ELSEVIER

Catalysis Today 44 (1998) 165–173

CATALYSIS TODAY

Hydrocarbon synthesis through CO_2 hydrogenation over $CuZnOZrO_2$/zeolite hybrid catalysts

Young-Kwon Park, Kwang-Cheon Park, Son-Ki Ihm*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1, Kusong-dong, Yusong-gu, Taejon 305-701, South Korea

Abstract

Direct syntheses of hydrocarbons from CO_2 hydrogenation were investigated over hybrid catalysts consisting of methanol synthesis catalyst ($CuZnOZrO_2$) and zeolites (MFI and SAPO). The yield of hydrocarbons was strongly depending upon the amount of zeolite's acid sites as measured by NH_3 TPD, while the product distributions were hardly affected by the change of acidity. The main product was ethane in the case of MFI hybrid catalyst and C_3 or C_4 hydrocarbon in the case of SAPO hybrid catalyst. This difference in product distribution was attributed to different mechanism of hydrocarbon formation. Investigation based on the ethene co-reaction suggested that the consecutive mechanism operated for HZSM-5 and the carbon pool mechanism for SAPO. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: CO; CO_2; Methanol; Acidity; SAPO-34; HZSM-5; Hybrid catalyst; Consecutive mechanism; Carbon pool mechanism

1. Introduction

Carbon dioxide is one of the most abundant carbon resources and its concentration in atmosphere has steadily increased. In order to improve climate conditions as well as to solve the carbon resource problem, it is desirable to develop techniques whereby carbon dioxide can be converted into valuable materials such as methanol or hydrocarbon. Although many investigations about hydrocarbon synthesis have been made on the carbon monoxide hydrogenation, little attention has been paid to the conversion of carbon dioxide into hydrocarbons due to the fact that carbon dioxide is a thermodynamically very stable compound. Iron-based catalysts [1–4], which were originally used in the Fischer–Tropsch (FT) synthesis reaction, have been applied to the hydrogenation of carbon dioxide for the synthesis of hydrocarbons, but they gave only a small yield of C_2^+ hydrocarbons with significant production of carbon monoxide and methane. More efficient catalysts should be developed for the production of C_2^+ hydrocarbons from carbon dioxide hydrogenation. Copper-based catalysts and zeolites were used for the methanol synthesis and methanol-to-hydrocarbon processes, respectively. Hydrocarbons can be synthesized by using these two processes in series [11]. However, direct synthesis of hydrocarbon from carbon dioxide is possible in a single reactor with hybrid catalysts consisting of methanol catalyst and zeolites [5–10].

---

*Corresponding author. Tel.: 00 82 42 869 3915; fax: 00 82 42 869 5955; e-mail: skihm@sorak.kaist.ac.kr

PII S0920-5861(98)00187-4

Fujimoto and Shikada [5] studied first the synthesis from carbon dioxide and hydrogen under pressurized conditions using hybrid catalysts composed of methanol catalyst (Cu–Zn) and high silica zeolite (DAY). It gave C_2–C_5 hydrocarbons with a selectivity higher than 90% but the yield of hydrocarbon is poor. Inui et al. [6] also reported that on a composite catalyst of Cu–Zn–Cr–Pd–Na combined with HZSM-5, a mixture of hydrogen and carbon dioxide is converted into methane and C_2–C_7 hydrocarbons with selectivity of 28.2% and 71.8%, respectively, at 10.1% conversion of carbon dioxide to hydrocarbons under severe conditions such as 50 atm and 320°C. Higher yield and selectivity for C_2^+ hydrocarbons were reported by Jeon et al. [7] and Fujiwara et al. [9] over hybrid catalysts; $CuZnOZrO_2$/SAPO-5 and CuZnCr oxide/HY zeolite, respectively. They proposed the following reaction pathway; methanol synthesis from carbon dioxide and hydrogen over copper catalyst, methanol/dimethyl ether to lower alkene over the zeolite, alkene oligomerization and isomerization over the zeolite, and hydrogenation to alkane over the copper catalyst.

Since the study of C_2^+ hydrocarbon synthesis over hybrid catalyst system has mainly been focused on the hydrogenation ability of methanol synthesis catalyst [8,9], the roles of zeolites in hybrid system should be elaborated in more detail in view of the nature of zeolite such as structure, acidity, etc. In addition, continued analysis on the hydrocarbon product distribution based on the reaction mechanism is highly desirable.

In the present work, two different types of zeolites such as MFI and SAPO were used to prepare the hybrid catalyst with $CuZnOZrO_2$ and their catalytic performances were compared in terms of zeolitic acidity.

2. Experimental

2.1. Catalyst preparation

$CuZnOZrO_2$ (60:30:10 wt%) precursors were prepared by co-precipitation. An aqueous solution of copper acetate, zinc nitrate and zirconium nitrate and an aqueous solution of sodium hydroxide (1.0 M) were mixed at 85°C and pH 7.0±0.3. The precipitate was aged for 1 h, separated by filtering, washed and dried. The precursors were calcined at 400°C for 12 h.

ZSM-5 was obtained through hydrothermal synthesis at 170°C for three days in a Teflon-lined 450 ml Parr bomb by following the procedures in a US patent [12]. After washing, the crystallized zeolites were calcined overnight at 550°C. The calcined NaZSM-5 sample was converted into the NH_4^+ form by ion exchange with 1 M NH_4Cl solution at room temperature and calcined at 550°C for 12 h to obtain HZSM-5. H–Ga–silicate and H–Fe–silicate were synthesized according to the procedure similar to that of HZSM-5 except that Al source was substituted with Ga nitrate and Fe nitrate. SAPO-5 was hydrothermally prepared from reactive gels containing a silicon source (Ludox HS-30), an aluminum source (pseudoboehmite), phosphoric acid, tripropylamine (TPA) and water [13]. This reaction mixture was heated in a Teflon-lined Parr bomb at 200°C for 48 h. After washing and drying, the resultant product was calcined at 550°C. SAPO-34 was synthesized according to the procedure similar to that of SAPO-5 except that the reaction time was 72 h at 200°C and the templating agent was morpholine.

Hybrid catalysts were prepared by physically mixing equal weight of a copper catalyst and a zeolite. They were pelletized and crushed to obtain sizes of 60–100 mesh.

2.2. Catalyst characterization

The surface areas were measured by the nitrogen BET method using a Micromeritics ASAP2000. The exposed copper surface area was measured by nitrous oxide titration following the procedure described by Chinchen et al. [14].

The structures of MFI type (HZSM-5, H–Ga–silicate, H–Fe–silicate) zeolites and SAPO (SAPO-5, SAPO-34) molecular sieves were confirmed by their powder X-ray diffraction (XRD) pattern using Cu K_α radiation.

Chemisorption measurements of carbon dioxide and hydrogen were performed at 25°C using a Micromeritics ASAP 2000. The samples used in the chemisorption studies were reduced for 12 h at 280°C in a flow of hydrogen, evacuated at the reduction temperature and cooled to the adsorption temperature.

Temperature programmed desorption (TPD) measurements were carried out to determine the acid properties of zeolites by using ammonia as an adsorbate. In a typical run, 0.3 g of a calcined sample was placed in a quartz tubular reactor and heated at 500°C under a helium flow of 45 ml/min for 1 h. The reactor was then cooled to 100°C and adsorption conducted at that temperature by exposing the sample to an ammonia flow of 23 ml/min for 1 h. Physically adsorbed ammonia was removed by purging the sample with a helium stream flowing at 45 ml/min for 30 min at 100°C.

2.3. Reaction studies

Carbon dioxide hydrogenation was performed in a continuous-flow fixed bed microreactor system made of stainless-steel tube. In a typical experiment, 1.0 g of hybrid catalyst was loaded into the reactor. Before reaction, the catalyst was reduced according to the following procedure; heating to 150°C at a rate of 5°C/min and heating to 280°C at a rate of 2°C/min in 5% H_2/Ar (60 cm^3/min) at atmospheric pressure. The hydrogen concentration was then increased stepwise in the sequence 10/20/40 to 100% (30 min per step). Subsequently the catalyst was held in a flow of pure hydrogen (60 cm^3/min) for 1 h at the same temperature. After the catalyst bed was reduced with hydrogen, the reactor was pressurized to 28 atm with helium, and CO_2 and H_2 were introduced into the reactor. CO_2 hydrogenation products were passed through a heated transfer line to a gas chromatograph (Hewlet–Packard 5890 series II) with TCD and FID detectors. Products were separated in a cross-linked methylsilicon capillary column (i.d.=0.2 mm, length=50 m) and Porapak Q column (o.d.=1/8 in., length=1.8 m).

3. Results and discussion

For the synthesis of hydrocarbons over a hybrid catalyst, CO hydrogenation has been investigated extensively so far [15,16] but CO_2 hydrogenation has not. Even if many works have been reported on the mechanism of CO_2 hydrogenation into methanol over copper-based catalysts [17,18], the study on hydrocarbon formation from CO_2 hydrogenation has chiefly been focused on the optimization of hydrogenation ability in the hybrid catalysts [8,9].

Table 1
CO/CO_2 hydrogenation over hybrid catalyst composed of CuZnO-ZrO_2 and HZSM-5

Reactant	CO	CO_2
Catalyst	$CuZnOZrO_2+$ HZSM-5	$CuZnOZrO_2+$ HZSM-5
Conversion (%)	48.3	38.4
Yield (%)		
HC	33.1	2.7
Oxygenates	0.2	1.0
HC Selectivity (wt%)		
C_1	14.7	18.1
C_2	12.4	76.4
C_3	29.0	4.5
C_4	38.5	0.8
C_{5+}	4.6	0.2
Aromatics	0.8	—

28 atm, 400°C, H_2/CO_2: 3, *W/F*: 20 g-cat h/mol.

Table 1 shows the product distribution from CO and CO_2 hydrogenations over the same hybrid catalyst with $CuZnOZrO_2$ and HZSM-5. In CO hydrogenation, the main products were C_4^+ hydrocarbons and aromatics. The initial intermediate, ethene, could grow into higher hydrocarbons including aromatics through the consecutive mechanism in CO hydrogenation [7,9,15,16]. In CO_2 hydrogenation, on the other hand, main hydrocarbon was ethane and no aromatics were formed. Ethene was hydrogenated mostly into ethane rather than propagated into higher hydrocarbons in CO_2 hydrogenation [19].

Hydrocarbon synthesis in CO/CO_2 hydrogenation can be described as follows:

1. CO hydrogenation

$$CO + 2H_2 \rightarrow CH_3OH$$

$$CH_3OH \rightarrow 1/n[CH_2]_n + H_2O$$

$$H_2O + CO \rightarrow CO_2 + H_2.$$

2. CO_2 hydrogenation

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

$$CO_2 + H_2 \rightarrow CO + H_2O$$

$$CH_3OH \rightarrow 1/n[CH_2]_n + H_2O$$

$$CH_3OH \rightarrow CO + 2H_2.$$

Table 2
Effect of water addition on the methanol conversion over hybrid catalyst composed of $CuZnOZrO_2$ and HZSM-5

	Catalyst				
	$CuZnOZrO_2$+HZSM-5				
Feed composition (MeOH: water)	1:0	1:1	1:3	1:5	1:9
Yields of $CO+CO_2$	17.2	38.5	57.9	80.1	94.8
Yields of HC	74.8	50.1	37.7	13.9	—
C_1	1.2	2.5	0.8	—	
C_2	15.2	28.5	40.0	54.0	
C_3	25.4	14.4	29.8	22.3	
C_4	10.4	18.4	11.1	20.0	
C_{5+}	12.2	23.5	14.8	3.7	
Aromatics	35.6	10.5	0.1		

1 atm, 400°C, *W/F*: 20 g-cat h/mol, conversion: 100%.

The presence of water in CO_2 hydrogenation can be the one of the main differences between the two hydrogenation reactions. In this regard, the reaction activity may be affected by the presence of water. In CO_2 hydrogenation, methanol conversion into hydrocarbon and methanol decomposition into CO are competing with each other [9]. The effect of water on the hydrocarbon distribution over hybrid catalyst could be demonstrated by changing the feed ratio in methanol conversion as shown in Table 2. With water increased, the methanol decomposition was enhanced and the formation of higher hydrocarbon was suppressed.

MFI type and SAPO type zeolites were used for methanol conversion reaction to compare the hydrocarbon distribution from methanol (Table 3). For an MFI type catalyst such as HZSM-5 or H–Ga–silicate, the main products were higher hydrocarbons such as aromatics and C_5^+ hydrocarbon. On the other hand, SAPO type catalyst such as SAPO-34 or SAPO-5, the main product was C_3 or C_4 hydrocarbon. Table 4 shows the results of CO_2 hydrogenation over hybrid catalysts. In view of main hydrocarbon from the methanol conversion in Table 3, it is expected that higher hydrocarbon can be obtained with HZSM-5 and C_3 hydrocarbon with SAPO-34. This is true in the case of SAPO hybrid system where C_3 hydrocarbons are major products. In the case of HZSM-5 hybrid system, however, the main hydrocarbon was ethane and neither higher hydrocarbons nor aromatics were formed.

For the same CO_2 conversion level, the yield of hydrocarbon over SAPO-34 (12.2%) was much higher than that (2.7%) of HZSM-5 hybrid system. NH_3 TPD of HZSM-5 and SAPO-34 as shown in Fig. 1 indicates that the amount of acid sites of SAPO-34 was much higher than that of HZSM-5 while the acid strengths characterized by high temperature peak were almost the same. Different acidic property must have affected the hydrocarbon yield or distribution.

Table 3
Methanol conversion to hydrocarbons over zeolites

	Catalysts			
	HZSM-5	H-Ga-Silicate	SAPO-34	SAPO-5
MeOH conversion (%)	100	100	100	100
C_1	0.3	1.5	0.3	1.1
$C_2^=$	6.6	4.2	30.5	2.5
C_2	—	—	0.6	—
$C_3^=$	8.9	23.8	38.3	18.3
C_3	5.3	—	10.6	—
$C_4^=$	6.5	12.0	13.3	36.4
C_4	10.8	—	1.7	8.6
C_5^+	20.6	18.5	4.6	33.1
Aromatics	41.0	40.0	—	
$C_2^= + C_3^= + C_4^=$	22.0	40.0	82.1	57.2

340°C, 1 atm, *W/F*: 60 g-cat h/mol.

Table 5 shows the CO_2 hydrogenation over HZSM-5 hybrid catalyst with varying SiO_2/Al_2O_3 ratio at similar conversion level. As the SiO_2/Al_2O_3 ratio decreased (or the amount of acid site increased), the hydrocarbon yield increased with the amount of acidity. However, the product distribution remains almost the same where ethane was the main hydrocarbon.

Table 4
CO_2 hydrogenation over hybrid catalysts

	Hybrid catalyst	
	$CuZnOZrO_2$+ HZSM-5	$CuZnOZrO_2$+ SAPO-34
CO_2 conversion (%)	38.4	33.9
Yield (%)		
HC	2.7	12.2
CO	34.7	20.5
MeOH	1.0	1.2
DME	0.0	0.0
HC selectivity (wt%)		
C_1	17.5	2.1
C_2	75.4	34.2
C_3	5.5	53.1
C_4	1.2	9.6
C_5	0.4	0.8
C_{6+}	0.0	0.2
C_2+yield (wt%)	2.2	11.9

28 atm, 400°C, H_2/CO_2: 3, *W/F*: 20 g-cat h/mol.

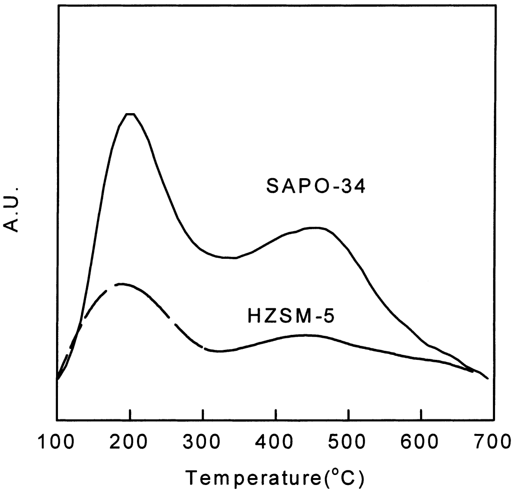


Fig. 1. NH_3 TPD of zeolites.

Table 5
CO_2 hydrogenation over hybrid catalysts composed of $CuZnOZrO_2$ and HZSM-5 with varying SiO_2/Al_2O_3 ratio

	SiO_2/Al_2O_3		
	400	100	70
CO_2 conversion (%)	38.9	38.8	38.4
Yield (wt%)			
HC	0.6	2.0	2.7
CO	37.4	35.7	34.7
MeOH	0.9	1.1	1.0
DME	—	—	—
HC Selectivity (wt%)			
C_1	24.8	21.7	18.1
C_2	70.9	72.4	76.4
C_3	4.2	5.9	4.5
C_4	—	—	0.8
C_{5+}	—	—	0.2
C_2+yield (wt%)	0.4	1.5	2.2

28 atm, 400°C, H_2/CO_2: 3, *W/F*: 20 g-cat h/mol.

Table 6
CO_2 hydrogenation over hybrid catalysts composed of $CuZnOZrO_2$ and different metallosilicates

	Catalyst		
	$CuZnOZrO_2$+ HZSM-5	$CuZnOZrO_2$+ H–Ga–silicate	$CuZnOZrO_2$+ H–Fe–silicate
CO_2 conversion (%)	38.4	38.9	38.5
Yield (wt%)			
HC	2.7	0.7	0.5
CO	34.7	37.3	37.0
MeOH	1.0	0.9	1.0
DME	—	—	—
HC selectivity (wt%)			
C_1	18.1	29.1	64.0
C_2	76.4	68.6	30.8
C_3	4.5	2.3	5.2
C_4	0.8	—	—
C_{5+}	0.2	—	—
C_2+yield (wt%)	2.2	0.5	0.2

28 atm, 400°C, H_2/CO_2: 3, *W/F*: 20 g-cat h/mol.

This implies that the product distribution is hardly affected by the amount of acidity in the case of hybrid catalyst with HZSM-5. However it seems that higher hydrocarbons such as C_4^+ could be obtained over a catalyst with sufficient acid sites as in the case of SiO_2/Al_2O_3=70.

Table 6 shows the results of CO_2 hydrogenation over various MFI type metallosilcate hybrid system. NH_3 TPD of Fig. 2 shows that HZSM-5 which is an aluminosilicate contains the largest amount of acid sites and the highest acid strength, and that H–Ga– and H–Fe–silicate follow the order in terms of the nature of acidity. For the same level of conversion, the hydrocarbon yield increased with the amount of acidity, not with the acid strength represented by high

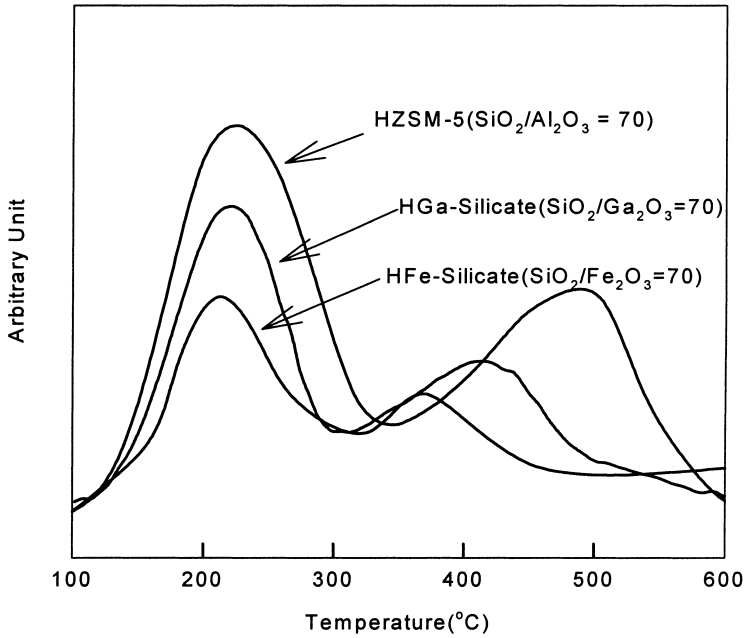


Fig. 2. NH_3 TPD of metallosilicates.

temperature peak. Also the product distribution was hardly affected by different metal and ethane was the main hydrocarbon. However in the case of H–Fe–silicate, methane instead of ethane was the main product. This is believed to be due to the Fischer–Tropsch activity of iron. Since Inui et al. [6] and Jeon et al. [7] proposed that higher hydrocarbon yield and selectivity could be obtained over a zeolite catalyst with medium acid strength, the catalytic activity of HZSM-5 with higher acid strength should have been lower than that of H–Ga–silicate or H–Fe–silicate with lower acid strength. Experimental results are somewhat unexpected in view of acid strength, and it could be suggested that hydrocarbon yield mainly depended upon the amount of acidity.

Table 7 shows the results of CO_2 hydrogenation over hybrid catalyst with Zn ion added zeolites. Compared with HZSM-5, the Zn impregnated/HZSM-5 did not change the hydrocarbon yield, while the ion exchanged Zn/HZSM-5 reduced the hydrocarbon yield. This seems to be due to the decrease in the amount of Brnøsted acid sites by ion exchanged zinc. In this case, the product distribution remained almost the same. This result shows again that hydrocarbon yield depended upon the amount of acid sites. Similar trends were observed in the case of SAPO hybrid system as shown in Table 8. It can be concluded that hydrocarbon distribution was hardly affected by varying the acidity.

On the other hand, crystal size or particle size may affect the product distribution due to their intra- or intercrystalline diffusion limitations. It was reported that the higher hydrocarbon was obtained with small crystal size, small particle size, or larger pore size in CO hydrogenation [16]. We observed, however, that the hydrocarbon yield and distribution was almost independent of crystal size or particle size in CO_2 hydrogenation. Even if the pore size of SAPO-34 (0.43 nm) is smaller than that of HZSM-5 (0.56 nm) or SAPO-5 (0.8 nm), the yield and selectivity to higher hydrocarbon of hybrid catalyst with SAPO-34 was higher. It is again suggested that hydrocarbon yield mainly depended upon the amount of acid sites.

If we roughly describe the CO_2 hydrogenation by Fig. 3, the $CuZnOZrO_2$ involved with step 1 and step 2 could be modified through solid–solid interaction with different zeolites during preparation of hybrid catalysts. These modifications may result in different selectivity in step 1 and step 2. If the hybrid catalyst with HZSM-5 has a poor ability of the methanol

Table 7
CO_2 hydrogenation over hybrid catalysts composed of $CuZnOZrO_2$ and HZSM-5 with Zn ion addition

	Catalyst		
	$CuZnOZrO_2$+HZSM-5	$CuZnOZrO_2$+Zn (impregnated)/HZSM-5	$CuZnOZrO_2$+Zn (ion exchanged)/HZSM-5
CO_2 conversion (%)	38.4	37.8	38.9
Yield (wt%)			
HC	2.7	2.8	1.6
CO	34.7	33.8	36.4
MeOH	1.0	1.2	0.9
DME	—	—	—
HC selectivity (wt%)			
C_1	18.1	19.2	19.5
C_2	76.4	75.2	76.2
C_3	4.5	4.6	4.3
C_4	0.8	0.9	—
C_{5+}	0.2	0.1	—
C_2+yield (wt%)	2.2	2.3	1.3

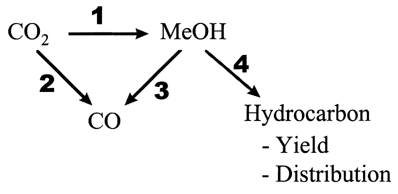
28 atm, 400°C, H_2/CO_2: 3, *W*/*F*: 20 g-cat h/mol.

Table 8
CO_2 hydrogenation over hybrid catalysts composed of $CuZnOZrO_2$ and SAPO (effect of acidity)

	Catalyst			
	$Cu/ZnO/ZrO_2$+ SAPO-34H	$Cu/ZnO/ZrO_2$+ SAPO-34L	$Cu/ZnO/ZrO_2$+ SAPO-5H	$Cu/ZnO/ZrO_2$+ SAPO-5L
Reaction temparature	400°C	400°C	350°C	350°C
CO_2 conversion (%)	33.9	38.3	31.8	29.9
Yield (wt%)				
HC	12.2	2.9	9.1	2.7
CO	20.5	33.3	21.0	26.7
MeOH	0.5	2.0	1.6	0.3
DME	0.0	0.1	0.1	0.2
HC selectivity (wt%)				
C_1	2.1	5.4	4.0	5.6
C_2	34.2	35.1	12.7	10.1
C_3	53.1	50.8	33.0	32.9
C_4	9.6	8.1	43.3	41.0
C_5	0.8	0.5	5.0	6.8
C_{6+}	0.2	0.1	2.0	3.6
C_2+yield (wt%)	11.9	2.7	8.8	2.6

28 atm, H_2/CO_2: 3, *W*/*F*: 20 g-cat h/mol.
H: Higher amounts of acid sites, L: Lower amounts of acid sites.

formation, it may result in lower hydrocarbon yield and higher CO yield. This kind of possibility has been checked as in Table 9. For two different hybrid catalysts with $CuZnOZrO_2$, CO_2 uptake and H_2 uptake were measured for each hybrid catalyst. The amount of chemisorption was almost the same for each catalyst, and also the catalytic activity of each of CO_2 hydrogenation into oxygenates (step 1) and reverse water gas shift reaction (step 2) was almost the same for each catalyst. Accordingly, it can be said that $CuZnOZrO_2$ does not seem to be modified significantly during preparation of hybrid catalyst. Or even if



1. $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$
2. $CO_2 + H_2 \rightarrow CO + H_2O$
3. $CH_3OH \rightarrow$ Hydrocarbons + H_2O
4. $CH_3OH \rightarrow CO + 2H_2$

Fig. 3. Schematic reaction path to hydrocarbons from CO_2.

Table 9
Checking the possibility of catalyst modification

	Hybrid catalyst	
	$Cu/ZnO/ZrO_2$+ HZSM-5	$Cu/ZnO/ZrO_2$+ SAPO-34
Chemisorption at 25°C		
CO_2 uptake (μ mol/g)	46.7	42.3
H_2 uptake(μ mol/g)	7.0	6.1
$^a CO_2$ *hydrogenation at* 28 atm, 250°C		
Oxygenates (MeOH+DME) yield (wt%)	9.9	9.8
^{a}*Reverse water gas shift reaction at* 1 atm, 400°C		
CO yield (wt%)	23.7	23.9

$^a H_2/CO_2$: 3, *W/F*: 20 g-cat h/mol.

modified, their effect on the catalytic activity of methanol synthesis catalyst does not seem to be significant. Since there is no difference between the two hybrid systems for step 1 and step 2, different hydrocarbon yield and selectivity should come from different path of methanol conversion. It is expected that the step 3 of methanol decomposition and the step 4 of hydrocarbon formation are competing with each other [9]. The lower hydrocarbon yield of hybrid catalyst with HZSM-5 must be due to its higher ability of methanol decomposition and lower ability of hydrocarbon formation. It was already demonstrated that the hydrocarbon yield strongly depended upon the amount of acid sites and also that the product distribution was hardly affected by acidity variation.

Table 10 shows the effect of ethene co-reaction on the changes of product distribution. In the case of HZSM-5 without ethene, ethane was obtained as a main product because water might prevent ethene from adsorbing on zeolite surface. However, the ethene addition has changed the hydrocarbon distribution dramatically. The selectivity to higher hydrocarbons increased tremendously and even aromatics were formed. If ethene is added in the feed, ethene would easily adsorb on zeolite surface and propagate into higher hydrocarbons. Ethene should have participated in the consecutive growth of olefinic intermediates into higher hydrocarbon. In the case of SAPO-34, however, most of the co-fed ethene were rejected without participating in the chain growth. This result implies that the mechanism of hydrocarbon formation may be different between HZSM-5 and SAPO-34. Considering the methanol conversion reaction, the reaction routes for the formation of olefinic product can be explained by two different mechanisms as shown in Fig. 4. The first one is a consecutive mechanism where ethene or olefinic intermediates grow consecutively into higher olefins. The second was a carbon pool mechanism proposed by Dahl and Kolboe [20] for SAPO-34 catalyst. According to their isotope labeling study, a various hydrocarbon pool such as $(CH_2)_n$ exists on zeolite surface and these

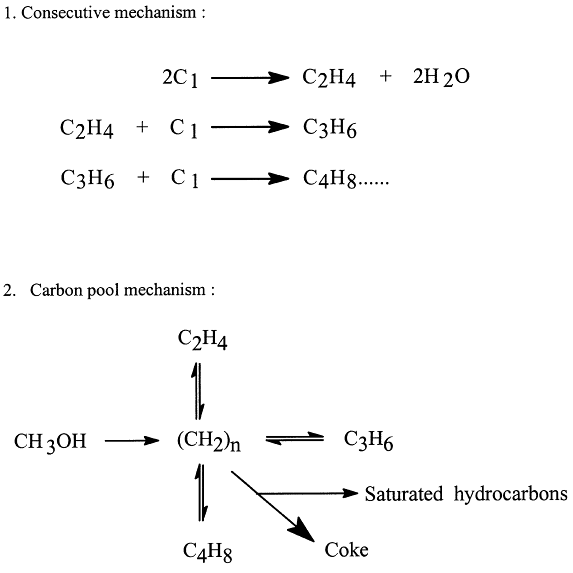


Fig. 4. Reaction mechanisms of methanol conversion.

Table 10
CO_2 hydrogenation over hybrid catalysts with ethene co-fed

	Catalyst					
	$Cu/ZnO/ZrO_2$ + HZSM-5(70) Selectivity (wt%)	$Cu/ZnO/ZrO_2$ +HZSM-5(70)[a] Selectivity (wt%)	R	$Cu/ZnO/ZrO_2$ + SAPO-34H Selectivity (wt%)	$Cu/ZnO/ZrO_2$ +SAPO-34H[a] Selectivity (wt%)	R
Hydrocarbon						
C_1	18.1	1.97	5.0	2.1	0.1	1.2
C_2	76.4	24.8	14.6	34.2	91.1	104.1
C_3	4.5	25.6	355.3	53.1	3.4	2.5
C_4+	1.0	46	503.8	10.6	5.4	13.8
Aromatics	0.0	1.6	∞	—	—	—

28 atm, 400°C, H_2/CO_2: 3/1, [a]H_2/CO_2/ethene: 3/1/0.3, *W/F*: 20 g-cat h/mol.
R: Hydrocarbon yield with ethene/hydrocarbon yield without ethene.

hydrocarbon pools may result in a corresponding olefin distribution. If some olefin such as ethene was added with methanol, most of the olefins were rejected by hydrocarbon pool. It is believed that the consecutive mechanism may operate for HZSM-5, and the carbon pool mechanism seems to operate for SAPO-34.

4. Summary

For the CO_2 hydrogenation over hybrid catalysts:

- The hydrocarbon distribution depends not only on the hydrogenating ability of methanol synthesis catalyst but also on the nature of zeolites.
- Methanol decomposition to CO and methanol conversion to hydrocarbon are competing with each other and their yields strongly depend upon the acidity of zeolites. The product distribution is hardly affected by the acidity variation.
- The difference in product distribution between CO and CO_2 hydrogenation may be due to the presence of water.
- HZSM-5 ($CuZnOZrO_2$) and SAPO-34 ($CuZnO\text{-}ZrO_2$) resulted in a different product distribution, which may be due to different mechanisms of hydrocarbon formation (consecutive vs. carbon pool).

Acknowledgements

This work was partially supported by the Clean Energy Program by R & D Management Center for Energy and Resources of MTI (Korea) and KAIST.

References

[1] D.J. Dwyer, G.A. Somorjai, J. Catal. 52 (1978) 291.
[2] G.D. Weatherbee, C.H. Bartholomew, J. Catal. 87 (1984) 352.
[3] M.D. Lee, J.F. Lee, C.S. Chang, T.Y. Dong, Appl. Catal. 72 (1991) 267.
[4] M.D. Lee, J.F. Lee, C.S. Chang, Bull. Chem. Soc. Jpn. 62 (1989) 2756.
[5] K. Fujimoto, T. Shikada, Appl. Catal. 31 (1987) 13.
[6] T. Inui, K. Kitagawa, T. Takeguchi, T. Hagiwara, Y. Makino, Appl. Catal. A 94 (1993) 31.
[7] J.K. Jeon, K.E. Jeong, Y.K. Park, S.K. Ihm, Appl. Catal. A 124 (1995) 91.
[8] M. Fujiwara, H. Ando, M. Tanaka, Y. Souma, Appl. Catal. A 130 (1995) 105.
[9] M. Fujiwara, R. Kieffer, H. Ando, Y. Souma, Appl. Catal. A 121 (1995) 113.
[10] K. Fujimoto, T. Shikada, Appl. Catal. 31 (1987) 13.
[11] T. Inui, T. Tageguchi, Catal. Today 10 (1991) 95.
[12] R.J. Argauer, G.R. Landolt, US Patent 3 702 886 (1972).
[13] B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajek, T.R. Cannan, E.M. Flanigen, US Patent 4 440 871 (1984).
[14] G.C. Chinchen, C.M. Hay, H.D. Vandervell, K.C. Waugh, J. Catal. 103 (1987) 79.
[15] C.D. Chang, W.H. Lang, A.J. Silvestri, J. Catal. 56 (1979) 268.
[16] K. Fujimoto, H. Saima, H. Tominaga, Ind. Eng. Chem. Res. 27 (1988) 920.
[17] S.K. Ihm, Y.K. Park, J.K. Jeon, K.C. Park, D.K. Lee, Stud. Surf. Sci. Catal. 114 (1998) 505.
[18] O.S. Joo, K.D. Jung, S.H. Han, S.J. Uhm, D.K. Lee, S.K. Ihm, Appl. Catal. A 135 (1996) 273.
[19] V. Bolis, J.C. Vedrine, J.P. Van de Berg, J.P. Wolthuizen, E.G. Derouane, J. Chem. Soc., Faraday I 76 (1980) 1606.
[20] I.M. Dahl, S. Kolboe, J. Catal. 149 (1994) 458.