

IRON GROUP METAL CATALYZED HYDROGASIFICATION  
IN THE PRESENCE OF SUPPORTED HYDROGENATION NICKEL CATALYST

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INTRODUCTION

The catalytic hydrogasification of "coal" is successfully carried out by Tomita<sup>1</sup> and Hüttinger<sup>2</sup> and their co-workers using nickel and iron as catalysts. On the other hand, hydrogasification of coal char and carbon has attracted a little attention because of strong thermochemical suppression at higher temperature and low gasification rate compared with the gasification by H<sub>2</sub>O or CO<sub>2</sub> and also because only noble metals such as platinum show high catalytic activity. But, it is known that iron group metals iron, cobalt and nickel also have catalytic activity for hydrogasification of carbonaceous materials like graphite. The activity and reaction mechanism are well studied using controlled atmosphere electron microscopy<sup>3</sup>.

This study shows the reactivity of iron, cobalt and nickel catalyzed char gasification with hydrogen at atmospheric pressure, and that the mixing of supported nickel catalyst with metal loaded char remarkably increases hydrogasification rate.

EXPERIMENTAL

Most experiments here were performed in a micro flow reactor at one atmospheric pressure. The effluent gas was analyzed using gaschromatography. Yallourn brown coal from Australia was used as starting material because of low ash and sulfur content. Coal was first crushed in 32-60 mesh and demineralized with hot HCl. Metals were loaded on demineralized coal by wet impregnation of aqueous metal nitrate solution and then heat treated to char in high purity argon at various temperatures. Supported nickel catalyst is a commercial hydrogenation catalyst in which about 45% of nickel is supported on diatomite and the particle size is under 150 mesh.

RESULT AND DISCUSSION

KINETICS

Fig. 1 shows the hydrogasification profiles of metal loaded and demineralized Yallourn chars heat treated at 1123K for 30 minutes. Catalytic effect of iron group metals is apparently shown. The catalytic activity decreases in the order of Co > Ni > Fe at this temperature and at this catalyst loading levels. One of the characteristics of the profiles is that the initial low reactivity is observed for all the catalyst loaded chars. Then gasification rates gradually increase with time to a steady

state. The time of this initial low reactivity was less than 30 minutes at 1173K in TGA analysis of heat treated chars at 1173K for 1 hour and became longer with temperature decreasing and lasted over 300 minutes at temperatures below 1043K. XRD study showed that all the catalysts were almost reduced to metallic phase during heat treatment of coals. These observations indicate that the initial low reactivity is due to poisoning of very small amount of sulfur which strongly chemisorbs on the catalyst surface.

Fig. 2 shows the catalytic activity of chars at 993K when mixed with the same weight of supported hydrogenation nickel catalyst. Despite no methane evolves at this temperature without supported nickel catalyst, higher reactivity is observed for all chars than the results in Fig. 1. Although supported nickel catalyst increases the gasification rate of demineralized char, the effect is distinguishing for metal loaded chars. And the time of initial low reactivity becomes short and almost negligible for Co loaded char. Gasification profile of catalyst loaded char is as follows; there is short and low reactivity at the initial stage and then after the gasification rate reaches a maximum, it decreases gradually. The decrease in rate is probably due to deactivation of supported nickel catalyst at high temperatures. The supported hydrogenation nickel catalyst not only increases the gasification rate catalyzed by iron group metals, but decreases the time of initial low reactivity, that is, removes the chemisorbed sulfur from catalyst surface. The decreasing order of catalytic activity is again  $\text{Co} > \text{Ni} > \text{Fe}$ .

Further two experiments were done to check the effect of supported nickel catalyst on catalyzed char hydrogasification. First, reaction temperature was changed. Methane formation was observed at 943K for Fe loaded char and even at 843K for Co loaded char. The gasification rate of Co loaded char at 843K is about 0.4 mg/g/min and the value of activation energy is 23.2 Kcal/mol in the temperature range between 843 and 993K.

Next, the amount of catalyst loading was changed. The results are depicted in Fig. 3. The chars in this experiment were heat treated at 1173K for 1 hour and a maximum gasification rate was employed. The gasification rate increases by only about 0.1% catalyst loading for all catalysts. However, the increase in gasification rate becomes small at the catalyst loading level over 0.2% and a leveling-off in the rate is observed for Fe. This rate-loading relation is the same as the relation observed for the gasification rate without supported nickel catalyst at higher temperature. This observation suggests that supported nickel catalyst increases gasification rate by enhancement of the catalytic activity of iron group metals.

#### MECHANISM

There are some ideas for the reason that supported hydrogenation nickel catalyst enhances the catalytic activity of iron group metals. One of the ideas is a bimetallic effect, that

is, nickel on the supported catalyst makes alloy with the iron group metals during gasification. To examine this idea, the same amount of iron and nickel was loaded on Yallourn coal and gasification rate was measured after charring. No methane was formed at 993K. This means that the enhancement of catalytic activity of supported nickel catalyst is not due to the bimetallic effect. It is supposed that some catalytic activities of supported nickel catalyst enhance the activity of Fe, Ni and Co for hydrogasification

It is well known that nickel catalyst for hydrogenation adsorbs hydrogen, where it dissociates to atomic hydrogen and also hydrogen atoms spill over to neighboring materials.<sup>4</sup> On the other hand, it is proposed that the rate controlling step of catalytic hydrogasification is the formation of atomic H.<sup>5</sup> Supported nickel catalyst is mixed with catalyst loaded char only mechanically in this study. However, supported nickel catalyst is very fine particles and there is a possibility that nickel catalyst contacts with iron group metals on the char. So, hydrogen atom can spill over to the catalyst species on char as illustrated in Fig. 4 and consequently supported nickel catalyst enhances the catalytic activity of iron group metals.

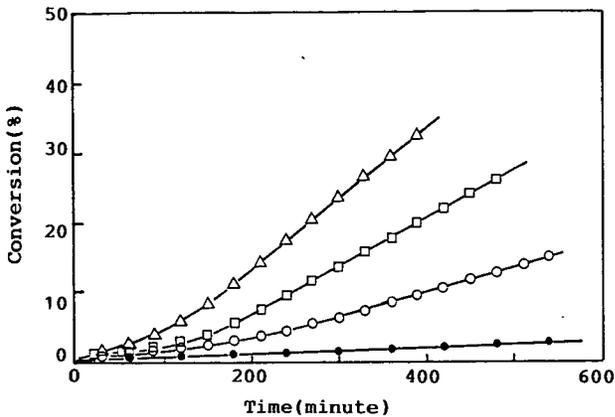
The mechanism mentioned above is only reasonable idea so far. But, there is another idea that hydrogen atom in supported nickel catalyst spills over to carbon directly and promotes the cleavage of C-C bond. In fact, supported nickel catalyst enhances the reaction rate of demineralized Yallourn char as depicted in Fig. 2. However, demineralized char contains a small amount of iron and iron shows hydrogasification activity at its low loading level as shown in Fig. 3. Therefore, the effect of supported nickel catalyst on demineralized char is mainly due to a trace of iron in the char and atomic H in the catalyst species is a very important factor on catalytic hydrogasification.

#### CONCLUSION

Iron, cobalt and nickel show catalytic activity for C-H<sub>2</sub> reaction. The hydrogenation nickel catalyst adsorbs hydrogen, and dissociated hydrogen atom spills over to catalyst species and consequently enhances the catalytic activity of those metals.

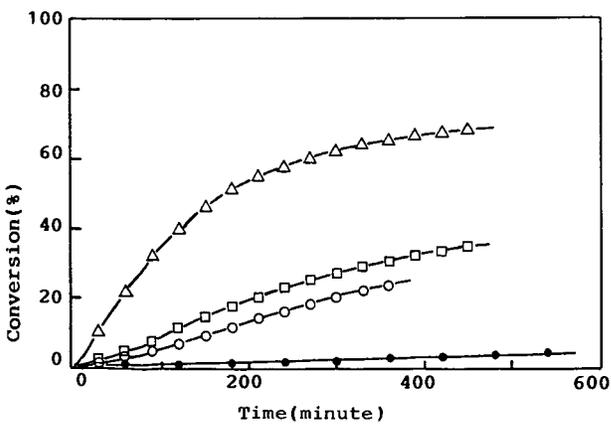
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○;0.80%Fe, △;0.92%Co, □;0.83%Ni, ●;Demineralized

FIGURE 1. HYDROGASIFICATION YALLOURN CHARS AT 1093K



○;0.80%Fe, △;0.92%Co, □;0.83%Ni, ●;Demineralized

FIGURE 2. HYDROGASIFICATION OF YALLOURN CHARS AT 993K WHEN MIXED WITH SUPPORTED HYDROGENATION NICKEL CATALYST

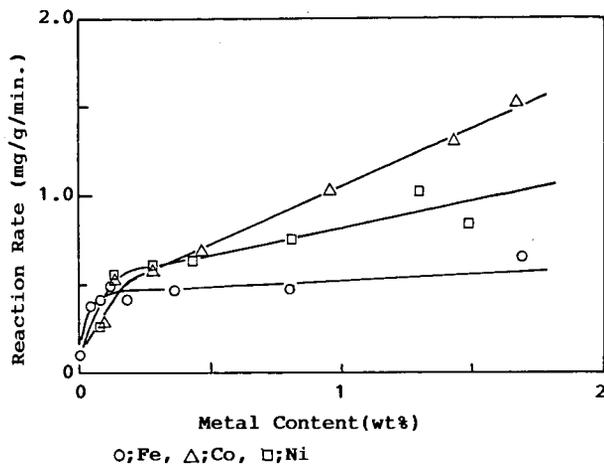


FIGURE 3. CATALYTIC ACTIVITY OF IRON GROUP METALS FOR HYDROGASIFICATION AT 973K WHEN MIXED WITH SUPPORTED HYDROGENATION NICKEL CATALYST

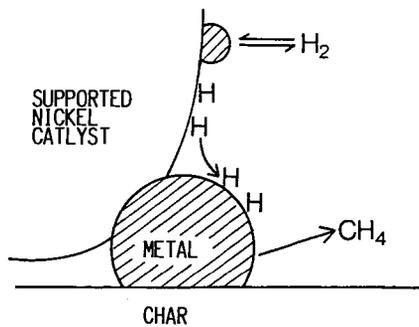


FIGURE 4. SCHEMATIC DIAGRAM OF HYDROGEN ATOM SPILL OVER IN THE SUPPORTED NICKEL CATALYST AND METAL LOADED CHAR SYSTEM