STUDY ON THE AKTIVITY AND STABILITY OF METHANOL SYNTHESIS CATALYST ADDED B_2O_3 UNDER LOW TEMPERATURE-INTERMEDIATE PRESSURE

Ho K.M.1, Ri Ju R.2, Hyon Ch.3 (Democratic People's Republic of Korea)

Email: Ho425@scientifictext.ru

[1]*Ho Kwang Min - Master of Chemistry,Lecturer;*

[2]*Ri Ju Ryol - Master of Chemistry, Associate professor, Lecturer,*

[3]*Hyon Chol - Master of Chemistry, Associate professor, Lecturer,*

DEPARTMENT OF ORGANIC CHEMISTRY, FACULTY OF ORGANIC CHEMISTRY ENGINEERING,

HAM HUNG UNIVERSITY OF CHEMICAL INDUSTRIAL, NORTH KOREA

Abstract: *generally the catalyst is used in the form of a $Cu/ZnO/Al_2O_3$ methanol from synthesis gas($CO+H_2$). The article shows the result of the analysis compared the activity of the catalyst, the surface into a single footprint and copper fewer adding B_2O_3 to a catalyst $Cu/ZnO/Al_2O_3$. More compared the activity of the catalyst for the ongoing management of time with a synthetic catalyst C207 methanol. Addition of B_2O_3 to Cu / ZnO / Al2O3 catalyst increases the copper dispersion and the optimum content of B_2O_3 is 1 ~ 2%. During the continuous operation for 600 hours, the activity of both $Cu/ZnO/Al_2O_3/B_2O_3$ and C207 catalyst decreases gradually. At this time, the catalyst containing B_2O_3 is always more active.*

Keywords: *methanol systhesis catalyst, Methanol synthesis, catalyst.*

ИССЛЕДОВАНИЕ ОБ АКТИВНОСТИ И СТАБИЛЬНОСТИ СИНТЕТИЧЕСКОГО КАТАЛИЗАТОРА МЕТАНОЛА С ДОБАВЛЕНИЕМ B_2O_3 ПРИ НИЗКОЙ ТЕМПЕРАТУРЕ И СРЕДНЕМ ДАВЛЕНИИ

Хо К.М.[1], Ли Ч.Р.[2], Хен Ч.[3] (Корейская Народно-Демократическая Республика)

[1]*Хо Кван Мин - кандидат химических наук, преподаватель;*

[2]*Ли Чжу Рел - кандидат химических наук, доцент, преподаватель;*

[3]*Хен Чхор - кандидат химических наук, доцент, преподаватель,*

кафедра органической химии, факультет технологии органической химии,

Хамхынский химико-технологический университет,

г. Хамхын, Корейская Народно-Демократическая Республика

Аннотация**:** *вообще используют катализатор в виде $Cu/ZnO/Al_2O_3$ для синтеза метанола из газа ($CO+H_2$). В статье показан результат анализа в сравнении активности катализатора, его поверхности в единице занимаемой площади и меди при меньшем количестве добавления B_2O_3 к катализатору $Cu/ZnO/Al_2O_3$. Ещё*

сравнили активность катализатора по времени непрерывного управления с синтетическим катализатором метанола C207. При добавлении B_2O_3 к катализатору $Cu/ZnO/Al_2O_3$ степень дисперсий повышается и наименьшее количество B_2O_3 составляет 1 - 2 процента. При непрерывном управлении 600 часов постепенно уменьшается активность в катализаторах $Cu/ZnO/Al_2O_3$/ B_2O_3 и C207, но при этом активность катализатора, содержащего B_2O_3, всегда сильна.

Ключевые слова: *катализатор синтеза метанола, синтез метанола, катализатор.*

The preparation method, structural characteristics, and industrialization of methanol synthesis catalysts under low temperature and under low pressure have been studied extensively, but there are very few studies under low temperature - intermediate pressure [1, 2] .

We have studied the activity and the stability of continuous operation when adding B_2O_3 to $Cu/ZnO/Al_2O_3$ ternary catalysts.

1. Experimental method

1) Catalyst preparation

In order to make the $Cu/ZnO/Al_2O_3$ (5/4/1) catalyst containing B_2O_3, Na_2CO_3 solution was added to an aqueous solution of zinc nitrate and zinc nitrate mixed in a constant amount and cocurrently precipitated while maintaining 8 at 80 ℃.

It was then aged, washed, and mixed with $Al(OH)_3$, which was made by precipitating alumium nitrate with NH_4OH at room temperature.

Next, we mixed the H_3BO_3 solution in an appropriate amount, dried at 120°C for 12 hours, and calcined at 350°C for 5 hours to form a product of φ5 × 5 mm [3].

2) Method of measuring activity

The prepared catalyst was used for the measurement of methanol synthesis activity in a fixed - bed flow reactor.

4mL of the catalyst having a particle size of 0.4 to 1 mm was filled and subjected to a reduction treatment at 373K to 523K for 27 hours with a mixed gas of H_2(5%) and N_2(95%).

The CO conversion rate (XCO) and the methanol discovery rate (STY) of the catalyst were measured while passing the gas, that is $CO/CO_2/H_2/(CH_4+N_2)$=4.5/0.5/85/10 at 493K and 15MPa, at a velocity Sv= $10000h^{-1}$.

3) Measurement of structural characteristics of catalyst

The specific surface area of the catalyst was measured using a high-speed gas adsorption analyzer (NOVA 1000e type). **XRD** diffraction analysis was carried out using Philips-3Max type at Cu K_α, 30KV, 20mA, and the content of B_2O_3 was determined by atomic absorption spectrometry.

2. Result and discussion

1) Effect of B_2O_3

Table 1 shows the relationship between the change in activity and the specific surface area and the surface area ratio according to the content of B_2O_3 after 100 hours of reaction.

In the experiment, the activity of the B_2O_3-$Cu/ZnO/Al_2O_3$ catalyst was compared with that of the imported

catalyst C207.

The composition of the C207 catalyst is Cu/Zn/Al(atomic ratio)=5/4/1.

As shown in Table 1, when the content of B_2O_3 was 1.5wt%, the activity of the methanol synthesis and the co-surface area were maximized, and the specific surface area was slightly decreased.

This can be the result of the physically mixed B_2O_3 covering the copper surface when B_2O_3 is included in the catalyst by more than 1.5wt%.

The activity of C207 catalyst was slightly decreased after 100 hours, and the copper specific surface area and specific surface area did not change much, but the specific surface area, copper surface area and activity were much smaller than that of the catalyst added with B_2O_3.

Table 1. Change of activity and surface area according to reaction time of B_2O_3-Cu/ZnO/Al_2O_3 catalyst and C207 catalyst

catalyst	B_2O_3 content (wt%)	activity Kg-CH_3OH/(Kg-catalyst·h)	Specific surface area ㎡/g-catalyst	Copper surface area ㎡/g-catalyst
B_2O_3-Cu/ ZnO/Al_2O_3	4.5 3.2 2.4 1.5 1.5	0.35 0.39 0.56 0.60 0.61	86.3 83.4 79.5 71.4 71.4	17.8 19.3 20.5 34.2 34.5
C207	0 0	0.45 0.40	69.3 69.1	21.0 21.0

Reaction condition 523K,15MPa,GHSV=10000h^{-1} CO/CO_2/H_2/(CH_4+N_2)=4.5/0.5/85/10

These results show that B_2O_3 increases the copper surface area and induces motion dispersion effect.

To confirm this, results of x-ray diffraction analysis are given in Fig 2.

From the XRD analysis results, it can be seen that the **XRD** intensity of the **C207** catalyst was much higher than that of the B_2O_3 added catalyst.

That is, the addition of B_2O_3 suppresses crystal growth of Cu and ZnO.

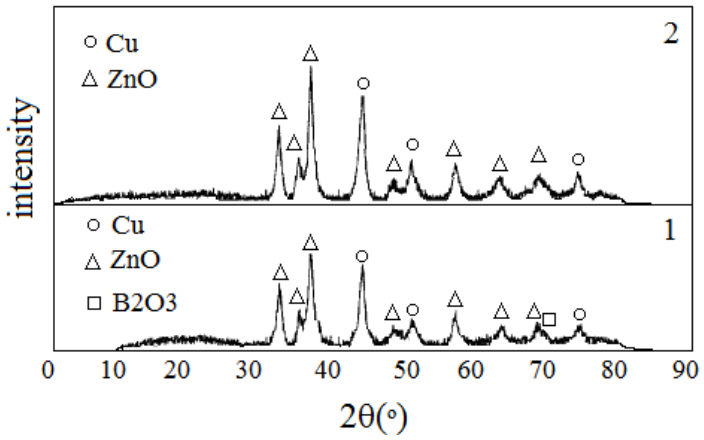

Fig. 1. XRD analysis of B_2O_3-Cu/ZnO/Al_2O_3 catalyst and C207 catalyst after 100 hours

1- B_2O_3-Cu/ZnO/Al_2O_3, 2- C207

2) Stability of activity in continuous operation

Figure 2 shows the results of the study of the activity of B_2O_3-Cu/ZnO/Al_2O_3 catalyst in 600-hour continuous operation.

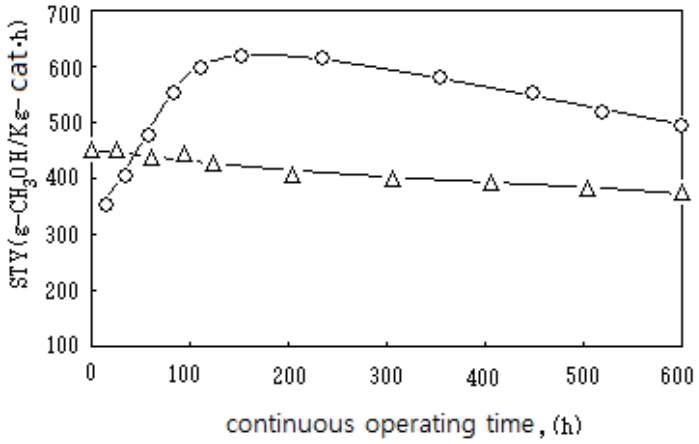

Fig. 2. Comparison of the activity of B_2O_3-Cu/ZnO/Al_2O_3 catalyst and C207 catalyst in 500-hour continuous operation

○- B_2O_3-Cu/ZnO/Al_2O_3, Δ-207

Reaction condition 523K, 15Mpa, Sv=10000h^{-1}, $CO/CO_2/H_2/(CH_4+N_2)$=4.5/0.5/85/10

As shown in Fig. 2, the catalyst when containing 2% of B_2O_3 has the maximum activity after 100 hours of reaction time and gradually decreases from the next.

C207 catalyst shows a tendency to decrease slowly during 600 hours of continuous operation.

In both catalysts, the decrease in activity due to the continuous operation can be attributed to the Cu-ZnO crystal destruction phenomenon in the water produced in the reaction. However, the activity of B_2O_3 catalyst after 100 hours is always higher than that of C207.

Conclusion

Addition of B_2O_3 to Cu / ZnO / Al2O3 catalyst increases the copper dispersion and the optimum content of B_2O_3 is 1 ~ 2%. During the continuous operation for 600 hours, the activity of both $Cu/ZnO/Al_2O_3/B_2O_3$ and C207 catalyst decreases gradually. At this time, the catalyst containing B_2O_3 is always more active.

References in English / Список литературы на английском языке

1. *Denisov E.T., Sarkisov O.M., Lihtenshtejn G.I.* Himicheskaja kinetika. M. Himija, 2000.
2. *Klier K.* Adv. Catal. 31 (1983) 243.
3. *Chinchen G.C., Hay C.M.,* Catal J. 103 (1987) 79.
4. *Morikawa Y., Iwata K., Terakura K.* Appl. Surf. Sci. 169/170 (2001) 11.

References / Список литературы

1. *Денисов Е.Т., Саркисов О.М., Лихтеншстейн Г.И.* Химическая кинетика. М. Химия, 2000.
2. *Клиер К.* Адв. Каеализатор. 31 (1983) 243.
3. *Чинчен Г.Ц., Хаы Ц.М., Каеализатор Й.* 103 (1987) 79.
4. *Морикаща Ы., Ищата К., Теракура К.* Аппл. Сурф. Сци. 169/170 (2001) 11.