

Influence of Ni Loading on Catalytic Activity of NiO/ γ -Al₂O₃ for Hydrogenation of Coal Pyrolysis

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(Received: 9 September 2012;

Accepted: 20 March 2013)

AJC-13140

Selecting γ -Al₂O₃ as support, a series of nickel nitrate with different concentrations (5, 8 and 10 %) were prepared by incipient impregnation while the equivalent volume impregnation method was applied to prepare NiO/ γ -Al₂O₃ supported catalysts. XRD, TPR, XPS and SEM were used for characterization of these catalysts. The catalytic activity of NiO/ γ -Al₂O₃ increased with the nickel loading increasing in 400-800 °C, but the catalytic activity of different loading NiO/ γ -Al₂O₃ had little difference in 900-950 °C, the catalyst with 10 % load showed a good catalytic activity in whole pyrolysis process. The XRD characterizations of catalysts with different loadings showed that, 10 % loading had the highest catalysis activity, 8 % secondly and 5 % last, in the temperature range of 400-800 °C. Therefore, it can be inferred that NiO acted as main catalyst during the reaction course. The SEM characterization of catalysts with different NiO loadings showed that the 10 % loading of active component Ni coarser crystalline grains was found. While distinct NiO crystals were analyzed by XRD. Therefore, it can be inferred that the coarse crystalline grains are NiO crystals, which were observed through SEM. The analytical result of SEM was consistent with the characterization results of XRD. The XPS with 10 % Ni loading inferred that existential form of Ni is NiO and NiAl₂O₄. On the specimen surface, the binding energy of Al2p is 74.00 ± 0.5 eV and the binding energy of O1s is 531.3 eV, which belong to the lattice oxygen in Al₂O₃. The value agreed well with the characterization results of XRD. The TPR analysis results indicate that the loading amount of NiO/ γ -Al₂O₃ is 9.12 %, which was very close to the theoretical data 10 %.

Key Words: Coal slime, Pyrolysis, Supported catalyst, Hydrogen.

INTRODUCTION

As an individual processing method, coal pyrolysis is calorified under the condition of air isolation. It is a complex process, consisting of a series of chemical reactions and physical changes and generating gas (coal gas), liquid (tar) and solid products(char), *etc.*¹⁻⁷. Coal pyrolysis leads to a high yield of gaseous products. Generally, coke-oven gas contains 55-60 % (volume) hydrogen. Hydrogen has various advantages *e.g.*, high combustion releasing heat and no pollution, so that it is unexampled coal, petroleum and natural gas, while it can solve world energy problem and environmental problem radically. Hydrogenation of coal pyrolysis has extensive significance in environmental protection, energy conservation and reasonable utilization of coal resources, therefore, it can reduce the environmental pollution caused by coal and can make full use of high economic value compounds in coal. At present, there are few systematic researches for hydrogenation of coal pyrolysis at domestic and abroad. In this paper, a series of NiO/ γ -Al₂O₃ catalysts were prepared by the dipping method with γ -Al₂O₃

as support. Characterized with XRD, TPR, XPS, SEM and other detection means, study on the influence of Ni loading on catalytic activity of NiO/ γ -Al₂O₃ for hydrogenation of coal pyrolysis.

EXPERIMENTAL

The experiments on coal pyrolysis for hydrogenation production were carried out in a programmed temperature fixed-bed reactor. The coal used in the experiments was steam coal obtained from Shenhua Power Plant. The ultimate analysis results of the coal were: C 67.07 %, H 2.711 %, N 0.587 %. Mass of 20 g coal. 2 % of coal quantity catalyst was heated from the ambient temperature up to 950 °C with the rate of 15 °C min⁻¹. Pyrolysis took place inside a quartz tube, which found itself in the constant temperature zone of the electric oven. Pyrolytic gases were cooled to enable tar and water condensation and were subsequently dried by means of a special filter. A SP-2100 type gas chromatographic instrument was modified and applied to analyze the composition of resulting gases, such as H₂, CH₄ and CO, *etc.*

Catalyst preparation: Selecting γ - Al_2O_3 (Tianjin Chemical Institute) as support, a series of nickel nitrate with different concentrations (5, 8 and 10 %) were prepared by incipient impregnation. The metal oxide precursor's weight was calculated according to the pure metal content. The condition of preparation of the catalyst was as follows: particle size: 200 mesh; baking 4 h at 450 °C.

X-ray diffraction: Running conditions of XRD are as follows: Incidence light source is Cu target; scan range is $2\theta = 10$ -70° and 10-90°; scan rate is 8°/min. The phase structures of the catalysts are characterized by TTR-III X ray diffraction (XRD).

Scanning electron microscope (SEM): Adopt JSM-6700 SEM (JEOL Manufacture) and the working voltage is 5000 KV.

Temperature programmed reduction: Adopt Micromeritics 2720 style chemisorption device, testing consumption amount of H_2 by utilizing thermal conductivity cell detector. Mass of 0.1230 g $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ were characterized in glass reactor by temperature programmed reduction under an atmosphere of 10 % H_2 -90 % Ar mixture from the ambient temperature up to 1000 °C with the rate of 10 mL min^{-1} .

X-Ray photoelectron spectroscopy: Adopt VG Scientific ESCALab220i-XL style photoelectron spectroscopy, using AlK_α X-ray as an excitation source under the condition of the power output of 300W. The based vacuum is 3×10^{-9} mbar when analyzing. Correct electron binding energy by C1s peak (284.8 eV) of the polluted carbon.

RESULTS AND DISCUSSION

Activity evaluation of catalysts with various Ni loadings:

A series of $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalysts (with different loadings 5, 8 and 10 %) have been prepared by incipient impregnation and the evaluation of activity has been performed. The results were shown in Fig. 1. It shows catalytic activity of $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ increases with the increasing of the loading amount of Ni in the temperature range of 380-420 °C, while at high temperature section (900-950 °C), the increasing of the loading amount of Ni has no significant effect on catalytic activity of $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$. Because the higher loading NiO can produce much more surface activity sites in $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst and result in activity increasing of the catalyst. During the whole pyrolysis process, the $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst with 10 % loading performed best.

XRD characterization of catalysts with different Ni loadings: XRD characterizations of catalysts with different loadings were given in Figs. 2 and 3. It showed that, no XRD peaks can be found with 5 and 8 % loading of $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$. It indicated that NiO in the $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst as microcrystal highly dispersed on the catalyst surface and the NiO loading amount is too low, therefore, it did not reach the XRD detection limit and resulted in no XRD peaks. In contrast, two very weak XRD peaks were observed at $2\theta = 43.536, 54.032$ with 10 % loading of $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$. The two XRD peaks are characteristic peaks of metal oxides NiO. The XRD spectra proved that the main phase was $\text{NiAl}_{32}\text{O}_{49}$ produced by reaction of NiO with Al_2O_3 .

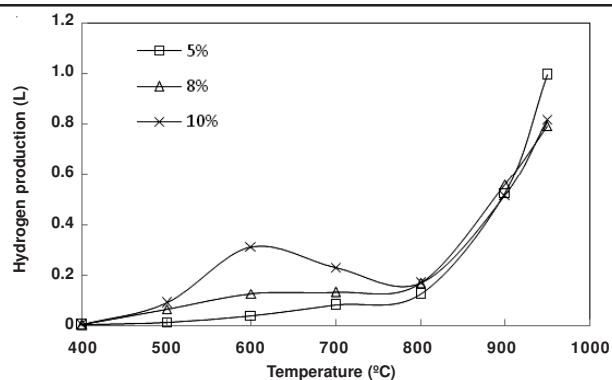


Fig. 1. Catalytic activity of Ni different loading

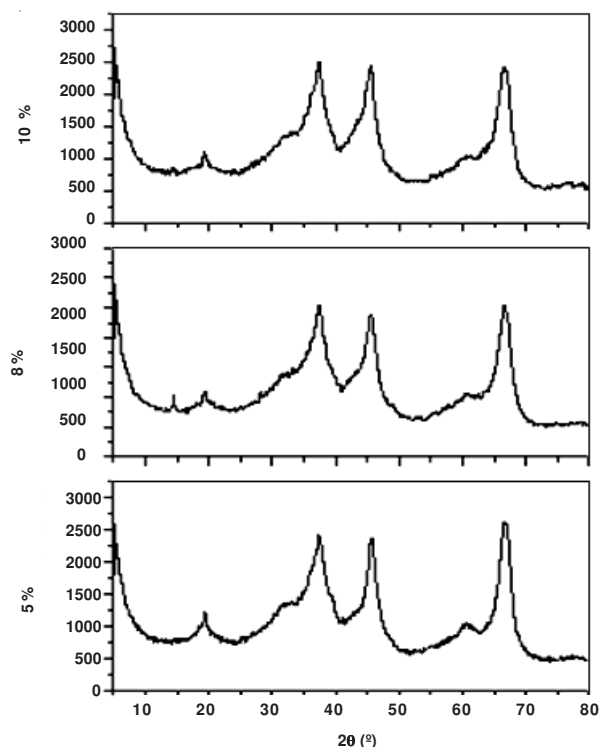


Fig.2. Comparison XRD of Ni different loading

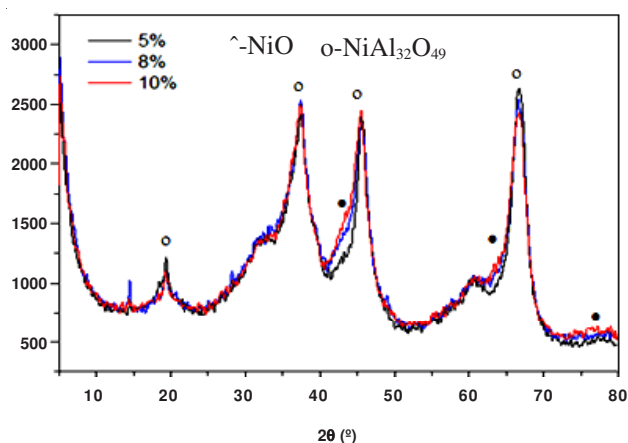
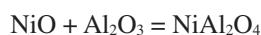


Fig. 3. XRD of Ni different loading

In addition, the relative intensities of NiO X-ray peaks increase with the increasing of Ni loading amount. Blunt peak-shapes indicate that NiO dispersed uniformly on the surface of $\gamma\text{-Al}_2\text{O}_3$ support.

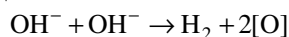
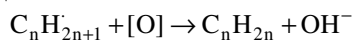
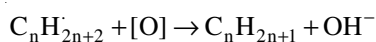
Comparing XRD analysis with the experimental results, as shown in Figs. 1-3 10 % loading had the highest catalysis activity, 8 % secondly and 5 % last, in the temperature range of 400-800 °C. Therefore, it can be inferred that NiO acted as main catalyst during the reaction course. It can also be found that catalytic activities were not obviously different from different loadings above 800 °C (Fig. 1).

The main factor is that the NiO reacts with Al₂O₃ to form difficult reduction of nickel aluminum spinel in the oxidizing atmosphere:

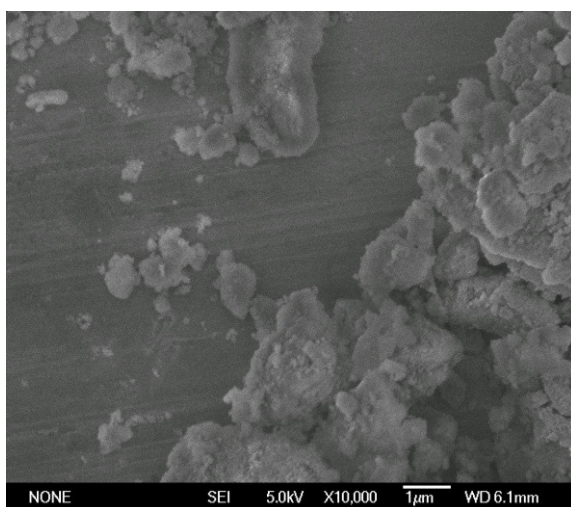


Generally, at 500 °C or lower temperature NiO reacts with Al₂O₃ to form Ni Al₂O₄ spinel structure and Ni Al₂O₄ formed in great quantities at 800 °C. Nickel oxide of NiAl₂O₄ spinel structure showed no catalytic activity in most catalysis process. Large amount of NiAl₂O₄ generated above 800 °C leads to catalytically activity decrease obviously, so catalytic activities were not obviously different from different loadings.

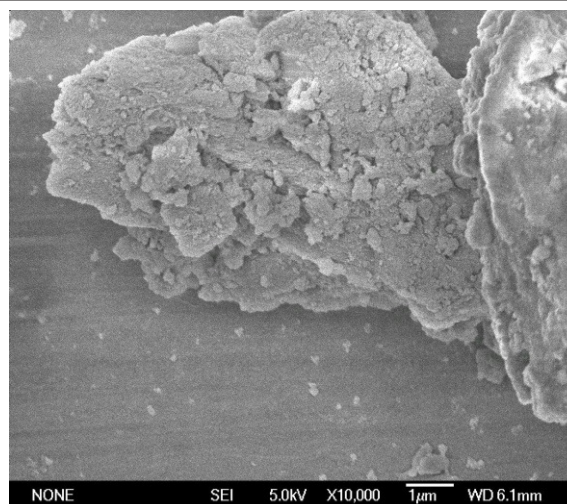
NiO acted as main catalyst in the whole pyrolysis process for hydrogen production. For NiO which is a *p*-type semiconductor has considerable non-stoichiometric oxygen. Coal mainly produces gas hydrocarbon in the pyrolysis stage (400-700 °C), so hydrogenation production was mainly from oxidative dehydrogenation of gas hydrocarbon. The mechanism of oxidative dehydrogenation of gas hydrocarbon on NiO is inferred⁸ as follows: firstly, gas hydrocarbon reacts with non-stoichiometric oxygen [O] in NiO extracting one -H to form hydrocarbyl free-radical; then one more extraction -H to form low-rank hydrocarbons. Therefore, we inferred that the mechanism was as follows:



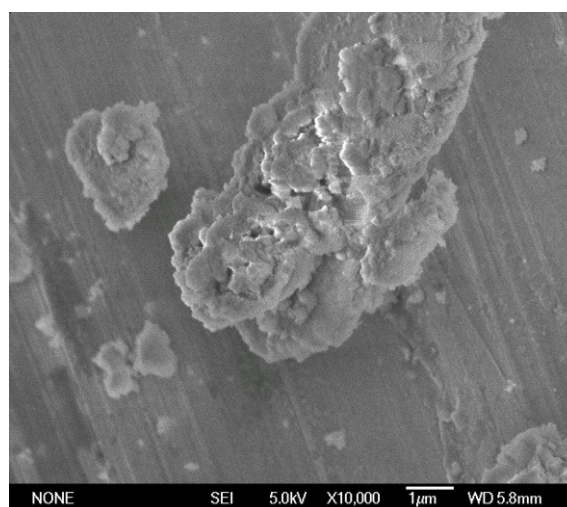
SEM characterization of catalysts with different NiO loadings: In Fig.4A-C represent morphologies with 5, 8 and 10 % loading, respectively.



(A)



(B)



(C)

Fig. 4. SEM image of Ni different loading (10000)

With 5 % loading of active component Ni, the metal oxide distribute in layer on the surface of γ -Al₂O₃ support, with no coarse crystalline grain (Fig. 4). It is also proved by the XRD analysis. With 8 % loading of active component Ni, a few smaller crystalline grain dispersed uniformly on the surface of γ -Al₂O₃ support through SEM. Combined with XRD, It can be inferred that the smaller crystalline grain is NiO crystal. With 10 % loading of active component Ni, coarser crystalline grains were found through SEM. While distinct NiO crystals were analyzed by XRD. Therefore, it can be inferred that the coarse crystalline grains are NiO crystals, which were observed through SEM. The analytical results of SEM were consistent with the characterization results of XRD.

XPS characterization of catalysts: Figs. 5-8, represent the XPS and spectra with 10 % Ni loading (Fig. 5). 10 % NiO/ γ -Al₂O₃ catalyst sample contains Ni, Al and O. Figs. 6-8, represent Ni2p_{3/2}, Al2p and O1s spectra of NiO/ γ -Al₂O₃, respectively. With reference to the standard combination energy of each element in related compounds, the binding energy of Ni2p_{3/2} is 851.3-856.2 eV, which was close to the theoretical data 853.8 eV. Therefore, we inferred existential form of Ni is NiO and NiAl₂O₄. On the specimen surface, the

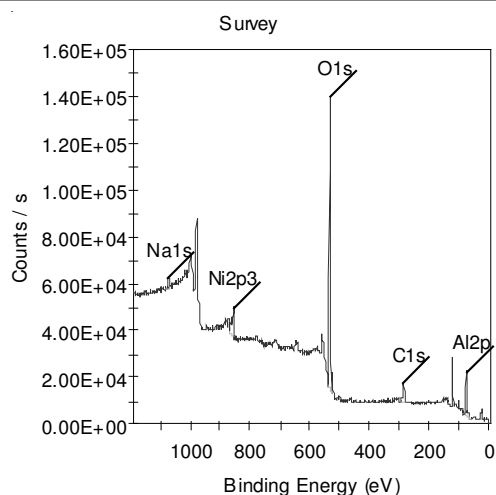
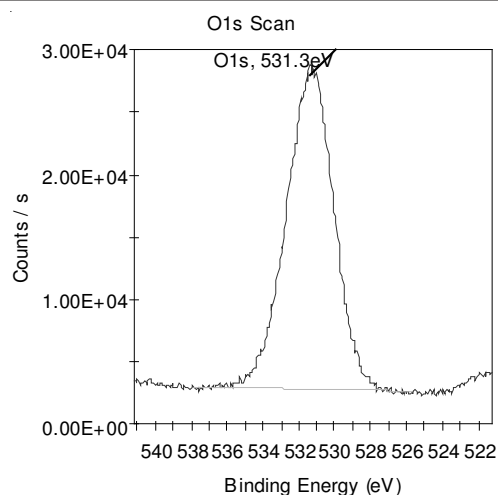
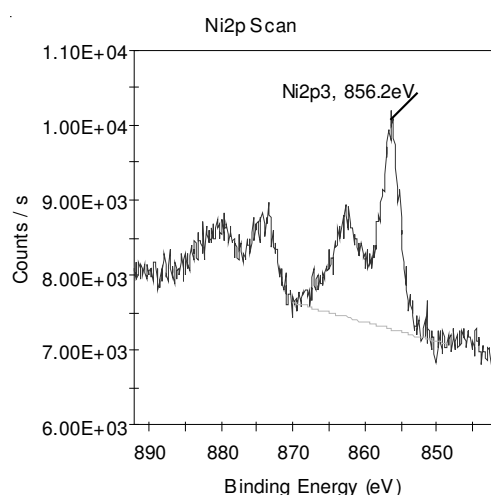
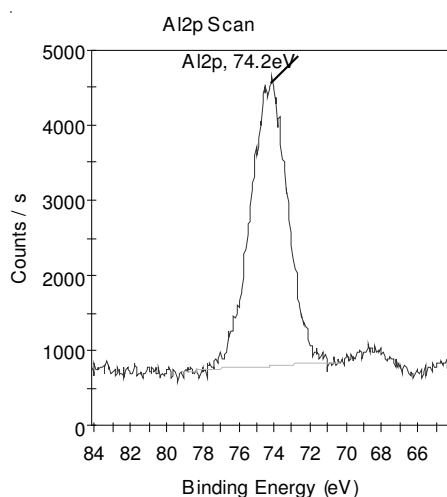
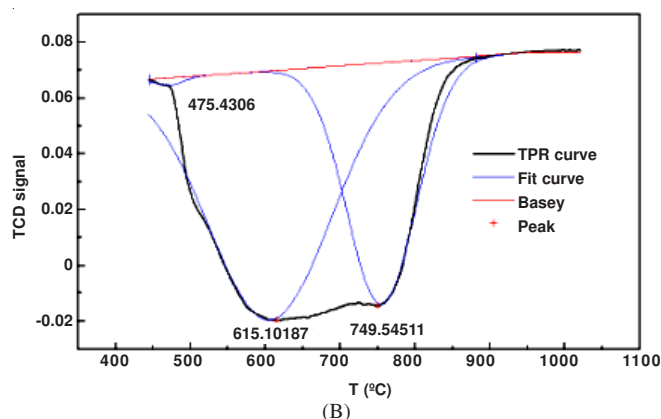
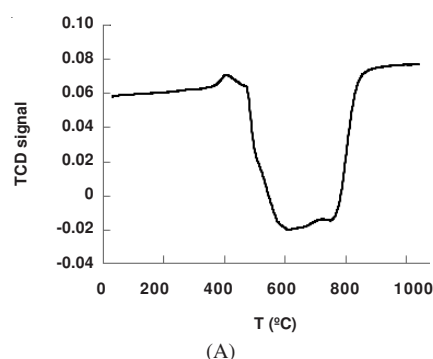


Fig. 5. XPS of 10 % Ni loading

Fig. 8. O1s spectra of NiO/γ-Al₂O₃Fig. 6. Ni2p3/2 spectra of NiO/γ-Al₂O₃Fig. 7. Al2p spectra of NiO/γ-Al₂O₃

binding energy of Al2p is 74.00 ± 0.5 eV and the binding energy of O1s is 531.3 eV, which belong to the lattice oxygen in Al₂O₃. The value is agreed well with the characterization results of XRD.

Temperature programmed reduction characterization of catalysts: Fig. 9 represents the XPS and the peak separation fitting spectra with 10 % loading NiO/γ-Al₂O₃. The H₂-

Fig. 9. TPR of the NiO/γ-Al₂O₃ catalyst

temperature programmed reduction curves exhibited that there are three reduction peaks at 475.4306, 615.10187 and 749.54511 °C, which were separately the reductions of crystalline NiO, high dispersed NiO and Surface NiAl₂O₄^{9,10}. TPR results further proved existential form of Ni in NiO/γ-Al₂O₃ is mainly highly dispersed NiO on the support and crystalline NiO occupies only a fraction. The value is agreed well with the characterization results of XRD. It was also found that Active component NiO reacts with Al₂O₃ support to form difficult reduction of NiAl₂O₄ spinel. In reduction process, the mainly concerning reduction reactions were:

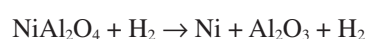
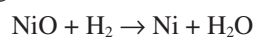


TABLE-1
TEMPERATURE PROGRAMMED REDUCTION ANALYSIS RESULTS FOR NiO/ γ -Al₂O₃ CATALYST

Catalyst	Reduction peak		
	Peak 1	Peak 2	Peak3
NiO/ γ -Al ₂ O ₃ (10%Ni)	Crystallized NiO	Dispersed NiO	NiAl ₂ O ₄
Composition			
Peak area	0.07166	11.94044	6.67162
Peak area (%)	0.38	63.9	35.7
Hydrogen consumption (mL)	0.0163	2.738	1.530
5 g catalyst content of metal (g)		0.293	0.163
5 g catalyst content of metal (%)		9.12	

The temperature programmed reduction analysis results indicate that the total hydrogen consumption is 34.83292 mL/g and the mass of catalyst is 0.1230 g. (According to peak separation fitting results (Fig. 9B), using hydrogen consumption of reduction peaks to calculate the loading amount. The results were shown in Table-1).

As shown in Table-1, the loading amount of NiO/ γ -Al₂O₃ is 9.12 %, which was close to the theoretical data 10 %.

ACKNOWLEDGEMENTS

The financial support of this research by Natural Science Basic Research Plan in Shaanxi Province of China (Program No. 2011JQ2015) in P.R. China is gratefully acknowledged.

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