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Deposition-precipitation approach for preparing core/shell SiO<sub>2</sub>@Ni-Rh nanoparticles as an advanced catalyst for the dehydrogenation of 2-methoxycyclohexanol to guaiacol

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# Graphical abstract



Fig.1. Schematic illustration of the formation of core/shell SiO<sub>2</sub>@Ni-Rh nanoparticles and their catalytic activity.

# Highlights

- A novel highly efficient and stable core-shell-like SiO<sub>2</sub>@Ni-Rh is successfully synthesized by deposition-precipitation.
- The as-synthesized catalysts possess high specific surface area (234.063 m<sup>2</sup>/g) and high dispersion of Ni on the surface of the catalyst.
- The dehydro-aromatization of 2-methoxycyclohexanol over the catalysts in a continuous fixed-bed reactor exhibits high conversion (98.3%) and selectivity (93.6%), high catalytic efficiency (0.47 s<sup>-1</sup>).
- The dehydrogenation of 2-methoxycyclohexanol to guaiacol is a high atom economy, high efficient, environmental friendliness, green and more promising synthesis.

Abstract: A novel core/shell nano-bimetallic catalyst SiO2 @ Ni-Rh was successfully prepared by depositionprecipitation method, using liquid ammonia as a precipitating agent. SEM, TEM, XRD, XPS, H2-TPR, H2-TPD and adsorption/desorption of nitrogen were employed to systematically investigate the surface morphology, size, chemical composition, reducibility, Ni dispersion and structure of the as-synthesized nanoparticles. It is found that the nickel and rhodium are uniformly dispersed on the silica surface to form core/shell SiO2@Ni-Rh nanoparticles with Ni atoms and Rh atoms as the outer shell and  $SiO_2$  as the core, which possess high dispersion of Ni on the surface and high specific surface area  $(234.063 \text{ m}^2/\text{g})$  of the catalyst with the mean particle size of ca. 130 nm. The dehydrogenation of 2-methoxycyclohexanol to guaiacol was used as the model reaction for evaluating the catalytic activity of the as-synthesized core/shell various Ni and Rh-containing bimetallic nanoparticles in a tubular stainless steel reactor. SiO2@15Ni-0.4Rh nanoparticles have exhibited remarkable catalytic performance, with 98.3% conversion and 93.6% selectivity of guaiacol, due to high dispersion of metal nanoparticles and synergistic effect of bimetallic Ni-Rh over the special core/shell SiO2@Ni-Rh by the addition of rhodium. Furthermore, turn over frequency value of SiO<sub>2</sub>@15Ni-0.4Rh nanoparticles achieves 0.47 s<sup>-1</sup>, showing high catalytic efficiency. In general, the dehydrogenation of 2-methoxycyclohexanol over the core-shell-like SiO2@Ni-Rh nanoparticles in a continuous fixed-bed reactor is a more promising, high atom economy, high efficient, easy separation, environmental friendliness, green synthetic pathway of guaiacol.

Keywords: bimetallic catalyst; core-shell structure; dehydrogenation; 2-methoxycyclohexanol; guaiacol.

# 1. Introduction

Guaiacol is a very important organic and pharmaceutical intermediates and fine chemical products, which has been extensively used in the synthesis of flavouring agents, fragrances, agricultural chemicals and pharmaceuticals, especially in the synthesis of sulfogaiacol and vanillin[1]. In general, diazotization and hydrolysis of 2-methoxyaniline is a widely used method for the synthesis of guaiacol. However, there are many other synthetic pathways of guaiacol to be proposed. For instance, it can be prepared from o-alkylation of catechol with dimethyl carbonate[2] and dimethyl sulfate[3] as single etherification reagents in the presence of phase transition catalyst, or the liquid phase reaction of methanol with o-halophenols[4, 5] in the presence of sodium hydroxide as a homogeneous catalyst, or the catalytic hydroxylation of anisole with H<sub>2</sub>O<sub>2</sub> in ambient conditions[6-10], or hydrolysis of 2-chloroanisole[11] or o-bromoanisole [12, 13] or 2-iodoanisole[14, 15]. However, these routes suffer from some drawbacks, such as corrosive and poisonous reagents, long and complex process, large consumption and emitting serious pollutants, which lead to environmental and economical problems.

In addition, it is very common for the vapor-phase selective alkylation of catechol with an alkylating agent including dimethyl carbonate[16-18] and methanol[19] to produce guaiacol over a heterogeneous catalyst. At present, the process of vapour-phase alkylation of catechol with an alkylating agent for the synthesis of guaiacol has been widely reported, which possesses many different advantages, such as low toxicity and corrosivity, simple separation, environmental friendliness and so on. Various heterogeneous catalysts referring to the process include metal oxides[20], molecular sieves[21], phosphates[22], supported catalysts[23-25]. However, a common and severe problem is that most of the tested catalysts are subjected to rapid deactivation on the long-running experiment, attributed to loss of acidic sites, which limits the application of this route to produce guaiacol. Hence, it is vital importance for facile synthesis of inexpensive and highly effective catalyst with high and exceptional catalytic activity in the synthesis of guaiacol under mild condition.

Comparatively, dehydro-aromatization of 2-methoxycyclohexanol over metal catalysts in a continuous fixed-bed reactor provides a novel more promising, green and more efficient synthesis for preparing guaiacol, which has received more attention because of its high conversion and selectivity, high atom economy, easy separation procedures, and environmental friendliness. Therefore, taking into account the above issues, the purpose of this paper is to design high-performance and low cost catalysts for the dehydrogenation of 2-methoxycyclohexanol to guaiacol by an eco-friendly approach. Recently, several supported monometallic metal catalysts are investigated in the synthesis of guaiacol by dehydrogenation. The active components for the supported monometallic metal catalysts are mainly palladium and nickel in the patents [26, 27]. Although the catalysts with containing Pd exhibits high conversion (92.1%) and high selectivity (93.5%) in the dehydrogenation of 2-methoxycyclohexanol [28], which restraints its industrial application due to their high cost. Nevertheless, Ni-based catalysts show unsatisfactory catalytic performances, and much more by-products are yielded. However,

the supported bimetallic catalysts has not yet been reported in the dehydrogenation of 2-methoxycyclohexanol to guaiacol. To be the best known, bimetallic catalysts often show more inspiring catalytic performances, ascribed to a remarkable synergistic and cooperative effect which likely changes the adsorption energy of reactants and intermediates on the catalyst surface. Thus, the monodisperse nano-SiO<sub>2</sub> with high surface area and chemical and thermal stability was served as the supporting material to immobilize cheap transition metal nickel as the main active component and small amount of precious metal Rh as promoter. The as-prepared catalyst possesses more unprecedented excellent activity than the corresponding Ni and Rh monometallic catalysts, which displays promising potential industrial application for preparation of guaiacol via dehydrogenation of 2-methoxycyclohexanol in a continuous fixed-bed reactor because of enhanced activity and low cost of preparation.

In this paper, monodisperse nano-SiO<sub>2</sub> spheres prepared by the well-known Stöber method[29] were used as supports to fabricate the core/shell various Ni and Rh-containing bimetallic nanoparticles by deposition– precipitation method, using liquid ammonia as a precipitating agent. Beside, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), hydrogen temperature-programmed desorption (H<sub>2</sub>-TPD), hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) and nitrogen adsorption/desorption analysis were employed to comprehensively characterize the as-synthesized silica nanospheres and core/shell SiO<sub>2</sub>@Ni-Rh. Then synthesis of guaiacol via dehydrogenation of 2-methoxycyclohexanol was used as probe reaction to investigate the catalytic performance of the as-synthesized core/shell SiO<sub>2</sub>@Ni-Rh catalysts in a tubular stainless steel reactor. And their catalytic properties and long-term stability were compared to these catalysts with various metal contents.

## 2. Experimental Section

#### 2.1 Reagents and materials

Nichel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, 98%), ammonia solution (AR, 25%), ethanol absolute (AR, 99.7%) and methanol anhydrous (AR, 99.5%) were purchased from Tianjin Sailboat Chemical Reagent Technology Co., Ltd., China. Phosphotungstic acid (AR) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., China. Tetraethyl orthosilicate (98%) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Cyclohexene oxide (98%), aluminum chloride (AR, 97.0%) and rhodium (III) chloride trihydrate (RhCl<sub>3</sub>·3H<sub>2</sub>O, 98%) were purchased from Shanghai Macklin biochemical Co. Ltd., China. All chemicals were used as received without any further purification. Deionized water was used in all experiments.

2.2 Preparation of nano-SiO<sub>2</sub> spheres

Based on the well-known Stöber method, silica microspheres were prepared by hydrolysis of tetraethyl orthosilicate in alcohol-water mixed solvent using ammonia as catalyst. Absolute ethanol (100mL), distilled water (1mL) and ammonia (11mL) were added into three-necked flask and ultrasonicated for 0.5 h. When the temperature was raised to 70 °C, 6.4545g of tetraethyl orthosilicate as a silicon source was slowly added dropwise to the resultant solution with continuous stirring. The resulting mixture was stirring and refluxed for 5 hours on a water bath, followed by aging for 24 hours at room temperature. The resulting suspension was centrifuged, washed with ethanol and water, and finally dried in vacuo overnight at 40 °C. The resultant mesoporous silica was calcined at 550 °C for 4 hours.

#### 2.3 Preparation of core/shell SiO2@Ni-Rh nanoparticles

Taking SiO<sub>2</sub>@Ni-Rh nanoparticles with 5 wt% of theoretical loading of Ni and 0.2 wt% theoretical loading of Rh for example, 0.3237g of mesoporous silica microspheres was added in 20mL of distilled water and ultrasonicated for 1 h. A homogeneous solution was obtained by dissolving 0.002g of RhCl<sub>3</sub> •  $3H_2O$  and 0.0967g of Ni(NO<sub>3</sub>)<sub>2</sub> •  $6H_2O$  in 30 mL of distilled water. The as-synthesised SiO<sub>2</sub> suspension was added to the resultant solution. Urea (0.6379g) was added into the mixture and ultrasonicated for 30 min, then the resultant mixture was heated on an oil bath under N<sub>2</sub> atmosphere at 100 °C for 5 h with being cooled by a condenser. After completing the reaction, the resulting precipitate was cooled and aged overnight at room temperature. The synthesized solid products were centrifuged and thoroughly washed with distilled water for 4-5 times, and dried in a vacuum oven at 50 °C for 24 hours. The dried solid was calcined at 450°C for 4 h to obtain SiO<sub>2</sub>/Ni-Rh nanocatalyst. For comparison, a series of SiO<sub>2</sub>/Ni-Rh with different Ni contents was also prepared by the same method.

# 2.4 Characterization of catalysts

SEM and TEM images, respectively, were obtained using a Zeiss Auriga FIB-SEM and a FEI Talos F200s electron microscope. X-ray diffraction (XRD) patterns for the powder samples was conducted using the PANalytical X'PERT POWDER with a Cu Kα radiation source (40 kV and 40 mA) as scan speed of 10°/min in the 20 range of 5° to 80°. The phase identification was made by comparison to the Joint Committee on Powder Diffraction Standards (JCPDSs). N<sub>2</sub>-absorption/desorption isotherms and the corresponding pore size distribution were performed on Quantachrome NOVA4200e. X-ray photoelectron spectroscopy (XPS) was recorded by AXIS Supra. H<sub>2</sub>-TPR experiments were operated on a Micromeritics AutoChem II 2920 TPD/TPR instrument. Before testing experiment, about 100mg of the sample loaded in a quartz reactor was first pretreated at 450 °C for 1 h under argon at a flow rate of 30 mL/min and cooled to room temperature. It was then heated to 780 °C at a heating rate of 10 °C/min in a stream of 10% H<sub>2</sub>/Ar with a flow rate of 50mL/min. The consumption of hydrogen was

collected by thermal conductivity detector (TCD). The instrument was calibrated with CuO of known amount. The amount of hydrogen consumption was denoted as X mol. H<sub>2</sub>-TPD experiments were also performed on a Micromeritics AutoChem II 2920 TPD/TPR instrument. When H<sub>2</sub>-TPR experiment was completed, the reactor was purged under argon flow for 2h to remove completely trace hydrogen, and cooled to room temperature under argon atmosphere. 10% H<sub>2</sub> /Ar was introduced into the reactor at a flow rate of 50mL/min at room temperature for 0.5h. After saturation, the reactor was purged again under argon flow for 2h in order to remove excess hydrogen. Finally, hydrogen TPD was carried out under argon atmosphere at a flow rate of 30 mL/min in programmed temperature mode up to 700 °C using a ramp of 10 °C min<sup>-1</sup>. Hydrogen consumption in H<sub>2</sub>-TPD was denoted as Y mol.

Dispersion of Ni and exposed Ni surface area were calculated according to the following equations[30-33]. Based on the hydrogen uptake, the dispersion (D) of Ni was calculated as:

$$D = \frac{2Y}{X} \times 100\%$$

And assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom (H/Nis = 1), exposed Ni surface area S was calculated as:

$$S = \frac{2Y \times N_{av} \times \sigma_{Ni}}{X \times M_{Ni}} \times 10^{-20}$$

Where  $N_{av}$  is the Avogadro's constant,  $M_{Ni}$  is the relative atomic mass (58.69 g/mol),  $\sigma_{Ni}$  is the surface area per nickel atom (6.33 Å<sup>2</sup>). Assuming a spherical shape, an average crystallite size (d) can be expressed as a function:

$$d_{v.s.} = \frac{6 \times 10^3}{(S \times \rho_{Ni})}$$

Where  $\rho_{Ni}$  is the density of nickel (8.9 g/cm<sup>3</sup>) [32].

### 2.5 Catalyst Evaluation

Dehydro-aromatization of 2-methoxycyclohexanol was performed in tubular stainless steel reactor ( $\varphi$ 10mm) embedded in a heating furnace and equipped with temperature control system. For a typical reaction, a certain amount of inert quartz granulates (8-12 mesh) was filled in the bottom of the tubular reactor, the as-synthesized catalyst (about 0.5g) was loaded in the middle of the tubular reactor, and the upper part of the reactor was filled with inert quartz granulates in order to fasten the catalyst bed securely in the middle of the tubular. After loading, the reactor was charged into the heating furnace and connected with the reaction line. A flow of N<sub>2</sub> was passed into the reaction system to purge the reaction tubes for 0.5h, while the temperature rose to 450 °C. Then hydrogen replaced of nitrogen was introduced to activate the catalyst at 450 °C for 4h. Finally, a 10 wt% solution of 2-methoxycyclohexanol in methanol was pumped into the reactor through a parallel flow pump at a constant liquid hourly space velocity (LHSV) of 11.5 h<sup>-1</sup>, while the flow of H<sub>2</sub> as a carrier gas was continuously introduced into

the reaction system to provide a reducing atmosphere and constant total pressure of 0.15 mPa. The reaction product was cooled through a condenser and was collected through a gas-liquid separator.

Turnover-frequency of catalytic reaction on supported metal catalysts was measured according to the following conditions: the amount of the catalyst weight was about 0.1g, LVSH of 10 wt% solution of 2-methoxycyclohexanol in methanol was 194.4  $h^{-1}$ , the total reaction pressure was 0.16Mpa, the flow of H<sub>2</sub> was a carrier gas, and the reaction temperature was 400 °C. The conversion rate of 2-methoxycyclohexanol was controlled in the range of 5-10% in order to ignore the effect of mass transfer. The quantitative analysis of the products mixture was performed using Agilent GC GC-7890A, which was equipped with a hydrogen flame detector.

### 3. Results and discussion

3.1Characterizations of catalysts

3.1.1 X-ray diffraction analysis



Fig.1. XRD patterns of the as-synthesized catalysts with various Ni or Rh contents.

As shown in Fig. 1, a broad diffraction peak of SiO<sub>2</sub> is observed in the range of 15°-30°, corresponding to the typical amorphous character of SiO<sub>2</sub> (JCPDS 29-0085)[34]. In the large-angle XRD patterns (Fig. 5), the reduced samples show reflections at 44.6°, 51.9° and 76.4°, respectively, assigned to the (111), (200) and (220) lattice planes of Ni Fm3m crystal structure (JCPDS 04-0850)[35, 36], indicating that nickel oxide loaded on SiO<sub>2</sub> surface are completely reduced to metallic nickel. In addition, it is noteworthy that the intensity of the nickel diffraction peak increases with the increase of Ni loading on the SiO<sub>2</sub>. Then the average crystal size of Ni was calculated using the half-width at half-height of most intense peaks of diffraction pattern and well-known Debye–Scherrer equation[37]. The results are summarized in Table 1, indicating that the average crystal size of Ni increases with the increases with the increase of Ni loading. Furthermore, XRD patterns of SiO<sub>2</sub>@Ni-Rh nanoparticles show no obvious

diffraction peak of the rhodium crystalline phase, suggesting that Rh is well dispersed or the content of Rh is too

low to be detected by XRD[38].

Catalyst	Ni surface area (S <sub>Ni</sub> ) <sup>a</sup>	Ni dispersion (D <sub>Ni</sub>	) <sup>a</sup> H <sub>2</sub> uptake <sup>a</sup>	Ni size (	nm)
	(m <sup>2</sup> /g-Ni)	(%)	(µmol/g-cat.)	XRD <sup>b</sup>	H <sub>2</sub> chem. <sup>a</sup>
SiO2@2Ni-0.1Rh	42.67	6.57	25.41	17.3	15.8
SiO2@5Ni-0.2Rh	27.97	4.31	39.84	22.3	24.1
SiO2@10Ni-0.4Rh	21.20	3.26	62.31	30.8	31.8
SiO2@15Ni-0.5Rh	15.71	2.42	65.84	46.5	42.9
SiO <sub>2</sub> @15Ni	13.46	2.07	55.55	48.8	50.1

Table1 The particle size and dispersion of Ni in the catalyst.

<sup>a</sup> Estimated from H<sub>2</sub> chemisorption at room temperature, <sup>b</sup> Estimated from XRD.

# 3.1.2 H<sub>2</sub>-TPD experiments analysis

Dispersion (D), exposed surface area (S) and average crystallite size (d) of Ni in the catalyst were calculated from H<sub>2</sub>-TPD experiments. The results are listed into Table 1. Ni dispersions (D<sub>Ni</sub>) of the samples decrease in the order: SiO<sub>2</sub>@2Ni-0.1Rh > SiO<sub>2</sub>@5Ni-0.2Rh > SiO<sub>2</sub>@10Ni-0.4Rh > SiO<sub>2</sub>@15Ni-0.5Rh> SiO<sub>2</sub>@15Ni, indicating that the increase with the loading of Ni has an adverse effect on the dispersion of Ni on the surface of the catalyst. D<sub>Ni</sub> of SiO<sub>2</sub>@15Ni-0.5Rh is larger and that of SiO<sub>2</sub>@15Ni, showing that the decoration of Rh can increase the dispersion of nickel in Ni-Rh bimetallic samples. Based on the adsorption stoichiometry of one hydrogen atom per nickel surface atom (H/Ni = 1), Ni surface areas (S<sub>Ni</sub>) of the catalysts vary in the range of 13.46–42.67 m<sup>2</sup>/g. Additionally, based on the Ni surface areas (S<sub>Ni</sub>), Ni particle sizes (d<sub>Ni</sub>) of samples increase in the order SiO<sub>2</sub>@2Ni-0.1Rh > SiO<sub>2</sub>@5Ni-0.2Rh > SiO<sub>2</sub>@10Ni-0.4Rh > SiO<sub>2</sub>@15Ni-0.5Rh> SiO<sub>2</sub>@15Ni (Table 1) from 15.8 nm to 50.1 nm, which is in consistent with the above XRD results.

3.1.3 Hydrogen – temperature programmed reduction (H2-TPR) analysis



Fig.2 H2-TPR patterns of SiO2@Ni-Rh catalysts with different Rh contents

H<sub>2</sub>-TPR profiles of SiO<sub>2</sub>@15Ni-0.5Rh, SiO<sub>2</sub>@15Ni-0.3Rh and SiO<sub>2</sub>@15Ni catalysts are illustrated in Fig.2. The profile of SiO<sub>2</sub>@15Ni shows two clear peaks, a strong peak at ca. 521°C and a shoulder at ca.626 °C, indicating that there are at least two distinct reducible species exist simultaneously over the surface of SiO<sub>2</sub>@15Ni. The peak at ca. 521 °C can be assigned to bulk NiO or particle agglomerates dispersed on the surface of catalysts. The peak at ca. 626 °C may be associated with the reduction of nickel oxide species embedded in the surface of SiO<sub>2</sub>. Significantly compared with reduction peak of pure nickel oxide at 220°C[39], the reduction peak of SiO<sub>2</sub>@15Ni widens and shifts towards higher temperature, owing to the strong interaction between Ni and support and the high dispersion of nickel on the surface of silicon oxide[40]. In addition, Fig.2 reveals that the main peaks in the H<sub>2</sub>-TPR trace of SiO<sub>2</sub>@15Ni, SiO<sub>2</sub>@15Ni-0.3Rh, SiO<sub>2</sub>@15Ni-0.5Rh are at ca.521°C, 450°C and 418°C, respectively. It can be found that for all catalysts, the main reduction peaks shift to lower temperature with Rh contents increasing, demonstrating that the decoration of noble metal Rh favors the reduction of nickel oxide because of H<sub>2</sub> spill-over at lower temperature[41]. However, the small reduction peak at around 310°C is observed on the H<sub>2</sub>-TPR profiles of the as synthesized catalysts modified by Rh, and can be interpreted to the reduction of rhodium oxide species or to rhodium in interaction with nickel [42, 43]. In general, the reducibility of the bimetallic catalyst modified with rhodium behaves more outstanding than that of the monometallic Ni catalyst.

3.1.4 N2-absorption/desorption isotherms and pore size distribution analysis

Catalyst	$S_{BET}$ (m <sup>2</sup> /g)	$V_{\text{pore,t}}(\text{cm}^{3}/\text{g})$	D <sub>pore,s</sub> (nm)
SiO <sub>2</sub> /Ni-Rh (400)	234.063	0.318	5.439
SiO <sub>2</sub> /Ni-Rh(500)	213.286	0.303	5.681

SBET: specific surface area; Vpore, t: total pore volume; Dpore,s: average pore size detected by BJH method.



Fig.3. (a) N<sub>2</sub>-adsorption/desorption isotherms and the corresponding pore size distribution of the SiO<sub>2</sub>@Ni-Rh catalysts reduced at 400 °C for 4h; (b) N<sub>2</sub>-adsorption/desorption isotherms and the corresponding pore size distribution of the SiO<sub>2</sub>@Ni-Rh catalysts reduced at 500 °C for 4h.

Porous structure of the SiO<sub>2</sub>@Ni-Rh catalysts at different reduction temperatures, including 400 °C and 500 °C, were characterized by N<sub>2</sub> adsorption/desorption instrument. Both the catalysts of the isotherms exhibit type-IV adsorption isotherm pattern with an obvious hysteresis loop in the range of P/P<sub>0</sub> 0.4-0.9 in Fig. 3, indicating the presence of mesopores in these catalysts[44]. The hysteresis loops for these catalysts belong to the type H1 according to the IUPAC classification[45, 46]. It indicates that the mesopores in both the catalysts have the complex and irregular shapes, e.g., the cylinder or spherical pores. The main textural properties of these catalysts are summarized in Table 2. In comparison with that of the SiO<sub>2</sub>/Ni-Rh catalyst reduced at 400 °C, the specific BET surface area and total pore volume of the SiO<sub>2</sub>/Ni-Rh catalyst reduced at 500 °C slightly drop. It is found that the reduction temperature has no significant influence on the textural properties of the catalysts in the temperature range of 400-500 °C. This fact could be explained by that the highly dispersed metal species strongly interact with the support SiO<sub>2</sub> to prevent the aggregation and enhance the stability of catalytic nanoparticles[47, 48].

3.1.5 Scanning electron microscope analysis and transmission electron microscopy analysis



Fig.4. SEM images of the as-prepared SiO<sub>2</sub> (a)-(b) and SiO<sub>2</sub>@Ni-Rh nanoparticles (c); TEM images of the as-prepared SiO<sub>2</sub>@Ni-Rh nanoparticles (d)-(e); the HAADE-STEM image (f): the corresponding high resolution Si mapping (i), the corresponding high resolution O mapping (ii), the corresponding high resolution Ni mapping (iii) and the corresponding high resolution Rh mapping (iiiv) of SiO<sub>2</sub>@Ni-Rh nanoparticles.

To reveal the morphology and microstructure of the as-prepared SiO<sub>2</sub> and SiO<sub>2</sub>@Ni-Rh nanoparticles, SEM, TEM and HRTEM observations were carried out in Fig. 4. As shown in Fig. 4a-4b, the as-synthesized monodisperse SiO<sub>2</sub> nanoparticles with uniform spherical shape and smooth surface have a narrow size distribution with a mean particle size of ca. 130 nm. After the deposition–precipitation, the as-prepared nanoparticles were coated with irregular floccules, and surfaces of the nanoparticles became rough. SEM results indicate that the nanoparticles after surface modification are still monodisperse, with coatings on individual nanoparticles. The floccules are composed of Ni-Rh bimetallic nanoalloy layers formed by the H<sub>2</sub> reduction of precursors of SiO<sub>2</sub>@Ni-Rh nanoparticles. The bimetallic layer covering the surface of the silica sphere has a thickness of ca. 2 nm as evidence of a large-scale TEM (Fig. 4e). To further illustrate the morphologies and distributions of Ni and Rh atoms in the particles of SiO<sub>2</sub>@Ni-Rh nanoparticles, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations were performed. The results show that Ni atoms (blue) and Rh atoms (pink) are anchored on the outside surface of the nanostructure and form Ni-Rh rich shell. The as-prepared SiO<sub>2</sub> composed of Si atoms (green) and O atoms (red) is obviously defined as a core. The random region HAADF-STEM mapping image of SiO<sub>2</sub>@Ni-Rh nanoparticles clearly defines that the core–shell structure with SiO<sub>2</sub> centered in the core and Ni-Rh atoms as a shell surrounding the SiO<sub>2</sub> core of bimetallic catalysts are successfully synthesized by deposition–precipitation.

3.1.6 X-ray photoelectron spectroscopy



Fig.5. XPS survey spectra of Ni 2p, Rh 3d of the as-prepared core-shell-like SiO2@Ni-Rh.

X-ray photoelectron spectroscopy (XPS) measurement was carried out to further investigate the elemental composition and chemical states of the as-prepared SiO<sub>2</sub>@Ni-Rh catalysts. Fig. 5a and 5b show XPS spectra of Ni 2p and Rh 3p in the SiO<sub>2</sub>@Ni-Rh catalysts. The survey spectrum reveals the presence of Ni and Rh in the samples, which is accordance with the results of the above HAADF-STEM mapping images. In the fine spectra of Ni 2p (Fig. 5a), the peaks at the binding energies of 852.6 eV and 876.9 eV are assigned to Ni 2p3/2 and Ni 2p1/2, respectively, suggesting that Ni<sup>2+</sup> precursor embedded in spherical silicon dioxide is successfully reduced to form metallic Ni on the surface of monodisperse SiO<sub>2</sub> nanoparticles[34]. Besides, two shake-up satellite signals at 858.6 eV and 876.9 eV are observed, which can be caused by multi-electron excitation[49, 50]. As shown in Fig. 5b, the peaks observed in the XPS spectra of Rh 3d at binding energies of 306.9 eV and 311.7 eV are characteristic of metallic Rh, demonstrating that Rh predominantly exists in Rh0 form on the surface of monodisperse SiO<sub>2</sub> nanoparticles[51]. It is notable that the Rh 3d5/2 peaks of the SiO<sub>2</sub>@Ni-Rh catalysts show negative shifts compared to those of pure Rh nanoparticles, which may be attributed to the transfer of electrons from Ni to Rh on the catalyst. The electronic transfer can lead to the downshift of the Rh d-band center position and the reduction of the adsorption energies of the reactants on the catalyst as well as their activation barriers, which has a dominant

influence in accelerating reaction rate and facilitates the improvement of catalytic activity[52].

3.2 Catalytic properties of the as-prepared core/shell SiO2@Ni-Rh nanoparticles

Dehydrogenation of 2-methoxycyclohexanol to guaiacol was adopted as a probe reaction to quantitatively evaluate the catalytic activity of core/shell SiO<sub>2</sub>@Ni-Rh nanoparticles. In the present work, the effect of Ni and Rh loading on the catalytic activity of the as-prepared catalysts for the dehydrogenation of 2-methoxycyclohexanol to guaiacol and the kinetics of this dehydrogenation reaction were systematically studied. Before the reactions, all the catalysts are uniformly reduced by hydrogen at 450 °C for 4 h.



Fig.6. The catalytic activity of core/shell SiO<sub>2</sub>@Ni-Rh with various Ni loading; reduction temperature, 450 °C; reaction temperature, 400 °C; reaction pressure, 0.16 mPa; LHSV, 11.5  $h^{-1}$ ; carrier gas, H<sub>2</sub>; TOS (time on stream), 3h.

Fig. 6 shows the effect of Ni loading on the catalytic properties of the as-prepared catalysts. With the increase of nickel loading, the activity of the catalyst firstly reached a plateau. The trend of the conversion rate is similar to that of selectivity with the variation of nickel loading in Fig. 6. When the conversion of the substrate reaches its maximum 98.6% at 20 wt% of Ni loading, the selectivity of guaiacol attains its maximum ca. 87.8% at 25 wt%. The further increase of nickel loading results in an obvious decrease of activity of the catalyst and selectivity of the main product because of the aggregation and agglomeration of the nickel species particles, attributed to the relatively high Ni loading [53]. Taking the above results into consideration, there is an optimal Ni loading of the catalysts for the dehydrogenation of 2-methoxycyclohexanol at ca. 15-20 wt%.



Fig.7. The dependence of catalytic activity on the weight ratios of Rh/Ni; reduction temperature, 450 °C; reaction temperature, 400 °C; reaction pressure, 0.16 mPa; LHSV, 11.5 h<sup>-1</sup>; carrier gas, H<sub>2</sub>; TOS (time on stream), 3h.

The catalytic activities of catalysts with various weight ratios of Rh/Ni at 0-5 wt% are shown in Fig. 7. On fixed 15% nickel loading supported catalysts, the catalytic activity increases with the increase of the weight ratios of Rh/Ni from 0 to 4wt%, showing surprisingly high 98.3% 2-methoxycyclohexanol conversion and 93.6% guaiacol selectivity, contributed to the increase of the number of active sites for high metal loading catalysts. However, when the mass ratio of Rh/Ni is higher than 4wt%, there is a slight decrease in the conversion and selectivity, ascribed to the agglomeration and aggregation of nanoparticles that has a negative impact on the catalytic activity of the catalyst. But SiO<sub>2</sub>@15Ni catalysts exhibit weak catalytic activity, 90.3% conversion and 77.7% selectivity. Due to the formation of a stable surface alloy, which improves the dispersion of the metal nanoparticles on the SiO<sub>2</sub> surface by the addition of rhodium, the core/shell bimetallic Ni-Rh catalysts show higher catalytic activity and selectivity than monometallic nickel catalysts in the dehydrogenation of 2-methoxycyclohexanol to guaiacol.



Fig.8. Catalytic performance of all the catalysts as a function of time on stream; reduction temperature, 450°C;

reaction temperature, 400°C; reaction pressure, 0.16 mPa; LHSV, 11.5 h<sup>-1</sup>; carrier gas, H<sub>2</sub>. SiO<sub>2</sub>@15Ni-0.4Rh: — conversion — selectivity; SiO<sub>2</sub>@15Ni: — conversion — selectivity; SiO<sub>2</sub>@5Rh: — conversion — selectivity.

For the purpose of comparison, the catalytic activities and long-term stabilities of all the catalysts were investigated. For SiO<sub>2</sub>@15Ni-0.4Rh, the conversion of reactant and the selectivity of aimed product (guaiacol) gradually achieve at ca. 85% within the first 180mins, then reach the maximum and remain for a long time in Fig. 8. In contrast, for SiO<sub>2</sub>@15Ni, the conversion of reactant achieves at only 80% after an upward tendency within the first 180mins, and is maintained at ca. 80% for only 150mins then it dropped rapidly to below 70 % after 360mins of time on stream. A sharp decline of selectivity of the catalytic test systems over SiO<sub>2</sub>@15Ni is observed during dehydrogenation process. Furthermore, it is found from Fig.8 that SiO<sub>2</sub>@5Rh presents more unsatisfactory activity and selectivity than SiO<sub>2</sub>@15Ni. In general, the as-prepared core/shell SiO<sub>2</sub>@15Ni-0.4Rh catalyst possesses higher catalytic activity and selectivity than the corresponding Ni and Rh monometallic catalysts prepared by the same method, which could be ascribed to a synergistic effect between Ni and Rh atoms generally caused by electronic (ligand) and geometric (ensemble) effects[54-57].

To further demonstrate the superior catalytic performance of bimetallic Ni-Rh supported on SiO<sub>2</sub> catalyst, the initial TOF values of SiO<sub>2</sub>@15Ni-0.4Rh and SiO<sub>2</sub>@15Ni were measured, respectively. For SiO<sub>2</sub>@15Ni-0.4Rh, the conversion of the reactant was 7.8% under the above reaction conditions. Based on the H<sub>2</sub> uptake of supported metal catalysts (Table 1 ), the initial TOF value of SiO<sub>2</sub>@15Ni-0.4Rh was determined to be 0.47 s<sup>-1</sup>, obviously higher than that of SiO<sub>2</sub>@15Ni (0.40 s<sup>-1</sup>). The result indicates that SiO<sub>2</sub>@15Ni-0.4Rh shows higher catalytic efficiency than the latter one, because the addition of rhodium is helpful for improving on dehydrogenation activity of the catalyst. In summary, Ni-Rh catalyst supported on SiO<sub>2</sub> exhibits high and exceptional catalytic activity for the dehydrogenation reactions of the model compounds and superior selectivity towards the aimed product compared with SiO<sub>2</sub>@15Ni, due to high dispersion and synergistic effect of Ni-Rh NPs, suggesting that the highly dispersed bimetallic Ni-Rh species are necessitated for obtaining optimum performance in the dehydrogenation of 2-methoxycyclohexanol to guaiacol.

#### 4. Conclusion

Firstly, the monodisperse SiO<sub>2</sub> nanospheres with mesoporous structure, high specific surface areas and thermal stability were prepared by the well-known Stöber method, which have a narrow size distribution with a mean particle size of ca. 130 nm. Then core/shell-structured bimetallic catalysts with SiO<sub>2</sub> centered in the core and Ni-Rh atoms as a shell surrounding the SiO<sub>2</sub> core are successfully synthesized by deposition–precipitation, and the

coatings of whose have a thickness of ca. 2 nm. The addition of rhodium in the catalyst drops the reduction temperature of the precursor and increases the dispersion of nickel on the surface silica. Meanwhile, SiO<sub>2</sub>@Ni-Rh catalysts show the transfer of electrons from Ni to Rh on the catalyst, leading to the downshift of the adsorption energies of the reactants on the catalyst as well as their activation barriers and favoring the improvement of catalytic activity. Subsequently, the dehydrogenation of 2-methoxycyclohexanol to guaiacol as a probe reaction was carried out under SiO<sub>2</sub>@15Ni-0.4Rh, which exhibits excellent performance with a 2-methoxycyclohexanol conversion of up to 98.3% and a guaiacol selectivity of 93.6% for a long time at 400 °C. In addition, the initial turnover frequency value of SiO<sub>2</sub>@15Ni-0.4Rh (0.47 s<sup>-1</sup>) proves obviously higher than that of SiO<sub>2</sub>@15Ni (0.40 s<sup>-1</sup>). Finally, considering its high catalytic activity and excellent stability, the core-shell-like SiO<sub>2</sub>@Ni-Rh nanoparticles have promising applications in the area of advanced heterogeneous catalysis, which are helpful for exploiting new synthesis method, engineering design and industry production of guaiacol.

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