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Effective synthesis of ethanol from CO_2 on polyfunctional composite catalysts

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Abstract

Synthesis of ethanol by hydrogenation of carbon dioxide has been investigated by developing the novel composite catalysts. The three different kinds of elementary reaction functions for ethanol synthesis were undertaken. The catalytic functions are partial reduction of CO_2 to CO, C–C bond formation, and –OH group insertion. For this purpose, supported Rh catalyst, Fe-based modified Fisher–Tropsch catalyst, and Cu-based modified methanol synthesis catalyst were combined by different ways. As a result, high space–time yields of ethanol as high as 0.8–0.9 kg/l h were obtained. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: CO_2; Polyfunctional composite catalysts; Synthesis of ethanol; Temperature-programmed reduction; TPR

1. Introduction

In order to mitigate accumulation of CO_2 in the atmosphere, a variety of countermeasures is now being undertaken. Among the methods of chemical fixation, catalytic hydrogenation of CO_2 into methanol and other alcohols on the solid catalyst is regarded as the most promising way from the viewpoints of rapid conversion rate and selectivity to the aimed products. Moreover, these alcohols can be used not only as it is for various significant purposes but also successive conversion to more valuable compounds, such as a high octane-number gasoline [1] and other raw materials for chemical industries.

As for ethanol, it is now synthesized industrially by the catalytic hydration of ethylene on solid-acid catalysts, however, the space–time yield of ethanol is fairly low (ca. 70–200 g/l h), and development of alternative synthesis routes has been expected. Therefore, in this presentation, the focus was concentrated on the increase in space–time yield of ethanol. For this purpose, the function of three kinds of catalytic functions, i.e., the function of partial reduction of CO_2 to CO, the function of C–C bond growth, and the function of –OH group insertion to products were combined by different ways and different ratios. The performances of these catalysts were compared by the reaction test under a pressurized condition with varying reaction temperature and space velocity of the reaction gas.

2. Experimental

2.1. Catalyst preparation

Five kinds of elementary catalysts designated as Cats. 1–5, and combinations of two of them were

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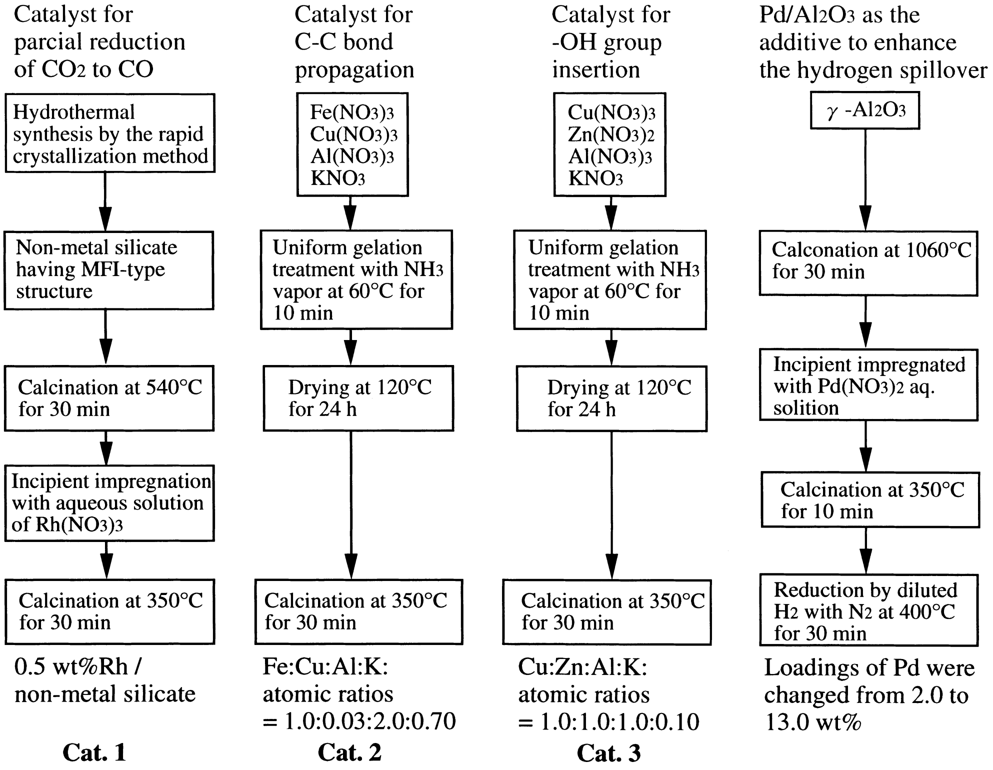


Fig. 1. Preparation procedures and compositions of elementary catalysts.

mainly used for the reaction test. Preparation procedures and compositions of Cats. 1–3 and Pd supported on alumina are shown in Fig. 1 as the elementary catalyst ingredients. In Cats. 4 and 5, Ga ingredient was combined with atomic ratios 0.16 and 0.32 to Cat. 2 and Cat. 3, respectively. Gallium nitrate was introduced from the stage of mixed aqueous solution before the uniform gelation as the source of Ga ingredient. In case of Pd-modification, 10 wt% Pd supported on the 1060°C calcined γ-alumina [2] was physically mixed at the stage of powder form with Cats. 4 and 5 to regulate the atomic ratio of Pd which became 0.03 [3].

A 0.5 wt% Rh supported on MFI-type non-metal silicate, designed as Cat. 1, was prepared as the catalyst for partial reduction of CO_2 to CO. The non-metal silicate was synthesized by the rapid crystallization method [4]. A Fisher–Tropsch type Fe-based catalyst composed of Fe:Cu:Al:K= 1:0.03:2.0:0.7 atomic ratios, designed as Cat. 2, was prepared as the catalyst for C–C bond propagation by applying the uniform gelation method [5].

A methanol synthesis catalyst, composed of Cu:Zn:Al:K atomic ratios=1.0:1.0:1.0:0.1, designed as Cat. 3 was prepared as the catalyst for –OH group insertion, also by the uniform gelation method.

All the catalysts in powder form were tabletted to 6.0 mm in diameter and 5.0 mm height by using a tablet machine, and it was crashed followed by sieving to 10–24 mesh to provide the reaction.

2.2. *Reaction method*

The reaction test was carried out using a pressurized flow reactor. A 0.50 g portion of catalyst was packed into the stainless tubular reactor of 10 mm inner diameter, and was reduced in situ in a stream of 10% H_2 diluted with N_2 at 450°C under the atmospheric pressure before the reaction. Once the reactor is cooled, the reduction gas was replaced by the reaction gas composed of CO_2, CO and H_2, and it was allowed to flow in the reactor under 80 atm, at the temperature range from 270°C to 370°C, and with the

Table 1
Performance of the elementary catalysts

Catalyst	Temperature (°C)	SV (10^4 h^{-1})	CO_2 conversion (%)	Selectivity (C-mol%)					STY (g/l h)		
				MeOH	EtOH	Ox.[a]	HC[b]	CO	MeOH	EtOH	(MeOH+EtOH)
Cat. 1	350	3.9	16.1	0.00	0.00	0.0	0.6	99.4	0	0	0
Cat. 2	350	3.2	43.3	5.53	8.17	4.1	64.9	17.3	274	291	565
Cat. 3	330	2.0	30.8	22.5	0.0	0.0	0.31	77.2	495	0	495

Reaction gas 25% CO_2–75% H_2).
[a] Methyl acetate was the major component.
[b] Methane was the major component; the products obeyed Shultz–Flory law.

space velocity range from 20 000 to 70 000 h^{-1}. All the products were analyzed by gas chromatographs equipped with the integrator.

3. Results and discussion

3.1. Reaction characteristics of the elementary catalysts

As shown in Table 1, the Rh single-component catalyst (Cat. 1) formed CO from CO_2 exclusively at 350°C.

The Fe-based Fisher–Tropsch type catalyst (Cat. 2) produced hydrocarbons with a selectivity of 64.9% under the same temperature and pressure for Cat. 1, and the composition obeyed Shultz–Flory law with an α-value of 0.54. However, besides the hydrocarbons, considerable amounts of ethanol and methanol were obtained. The Cu-based methanol synthesis catalyst (Cat. 3) produces only methanol as the oxygen containing product, and the major product was carbon monoxide. Therefore, Cat. 3 is regarded as not only the methanol synthesis catalyst but also the partial reduction catalyst for CO_2.

3.2. Effect of combination of the partial reduction catalyst with the alcohol synthesis catalyst by different ways on the catalytic performance

In the case of the Rh catalyst (Cat. 1) and the Fe-based catalyst (Cat. 2) the combination of these catalysts by packing in series gave a better result than the case of physical mixing (Table 2). The yield of alcohols in case of packing in series evidently increased due to the increase of CO in the reaction gas before introduction of the Fe-based catalyst. On the contrary, in the case of a combination of the Fe-based catalyst (Cat. 2) with a Cu-based catalyst, Cat. 5 modified with Pd (designated Cat. 6), the physical mixing gave a much better result in alcohol synthesis. The reason is ascribed to the degree of change in the reduction state of the catalyst surface during the reaction. Namely, in the case of combination with Rh, physical mixing

Table 2
Effect of combination of the different kinds of catalysts

Catalyst	Combinated method	Temperature (°C)	CO_2 conversion (%)	Selectivity (C-mol%)				EtOH yield (%)	STY (g/l h)	
				EtOH	MeOH	HC	CO		EtOH	MeOH
Cats. 1+2[a]	Physical mixing	350	40.8	8.04	4.61	67.4	14.1	3.28	276	220
Cats. 1+2[a]	Packed in series	350	41.9	11.0	8.51	58.4	19.2	4.60	378	418
Cats. 2+6[b]	Physical mixing	330	47.0	17.4	5.84	62.8	12.3	8.18	420	196
Cats. 2+6[b]	Packed in series	330	40.1	7.27	14.9	55.8	20.5	2.92	150	427

25% CO_2–75% H_2, 80 atm, SV 20 000 h^{-1}; Cat. 6: Pd-modified Cat. 5.
[a] Mixed weight ratio was 2 to 1. In case of Cats 1+2, STYs were based on the catalyst volume of Cat. 2.
[b] Mixed weight ratio was 1 to 1.

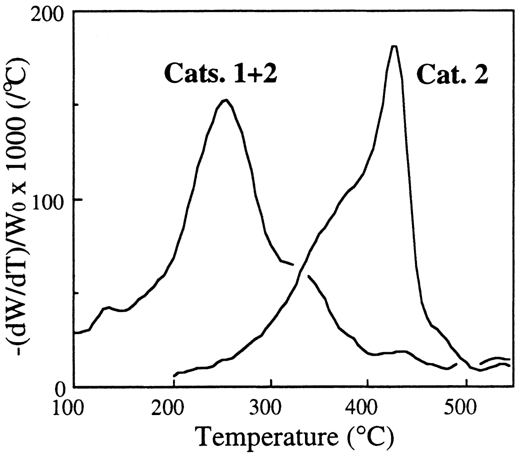


Fig. 2. Temperature-programmed reduction (TPR) profiles for Cat. 2 and Cats. 1+2 (physical mixing). 5% H_2–95% N_2, 10°C/min. Cat. 2 – Fe-based catalyst; Cats. 1+2 (physical mixing of Rh/Al_2O_3 (Cat. 1) and Fe-based catalyst (Cat. 2)).

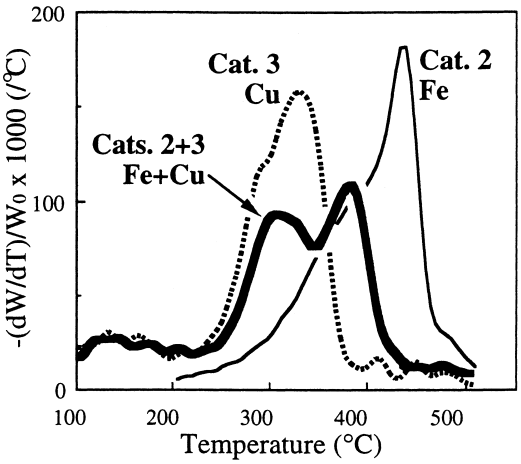


Fig. 3. TPR profiles for Cat. 2, Cat. 3, and Cats. 2+3. 5% H_2–95% N_2, 10°C/min. Cat. 2 – Fe-based catalyst; Cat. 3 – Cu-based catalyst; Cat. 6 physical mixing of Cats. 2 and 3.

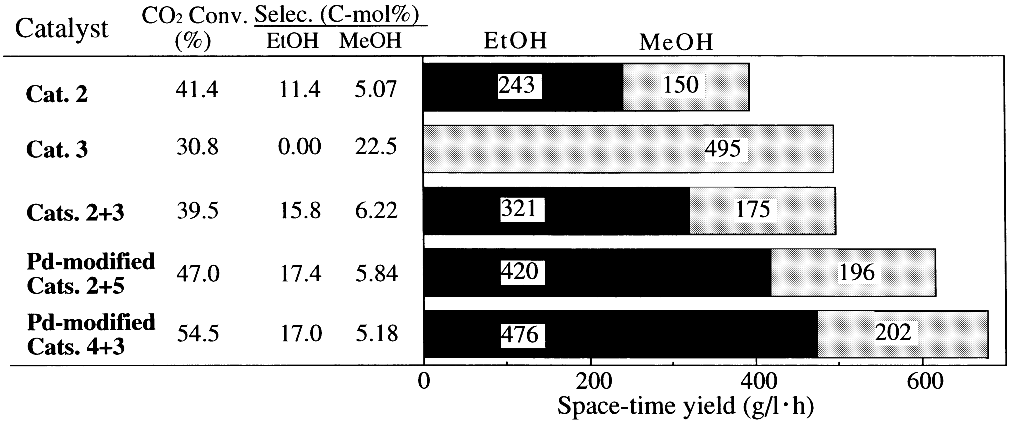
induces excess reduction by the role of too strong hydrogen spillover effect on the Fe-based catalyst part, resulting in the increase in hydrocarbon synthesis and decrease in alcohols. On the other hand, the Cu-based catalyst exhibited more mild reduction role than that in Rh catalyst for the Fe-based catalyst, and as a result, it gave more alcohols. In the case of packing in series it seems to be the methanol produced in the front part of the catalyst bed, i.e. Cat. 2 passed through the part of Cat. 6.

The reduction state of catalysts was confirmed by the measurement of temperature-programmed reduction (TPR) for the pre-oxidized catalysts. In Fig. 2, the effect of the combination of the Fe-based catalyst (Cat. 2) with Rh catalyst (Cat. 1) on the temperature-programmed reduction (TPR) profiles is shown. The peak of TPR profile for Cat. 2 was shifted to lower temperature side ca. 180°C by the combination of the Rh catalyst. The reason must be ascribed to the role of Rh particles supported on alumina as the porthole of hydrogen spillover, and consequently, the Fe-based catalyst could be reduced easily. On the other hand, the effect of combination of the Fe-based catalyst (Cat. 2) and the Cu-based catalyst (Cat. 3) on the TPR profiles is shown in Fig. 3. As shown, by combining the Cu-based catalyst (Cat. 3), and the TPR profiles of the Fe-based catalyst (Cat. 2), the two peaks that come from Cat. 2 and Cat. 3 appeared. However, the decrease in the peak temperature from the Fe-based catalyst was ca. 60°C, which is about one-third compared with the combination of Cats. 1+2. The decrease in the peak temperature of the Cu-based catalyst was small (ca. 20°C). These results indicate that Cu component in the role of porthole for hydrogen spillover is much lower than that of the Rh catalyst.

3.3. *Effect of the way of Ga-modification*

In Fig. 4 comparison of the catalytic performance is made for various catalysts, especially the different modification method of Ga ingredient, which was used with an expectation of its strong inverse hydrogen spillover, i.e., this property protects excess reduction of the catalyst surface by hydrogen during the reaction [6]. As shown in this figure catalysts exerted the best performance for the ethanol synthesis. At 54.5% conversion of CO_2, ethanol selectivity was 17.0%, and space–time yield of ethanol reached 476 g/l h.

In Fig. 5, in the case of Pd-modified Cats. 4+3, which is shown in the bottom of the bar graph in Fig. 4, distribution of alcohols produced is shown as the bar graph, and in Fig. 6 its Shulz–Flory plot is shown. The olefin to paraffin C-mol ratio for C_2 and C_3 hydrocarbons was 0.68 and 4.49, respectively, indicating that ethene was consumed on the catalyst surface to alcohols much more than higher alcohols



Catalyst	CO_2 Conv. (%)	Selec. (C-mol%) EtOH	Selec. (C-mol%) MeOH
Cat. 2	41.4	11.4	5.07
Cat. 3	30.8	0.00	22.5
Cats. 2+3	39.5	15.8	6.22
Pd-modified Cats. 2+5	47.0	17.4	5.84
Pd-modified Cats. 4+3	54.5	17.0	5.18

Fig. 4. Performance of catalysts prepared by different modification methods. Cat. 2: Fe-based catalyst; Cat. 3: Cu-based catalyst, mixing of different kinds of catalysts was done by physical mixing; Cat. 5: Ga-modified Cu-based catalyst; Cat. 4: Ga-modified Fe-based catalyst, Pd was combined by the physical mixing method. Reaction conditions: 25% CO_2–75% H_2, 80 atm, SV=20 000 h^{-1}, 330°C.

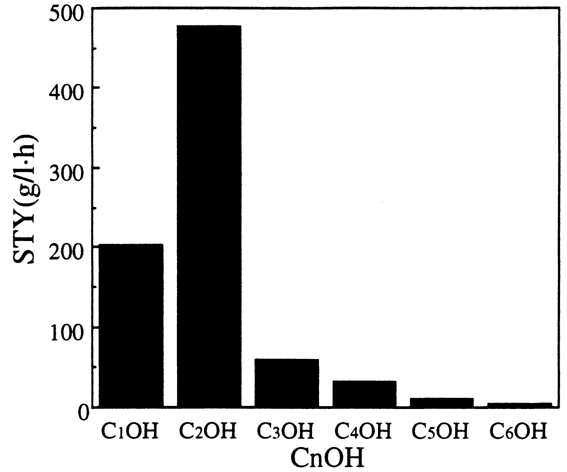


Fig. 5. Distribution of alcohols produced. Catalyst: Pd-modified Cats. 4+3, 25% CO_2–75% H_2, 80 atm, SV=20 000 h^{-1}, 330°C.

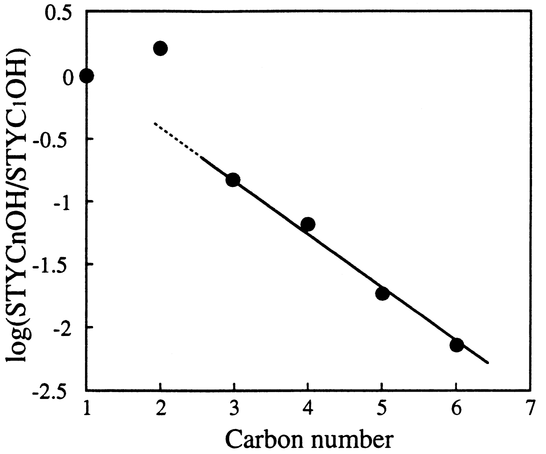


Fig. 6. Shultz–Flory plot for alcohols produced. Catalyst: Pd-modified Cats. 4+3, 25%CO_2–75%H_2, 80 atm, SV=20 000 h^{-1}, 330°C.

having carbon number 3. As shown in Fig. 6, above C_3 alcohols formed obeyed Shultz–Flory law, however, ethanol far deviated from the law, according to the synergistic effect of combination of the three elementary functions.

3.4. *Other factors influencing the catalytic performance*

The contents of Ga and Pd were varied for the Pd-modified Cats. 2+5, and the optimum performances for ethanol synthesis were obtained at the atomic ratios of 0.16 and 0.017, respectively.

The addition of small concentration (3 mol%) of CO enhanced the activity and ethanol yield by about 34%.

The effect of contact time on the catalytic performance showed that CO was the initial product and with an increase of contact time hydrocarbons and ethanol increased distinctly and CO decreased in counterpart. Hydrocarbons increased independently from other products.

Table 3
Results obtained at high space velocities on the optimally combined catalysts

Catalyst	Temperature (°C)	SV (10^4 h^{-1})	CO_2 conversion (%)	Selectivity (C-mol%)					STY (g/l h)		
				MeOH	EtOH	Ox.[c]	HC[d]	CO	MeOH	EtOH	(MeOH+EtOH)
(Cats. 1+2)[a]	350	7.0	29.4	2.85	9.33	0.5	46.7	40.6	335	787	1122
(Cats. 2+3)[b]	330	5.0	31.1	4.97	14.8	2.1	51.5	26.6	408	874	1282

[a] Packed in series with a wt. ratio of 1 to 2.
[b] Physically mixed with a ratio of 1 to 2.
[c] Methyl acetate was the major component.
[d] Methane was the major component; the products obeyed Shultz–Flory law.

It is noteworthy that the contact time dependency on the ethanol synthesis depended on the kind of catalyst, indicating that the reduced state of the composite catalyst depends on the composition of the reaction gas, especially the partial pressure of hydrogen. In the case of the catalyst having proper characteristics to maintain the optimum reduced state of the catalyst exhibits higher space–time yield of ethanol. In Table 3, some results obtained with higher space velocities or lower contact times are shown. As it can be seen in this table, very high STY values of ethanol as high as 0.8–0.9 kg/l h were achieved at higher space velocities under ca. 30% CO_2 conversion level.

4. Conclusion

Carbon dioxide was efficiently converted to ethanol by using composite catalysts involving three different kinds of elementary catalytic functions; i.e., partial reduction of CO_2 to CO, C–C bond formation, and –OH group insertion. Although the selectivity to ethanol is still not high, the space time yield corresponds to one order higher than the conventional industrial yield by the process of ethene hydration. Therefore, these kinds of catalytic routes have a high potential to replace the conventional route for ethanol synthesis.

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