

A New Preparation Method of Environmental Friendly Reforming Catalyst—Ni₂O₃/PG and its Performance Test

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Abstract

The utilization of biomass energy has an important role of the ecological environment protection. Removal of tar produced in the process of biomass energy use and reforming to small molecular combustible gas can effectively improve the heating value of biomass energy. This thesis introduces coordination homogeneous precipitation method to prepare Ni₂O₃/PG catalyst, with high nickel oxide as catalyst active component, micro/nano level chemical purification attapulgite as the carrier. These catalysts were characterized by using a combination of X-ray diffraction (XRD), specific surface area measurement (BET), field emission scanning electron microscopy (SEM), high resolution transmission electron microscopy (TEM), and CO₂ catalytic reforming of paraxylene as tar model compounds, investigated the effects of the different Ni₂O₃ load, and different reaction temperature paraxylene CO₂ catalytic reforming reaction influence. The result indicates that Ni₂O₃/PG catalyst has good activity for the CO₂ reforming of paraxylene, it can effectively reduce the activation energy of conversion of paraxylene. Removal efficiency of paraxylene shows an obvious increase at 600 °C when using Ni₂O₃/PG catalyst, and small molecular combustible gas yield also present a large increase at 500 °C to 700 °C. The carbon deposition rate of Ni₂O₃/PG catalyst is investigated by a novel experiment, and the result shows that the carbon deposition rate is on the rise under 500 °C, and then decline as the temperature rises.

Keywords: Biomass energy, ecological environment protection, nickel oxide; attapulgite clay, semiconductor catalysis, catalytic reforming, coordination homogeneous precipitation method.

Introduction

Since the traditional fossil energy increasingly exhausted, new energy technology development has been put on the agenda. As the fourth largest energy after oil, coal and natural gas, biomass has been received more and more attention as a kind of renewable energy.¹

Straw, livestock manure, municipal waste, industrial organic waste, etc. all belong to the category of biomass. Thus, the utilization of biomass energy has an important role of the

ecological environment protection. Gasification is an effective means of high grade utilization of biomass energy.² However, besides the production of gas, tar will also be produced in the gasification process, which can cause the reduction of the gasification efficiency, corrosion of gasification equipment, stoppage of pipeline and harm the operation of equipment.³ Therefore, removing of tar is an important research direction of biomass gasification.

Thermalization method has been widely studied in removing tar, including the thermal cracking method and catalytic cracking method.⁴⁻⁷ The thermal cracking of tar generally requires high reaction temperature. To totally remove tar, the high temperature should be over 1100 °C, which makes the tar removal equipment should not only be made of structures and materials can withstand high temperature, but also possess good heat-preservation property. To achieve desired effect of tar removal, it needs to consume huge amounts of energy to get the necessary reaction temperature for thermal cracking, which is very unreasonable in economic terms.⁸ Orio et al.⁹ conduct comparative studies on tar catalytic cleavage reactions which use dolomites from different places as catalyst. The study shows that the content of Fe₂O₃ in dolomite affects its catalytic effect in tar catalytic cleavage reaction. The higher content of Fe₂O₃ leads to the better catalytic effect of dolomite. The dolomite rich in Fe₂O₃ can make the transformation efficiency of tar catalytic cleavage reaction reaches 95%, the gaseous product increases by 10% to 20%, the lower calorific value increases by 15%. Among the components of reaction gas, hydrogen increases by 4%, carbon monoxide, carbon dioxide and methane remains almost same. Rapagna et al.¹⁰ observe the tar catalytic cleavage reaction which uses olivine as catalyst. In their paper, the catalytic activity of olivine is contiguity with dolomite. In the tar thermal cracking experiment which uses quartz stone as inert bed materials, the absolute amount of tar in gasified gases is 43 g/Nm³. However, in the tar catalytic cleavage experiment which uses olivine as catalyst, the amount of tar decreases by 90% and the absolute amount is 24 g/Nm³. Since the mechanical strength of olivine is higher than that of dolomite, the olivine can replace dolomite in circumstances where need catalyst of high mechanical strength, such as fluidized bed.

Supported catalysts have been studied extensively in recent years. Swierczynski et al.¹¹ use forsterite as carrier to load nickel to prepare catalyst, use methylbenzene as model compound of tar to make tar catalytic cleavage experiment. The study shows that the forsterite loaded nickel catalyst's effect of catalytic cleavage removal on tar is much better

than that of pure forsterite, the catalytic cleavage conversion efficiency of nickel-based forsterite catalyst on toluene at 560°C is equivalent to that of pure forsterite at 850°C. Pure forsterite will produce benzene below 20% in the catalytic cleavage reaction; however, nickel-based forsterite catalyst can totally convert toluene into carbon monoxide, carbon dioxide and hydrogen. Miyazawa et al. ¹² respectively load nickel onto the surface of Al₂O₃, ZrO₂, TiO₂, CeO₂, MgO to make supported catalyst. At the reaction temperature of 823K, the order of tar catalytic cleavage conversion activity of catalysts above is Ni/Al₂O₃>Ni/ZrO₂>Ni/TiO₂>Ni/CeO₂>Ni/MgO>no catalyst. From the result of catalyst characterization, the catalytic activity of catalyst is relevant to the percentage of nickel on the surface of catalyst. During the process of the experiment, Ni/CeO₂ shows up best performance of the resistance carbon. Kimberly ¹³ conducts a study on the nickel base catalyst's tar catalytic cleavage removal effects in fluidized bed. As the fluidized bed demands a high strength of catalyst, Kimberly chooses alumina with high abrasion-resistant capability as carrier and nickel oxide as active components to load. In order to further improve the abrasion-resistant capability and the carbon-resistance capability of catalyst, Kimberly also loads magnesia and kali on the carrier. The study presents that this kind of catalyst possesses good abrasion-resistant and carbon-resistance capability, moreover, its catalytic cleavage removal efficiency to tar in fluidize bed can reach over 80%. Courson et al. ¹⁴ make and prepare catalyst, with nickel oxide as active component and forsterite as carrier. They also conduct a study on how calcination temperature influences catalytic performance. By characterizing catalyst, they found that catalyst's carrier can powerfully interact with active component. Catalyst with active component of 2.8% have best properties of tar catalytic cleavage at 1100°C. During the test, no carbon sintering is found, while few carbon deposits are produced on the surface of catalyst.

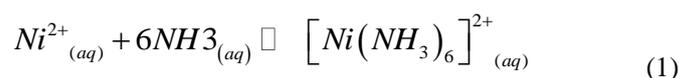
The thesis focuses on the CO₂ reforming reaction of tar on the surface of catalyst with Ni₂O₃ as active component. Ni₂O₃ is non-stoichiometric with vacancy of cation, belongs to P-type semiconductor. When its temperature rises, it will excite the electron in filled band and step to the acceptor level, leading to electron hole in filled band. Ni₂O₃ which becomes conductor can transfer electrons as well as trap electrons from environment outside, so that it can accelerate oxidation reactions and dehydrogenation reactions with the characteristic of electron transfer. As semiconductor oxide, Ni₂O₃ has special features of high melting point, good heat resistance and insensitive to toxic. This paper shows an experiment which uses paraxylene as tar model compound, evenly loads nanometer Ni₂O₃ on micro-nanometer attapulgite after chemical purification through the coordination homogeneous precipitation method. It expedites how different loading capacity of Ni₂O₃, different reaction temperature influences the reaction efficiency and gas production of CO₂ catalytic reforming of paraxylene, as

well as measures the carbon amount of catalyst at different reaction temperatures in given time.

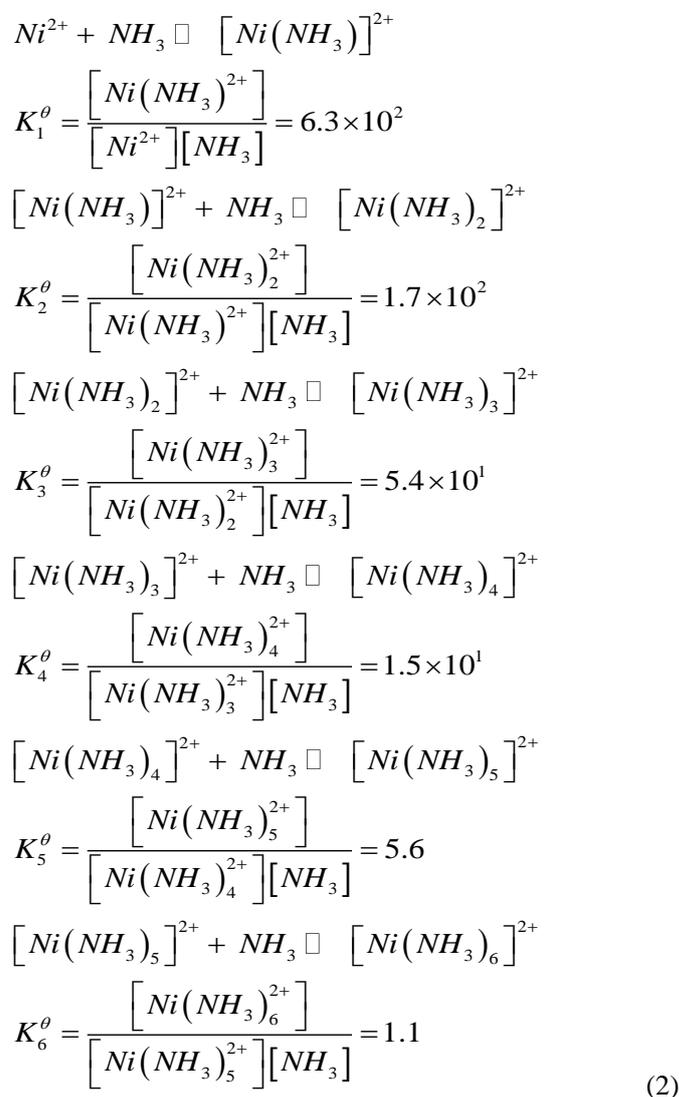
Preparation of the catalyst

The preparation principle of catalyst: The high nickelic oxide/ attapulgite catalysts were prepared by coordination homogeneous precipitation method with NH₃•H₂O as complexing liquid and Ni(NO₃)₂•6H₂O as the material of catalyst active components. NH₃•H₂O is added to the Ni(NO₃)₂•6H₂O solution and Ni-NH₃ coordination compound solution is achève.

When NH₃•H₂O is added to the Ni(NO₃)₂•6H₂O solution, make sure the concentration of NH₃ is big enough, can we eventually establish the following balance:



In fact, Ni²⁺ is cooperate with six NH₃ gradually to form [Ni(NH₃)₆]²⁺, therefore there are the following series of balance:



Thus, the atability constant of $[Ni(NH_3)_6]^{2+}$ is:

$$K_S^\theta = K_1^\theta K_2^\theta K_3^\theta K_4^\theta K_5^\theta K_6^\theta = 534386160 \quad (3)$$

The instability constant of $[Ni(NH_3)_6]^{2+}$ is:

$$K_{IS}^\theta = \frac{1}{K_S^\theta} = 1.8713 \times 10^{-9} \quad (4)$$

The relationship between coordination equilibrium and precipitation dissolving balance can be regarded as the process that ligands contest metal ion with precipitant.

Ammonia dissolved in solution, the ionization equation is :



The wake base ionization balance constant of ammonia is :

$$K_b = \frac{[OH^-][NH_4^+]}{[NH_3]} = 1.8 \times 10^{-5} \quad (6)$$

The precipitation and dissolution equilibrium of $Ni(OH)_2$ can be represented by the following formula :

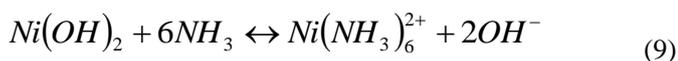


The solubility product constant of $Ni(OH)_2$ is :

$$K_{sp}(Ni(OH)_2) = 2 \times 10^{-15} \quad (8)$$

From the above content, in order for make sure no $Ni(OH)_2$ appear in the solution, it must make sure that $[Ni^{2+}][OH^-]^2 < K_{sp}(Ni(OH)_2)$, the solution is unsaturated under this condition, and there is no precipitate formed. If there are solid in the system, the balance will move to dissolve direction, until saturated.

Assume that all the Ni^{2+} react with NH_3 to get $Ni(NO_3)_6 \cdot 6H_2O$:



$$\frac{[Ni(NH_3)_6^{2+}][OH^-]^2}{[NH_3]^6} = K_S^\theta \times K_{sp} \quad (10)$$

Let y_0 be the the least concentration of $[NH_3]$ should be contained in $Ni-NH_3$ coordination compound solution, x_0 be the concentration of $[Ni(NH_3)_6]^{2+}$ of $Ni(NO_3)_2 \cdot 6H_2O$ solution when the Ni^{2+} are totally converted to $[Ni(NH_3)_6]^{2+}$. The formula can be obtained :

$$y_0 = \sqrt[5]{\frac{x_0 K_b}{K_S^\theta \times K_{sp}}} \quad (11)$$

Accroding to the formula :

$$w_0 = \frac{K_{IS}^\theta [Ni(NH_3)_6^{2+}]}{[NH_3]^6} = \frac{K_{IS}^\theta x_0}{y_0^6} \quad (12)$$

It can be figured out that the concentration of Ni^{2+} in the $Ni-NH_3$ coordination compound solution is w_0 . $x=x_0$, $y=y_0$, $w=w_0$.

According to the formula :

$$x_{i+1} = x_i - w_i \quad (13)$$

It can be concluded that the least concentration's modification value of $[Ni(NH_3)_6]^{2+}$ should be contained in the solution is x_{i+1} . Besides, according to the formula :

$$y_{i+1} = \sqrt[5]{\frac{x_{i+1} K_b}{K_S^\theta \times K_{sp}}} \quad (14)$$

The concentration's modification value of $[NH_3]$ in the solution is y_{i+1} , among which i is iterations and $i=0$ at the initial time.

According to the formula :

$$w_{i+1} = \frac{K_{IS}^\theta [Ni(NH_3)_6^{2+}]}{[NH_3]^6} = \frac{K_{IS}^\theta x_{i+1}}{y_{i+1}^6} \quad (15)$$

The concentration's modifier of Ni^{2+} in $Ni-NH_3$ coordination compound solution can be figured out as w_{i+1} and be judged whether the number of w_{i+1} is converged. If it is, we can culcaluate the volume of ammonia totally needed to prepare $Ni-NH_3$ coordination compound solution by the following formula :

$$V_a = \frac{17 \cdot (y_i + 6x_i) V_{CS}}{0.28 \times 0.87} \quad (16)$$

Otherwise, let i be $i+1$ and return to continue culcalating.

Table 1
The notes of symbols in the formulas

Symbol	Note
K_C^θ	stability constant
K_b	wake base ionization balance constant
K_{sp}	solubility product constant
w_i	the concentration of Ni^{2+} in $Ni-NH_3$ coordination compound solution
x_i	the concentration of $[Ni(NH_3)_6]^{2+}$ in $Ni-NH_3$ coordination compound solution
y_i	the concentration of $[NH_3]$ in $Ni-NH_3$ coordination compound solution
V_{CS}	the volume of $Ni-NH_3$ coordination compound solution
V_a	the volume of ammonia

Catalyst preparation: Catalyst preparation device is shown in figure1, consist of electro-thermostatic water bath, three-necked flask, condenser pipe, syringe and syringe pump.

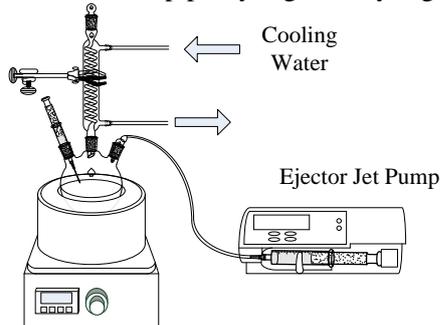
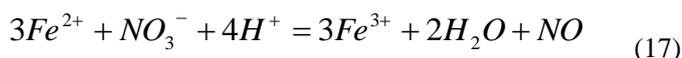


Figure 1: catalyst preparation device

Preparation of Ni-NH₃ complex first. Assume that all Ni²⁺ in the 100ml solution react with NH₃ to get Ni(NO₃)₆.6H₂O, its concentration x is 0.1893 mol/L. The calculations show that the concentration of NH₃ is 1.2610mol/L. It takes 1.1358mol/L of NH₃ to get Ni-NH₃ complex, so at least 0.2397mol NH₃ in the ammonia, that is to say, at least 16.7ml ammonia(mass fraction of 28%, relative density of 0.87g/ml) is needed.

Because nickel oxide is non-stoichiometric compound, loading amount is measured by nickel. Dissolve 5.5g Ni(NO₃)₆.6H₂O in ultrapure water, and dilute with water to 30ml. Pour 20ml ammonia into the solution and stir with electro-magnetic stirrer, 50ml Ni-NH₃ complex is prepared. Attapulgate is purified by chemical method, take 10g attapulgate into the 1000ml three-necked flask and set the temperature of electro-thermostatic water bath to 60°C. Pour Ni-NH₃ complex into the three-necked flask, and drip 2ml polysorbate80 mix until completely incorporated. Change the temperature to 70°C, open the cooling water pipe. Set the syringe pump flow rate and total flow respectively to 500ml/h and 400ml.

Stir Ni-NH₃ complex, attapulgate and polysorbate for 1 hour until get green turbid liquid, and then filter by vacuum filtration. In order to weaken the agglomeration between the Ni₂O₃ particles, turbid liquid must be repetitive scrubbed by anhydrous ethanol. Drop the ferrous sulfate solution into the filtrate after each wash, if color turns light, it means nitrite ion in the filtrate:



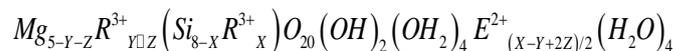
Washing the filtrate until the color of solution no longer change.

Vacuum drying the filtrate under 105°C, and then crushing adequately by mortar. After calcinating for 1 hour in the muffle furnace under 400°C, 10Ni₂O₃/PG catalyst finally obtained.

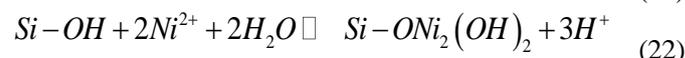
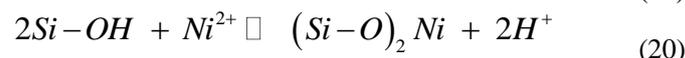
The performance test and analysis of the catalyst

XRD: Rigaku D/Max 2500VL/P type X-ray diffraction was carried out on the phase analysis of catalyst.

The crystallochemical formula is :



R³⁺ represents Al³⁺ and Fe³⁺, □ represents octahedral voids, E²⁺ represents exchangeable cations. The phenomenon of replacement of isomorphism is common in the octahedral voids, Al occupy about 28%~59% of octahedral voids. In the process of the preparation of catalyst, Ni²⁺ can occupy the place of octahedral, also can exchange E²⁺ in the crystal.



Thus, except Ni₂O₃, we can find characteristics diffraction peaks of (Ni,Mg)₃Si₄O₁₀(OH)₂ and (Ni,Mg)₄Si₆O₁₅(OH)₂.6H₂O in the chromatogram as shown in the figure 2.

According scherre equation, normal size of crystal face of Ni₂O₃ on the catalyst can be calculated :

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (23)$$

$$D = \frac{0.89 \times 0.154056}{\frac{0.269\pi}{180} \times \cos 27.579} = 32.96 \quad (24)$$

The average normal size of crystal face is 32.96nm.

BET: Table 2 shows the BET test results of catalysts of different loading capacity which are prepared by coordination homogeneous precipitation method. It is concluded that the specific surface area of 6 Ni₂O₃ /PG on catalyst loading Ni₂O₃ is a little smaller than that of pure PG. Besides, the specific surface area of 10Ni₂O₃ /PG and 14Ni₂O₃ /PG becomes bigger than that of pure PG. When the loading amount is 10%, the specific surface area reaches the maximum point. In general, with the increase of loading amount, the specific surface area appears the trend of becoming smaller and then bigger and smaller at last. While the average pore volume and the average pore size appears the trend of becoming bigger and then smaller and bigger at last. Because the loaded Ni₂O₃ nanometer particle covers the PG crystal's nanometer channel, while increasing the surface area of mesoporous and macroporous formed by rod-like crystal.

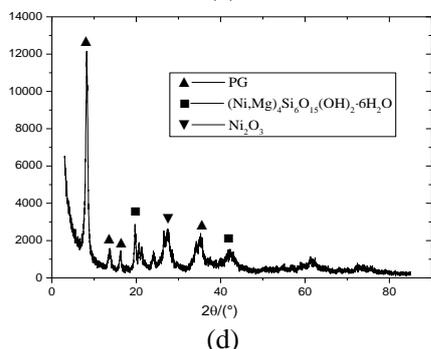
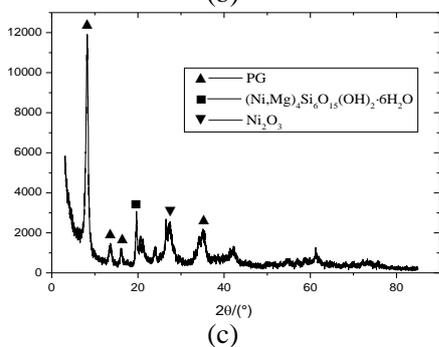
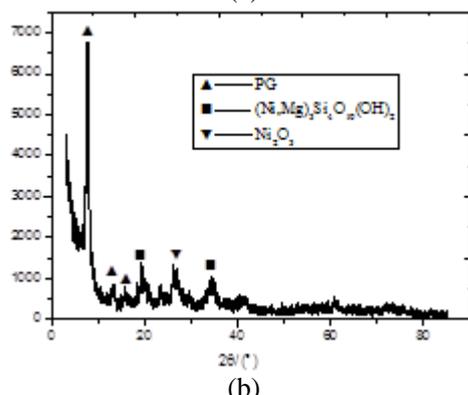
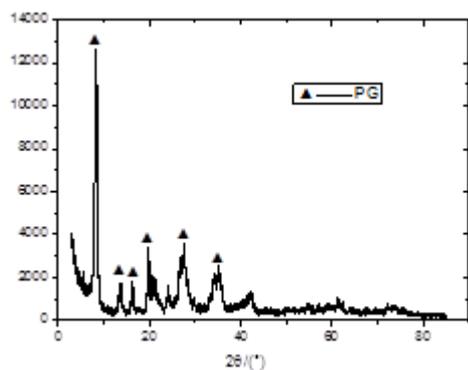


Figure 2: (a) PG (b) 6Ni₂O₃/PG (c) 10 Ni₂O₃/PG (d) 14 Ni₂O₃/PG

Table 2
BET test results of the catalyst

Catalyst types	BET surface area (m ² · g ⁻¹)	Pore volume (cm ³ · g ⁻¹)	Pore diameter (nm)
PG	120.9	0.5266	17.423
6Ni ₂ O ₃ /PG	118.01	0.6182	20.954
10Ni ₂ O ₃ /PG	133.23	0.5602	16.819
14Ni ₂ O ₃ /PG	131.2	0.6533	19.918

Figure 3 shows the adsorption isotherm of each catalyst. As the figure presents, PG, 6Ni₂O₃/PG, 10Ni₂O₃/PG and 14Ni₂O₃/PG is typical IV type adsorption isotherm, appearing hysteresis loop at 0.7, which means the pore size is larger. The absorptive capacity of high pressure area rises more rapidly, showing that there are more pore of big pore size. From the result of BET test, the average pore size of catalyst is between 17nm and 21nm. Relating to SEM, among them the macropore whose pore size is bigger than 50nm mainly is rod-like crystal pile hole.

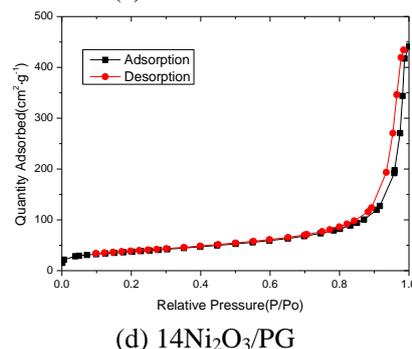
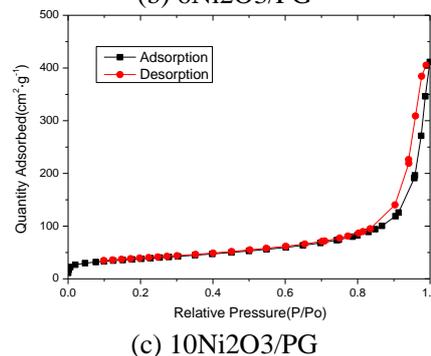
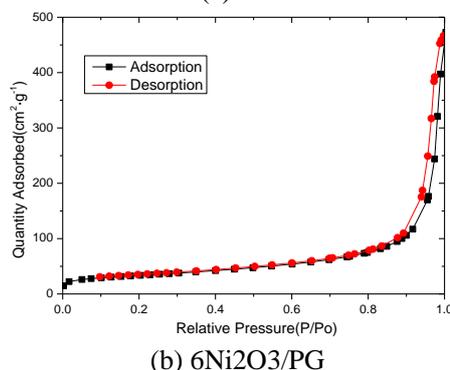
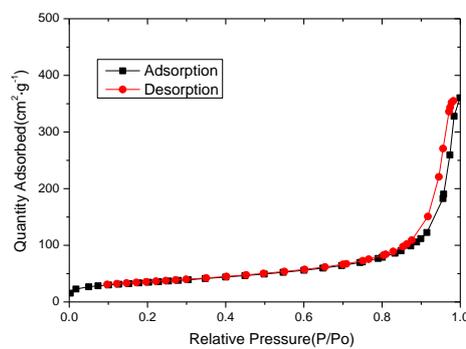
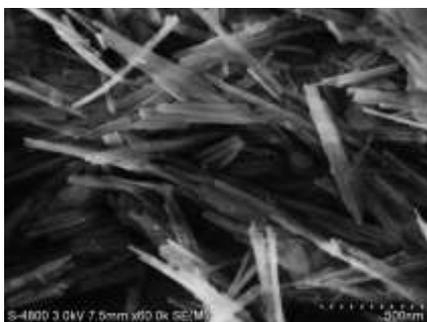
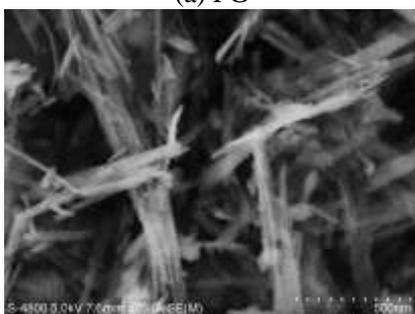


Figure 3 : Adsorption isotherm of each catalyst

SEM: Figure 4 shows the catalyst microstructure done by hitachi S-4800 field emission scanning electron microscope. Figure 4(a) is pure attapulgite, Figure 4(b) is 6Ni₂O₃/PG made by coordination homogeneous precipitation method. It can be found that the attapulgite loaded Ni₂O₃ looks the same as pure attapulgite from the appearance. Single crystal stays rodlike and crystals stack each other, forming many macropores.



(a) PG



(b) 6Ni₂O₃/PG

Figure 4 : SEM images

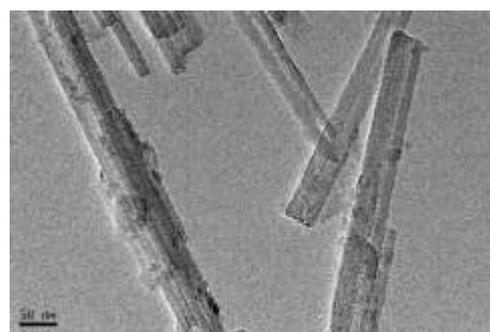
TEM: Figure 5 shows the microstructure done by high resolution transmission electron microscopy. It is observed that Ni₂O₃ homogeneously dispersed on attapulgite crystal. Homogeneous dispersion can improve the contacting of active components and gas molecules effectively in the reaction process, to obtain high reaction rate of reaction in a less loading amounts accordingly and improving the utilization rate of catalytic active component and reduce the manufacturing cost of the catalyst.

Experimental apparatus: The catalyst is tested in the vertical fixed tubular furnace as figure 6 shows, to simulate the fixed catalytic bed in the actual industry. Heating curves and the reaction temperature in the tubular furnace can be set by programmed temperature controlling. Catalytic bed made from $\phi 8mm \times 400mm$ quartz tube, the middle part of the catalytic bed made from a quartz plate with many small holes to place the catalyst. Before the experiment, 3g catalyst was placed in the catalytic bed first, and then N₂ pass into the bed at flow rate of 30ml/min to replace the air in the system. Set the temperature of the steam generator and the tubular furnace to experimental temperature. Open the switch of the mass flowmeter and the CO₂ passes through the system at flow rate of 80ml/min when the temperature of the steam generator and the tube furnace rise to setting temperature.

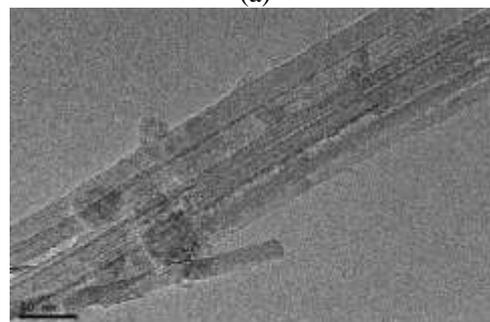
Switch on the injection pump, and inject xylene at flow rate of 0.4mmol/min. Xylene can be changed into gas in the steam generator, and passes through the catalytic bed with the mixture of CO₂ and N₂. In the end, the gas passes through the condenser, unreacted xylene will be condensed and collected, the filtered gases run through dryer, the flowmeter which connected with data connection computer, and sent to the gas chromatograph to analysis the gas components. The conversion rate of xylene can be calculated as the following formula :

$$\eta = (m_{in} - m_{out}) / m_{in} \tag{25}$$

In the formula, m_{in} is the weight of the xylene which be injected into the system, and m_{out} is the weight of which be condensed.



(a)



(b)

Figure 5 : TEM images of 10Ni₂O₃/PG

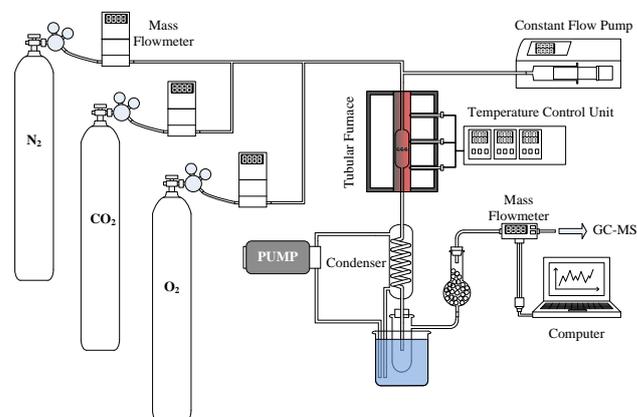


Figure 6: Catalyst performance test experiment system

Results and analysis of catalyst performance: Effects of temperature on tar reforming

In the experiment of testing the catalyst's property, the paraxylene's conversion rate is tested under five different working conditions of 400°C, 500°C, 600°C, 700°C, 800°C and different conditions of catalyst-free, using pure PG as catalyst and using Ni₂O₃/PG of varied loading amounts as catalyst. The testing result is presented in figure 7. Among above situations, silica sands of the same grain size are used to imitate the catalyst-free situation.

The experiment also measures how gas production rate of every gas among the reaction gas per minute changes with the change of temperature, the testing results are respectively presented in figure 8, 9, 10, 11 and 12.

Experiments of CO₂ reforming of tar were carried out during a temperature range of 400~800°C. Fig 7 shows that paraxylene conversion rate rises as the temperature increases. Silica sand as inert material was used to simulate the condition without catalyst. Silica sand showed almost no activity until 500°C. Below 500°C, paraxylene conversion rate was low (4.64% at 500°C) and increased slowly. With the further elevation of temperature, the conversion rate of paraxylene increases. As is shown in Fig 7, adding catalyst can effectively improve the efficiency of paraxylene carbon dioxide reforming reaction, and reduce the reaction activation energy, which cause that reactions can be performed at the low temperature. Palygorskite has a larger surface area, according to the results of the BET test, the specific surface area of chemically purified attapulgite can be 120.9 m² · g⁻¹. Moreover, there are three kinds of adsorption center on the surface of attapulgite¹⁵: (I) Because the replacement of isomorphism, silica tetrahedral produces weak electron supplying for oxygen atom, the interaction between adsorption center and them is weak. (II) The crystal water molecular (OH)₂ which coordinate with metal cation Mg²⁺ on the edge of fiber can form hydrogen bond with adsorption center. (III) The Si-OH formed by the break of Si-O-Si oxo-bridged oxygen bond on the outside surface of silica tetrahedral layer can accept ions, as well as mutually combine with absorbed molecule on the outside surface of crystal. Therefore, physical absorption and chemisorption can be done to areme, naphthenic hydrocarbon, alkane and others. When dimethylbenzene molecule attaches to the surface of macropore inside the PG crystal, its reaction rate with CO₂ accelerates. Besides, the resultant of reaction H₂, C₂H₄, C₂H₆, CH₄ and CO can be diffused and released through the PG crystal while the framework of PG crystal will not be destroyed. After using xNi₂O₃/PG made by coordination homogeneous precipitation method as catalyst, the conversion rate of paraxylene at 500°C to 700°C increases a lot compared to the situation using pure PG as catalyst. At 600°C, in the reaction using 6Ni₂O₃ /PG, 10Ni₂O₃ /PG and 14Ni₂O₃ /PG as catalyst, the conversion rate of paraxylene respectively reaches 95.75%, 97.85% and 92.60%. It states that the high dispersity load of active component Ni₂O₃ primely decreases

the converted activation energy of paraxylene, making it can be converted at low temperature.

When paraxylene molecule adsorbs on the surface of the big hole inside attapulgite crystal, its reaction rate with carbon dioxide accelerates, forming H₂, C₂H₄, C₂H₆, CH₄ and CO, which can be released through the internal diffusion of attapulgite. During this process, the crystal framework of attapulgite is not destroyed. Relative to pure attapulgite, when xNi₂O₃/PG is utilized as a catalyst, the reaction efficiency has been significantly improved from 500°C to 700°C. When the temperature rises to 600°C, the conversion rate can be reach 95.75%, 97.85%, 92.60% respectively, as 6Ni₂O₃ /PG, 10Ni₂O₃ /PG, 14Ni₂O₃ /PG is utilized as catalyst. This illustrates that the dispersible loading of active component can reduce the activation energy of conversion of paraxylene.

When the temperature rises from 500°C to 600°C, the reaction rate has been obviously improved under the circumstance of using catalyst. Comparing figure 5 and figure 6, it can be found that in the condition of catalyst-free, the gas production rates of H₂, C₂H₄, C₂H₆, CH₄ and CO present a large increase at 600°C. Removal efficiency of xylene shows an obvious increase at 600°C when using xNi₂O₃/PG as catalyst which are prepared by coordination homogeneous precipitation method. As can be seen from figure 9, figure 10, figure 11 and figure 12, the gas production rates of H₂ and CO at 600°C increase significantly when compare with that at 500°C.

Comparing the different rate of gas production according to changing temperature of each gas components among the gas produced in the case of different catalyst, we can find that under the conditions in which the catalyst is not used or only attapulgite is used as catalyst, CH₄, C₂H₄, and C₂H₆ are produced between 500°C to 700°C. When temperature further increases, C₂H₄ and C₂H₆ are no longer produced among the produced gas and the gas production of CH₄ is also stabilized with the increase of temperature. CH₄ is produced between 500°C to 700°C as xNi₂O₃/PG is utilized as the catalyst. With the increase of temperature, CH₄ is no longer produced.

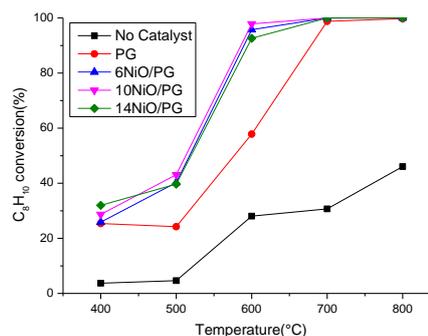


Figure 7: Effect of temperature on paraxylene conversion rate

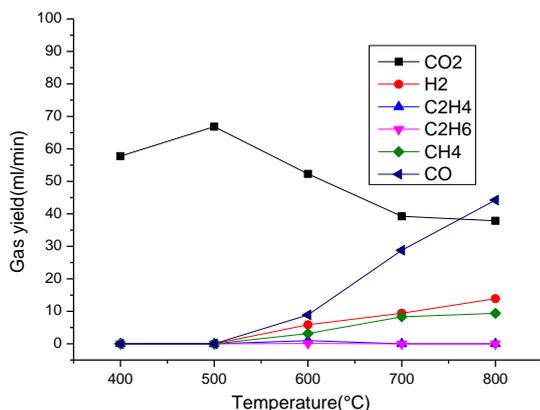


Figure 8: Effect of temperature on gas yield when non catalyst is utilized

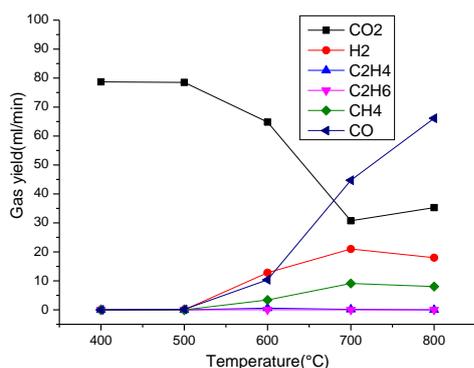


Figure 9: Effect of temperature on gas yield when PG is utilized as a catalyst

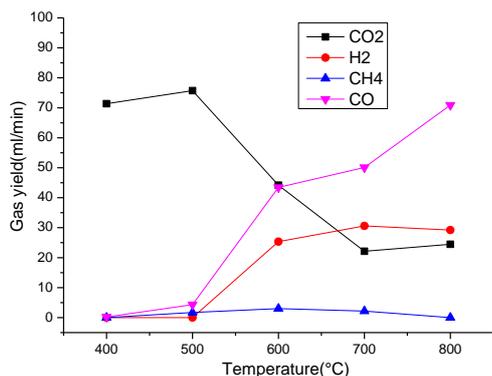


Figure 10: Effect of temperature on gas yield when 6NiO/PG is utilized as a catalyst

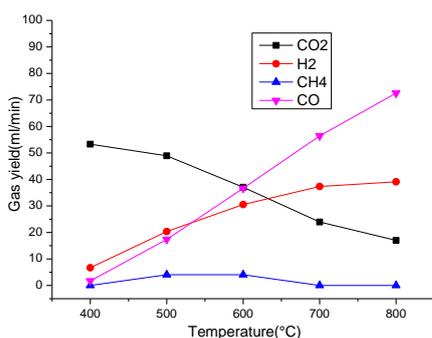


Figure 11: Effect of temperature on gas yield when 10NiO/PG is utilized as a catalyst

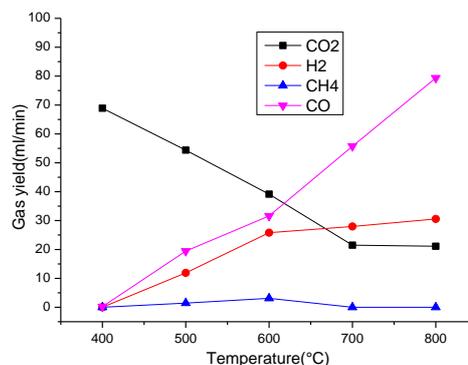


Figure 12: Effect of temperature on gas yield when 14NiO/PG is utilized as a catalyst

In the determination experiment of catalyst's carbon deposition rate, the author chooses 10Ni₂O₃/PG as sample and puts 3g catalyst in the catalyst bed everytime, while setting the flow rate of paraxylene as 0.405mmol/min and flow rate of carbon dioxide as 75 ml/min, setting reaction time of every operating condition is fifteen minutes. When every operating condition finishes, the catalyst is taken out, weighed, put into the tube furnace, and calcined in air atmosphere under the condition of 800°C for one hour. After that, it is taken out and weighed again. Let the weight before calcination be m_1 and the weight after calcination be m_2 , the author calculates the carbon deposition rate of catalyst through the formula :

$$\eta_c = (m_1 - m_2) / m_2 \tag{26}$$

Figure 13 shows the change of catalyst's carbon deposition with temperature when using 10Ni₂O₃/PG as catalyst. It can be observed that as the temperature rises, the carbon deposition rate of catalyst increases and then decreases. In the reaction of CO₂ reforming of dimethylbenzene using Ni₂O₃/PG as catalyst, the carbon deposition on the surface of catalyst is the side reaction appearing with the reaction, belonging to catalysis carbon deposition. The dimethylbenzene absorbed on the active component of

catalyst is oxidized, the π_6 bond on benzene is under attacked and break. Besides, part of carbon-hydrogen bonds break and form H₂ while the rest attach to the surface of active component, forming carbon deposition. These carbon deposition then react with CO₂ to form CO and H₂.

From figure 13 it can be concluded that the carbon deposition rate is on the rise under 500°C, however after that, the carbon deposition rate is decline as the temperature rises. Combining with figure 7, we can find that 500°C is not only the watershed of carbon deposition's change, but also the watershed of paraxylene conversion rate's change. During the reaction process, the carbon deposit is in the dynamic equilibrium of being produced and consumed. When the reaction temperature is low, dimethylbenzene molecule is absorbed and ring opened on the surface of catalyst and the

equilibrium drift towards the direction of carbon deposition production. When the temperature is over 500°C, the equilibrium develops towards where carbon deposit and CO₂ reacts and the carbon deposition rate starts to decrease.

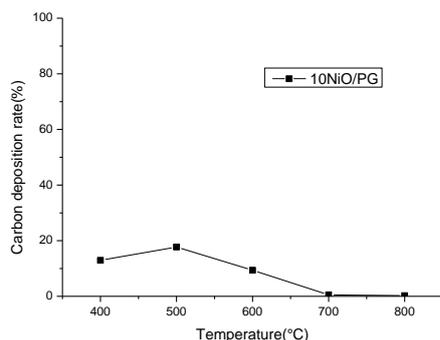


Figure 13 : The change of catalyst's carbon deposition with temperature when using 10Ni₂O₃/PG as catalyst

Conclusion

Nickel Oxide is nonstoichiometric compounds with vacancy of positive ions—Ni²⁺. The “□” in figure 14 shows the vacancy of Ni²⁺ and there is a lack of two units of positive charges, therefore, there must be two Ni²⁺ valence rising to Ni³⁺, which can be regarded as Ni²⁺ restricting the hole with one unit of positive charge so as to keep the crystal's electric neutrality. When the temperature rises, it excites the electrons in full filled band to step into the hole, resulting in electron-hole in full filled band. The oxidation mechanism which hydrocarbons act on Ni₂O₃/PG can be considered as the process of reduction-oxidation, and there are four steps of this process.

Hydrocarbons adsorb on the catalyst react with the oxygen in the Ni₂O₃ and it is deeply oxidated. The side chain of the

paraxylene interrupts first, and then the π_6^6 chain can be broke by the Ni₂O₃ and the electrons of the paraxylene step into the conduction band of Ni₂O₃. Trivalent nickel turn into divalent. The conduction band is filled with electrons as the amount of Ni³⁺ ions reduce. In this condition, CO₂ can obtain electrons from NiO and react to form CO and H₂. The reduction of catalyst active component Ni³⁺ ions hinder molecules from absorbing onto the surface of catalyst, promoting the detachment of CO, H₂O, CO₂ and other gases from the surface of catalyst. Fermi level rise into the center of forbidden band under the reaction temperature. The electrons in the valence band are excited and jumped into the conduction band, supply the electrons required in the reaction, and the valence state of Ni³⁺ ions rises again.

So far, xNi₂O₃/PG turns back to the original state without being consumed. Because of the excitation and activation which xNi₂O₃/PG does to reacted molecular, the CO₂ reforming reaction of whole dimethylbenzene is accelerated.

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