

Study on Supported Metal Catalysts for Hydrogen Production from Coal Slurry Pyrolysis

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(Received: 14 September 2012;

Accepted: 11 April 2013)

AJC-13225

The objective of this paper is to study the effect of supported metal catalysts on hydrogen production from coal slurry pyrolysis and to explain their catalytic mechanism. Experimental results show that Ag/ γ -Al₂O₃ and Fe/ γ -Al₂O₃ have good catalytic activity at 700 °C to 1100 °C with the higher yield of H₂ being mainly resulted from the phenomenon of hydrogen spillover. Ni/ γ -Al₂O₃ shows good catalytic activity at both medium temperature and higher temperature. Because Co inhibits the activity of catalyst, the Co/ γ -Al₂O₃ shows good catalytic activity only at medium temperature. The characteristic diffraction peaks of Cd/ γ -Al₂O₃, Zn/ γ -Al₂O₃ and Cu/ γ -Al₂O₃ are CdO, ZnO and CuO, respectively. These three oxides are *n*-type oxides, so they show better catalytic activity at medium temperature.

Key Words: Catalyst, Coal pyrolysis, Hydrogen production.

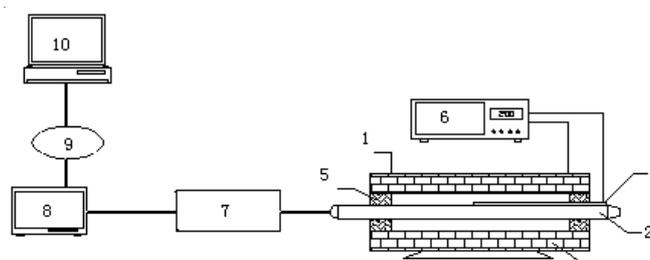
INTRODUCTION

Coal slurry is a main by-product during coal preparation. If discharged, it will not only cause serious environmental pollution, but also waste enormous valuable coal resources¹. Therefore, much more effects must be done to utilize the coal slurry as soon as possible. The existing treatment methods of coal slime need to separate the coal from water. In fact it is difficult to make an effective use of the coal and the separation process is difficult and complex due to the nature of the coal slime. To directly produce the hydrogen from coal slurry with high moisture contents through catalytic pyrolysis was focused². In this study, seven supported metal catalysts were tested to investigate the feasibility of the supported metal catalysts for hydrogen production from coal slurry pyrolysis.

EXPERIMENTAL

Preparation of catalysts: In this study, seven metal nitrate solutions *i.e.*, silver nitrate, copper nitrate, nickel nitrate, cobalt nitrate, zinc nitrate, cadmium nitrate and iron nitrate were selected as impregnating solutions. Spherical γ -Al₂O₃ with particle size of 2~3 mm was chosen as a carrier which was produced by the Chemical Engineering Research and Design Institute of Tianjin. The supported metal catalysts are prepared by an equivalent-volumetric impregnation method with a metal loading of 5 %.

Evaluation of catalytic activity: In this experiment, samples were placed in a tubular reactor housed in a furnace. In each test, the inside temperature of the furnace was raised from room temperature to 1100 °C at a rate of 17.8 °C min⁻¹ at the system pressure of 101.3 kPa with 1 h of reaction time. The gas product of pyrolysis was collected at an increase of every 100 °C, dedusted, dried and analyzed by gas chromatography. The hydrogen concentration was analyzed using nitrogen as the carrier while helium was used for analysis of carbon dioxide and carbon monoxide. The gas product can be calculated using $V = c \times v$ where *V* is the yield of interested gas (mL), *c* is the gas concentration and *v* is the total volume (mL) of the gas. The schematic diagram of experimental device is showed in Fig. 1.



1. Pyrolysis furnace, 2. Reactor, 3. Thermocouple, 4. Refractory lining, 5. Fire-resistant cotton, 6. Temperature control devices, 7. Condensation and purification, 8. Flow meter, 9. Gas collection, 10. GC

Fig. 1. Schematic diagram of the pyrolysis reactor

RESULTS AND DISCUSSION

Effect of Ag/ γ -Al₂O₃ and Fe/ γ -Al₂O₃ on the hydrogen production from coal slurry pyrolysis: It can be observed from Fig. 2 that Ag/ γ -Al₂O₃ and Fe/ γ -Al₂O₃ have good catalytic activity on coal slurry pyrolysis during 600–1100 °C. In particular the catalytic activity has markedly improved between 900 and 1100 °C. The pyrolysis reaction is sped up and a large amount of hydrogen is generated during 900–1000 °C and the hydrogen mainly comes from secondary cracking of the products coming from coal slurry pyrolysis. For example the direct cracking of alkanes, aromatics isomerization, condensation reactions, *etc.* The additions of Ag/ γ -Al₂O₃ or Fe/ γ -Al₂O₃ are beneficial for the above reactions, so they promote hydrogen production significantly.

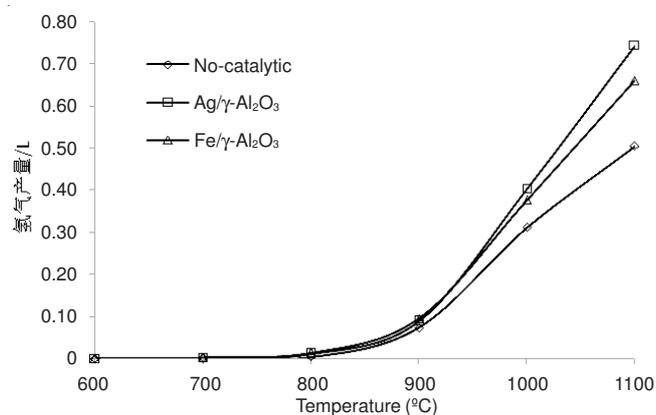


Fig. 2. Effect of Ag/ γ -Al₂O₃ and Fe/ γ -Al₂O₃ on hydrogen production from pyrolysis of coal slurry

In Figs. 3 and 4 the characteristic diffraction peaks of Ag and Fe are emerged in the spectra respectively. This shows that the active component of Ag/ γ -Al₂O₃ and Fe/ γ -Al₂O₃ are Ag and Fe. They have a significant catalytic activity on the preparation of hydrogen from coal slurry pyrolysis which is mainly due to the phenomenon of hydrogen spillover^{1,2}. The alumina around Ag and Fe particles can be activated and the volume of activated alumina is much larger than the size of catalyst particle itself. It means that the catalytic reactions activate on the surface of catalyst and activated alumina at the same time, so it can lead to such a high level of reaction activity.

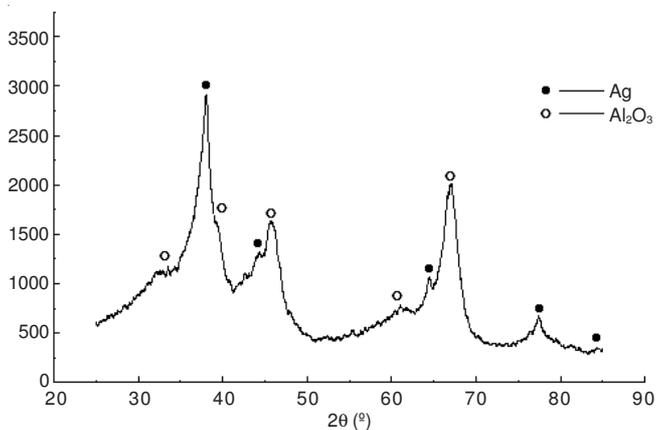


Fig. 3. XRD spectra of Ag/ γ -Al₂O₃

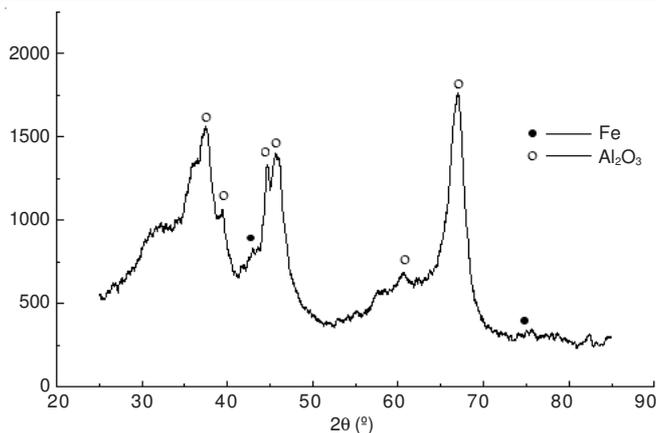
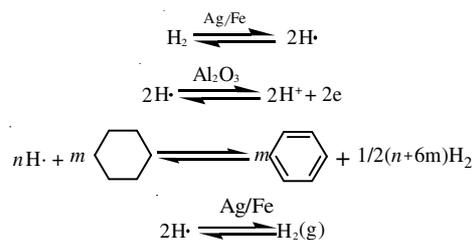


Fig. 4. XRD spectra of Fe/ γ -Al₂O₃

The coal slurry has generated a certain degree of hydrogen in 800–900 °C, so the hydrogen dissociates to hydrogen atom on the surface of Ag/ γ -Al₂O₃ and Fe/ γ -Al₂O₃ and migrates to the surrounding inert alumina. The inert alumina can be activated by the migratory hydrogen atom, then the hydrogen atoms around the activated alumina make the dehydrogenation of alkanes, alkenes and aromatic hydrocarbons. Taking cyclohexane for example to conclude the catalytic rules on the Ag/ γ -Al₂O₃ and Fe/ γ -Al₂O₃ for hydrogen production from coal slurry pyrolysis.



Effect of Ni/ γ -Al₂O₃ and Co/ γ -Al₂O₃ on the hydrogen production from coal slurry pyrolysis: Fig. 5 illustrates the effect of Ni/ γ -Al₂O₃ and Co/ γ -Al₂O₃ on hydrogen production from coal slurry pyrolysis. Ni/ γ -Al₂O₃ shows higher catalytic activity than Co/ γ -Al₂O₃ especially after the 900 °C. Ni/ γ -Al₂O₃ has obvious catalytic activity that results in the yield of hydrogen twice as much as Co/ γ -Al₂O₃.

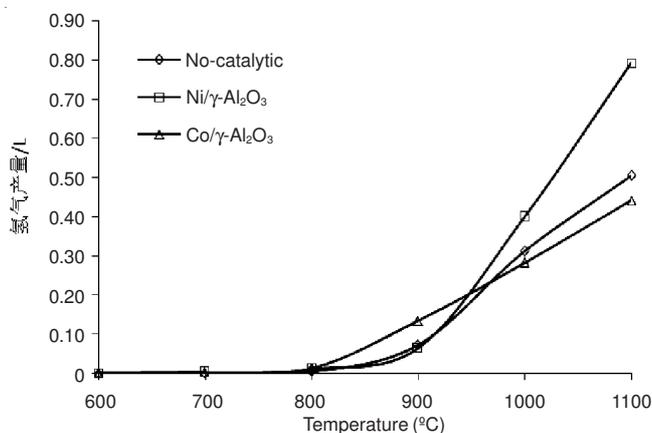
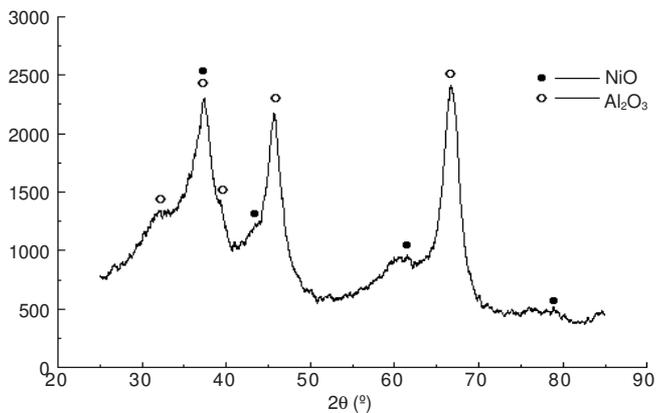
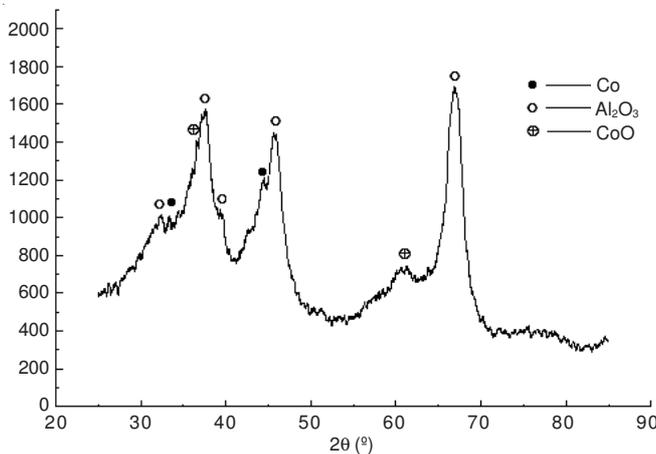


Fig. 5. Effect of Ni/ γ -Al₂O₃ and Co/ γ -Al₂O₃ on hydrogen production from pyrolysis of coal slurry

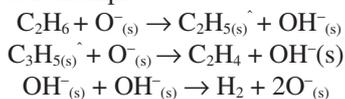
The XRD spectra of Ni/ γ -Al₂O₃ and Co/ γ -Al₂O₃ are given in Figs. 6 and 7. Ni/ γ -Al₂O₃ mainly exists in crystal NiO form and does not have the diffraction peaks of Ni. Co/ γ -Al₂O₃ appears the characteristic diffraction peaks of Co and CoO simultaneously.

Fig. 6. XRD spectra of Ni/ γ -Al₂O₃Fig. 7. XRD spectra of Co/ γ -Al₂O₃

Element Ni and Co belong to the same cycle and group, but there is such a large difference of the catalytic activity. To reveal the difference of catalytic activity between Ni/ γ -Al₂O₃ and Co/ γ -Al₂O₃, we will study combining the results of XRD and the analysis of Fig. 5.

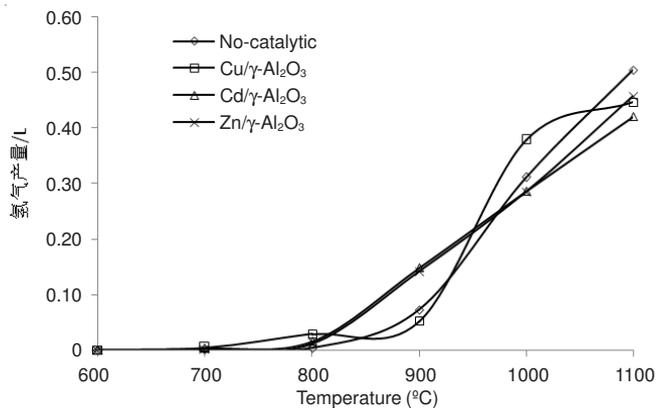
NiO and CoO are typical *p*-type oxides, they have excess amount of oxygen than the molecular formula of NiO and CoO showed, that is, non-stoichiometric oxygen, which has some relevance to catalytic activity^{1,2}. The catalytic activity of NiO and CoO is mainly derived from the mobile oxygen with high-concentration and high-active in the lattice of the catalyst. This part of oxygen is neither the lattice oxygen as conventionally understood, nor the oxygen of physical adsorption, we called that a mobile oxygen or "non-stoichiometric oxygen".

To conclude the reaction mechanism of oxidative dehydrogenation that occurred on the catalyst of NiO and CoO, we take ethane as an example.



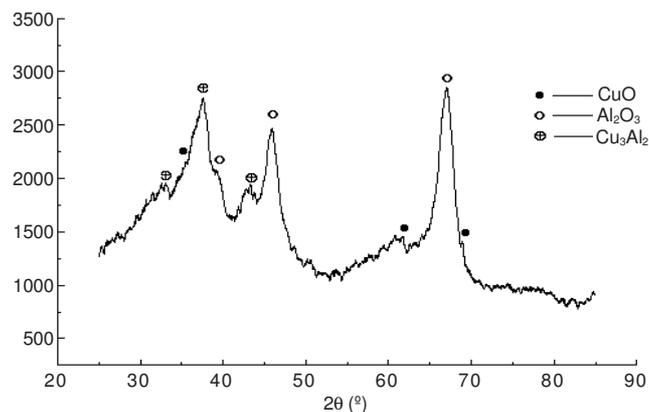
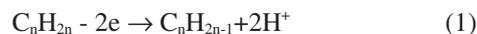
The previous experiment results that adopt Co as a catalyst show that Co restrains the generation of hydrogen from coal slurry pyrolysis. Co/ γ -Al₂O₃ contains Co which inhibits the catalytic activity of Co/ γ -Al₂O₃. So the yield of hydrogen choosing Co/ γ -Al₂O₃ as a catalyst is more less than Ni/ γ -Al₂O₃ as a catalyst for hydrogen production during 900-1100 °C.

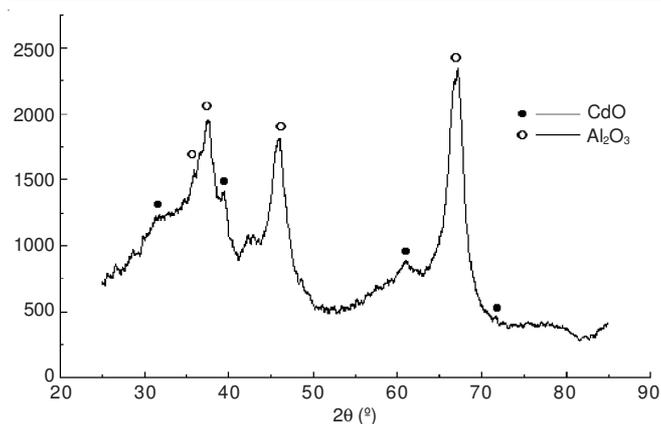
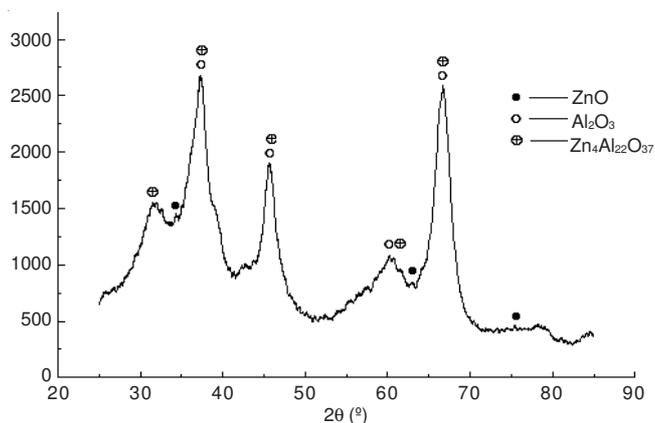
Effect of Cu/ γ -Al₂O₃, Cd/ γ -Al₂O₃ and Zn/ γ -Al₂O₃ on the hydrogen production from coal slurry pyrolysis: It can be seen from Fig. 8 that Cd/ γ -Al₂O₃ and Zn/ γ -Al₂O₃ show good catalytic activity between 700 to 900 °C, then the activity is significantly reduced in 900~1100 °C; Cu/ γ -Al₂O₃ has a better catalytic activity than Cd/ γ -Al₂O₃ and Zn/ γ -Al₂O₃ within 700~800 °C. Integrating the three catalysts, they show good catalytic activity in the range of 700~900 °C.

Fig. 8. The impact of Cu/ γ -Al₂O₃, Cd/ γ -Al₂O₃ and Zn/ γ -Al₂O₃ on hydrogen production from pyrolysis of coal slurry

The characteristics diffraction peaks of Cu/ γ -Al₂O₃, Cd/ γ -Al₂O₃ and Zn/ γ -Al₂O₃ are shown in Figs. 9-11 respectively. They show that all of them exist in the structure of oxide. The XRD spectra of Cu/ γ -Al₂O₃ appears the characteristics diffraction peak of CuO, Zn/ γ -Al₂O₃ and Cd/ γ -Al₂O₃ appear diffraction peaks of CdO and ZnO respectively.

CuO, CdO and ZnO are *n*-type oxides. Gaseous hydrocarbon was produced from coal slurry pyrolysis in the medium temperature phase and then the olefin chemisorbs the surface of oxide. It means that the olefin as an electronic donor absorb on the metal cation of the oxide.

Fig. 9. XRD spectra of Cu/ γ -Al₂O₃

Fig. 10. XRD spectra of Cd/ γ -Al₂O₃Fig. 11. XRD spectra of Zn/ γ -Al₂O₃

The second step is the control reaction, in fact it is a process that H⁺ on the surface of catalyst changes into H₂ and then desorbs from the catalyst. The gaseous olefin as an electron donor adsorbs on *n*-type metal-oxide, so it lead to the electron work function decrease, the conductivity increase and a raise of surface charge. The *n*-type transition metal-oxide

catalyst can provide more electron than the *p*-type transition metal-oxide catalyst, so it is conducive to the second reaction. Therefore *n*-type transition metal-oxide catalyst is in favour of hydrogen production in the medium temperature phase.

Conclusion

(1) Ag/ γ -Al₂O₃ and Fe/ γ -Al₂O₃ show good catalytic activity at 700~1100 °C, its catalytic activity is mainly derived from the phenomenon of hydrogen spillover.

(2) NiO and CoO are typical *p*-type oxides. Ni/ γ -Al₂O₃ shows good catalytic activity in the medium temperature section (700~800 °C) and higher temperature section (1000~1100 °C), while Co/ γ -Al₂O₃ only has good catalytic activity in the medium temperature section, the main reason is that there is Co existing in Co/ γ -Al₂O₃ which inhibits the catalytic activity.

(3) The XRD analysis of Cd/ γ -Al₂O₃, Zn/ γ -Al₂O₃ and Cu/ γ -Al₂O₃ shows that their characteristic diffraction peaks are CdO, ZnO and CuO respectively. They are all *n*-type oxide, so they show a good catalytic activity in the medium temperature.

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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