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SELECTIVE SYNTHESIS OF ETHANOL OVER Rh-Ti-Fe-Ir/SiO_2 CATALYST AT HIGH PRESSURE SYNGAS CONVERSION

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A high performance catalyst for ethanol production has been developed. Ethanol was produced with more than 50% selectivity from syngas over Rh-Ti-Fe-Ir/SiO_2 under the condition of 50 atm and 260 °C. The roles of additives were discussed from the point of the reaction behavior and physical property of this catalyst.

It is well known that Rh/SiO_2 catalyst produces C_2-oxygenated compounds such as ethanol, acetaldehyde, and acetic acid from syngas with high selectivity.1) However, it is very difficult to produce ethanol selectively without any production of other C_2-oxygenates even over Rh/SiO_2. In addition to this, the activity of CO conversion over Rh/SiO_2 is not enough in consideration of a practcal use. This is the reason why additives are used to improve such catalyst performances as CO conversion activity and product selectivity. For example, Mn additive is proved to improve the catalyst activity of Rh/SiO_2.2) On the other hand, Fe additive improves ethanol selectivity.3) Nevertheless, these additive effects are not enough to produce ethanol in good yield.

We have developed several multi-promoted Rh/SiO_2 catalysts with a high performance for ethanol production.4) In this letter, we wish to report that the Rh-Ti-Fe-Ir/SiO_2 acts as a good catalyst for the selective production of ethanol.

Catalysts were prepared by a conventional co-impregnation method. SiO_2(#57, Davison) of 16-32 mesh were impregnated with an ethanol solution containing some amount of $RhCl_3 3H_2O$ and additive salts. $TiCl_4$, $FeCl_3 6H_2O$, and $IrCl_4 H_2O$ were used as additive precursors. After impregnation, catalyst was dried carefully by a rotary evaporator up to 120 °C, and reduced gradually with H_2 flow at the temperature from 20 °C to 400 °C, finally at 400 °C for 2 h. High pressure reaction was conducted with a flow type fixed-bed stainless steel micro reactor. The effluent gas was directly introduced to GC and analized by 4 GC columns.1) The volumetric adsorptions of H_2 and CO on each catalyst were measured by a conventional glass vaccum apparatus.

Table 1. Reaction behavior of promoted Rh/SiO_2 catalyst

Catalyst	CO conv.	Selectivity / %							
		MeOH$^{a)}$	EtOH$^{a)}$	AcH	AcOH$^{a)}$	C_2-oxy.	CH_4	C_2^+	CH_4/C_2^+
Rh/SiO_2	2.9	2.3	6.5	34.2	34.9	75.5	18.4	2.3	8.2
Rh-Ir(1:0.5)/SiO_2	3.1	2.3	17.5	31.2	25.8	74.5	20.3	1.4	14.3
Rh-Ti(1:1)/SiO_2	12.2	9.1	22.5	6.8	13.7	43.2	32.7	9.2	3.6
Rh-Fe(1:0.3)/SiO_2	5.9	11.7	39.0	1.7	7.3	48.0	32.8	2.0	16.4
Rh-Ti-Fe(1:1:0.3)/SiO_2	14.3	3.4	42.2	2.9	12.0	57.0	30.6	3.3	9.3
Rh-Ti-Fe-Ir(1:1:0.3:0.5)/SiO_2	12.5	3.7	50.7	1.8	12.5	65.0	21.5	2.6	8.3

Each catalyst contains 4.7wt% of Rh. Number in a parenthesis shows an atomic ratio of additives to Rh. Data were obtained at a time on stream of 2 h. a) denotes the sum of neat product and ester. C_2^+ denotes the sum of hydrocarbons other than CH_4. Reaction conditions;catalyst charge:1.0g,reaction pressure:50 atm,reaction temperature:260 °C,flow rate:100 ml/min,syngas ratio(H_2/CO):1.

Table 1 shows the reaction behavior of several catalysts. The amount of additives included in each catalyst was optimized for ethanol production. C_2-oxygenates were produced with 76% selectivity, but acetaldehyde(AcH) and acetic acid(AcOH) were main products in stead of ethanol(EtOH) over Rh/SiO_2. By the addition of Ir to Rh/SiO_2, ethanol selectivity was increased three times with a decrease of AcOH, but CO conversion and the selectivity of C_2-oxygenates were not changed compared with Rh/SiO_2. Hydrogenation ability of Rh-Ir/SiO_2 to acetyl intermediate is supposed to be higher than that of Rh/SiO_2 because of the high value of CH_4/C_2^+. By the addition of Ti to Rh/SiO_2, CO conversion was increased to 12.2% which was 4 times as much as the case of Rh/SiO_2, but the selectivity of C_2-oxygenates were decreased followed by an increase of hydrocarbons. In addition, ethanol selectivity in C_2-oxygenates was relatively high. The low value of CH_4/C_2^+ suggests that chain propagations are accelerated on this catalyst. By the addition of Fe to Rh/SiO_2, the selectivity of ethanol was strikingly increased from 6.5% to 39.0%, but C_2-oxygenates were decreased in the same way as the case of Rh-Ti/SiO_2. CH_4 was predominant in hydrocarbons produced. This is different from the case of Rh-Ti/SiO_2. High CH_4/C_2^+ suggests that the ability to hydrogenate acetyl intermediate is higher than that of Rh-Ti/SiO_2. Though Ti additive increases CO conversion, the significant disadvantage for the ethanol production is the production of lots of hydrocarbons. On the other hand, Fe additive increases ethanol selectivity, but the increase of CH_4 formation should be avoided for more selective production of ethanol. Ir additive increases the ethanol selectivity without any disadvantage, but its selectivity and activity are not enough.

From these results, the combination effects of these additives to Rh/SiO_2 were investigated. In the case of Rh-Ti-Fe/SiO_2, doubly promoted effect was revealed in both CO conversion and ethanol selectivity, but the disadvantage, that is, high CH_4 formation, was still present. To avoid this disadvantage, Ir additive was added to Rh-Ti-Fe/SiO_2. CH_4 formation was suppressed to the same magnitude of the case of Rh/SiO_2 and the C_2-oxygenates selectivity was increased by these combination. As a result, the efficiency of ethanol production was remarkably enhanced by the triply promoted Rh/SiO_2 catalyst. This is the first presentation that ethanol is possible to be produced from syngas with more than 50% selectivity over Rh-Ti-Fe-Ir/SiO_2. The enhancement of catalyst performance by the combination of two different types of additives, additives for increasing activity and for improving selectivity, has been shown in this work. These combination effect is expected to be a guiding principle to design a high performance catalyst for syngas conversion.

Table 2. Gas chemisorption character of catalyst

Catalyst	Adsorbed CO (mlSTP/g-cat.)	Adsorbed H_2 (mlSTP/g-cat.)	CO/H_2
Rh/SiO_2	4.1	2.2	1.9
Rh-Ir/SiO_2	5.2	2.3	2.2
Rh-Fe/SiO_2	3.2	1.6	2.1
Rh-Ti/SiO_2	4.3	1.3	3.3
Rh-Ti-Fe/SiO_2	3.7	1.1	3.3
Rh-Ti-Fe-Ir/SiO_2	3.3	1.1	3.0

Each catalyst contains 4.7 wt% of Rh.

Table 2 shows gas chemisorption behavior of each catalyst. In the case of Rh-Ir/SiO_2, some amount of chemisorbed gas was indebted to the adsorption on Ir metal itself. The amount of chemisorbed H_2 and CO was decreased with the increase of additive amount. Chemisorption seems to be blocked by additives. From CO/H_2 value of each catalyst, it is noteworthy that H_2 chemisorption is remarkably suppressed compared with CO chemisorption on catalysts containing Ti additive.

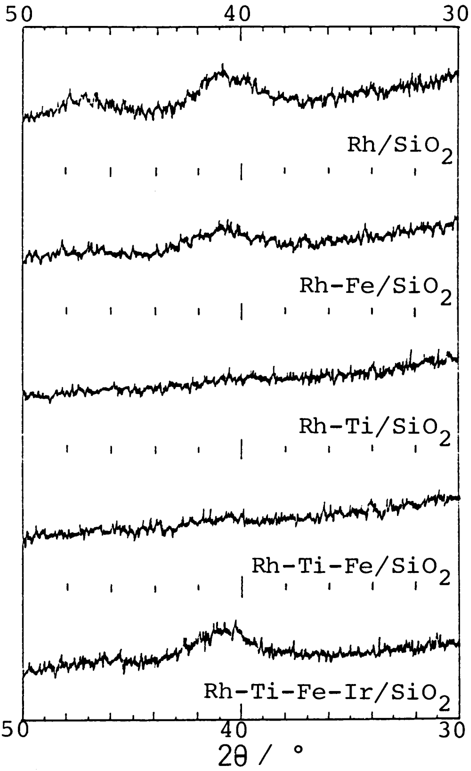

Fig.1. XRD patterns of various catalysts.

Figure 1 shows the X-ray diffraction pattern of each catalyst. Two peaks assigned to Rh crystallite were observed at 2θ = 41° and 48° in the case of Rh/SiO_2 and Rh-Fe/SiO_2 catalysts. From X-ray diffraction line broadening, Rh crystallite size on Rh/SiO_2 was estimated at about 33 Å. Rh crystallite size on Rh-Fe/SiO_2 seems to be reduced by some alloy formation with Fe additive. This alloy formation has been confirmed by Mossbauer spectroscopy.5) Most interesting is that the peaks due to Rh crystallite are not observed in the case of catalysts containing Ti additive except for Rh-Ti-Fe-Ir/SiO_2. There are two possibilities for explanation of this phenomenon. Rh crystallite may be so highly dispersed by the addition of Ti additive that it can not be observed by XRD. Or, Ti additive may change the morphology of Rh crystallite from hemisphere state to thin laft-like state which might be difficult to be observed by XRD. From the result that the amount of CO chemisorbed on Rh-Ti/SiO_2 is comparable to that of Rh/SiO_2, the dispersion of Rh crystallite on Rh-Ti/SiO_2 is supposed to be the same order as that on Rh/SiO_2. Therefore, the latter possibility is favorable to explain this change of XRD pattern. This disappearance of Rh peaks is supposed to be strongly related to the enhancement of CO conversion activity as well as the suppression of H_2 adsorption. In the case of Rh-Ti-Fe-Ir/SiO_2, two peaks recovered in XRD pattern are perhaps assigned to Ir metal which peak positions are almost the same as that of Rh metal.

Figure 2 shows the temperature programmed reaction pattern of adsorbed CO on each catalyst. The peak temperatures of CH_4 formation on catalysts containing Ti additive were decreased remarkably compared with that on Rh/SiO_2. On the other hand, the peak temperatures on $Rh-Ir/SiO_2$ and $Rh-Fe/SiO_2$ which have good ethanol selectivities were increased significantly compared with that on Rh/SiO_2. It is shown that the selectivity of ethanol in C_2-oxygenates is increased with an increase of Rh dispersion in the case of Rh/SiO_2.[1)] In addition, CH_4 formation peak temperature is also increased with an increase of Rh dispersion.[6)] From these findings, increasing selectivity of ethanol in the case of $Rh-Fe/SiO_2$ and $Rh-Ir/SiO_2$ is supposed to be responsible for the presence of highly dispersed Rh caused by alloy formations which reduce Rh ensemble size. The correlation between the catalyst performance and its physical properties is now under investigation in detail.

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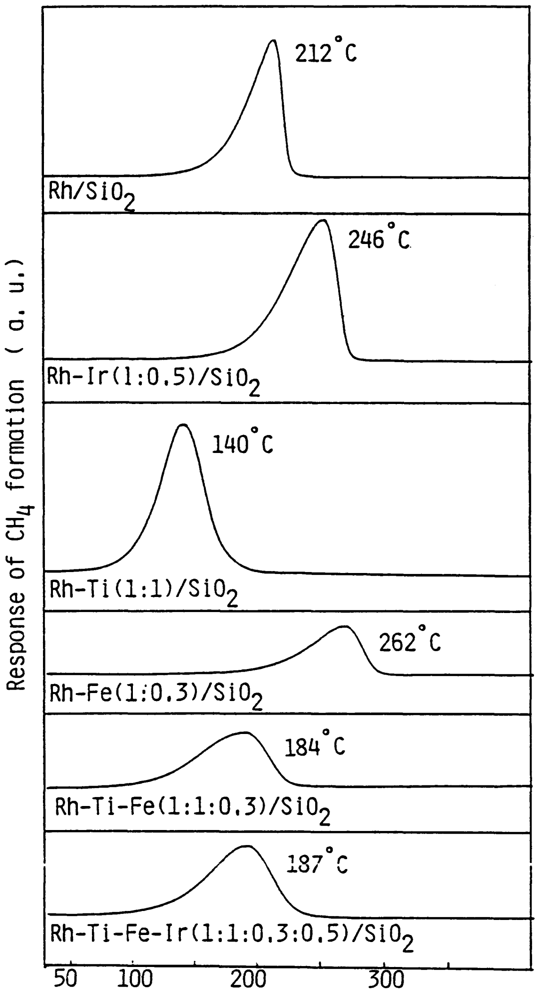

Fig.2. TPR patterns of adsorbed CO on catalysts.
Temperature was programmed from 30 °C to 370 °C with the rate of 7 °C/min. H_2 carrier flow rate: 60 ml/min.

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