Research Article

Influences of Different Preparation Conditions on Catalytic Activity of $\text{Ag}_2\text{O-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ for Hydrogenation of Coal Pyrolysis

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A series of catalysts of $\text{Ag}_2\text{O-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ was prepared by equivalent volume impregnation method. The effects of the metal loading, calcination time, and calcination temperatures of Ag and Co, respectively, on the catalytic activity were investigated. The optimum preparing condition of $\text{Ag}_2\text{O-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ was decided, and then the influence of different preparation conditions on catalytic activity of $\text{Ag}_2\text{O-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ was analyzed. The results showed the following: (1) at the same preparation condition, when silver loading was 8%, the $\text{Ag}_2\text{O-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ showed higher catalyst activity, (2) the catalyst activity had obviously improved when the cobalt loading was 8%, while it was weaker at loadings 5% and 10%, (3) the catalyst activity was influenced by different calcination temperatures of silver, but the influences were not marked, (4) the catalyst activity can be influenced by calcination time of silver, (5) different calcination times of cobalt can also influence the catalyst activity of $\text{Ag}_2\text{O-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, and (6) the best preparation conditions of the $\text{Ag}_2\text{O-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ were silver loading of 8%, calcination temperature of silver of 450°C, and calcinations time of silver of 4 h, while at the same time the cobalt loading was 8%, the calcination temperature of cobalt was 450°C, and calcination time of cobalt was 4 h.

1. Introductions

Humans suffered from serious environmental pollution owing to the burning of fossil fuels. Moreover, as a kind of nonrenewable energy, fossil fuels are decreasing gradually even drying up in some cases [1]. In order to maintain the sustainable development of society, we have to develop and use reusable energy and new energy. New energies like hydrogen are becoming important as a kind of replaced energy and playing a more and more important role in primary energy [2–4]. Hydrogen can be prepared with fossil fuels or nonrenewable energy [5–7]. But according to the characteristics of China's coal resource [1], the preparation for hydrogenation of coal pyrolysis may be more appropriate

in reality. Because the pyrolysis temperature is low and the technical process is fixable, therefore, it can be both final disposal to prepare some hydrogen-rich gas, tar, and semicoke, and so forth, for the future of the people's demand and middle disposal to realize the polygeneration with gases, tar, and semicoke which produced in pyrolysis process [8–10]. But the output in simple hydrogenation of coal pyrolysis is low presently, and adding appropriate catalysts will improve the efficiency of traditional coal pyrolysis process because the study of catalyst plays a vital role. This paper discussed the influences of six different preparation conditions of catalyst ($\text{Ag}_2\text{O-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$) activity in loading, calcination time, and calcination temperatures of silver and cobalt, analyzed the influences of different preparation conditions on catalytic

activity of $\text{Ag}_2\text{O}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ for hydrogenation of coal pyrolysis, and then found the optimum conditions to prepare $\text{Ag}_2\text{O}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$.

2. Experiment Device and Method

2.1. Catalyst Preparation. Catalysts were prepared with equivalent volume impregnation method. Optimum dose of AgNO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was taken to prepare a certain concentration liquor according to the 5%, 8%, and 10% loadings of silver and cobalt. Primarily, move corresponding $\text{Co}(\text{NO}_3)_2$ soak into $\gamma\text{-Al}_2\text{O}_3$ and bake or dry it with a slow fire after placing 24 h. Then, put it into an oven and let it dry overnight. Thirdly, place it into a muffle furnace to roast. Finally, soak $\gamma\text{-Al}_2\text{O}_3$ in AgNO_3 and repeat above steps; then $\text{Ag}_2\text{O}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ bimetallic catalyst can be prepared.

2.2. 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 $17.8^\circ\text{C min}^{-1}$ 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 gas the total volume (mL). The schematic diagram of experimental device is shown in Figure 1.

3. Results and Discussions

3.1. The Influence of Different Silver Loadings on Catalytic Activity. The relationship graph between catalytic activity of $\text{Ag}_2\text{O}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ and silver loading is referred to in Figure 2. From Figure 2 we can see that the catalytic activity of different silver loadings was not distinct in $700^\circ\text{C} \sim 950^\circ\text{C}$. When the temperature was within $900^\circ\text{C} \sim 950^\circ\text{C}$, catalytic activity with silver loading at 10% showed better performance. From the above analysis, it can be seen that catalytic activity of $\text{Ag}_2\text{O}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ was not increased with the silver loading increase.

Figure 3 showed the XRD of different silver loadings; it can be seen from Figure 3 that all the samples had the complete Co_3O_4 crystal structure, which showed the characteristic peak of Co_3O_4 at $2\theta = 31.249^\circ, 36.840^\circ, 45.005^\circ, 55.916^\circ, 59.508^\circ, \text{ and } 65.458^\circ$; however when the silver loading was 8%, characteristic peak of the Ag_2O was shown at $2\theta = 32.839^\circ$ and 38.109° in the XRD, but the characteristics' peak of Ag_2O was not obvious when the silver loading was 5% and 10%. The reason was that Ag_2O and Co_3O_4 presented a strong interaction with the increasing of the silver loading, which caused the Ag_2O dispersed as the microcrystalline on the surface of catalyst.

Finally several good conclusions were drawn from the former analyzing conclusion. As a result of the above analysis

FIGURE 1: The schematic diagram of the pyrolysis reactor.

FIGURE 2: The catalytic activity of different silver loadings.

Co_3O_4 is a kind of p-type semiconductor and conducts by cavitations. When Ag_2O loaded on Co_3O_4 , as the valence state of Ag^{+1} is lower than cobalt, it plays a role as acceptor impurity, which can increase the cavitations and the conductivity of Co_3O_4 semiconductor [11–13]. Take produced hydrogen occurring on the metal cobalt oxide catalysts for propane secondary cracking as an example. Propane became positive ions adsorbed on the catalyst, and the function of propane can be a donor impurity; the propane gave electronics to Co_3O_4 ; then the cavitations were decreased; thus decrease of the

FIGURE 3: The XRD of different silver loadings.

cavitations became unhelpful to accept propane electronic. If Co_3O_4 was added to the acceptor impurity Ag^{+1} , the cavitations' number will be raised, which improved the electric conductivity remarkably, availed surface adsorption step, and reduced the activation energy of hydrogen production from propane secondary cracking correspondingly. As a result, it has the highest catalytic activity when silver loading was 8% [14, 15].

3.2. The Influences of Different Cobalt Loadings on Catalytic Activity. Figure 4 was catalytic activity curves for hydrogenation of coal pyrolysis when cobalt loading was 5%, 8%, and 10%. From those curves it can be seen that the catalyst activity has obviously shown improvement when loading of the Co was 8%, but it was weaker when loading of Co was 5% and 10%.

Figure 5 showed that all the catalysts have shown the characteristics of diffraction peak of Co_3O_4 , but the intensity of the diffraction peak differs with the change of cobalt loading. The intensity of diffraction peak was weakest at 5% cobalt loading; the diffraction peak of 8% cobalt loading showed both the characteristics of Ag_2O diffraction peak and the characteristics of diffraction peak of Co_3O_4 , while the intensity of diffraction peak was strongest at 10% cobalt loading. Then, by comparing Figure 4 with Figure 5, crystalline phase of Co_3O_4 was not the main active center for hydrogenation of the coal pyrolysis. The reason was that the catalytic activity of 8% the cobalt loading was optimal, but the intensity of characteristics diffraction peak at cobalt 8% loading was lower than 10% loading. This means that intense interactions exist in Ag_2O and Co_3O_4 . The catalyst activity can be influenced by this interaction mainly.

3.3. The Influence of Different Silver Calcination Temperatures on Catalytic Activity. Figure 6 showed the influence of different silver calcination temperatures on $\text{Ag}_2\text{O}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalytic activity. The results showed that catalytic activity was the best when calcination temperature was at 450°C , while the change was unobvious at 400°C and 500°C . It can be inferred

FIGURE 4: The catalytic activity of different cobalt loadings.

FIGURE 5: The XRD of different cobalt loadings.

that the different calcination temperatures had influenced the catalyst activity, but the influences were not marked.

It can be seen from Figure 7 that the characteristics' diffraction peak of Co_3O_4 was sharp; the intensity was the strongest and formatted the Ag_2O crystal phase simultaneously when the calcination temperature was 450°C . While the Ag_2O crystalline degree was bad when the calcination temperature was 400°C , so presumably the Ag_2O crystal phase has not formed not yet; therefore this made the catalyst activity low relatively. When the calcination temperature was 500°C , with the increasing of calcination temperature, silver can disperse the surface of $\gamma\text{-Al}_2\text{O}_3$ preferably because of the interaction of Co-Ag.

Combined with Figure 6 and Table 1, it can be inferred that although the main phase of catalyst existed was Co_3O_4 when the calcination temperature was 400°C and 500°C , but the specific surface area had changed. Table 1 showed that the specific surface area of 400°C had greatly improved compared to that of the 500°C ; the high temperature roasting may be the main reason causing the sintering on surface, which

FIGURE 6: The catalytic activity of different silver calcination temperatures.

FIGURE 7: The XRD of different silver calcination temperatures.

TABLE 1: The catalyst surface area of different silver calcination temperatures.

	$T/^{\circ}\text{C}$	$\text{BET}/\text{m}^2\cdot\text{g}^{-1}$
$\text{Ag}_2\text{O}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$	400	234.862
	450	199.787
	500	202.683

led to the decreasing of specific surface area. Those reasons can make the catalyst activity decrease. On account of the catalyst Ag_2O crystalline phase existed obviously when the calcination temperature was 450°C . Thus the catalyst activity had increased; its specific surface area was reduced, so that the catalyst activity, which existed two crystalline phases, had no corresponding relation obviously with the structure and the specific surface area of catalyst. Therefore, it was concluded

(a)

(b)

FIGURE 8: The catalytic activity of different cobalt calcination temperatures.

that the interaction between Co_3O_4 and Ag_2O may be more important factors affecting catalytic activity.

3.4. The Influence of Different Cobalt Calcination Temperatures on Catalytic Activity. The influence of different cobalt calcination temperatures on catalytic activity is referred to in Figures 8 and 9. The catalyst showed best activity when cobalt calcination temperature was 450°C at the range of $400^{\circ}\text{C}\sim 800^{\circ}\text{C}$ while at different temperatures catalytic activity's changes were not distinct at the range of $800^{\circ}\text{C}\sim 950^{\circ}\text{C}$. When cobalt calcination temperature was 400°C , the catalytic activity was better than the other two catalysts. The catalyst showed higher activity when the cobalt calcination temperature was 450°C in the whole temperature range. It was due to the fact that intensity of Co_3O_4 characteristic diffraction peak was lower than the other two catalysts, so the activity was awful [16–18]. The catalytic activity component particle may be sintering at 500°C ; thus the number of the surface active sites was decreased, so the catalytic activity for hydrogenation of coal pyrolysis was reduced.

FIGURE 9: The XRD of different cobalt calcination temperatures.

FIGURE 11: The XRD of different silver calcination times.

FIGURE 10: The catalytic activity of different silver calcination times.

FIGURE 12: The catalytic activity of different cobalt calcination times.

3.5. The Influence of Different Silver Calcination Times on Catalytic Activity. Figure 10 showed the different silver calcination times' influence on catalytic activity. It can be inferred from Figure 5 that different calcination times can also influence the catalytic activity. Catalyst showed the best activity while calcination time was 4 h; in contrast the catalytic activity's change was not distinct when the calcination time was 3 h or 5 h.

From Figure 11 it can be inferred that all catalysts showed the characteristics diffraction peak of Co_3O_4 , but the intensity of the diffraction peak varied with the silver calcination time change. The intensity of the Co_3O_4 diffraction peak was the strongest when the calcination time was 4 h, and also the characteristic diffraction peak of Ag_2O at $2\theta = 32.839^\circ$ and 38.109° was observed while the catalysts whose calcination times were 3 h and 5 h had not shown the characteristic diffraction peak of Ag_2O almost. Because when the calcination time was 3 h the transformation from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and AgNO_3 to Co_3O_4 and Ag_2O was incomplete, and some

of cobalt and silver cannot be transformed to Co_3O_4 and Ag_2O which possess catalytic activity [19, 20]. But when silver calcination time was 5 h, the time was too long to make catalyst grow up and gather on the surface and reduced the active particles, which lead to catalytic activity decrease.

3.6. The Influence of Different Cobalt Calcination Times on Catalytic Activity. Figure 12 showed the different cobalt calcination times influencing catalytic activity. Different calcination times of Co can also influence the catalyst activity of $\text{Ag}_2\text{O}-\text{Co}_3\text{O}_4/\gamma-\text{Al}_2\text{O}_3$ in Figure 12. The catalytic activity of $\text{Ag}_2\text{O}-\text{Co}_3\text{O}_4/\gamma-\text{Al}_2\text{O}_3$ was the best when the calcination time was 4 h; on the contrary, when calcination time was 3 h or 5 h, the change of catalytic activity was not distinct.

4. Conclusions

At the same preparation condition, $\text{Ag}_2\text{O}-\text{Co}_3\text{O}_4/\gamma-\text{Al}_2\text{O}_3$ with loading 8% silver showed higher catalyst activity. When

the range of calcination temperature was 700°C~950°C, the change of catalytic activity was not distinct for different silver loadings, while catalytic activity only showed enhanced activity of 10% silver loading in 900°C~950°C. The activity had obviously improved when loading of the Co was 8%, while it was weaker by loadings 5% and 10%. Catalytic activity was the best when calcination temperature of silver was at 450°C, while it had a little change at 400°C and 500°C. It can be inferred that the different calcination temperatures can influence the catalyst activity, but the influence was not marked. Different calcination times can also influence the catalyst activity. Catalytic activity was the best at 4 h, while the change of catalyst activity was not distinct when the calcination time was 3 h or 5 h. When loading of the silver was 8%, the calcination temperature of silver was at 450°C and the calcination time of silver was 4 h, while at the same time the Co loading was 8%, the $\text{Ag}_2\text{O}-\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ showed the best catalytic activity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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