(N) catalysts with different nickel loading amounts (varied from 6 wt% to 18 wt%) were synthesized and their XRD patterns are presented in Fig. 4. The sharp and symmetric peaks are evidently observed, indicating the good crystallization of Ni nanoparticles. Peaks at  $44.6^\circ$ ,  $51.3^\circ$ , and  $76.4^\circ$  could be assigned to diffractions of the (111), (200), and (220) planes of metallic Ni, respectively.

TEM images of supported Ni nanoparticles with different nickel loading amounts are shown in Fig. 5(a) to (c). The corresponding particle size distributions are shown in Fig. 5(d) to (f). Ni nanoparticles are homogeneously immobilized on the surface of carbon. With the loading amount increased from 9 wt% to 18 wt%, the mean particle size of Ni nanoparticles increased steadily from 5.1 nm to 9.8 nm.

$\text{H}_2$ -TPR profiles of the as-prepared catalyst are shown in Fig. 6. Two reduction peaks are distinguished, the one at temperature  $\sim 586$  K could be assigned to the reduction of NiO species, and the other at higher temperature  $\sim 821$  K corresponded to the reduction of larger NiO nanoparticles or nickel oxides with interaction with AC.

### 3.2. Effect of residence time on conversion

After the adjustment in the loading amount and particle size of supported Ni catalysts, their catalytic performances were further explored for steam reforming of toluene. The effects of several important parameters were investigated.

Residence time of the reactants in the catalyst bed directly affects the conversion of toluene. Longer residence time means longer reaction duration, as a result, the conversion is higher. Fig. 7 illustrates the effect of residence time of the conversion of toluene with catalysts prepared with different Ni precursors. As expected, for all three catalysts, the toluene conversion increased by extending the residence time. And catalysts prepared based on different nickel precursors presented different catalytic performances. The conversion of toluene follows the order

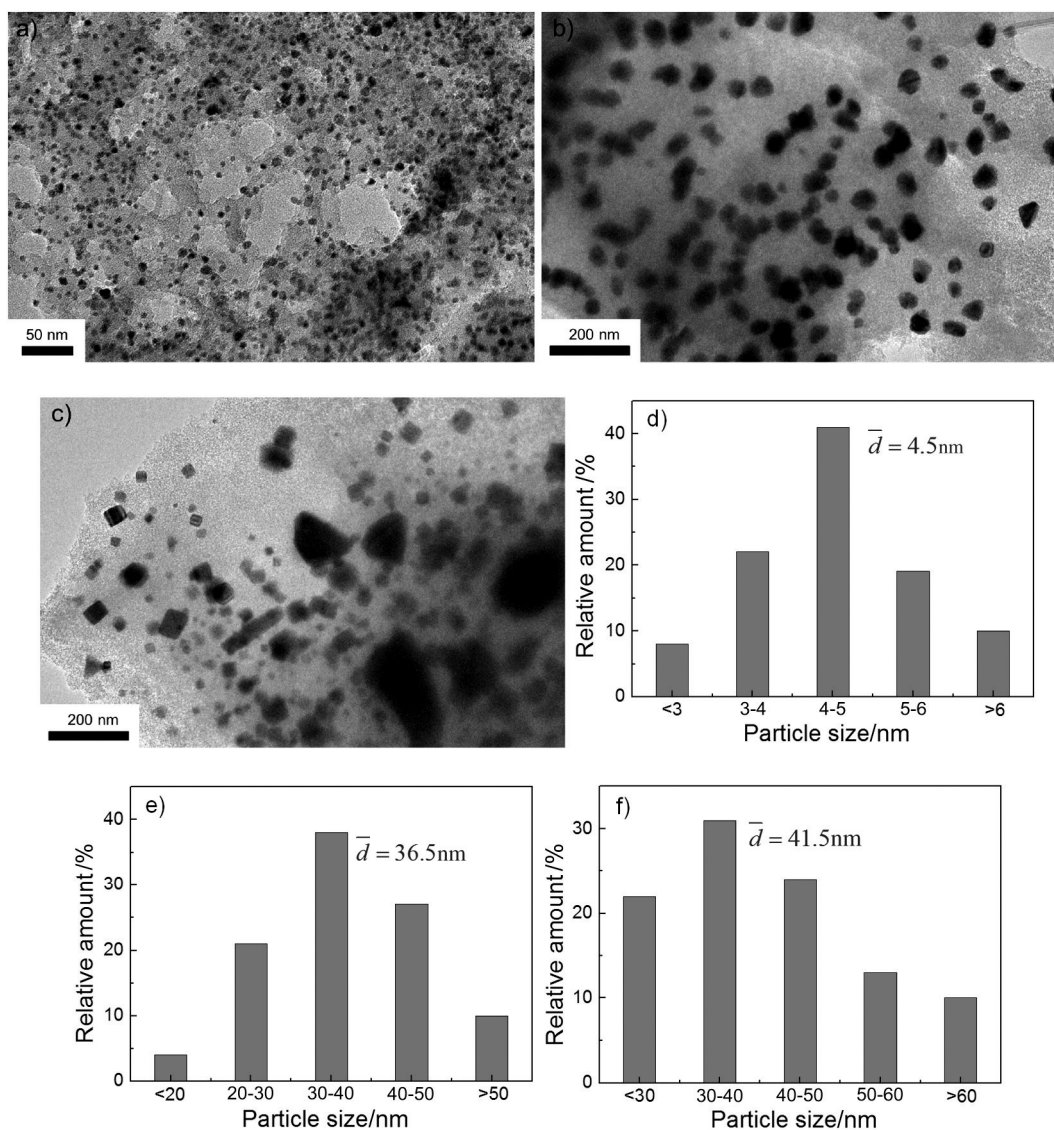


**Fig. 3.** (a), (b) and (c): TEM images of Ni/AC catalysts synthesized with nickel nitrate, nickel acetate and nickel chloride, respectively; (d), (e) and (f): histograms of particle size distribution prepared with nickel nitrate, nickel acetate and nickel chloride respectively. (Ni loading amount was 6 wt%).

Ni-AC(N) < Ni-AC(AC) < Ni-AC(C), which matches with the order of the nickel particle sizes. As for Ni-AC(N), with the residence time increased from 0.15 s to 0.31 s, a sharp increase from 39.5% to 95.1% of

toluene conversion was observed. The highest conversion of 97.4% was reached when the residence time was 0.48 s.

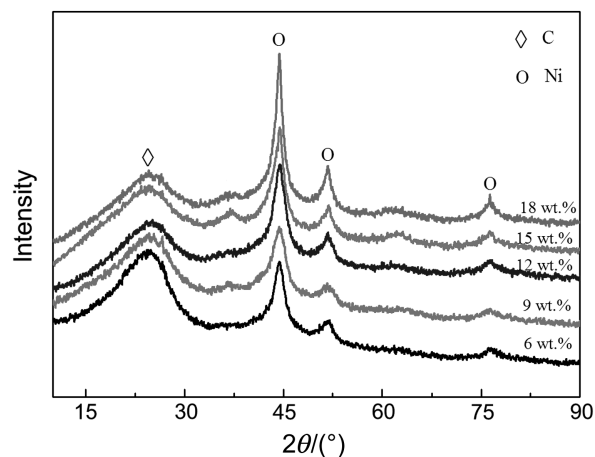


**Fig. 4.** XRD spectra of catalysts with different Ni loading amounts.

### 3.3. Effect of S/C ratio on conversion

Major reactions occur during toluene steam reforming are shown in Eqs. (3) to (9). As shown in Eqs. (3) and (4), water is one of the reactants, the steam reforming would be enhanced and  $\text{CO}_2$  instead of CO would be the favorable product by increasing water content in the feed. It indicates that the S/C ratio plays an important role in determining the conversion of toluene. Conversions of toluene increased steadily from 70.1% to 93.3% with the S/C ratio increased from 1 to 4 (Fig. 8). Besides, the water content in the feed also has a major impact on the carbon formations. In the water-less environment, carbon and hydrogen would be produced according to Eq. (9). Therefore, layers of carbon would be accumulated in a relatively short time leading to catalyst deactivation. While in a water-rich environment, Eqs. (3) and (4) are favored and the carbon accumulating rate on the Ni surface is slow; at the same time, water may clean part of the formed carbon on the surface of catalysts by oxidizing it to CO or  $\text{CO}_2$  [47].

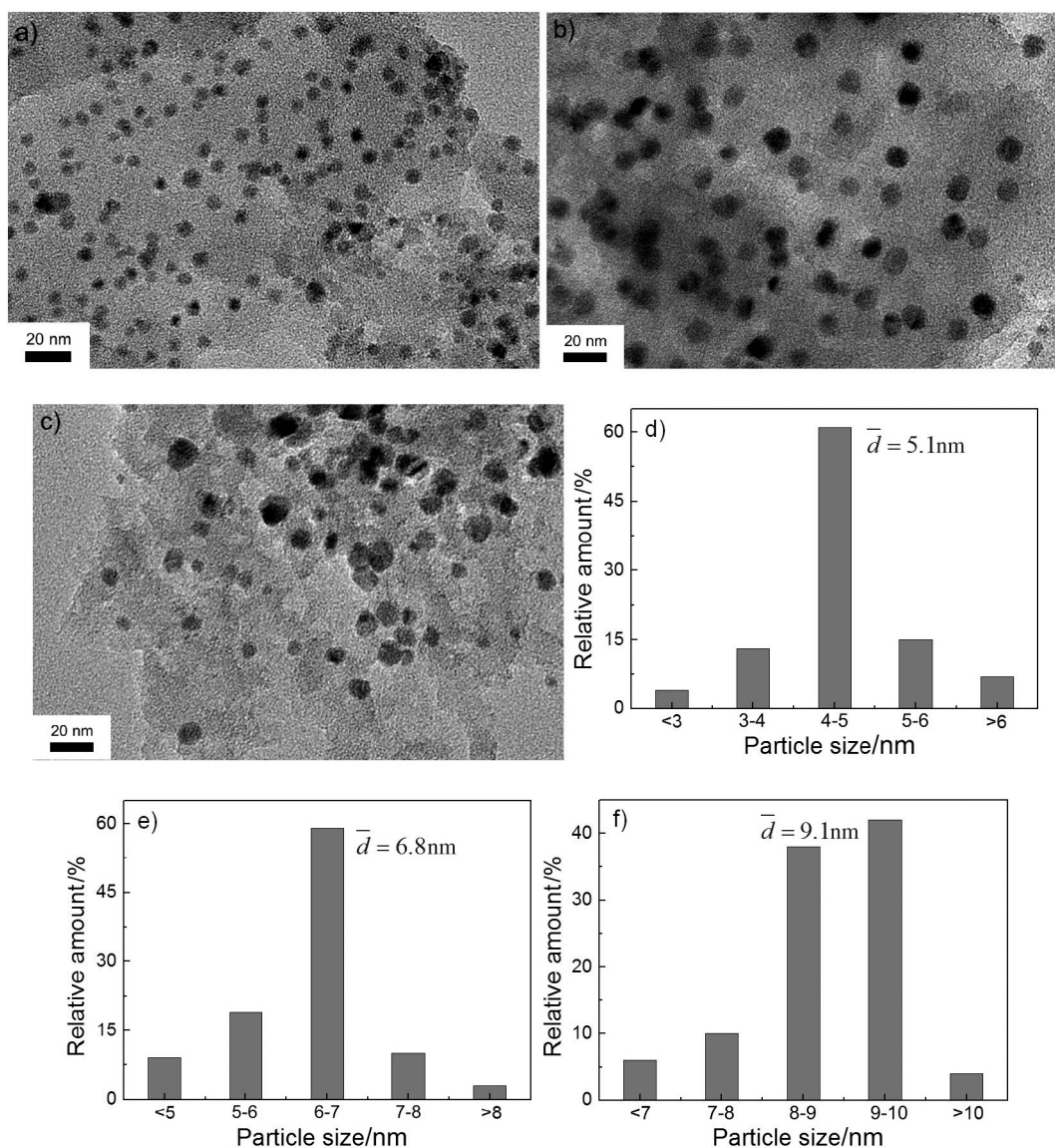


**Fig. 5.** (a) (b) and (c): TEM images of Ni nanoparticles supported on AC with Ni loading amount of 9 wt%, 15 wt% and 18 wt%, respectively; (d), (e) and (f): histograms of particle size distribution for Ni content of 9 wt%, 15 wt% and 18 wt%, respectively.

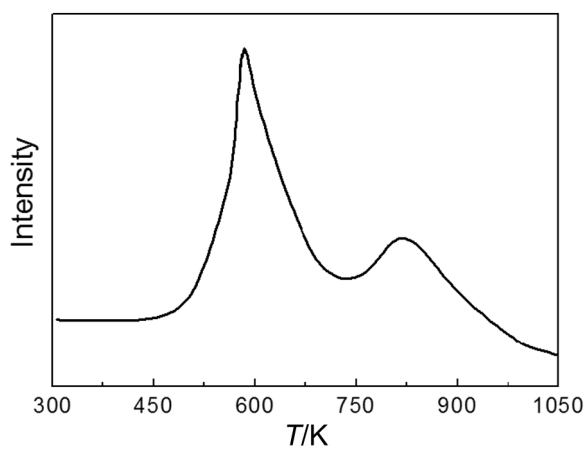


**Fig. 6.**  $H_2$ -TPR profile of 12 wt% Ni-AC(N) catalyst.

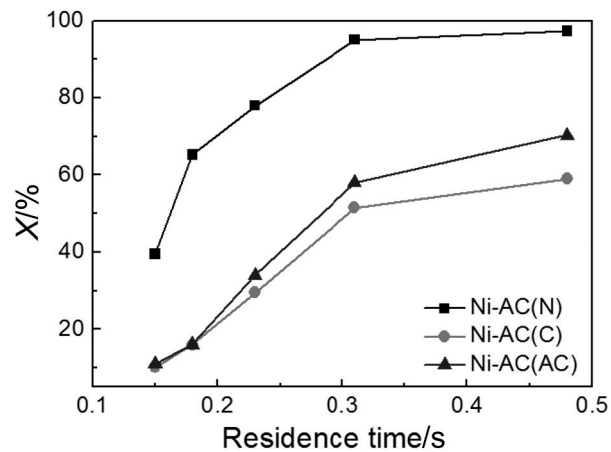


**Fig. 7.** Effect of residence time on the conversion of toluene (reaction temperature: 973 K; Ni content: 12 wt%; S/C: 1.3; toluene flow speed: 1–5  $ml \cdot h^{-1}$ ).

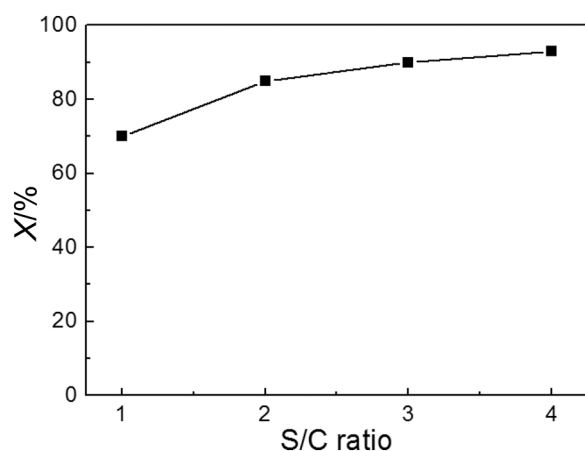


Fig. 8. Effect of S/C ratio on conversion (reaction temperature: 973 K; Ni content: 12 wt%; S/C: 1–4; toluene flow speed:  $3 \text{ ml} \cdot \text{h}^{-1}$ ).

Steam reforming:



Water gas shift:



Dry reforming:



Hydroalkylation:



Methanation:



Carbon formation:



### 3.4. Effect of nickel loading amount on conversion

The effect of Ni loading amount was determined in relation to the changes in toluene conversion, as shown in Fig. 9. The Ni content in catalyst shows much profounder effect on conversions. With the increase in Ni loading amount, the toluene conversion first increased and then decreased. The catalyst with the Ni content of 12 wt% exhibited the best catalytic performance: the conversion of toluene reached 98.1% under the experimental conditions (reaction temperature: 973 K; S/C: 2; toluene flow speed:  $2 \text{ ml} \cdot \text{h}^{-1}$ ). When the Ni amount was not bigger than 12 wt%, the reaction rate was elevated by increasing Ni amount. The conversion was promoted from 60.8% to 98.1% when the Ni content increased from 6 wt% to 12 wt%. As shown in Figs. 2 and 5, when the Ni content increased from 6 wt% to 10 wt%, the change in mean particle size of Ni is minor, while the amount of active centers increased. This may explain the promotion in toluene conversion when the Ni content varied from 6 wt% to 9 wt%. However, further increase in the Ni amount reduced the conversion. Catalysts with the highest Ni content of 18 wt% showed even worse performance than that of the catalysts with lower Ni content. The toluene conversion was reduced from 98.1% to 65.0% when the Ni content increased from 12 wt% to 18 wt%. This may be resulted from the increased Ni particle size as shown in Fig. 5.

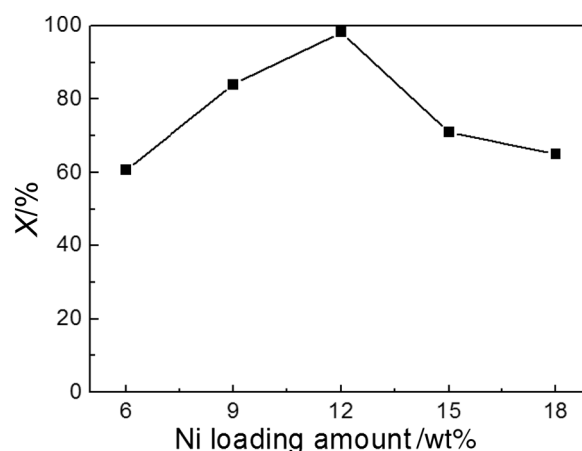


Fig. 9. Effect of nickel loading amount on conversion (reaction temperature: 973 K; S/C: 2; toluene flow speed:  $2 \text{ ml} \cdot \text{h}^{-1}$ ).

### 3.5. Stability of the Ni-AC(N) catalyst

The stability of the 12 wt% Ni-AC(N) catalyst during the steam reforming of toluene was tested and the results are shown in Fig. 10. A slight decrease in the conversion of toluene (from 98.1% to 92.0%) was observed during the first 200 min. Then in the subsequent 200–700 min, the toluene conversion almost remained at 92.0% and no obvious changes of the gas composition were observed. The catalyst stability for steam reforming of toluene also has been investigated in other studies. Sekine [48] tested the stability of  $\text{Ni-La}_{1-x}\text{Sr}_x\text{AlO}_{3-\delta}$ , and the conversion of toluene decreased from 60% to 40% after 180 min. Kong *et al.* [49] tested the stability of Ni-MgO, the toluene conversion decreased from 70% to 30% after 400 min. As reported by Zhang *et al.* [50], the toluene conversion decreased from 50% to 25% after 200 min over Ni-Ce-Mg-olivine catalyst. Hence, the as-prepared catalyst in our work showed a high catalytic activity and a good stability for toluene steam reforming.

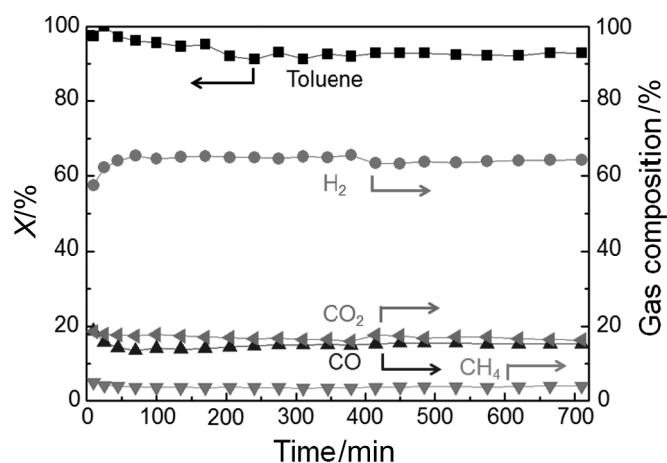


Fig. 10. Stability test of toluene steam reforming on Ni-AC(N) catalyst (reaction temperature: 973 K; Ni content: 12 wt%; S/C: 2; toluene flow speed:  $2 \text{ ml} \cdot \text{h}^{-1}$ ).

Steam reforming of toluene has been conducted in other studies [8,10,15,51,52]. The comparisons of catalytic performances are listed in Table 1. Hence, the as-prepared catalyst in our work showed a high catalytic activity and a good stability for toluene steam reforming. The excellent catalytic performance of Ni nanoparticles supported on AC was mainly contributed to the small particle size of Ni nanoparticles.

**Table 1**  
Comparisons in catalytic activity for steam reforming of toluene with other works

| Catalyst                                                                               | Reaction conditions   | Conversion/% | References |
|----------------------------------------------------------------------------------------|-----------------------|--------------|------------|
| Ni-AC(N)                                                                               | S/C = 2, T = 973 K    | 98           | This work  |
| Ni-olivine                                                                             | S/C = 3.5, T = 1063 K | 56           | [10]       |
| Ni-Ce-olivine                                                                          | S/C = 3.5, T = 1063 K | 75           | [10]       |
| Ni-Ce-Mg-olivine                                                                       | S/C = 3.5, T = 1063 K | 93           | [10]       |
| La <sub>0.8</sub> Mg <sub>0.2</sub> Ni <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub> | S/C = 3.4, T = 923 K  | 30           | [51]       |
| Ni-La <sub>0.8</sub> Sr <sub>0.2</sub> AlO <sub>3</sub>                                | S/C = 1, T = 923 K    | 21           | [52]       |
| Ni-LaAlO <sub>3</sub>                                                                  | S/C = 1, T = 923 K    | 15           | [52]       |
| Ni-α-Al <sub>2</sub> O <sub>3</sub>                                                    | S/C = 1, T = 923 K    | 5            | [52]       |
| NiO-CaO-Al <sub>2</sub> O <sub>3</sub>                                                 | S/C = 1, T = 923 K    | 70           | [8]        |
| NiO-CaO                                                                                | S/C = 1, T = 923 K    | 50           | [8]        |
| NiO-Al <sub>2</sub> O <sub>3</sub>                                                     | S/C = 1, T = 923 K    | 45           | [8]        |
| Ni-CaO-Al <sub>2</sub> O <sub>3</sub>                                                  | S/C = 3.4, T = 923 K  | 20           | [15]       |

## 4. Conclusions

In this work, the mean particle size of immobilized Ni nanoparticles was adjusted by modifications in surface properties of the support and nickel precursors. The acid treatment with the support helped to reduce the mean particle size of Ni nanoparticles from 22.4 nm to 5.7 nm by better wettability in aqueous solutions. The mean particle size of Ni nanoparticles was also affected by thermal decomposition products of nickel precursors. Ni nanoparticles prepared using nickel nitrate as the precursor showed the smallest mean particle size and the highest catalytic activity for toluene steam reforming. The mean diameter varied from 4.5 nm to 9.1 nm with the loading amount increased from 6 wt% to 18 wt%. The effects of residence time, S/C ratio and nickel loading amount on conversions were systematically investigated. The highest toluene conversion of 98.1% was obtained when the S/C ratio was 2, the Ni loading amount was 12 wt% and the toluene flow speed was 2 ml·h<sup>-1</sup>. Besides, Ni-AC(N) catalyst also showed high stability: the conversion of toluene only decreased from 98.1% to 92.0% after 700 min. The as-prepared catalysts are low-cost, highly catalytic active, and highly stable, and are thus providing promising alternative for treating tar-rich streams from biomass gasification.

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