

Selectivity Changes in CO Hydrogenation over Potassium Added Titania-supported Cobalt Catalysts

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티타니아 담지 코발트 촉매를 이용한 일산화탄소 수소화 반응에서 칼륨 첨가에 의한 선택성 변화

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Abstract : Small amounts of potassium were added to the titania-supported cobalt catalysts in order to produce higher and olefinic hydrocarbons in CO hydrogenation. Titania and potassium played important roles not only for the enhancement of the production of higher and olefinic hydrocarbons, but also for the prevention of the catalyst deactivation by carbon deposits. Titania support induced the so-called SMSI, and potassium seemed to act as an electronic modifier, giving rise to an electron enrichment of the metallic phase.

요 약

칼륨과 티타니아 담체가 일산화탄소 수소화 반응에서 분자량이 큰 불포화 탄화수소의 합성에 유리할 것으로 예상하여, 칼륨염이 첨가된 티타니아 담지 코발트 촉매를 제조하여 일산화탄소 수소화 반응에 사용하였다. 칼륨과 티타니아 담체는 일산화탄소 수소화 반응에서 분자량이 큰 불포화 탄화수소 화합물을 합성하는 데 있어 중요한 역할을 하였을 뿐 아니라, 탄소 누적에 의한 촉매의 비활성화 방지에도 기여하였다. 이는 티타니아 담체가 코발트 금속과 강한 상호작용을 하고, 칼륨은 코발트 금속에 전자를 풍부하게 하는 전자 공급자로 작용하여 일산화탄소의 흡착력을 증가시켰기 때문으로 믿어진다.

1. INTRODUCTION

The addition of small amounts of alkali to supported group VIII metals has long been known to enhance the formation of both the higher and olefinic hydroca-

rbons in CO hydrogenation[1,2], and its role was generally interpreted in terms of electronic effects of transferring electrons to the metallic phase[3,4]. If the promoting role of alkali is combined with secondary supplemental component which can increase the

production of higher and olefinic hydrocarbons, an outstanding effect may be obtained in the hydrocarbon product distribution. In this respect titania support appears as a promising secondary component. Titania is distinguished from the conventional supports of alumina and silica by its reducibility under high temperature reduction conditions. The partially reduced titania caused the so-called strong metal support interaction(SMSI) for titania-supported group VIII metal catalysts, and induced some interesting behaviors[5].

In this paper small amounts of potassium salt were added to titania-supported cobalt catalyst, and their effects on CO hydrogenation were investigated.

2. EXPERIMENTAL

Titania(Degussa, surface area $50\text{m}^2/\text{g}$) and $\gamma\text{-Al}_2\text{O}_3$ (Strem Chemicals, surface area $225\text{m}^2/\text{g}$) were used as supports for cobalt catalysts. Hydrogen(Matheson, 99.999%) and helium(Matheson, 99.999%) were further purified by passing them through oxytraps(Alltech) and molecular sieve traps. Carbon monoxide (Takachiho, 99.95%) was passed through a molecular sieve trap to remove water and metal carbonyls. Alumina- and titania-supported cobalt catalysts were prepared by an aqueous impregnation method to have 2% cobalt and 0-2% potassium loadings by weight, respectively. The catalysts were heated to 550°C linearly at $5^\circ\text{C}/\text{min}$ in hydrogen stream, and were reduced at the temperature for 12 h. All the catalysts used in the present study are designated by the symbols of (cobalt loading, wt%)-(support, Al or Ti)-(potassium loading, wt%). The 2-Ti-1.0 catalyst, for example, denotes the titania-supported cobalt catalyst having 2 wt% cobalt and 1wt% potassium loadings, respectively.

Temperature programmed desorption(TPD) spectra of CO were obtained by heating the reduced catalyst linearly at $5^\circ\text{C}/\text{min}$ under helium stream. The exit stream from the catalyst bed was analyzed with a TCD located at immediate downstream of the reactor. CO_2 , produced from CO disproportionation ($2\text{CO} \rightarrow$

$\text{C} + \text{CO}_2$) during TPD experiment, was removed before entering the detector by using Ascarite(Arthur H. Thomas Co.) which absorbs CO_2 rapidly. The normal light greenish-brown color turned into white color due to the absorption of CO_2 and the formation of sodium carbonates.

H_2 and CO chemisorption uptakes were measured in a conventional Pyrex glass volumetric adsorption apparatus. The gas uptakes were determined by extrapolating the straight portion of the adsorption isotherms to zero pressure, and the difference between the total and reversible uptake was taken for the chemisorption.

CO hydrogenation reaction was performed in a differential reactor. The H_2/CO ratio was 2. Products were analyzed in a differential reactor in an on-line G.C.(Hewlett Packard 5710A) equipped with Chromosorb 102 column and TCD and FID detectors connected in series. Reaction rate, R_{CO} , was expressed in terms of the moles of CO reacted per gram of catalyst per second.

3. RESULTS AND DISCUSSION

3. 1. Activity

The changes in activity with potassium concentration in the titania-supported cobalt catalysts are shown in Figure 1. A sharp drop in activity is observed as the potassium concentration increases. Although the role of potassium had once been considered as a poison which selectively blocks specific sites of the metallic surface[2], alkali doping has generally been interpreted in terms of electronic effects[3,6]. Praliaud et al[4] have also showed that potassium can act as an electronic modifier which gives rise to an electron enrichment of the metallic phases. The electron-rich metal surface will then increase the bond strength of electron-acceptor molecule CO, shifting the TPD peaks to high temperatures as shown in Figure 2.

As the adsorption strength of CO increases, hydrogen will compete less strongly with CO for the adsorption sites. The surface concentration of hydrogen

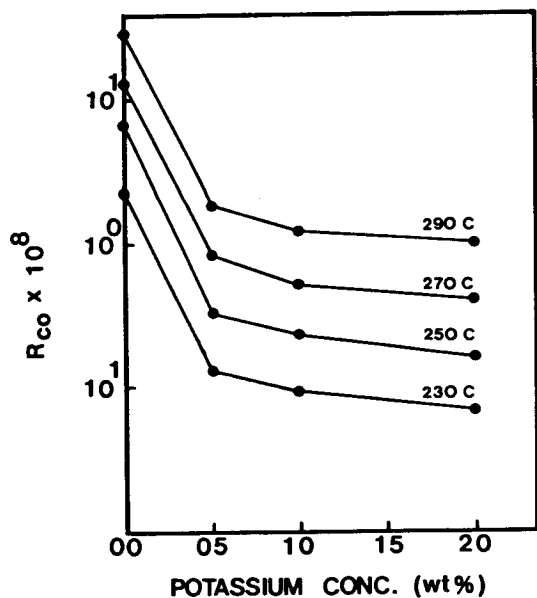


Fig. 1. Changes in CO hydrogenation activity with potassium concentration in the titania-supported cobalt catalysts.

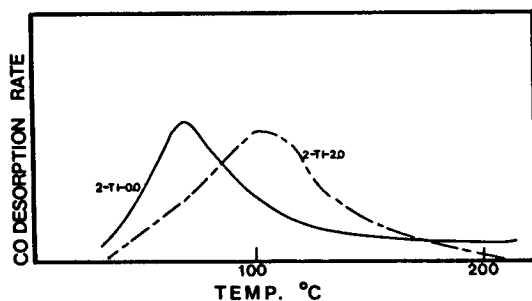


Fig. 2. TPD spectra of CO on the titania-supported catalysts.

will then be reduced, and thereby CO hydrogenation activity is believed to drop with potassium concentration. This is consistent with the suggestion by Vannice [7] that the most active metal surface is that on which CO adsorbs least strongly.

3. 2. Hydrocarbon Product Distribution

Table 1 shows the hydrocarbon product distributions of the supported cobalt catalysts. Comparing the

Table 1. Hydrocarbon Product Distributions in the Supported Cobalt Catalysts (reaction temp. = 290 °C, conversion = 0.7%)

catalyst	product distribution (wt%)					
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
2-Al-0.0	78.2	8.3	9.1	3.9	0.5	—
2-Al-0.5	64.3	11.6	12.8	6.9	3.8	0.6
2-Al-1.0	60.2	13.4	13.7	8.2	2.9	1.6
2-Al-2.0	58.7	16.5	14.9	8.4	1.1	0.4
2-Ti-0.0	52.6	16.3	18.7	8.4	4.0	—
2-Ti-0.5	43.2	17.2	21.3	12.7	4.3	1.3
2-Ti-1.0	38.6	17.1	24.9	14.2	4.9	0.3
2-Ti-2.0	33.7	16.4	31.1	12.9	4.6	1.3

2-Ti-0.0 and 2-Al-0.0 catalysts which contain no potassium, much higher hydrocarbons are produced on the titania-supported catalyst. This indicates that titania support has an advantage over alumina for the production of higher hydrocarbons. On some titania-supported metal catalysts, the production of higher hydrocarbons had been observed owing to SMSI [9, 10]. The most common feature of SMSI-induced catalysts is the suppression of hydrogen chemisorption [8]. From the chemisorption data in Table 2 the hydrogen uptakes on the titania-supported catalysts are known to be highly suppressed when compared with the alumina-supported ones. Therefore, the titania-supported

Table 2. Data for CO and H₂ Gas Uptakes on the Supported Cobalt Catalysts (temp. = 20 °C)

catalyst	uptakes (μmole/g cat)	
	H ₂	CO
2-Ti-0.0	0.12	0.43
2-Ti-0.5	0.11	0.37
2-Ti-1.0	0.10	0.31
2-Ti-2.0	0.10	0.28
2-Al-0.0	2.7	11.7
2-Al-0.5	2.4	8.6
2-Al-1.0	2.1	6.7
2-Al-2.0	1.5	3.8

cobalt catalysts seem to show SMSI to a certain extent, and the production of higher hydrocarbons on the titania-supported catalysts seems to be due to the SMSI. Owing to the suppression of hydrogen chemisorption, more olefinic hydrocarbons were produced on the titania-supported catalysts than on the alumina-supported ones.

The addition of potassium enhanced the production of higher hydrocarbons. Fu and Bartholomew[11] showed that the more higher hydrocarbons were produced on the surface with the more strongly bound CO owing to the longer residence time of carbon-containing reaction-intermediates on the surface. Since the potassium increased the adsorption strength of CO (Figure 2), the production of higher hydrocarbons with potassium concentration seems to result from the stronger CO adsorption strength.

The changes in olefin fraction with potassium concentration in the titania-supported catalysts are shown in Figure 3. The olefin fractions increase with increasing potassium concentration. This provides further

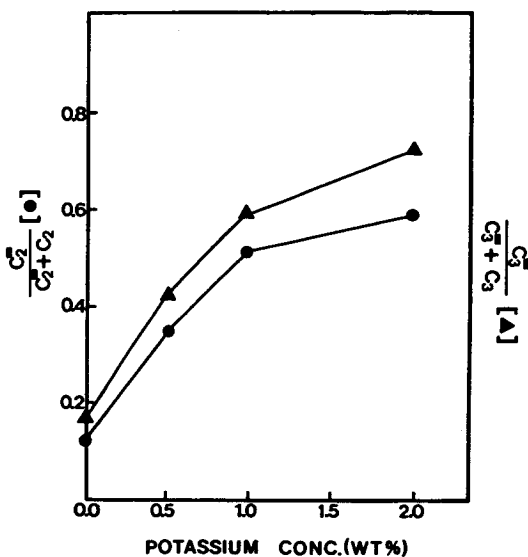


Fig. 3. Changes in olefin fraction with potassium concentration on the titania-supported catalysts (reaction temperature=290°C).

evidence for the aforementioned suggestion of an electronic role of potassium. The strong chemisorption of carbon monoxide on the potassium-added catalysts will weaken the competition of hydrogen with carbon monoxide for the adsorption sites. The resultant reduction in the surface hydrogen concentration retards the hydrogenation of the primarily formed olefins to corresponding paraffins.

3. 3. Deactivation

Arrhenius plots between the activity and inverse reaction temperature are shown in Figure 4. In the 2-Al-0.0 catalyst satisfactory constant slope appears over the wide temperature range for the data obtained at 1h from the introduction of reactants, while shift in the slope is observed at high temperatures for the data obtained at 4h. Agrawal et al.[12] observed that Co catalyst was more rapidly deactivated as compared with Ni and Ru catalysts, and the activation energy

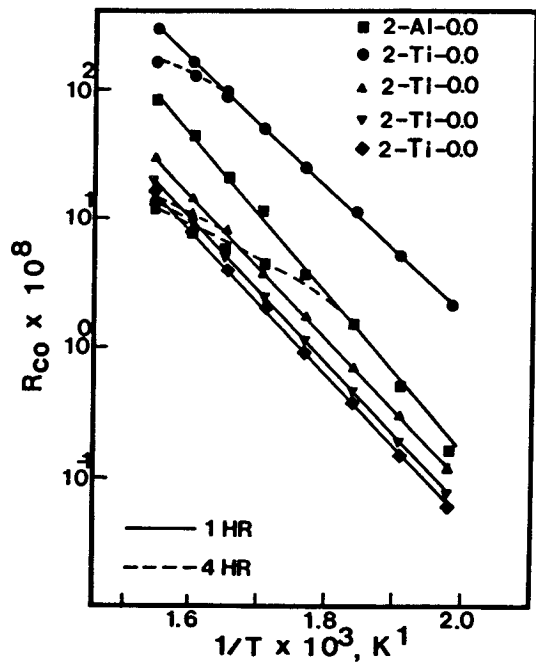


Fig. 4. Arrhenius plots for the supported cobalt catalysts.

on the $\text{Co}/\text{Al}_2\text{O}_3$ catalysts was reduced to almost half as the catalysts were deactivated by carbon deposits. The reduction in activation energy by carbon deposits had also been observed for $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst [13]. Figure 5 shows the normalized activity on the 2-Al-0.0 catalyst versus reaction time. At temperatures lower than 290°C , no significant catalyst deactivation was observed, but as the temperature was increased above 290°C , rapid deactivation began to occur. Auger electron spectra of the 2-Al-0.0 catalyst were recorded after CO hydrogenation reaction at 350°C for 1h (Figure 6-A) and for 4h (Figure 6-B) and for 4h (Figure 6-A), while the carbon accumulation becomes evident after 4h reaction. Therefore, the shift in the activation ene-

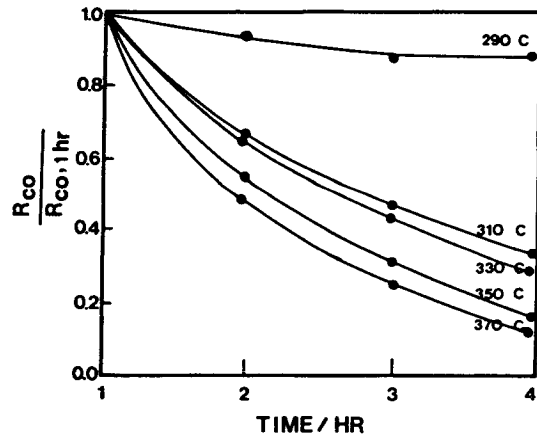


Fig. 5. Changes in activity with reaction time on the 2-Al-0.0 catalyst.

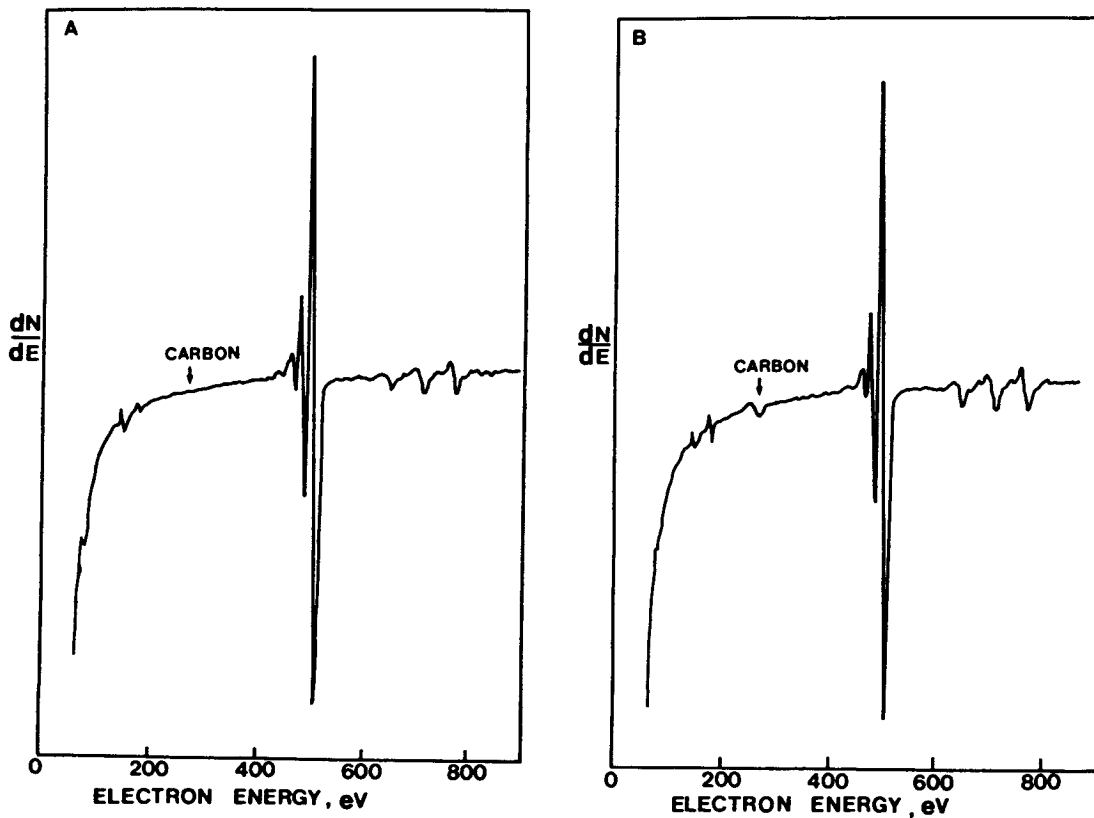


Fig. 6. Auger electron spectra of the 2-Al-0.0 catalyst after CO hydrogenation for 1 h (A) and for 4 h (B) (conversions were adjusted to have 0.8%).

rgy at temperatures higher than 290°C in the 2-Al-0.0 catalyst resulted from the catalyst deactivation by carbon deposits. In addition the shift in the activation energy of the 2-Ti-0.0 catalyst occurred at much higher temperature than the 2-Al-0.0 catalyst. Titania support is then said to be more suitable for the preparation of the highly resistant catalyst to the catalyst deactivation by carbon deposits. Since potassium also increased the temperature at which the shift in the activation energy occurred, it must have played a role of protecting the catalyst from the deactivation by carbon deposits.

4. CONCLUSION

Titania support had greater advantages over alumina for the preparation of cobalt catalysts which could not only enhance the production of higher and olefinic hydrocarbons in CO hydrogenation, but also be resistant to its deactivation by carbon deposits.

When potassium was added to the titania-supported cobalt catalyst, the selectivity for higher olefinic hydrocarbons increased. This was attributed to the electronic modification of the catalyst by potassium. Potassium also prevented the catalyst from deactivating by carbon deposits.

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