Light alkenes from syngas via dimethyl ether

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Abstract

A new route, named the SDTO method, for the synthesis of light alkenes from syngas is proposed. The method consists of the conversion of syngas to dimethyl ether, followed by the conversion of dimethyl ether to light alkenes. Catalysts for the two reactions have been developed. For the first reaction, the catalyst was synthesized by combining a methanol synthesis catalyst with γ-Al_2O_3 or zeolites, which possess both metallic and acidic functions. The conversion of the reaction is much higher than that of the methanol synthesis reaction. Suitable reaction conditions are: 210–280°C; $P > 3.0$ MPa and gas hourly space velocity (GHSV) < 1500 h^{-1}. The catalyst for the second reaction was a modified SAPO-34 molecular sieve. The effects of the modification on the catalyst and the factors influencing the reaction have been investigated. A fluid bed reactor is considered to be a suitable reactor type for these catalysts. Under the reaction conditions of 550°C and weight hourly space velocity (WHSV MeOH) > 6 h^{-1} or line velocity of MeOH > 15, the selectivity for ethylene and total light alkenes are ca. 60 and ca. 90, respectively (conversion = 100%). The stability of the modified SAPO-34 catalyst has been tested under severe conditions. The results from the serial connection of the two conversion steps without any separation show that the yield of $C_2^=$–$C_4^=$ alkenes could be > 100 g/(m^3 syngas).

Keywords: Alkenes; Dimethyl ether; Light alkenes; Molecular sieves; SAPO-34; Synthesis gas

1. Introduction

Synthesizing lower alkenes from coal or natural gas via syngas is one of the most important non-oil routes for ethylene and propene production. Two methods were suggested for the synthesis of light alkenes from syngas, one is the direct method by which syngas is directly converted to light alkenes [1], the other is the indirect method via methanol or the MTO method [2], that is to convert syngas to methanol

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and then to convert methanol to light alkenes. Many significant results have been obtained since the 1970's on these two methods [3–8]. In accordance with the facts that the direct method is thermodynamically unfavorable and the products may be restricted by the Schulz–Flory rule, and the methanol has to be converted to dimethyl ether prior to the synthesis of light alkenes during the indirect conversion process, we propose a new route, named the SDTO (Synthesis gas via Dimethyl ether To Olefins) method, to convert syngas to dimethyl ether and then to convert dimethyl ether to light alkenes. The new route has apparent advantages in enhancing carbon monoxide conversion and simplifying the process.

2. Experimental

The catalyst for conversion of synthesis gas to dimethyl ether was prepared by combining a methanol synthesis catalyst (Cu–Zn–Al, commercial product C301, Shanghai) with an acidic component such as γ-Al$_2$O$_3$ or zeolites. The catalysts were pressed into tablets and crushed to 15–35 mesh before reaction. The reaction was carried out on a 8 mm diameter × 300 mm long stainless steel, fixed-bed, continuous flow reactor. On-line thermal conductivity detector (TCD) chromatography with Porapak-Qs and carbon molecular sieve type 601 (Shanghai) columns were used to analyze the reaction products. Before reaction, the catalyst was reduced in 2% H$_2$ + 98% N$_2$ (volume) gas flow at elevated temperature from 20°C to 280°C with a rate of 1°C/min, and the temperature was then kept at 280°C for 100 min. The selectivity for dimethyl ether (DME) and methane are calculated from following formulae, respectively:

$$S_{DME}(\text{mol-\%}) = \frac{\text{moles of DME}}{\text{moles of DME and methanol}} \times 100$$

$$S_{CH_4}(\text{mol-\%}) = \frac{\text{moles of CH}_4 \text{ in products}}{\text{total moles of organic products}} \times 100$$

Silicoaluminophosphate SAPO-34 and modified SAPO-34 were used as catalysts for the conversion of dimethyl ether to lower alkenes. The SAPO-34 molecular sieve was synthesized using pseudoboehmite, phosphoric acid and silica sol as source of aluminum, phosphorus and silicon, respectively. Triethylammonium was used as templating agent. The synthesis procedure was described elsewhere [9,10].

The catalytic reaction was carried out both on a 12 mm diameter × 285 mm long quartz fixed bed reactor and on a 20 mm diameter × 500 mm long fluid bed reactor under normal pressure. For the fixed bed reaction, the catalyst was 20–40 mesh and 1.28 g. The reactant methanol was fed either by the nitrogen carrier gas flow through a saturator or by a pump. Before reaction, the catalyst was activated at 500°C in a nitrogen gas flow for 1 h. The catalyst for the fluid-bed reaction was prepared by the spraying desiccation method with an inert binder. The average

Table 1
Reaction results of the bifunctional catalysts[a]

Acidic component	Temp. (°C)	CO conv. (mol-%)	S_{DME} (mol-%)	S_{CH_4} (mol-%)
γ-Al$_2$O$_3$	260	85.27	91.59	2.89
M-γ-Al$_2$O$_3$[b]	260	87.94	93.50	2.24
HY Zeolite	265	81.65	91.63	3.12
M-HY[b]	265	69.30	92.12	1.89
SAPO-5	265	58.81	59.17	1.76
HMd Zeolite	260	92.28	94.00	5.24
M–HMd[b]	260	92.17	94.96	2.12
H-ZSM-5	240	90.33	91.40	3.09
M-ZSM-5[b]	238	92.37	92.57	1.43

[a] Metallic component: Cu–Zn–Al, metal:acid = 2:1 (weight); P = 3.0 MPa; WHSV = 1000 h^{-1}; H$_2$:CO = 2:1.
[b] Modified γ-Al$_2$O$_3$, HY, HMd or ZSM-5.

particle size of the spherical catalyst was about 50 μm. Prior to the fluid bed reactor, the liquid methanol was pumped to a fixed bed reactor to be preheated (at 100°C) or dehydrated by a γ-Al$_2$O$_3$ catalyst (at 275°C). Products of both fixed bed and fluid bed reactions were analyzed on line by using a Porapak-Qs column with TCD and FID detector. The selectivity for light alkenes was defined as 'the weight percentage in organic products'.

The acidity of the catalyst was measured by temperature-programmed desorption (TPD) of ammonia with helium carrier gas (30 ml/min) and a TCD conductor. The rate of temperature rise was 15°C/min.

3. Results and discussion

3.1. Conversion of syngas to dimethyl ether

The conversion of methanol on conventional metallic catalysts is not very high because the reaction is thermodynamically restricted. When the catalyst possesses both metal and acid properties, there exist three main reaction paths:

$$CO + 2H_2 \rightarrow CH_3OH \tag{1}$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{2}$$

$$H_2O + CO \rightarrow H_2 + CO_2 \tag{3}$$

The methanol formed in reaction (1) can convert to dimethyl ether immediately through dehydration reaction (2) on acidic sites. Therefore, a higher conversion of syngas could be obtained.

The reaction results of the metal–acid bifunctional catalysts, which were made from Cu–Zn–Al methanol synthesis catalyst in which various dehydration components were incorporated, are listed in Table 1. The dehydration ability of the acid
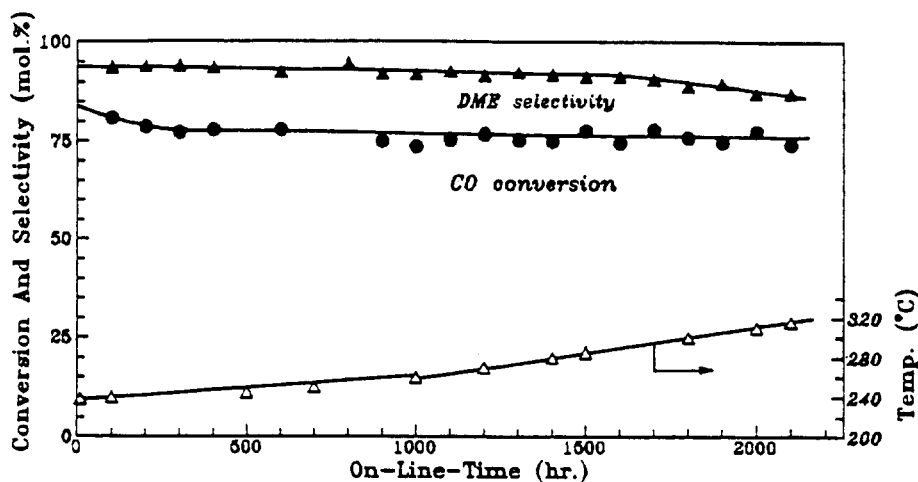
Fig. 1. Long-term test of the catalyst for the conversion of syngas to dimethyl ether (catalyst: Cu–Zn–Al + M-HMd; reaction conditions: GHSV = 1000 h^{-1}, P = 3.5 MPa).

components was found to have effects on the catalytic behavior of the syngas conversion reaction. A high conversion could be obtained when these components are strongly acidic. However, too high an acidic strength would cause an increase of methane in the product. An example is the case of the HMd zeolite in Table 1, where the selectivity for methane is up to 5.24%. To decrease the acidity of the HMd zeolite (i.e. MHMd) would result in the decrease of the methane content. The selectivity for DME was also found to be related to the manner of coordination between the metal and acid sites, apart from the acid properties of the acid components (in the case of SAPO-5 in Table 1). The catalysts made up of γ-Al$_2$O$_3$, modified HMd or modified ZSM-5 zeolite exhibit a higher carbon monoxide conversion and DME selectivity.

The process variables of the reaction have been investigated on M-ZSM-5 and MHMd modified catalysts. The results show that an increase of temperature and pressure promotes the conversion of synthesis gas to DME. Suitable reaction conditions are 210–280°C; P > 3.0 MPa and GHSV < 1500 h^{-1}.

A long-term test of the catalyst was carried out with CO + 2H$_2$ gas under the following reaction conditions; GHSV = 1000 h^{-1} and P = 3.5 MPa (Fig. 1). The temperature was non-periodically raised to maintain the carbon monoxide conversion above 75%. Although some accidents happened during the test, as for example a frequent overshoot of the reaction temperature, the selectivity for dimethyl ether still remained at 90% over a period of 2000 h and the selectivity for the by-product methane was less than 3%. The newly developed catalyst has been tested in a pilot plant up to 1000 h. The results are as follows: temperature maintained at 240°C, CO conversion > 75%, S$_{DME}$ > 96%.

3.2. Conversion of DME to light alkenes

The conversion of DME and other small oxygenated compounds in the products of the previous reaction, such as methanol, to light alkenes is the key step of the

Table 2
Reaction results of modified SAPO-34 catalysts for methanol conversion[a]

Catalyst	SAPO-34	SPNi04	SPBa05	SPCa01	SPMg03	SP05-58
Conversion (wt.-%)	100	100	79.99	100	100	100
Hydrocarbon (wt.-%)[b]						
CH_4	8.19	3.81	2.87	2.42	2.68	1.70
C_2H_4	38.66	45.74	51.15	49.03	40.05	57.57
C_2H_6	1.18	1.16	1.50	1.37	2.18	0.76
C_3H_6	33.70	35.00	32.68	34.15	36.11	37.14
C_3H_8	4.52	3.36	2.60	3.66	6.56	1.91
C_4H_8	12.15	9.07	6.12	7.38	9.78	0.93
C_4H_{10}	1.46	2.27	3.08	2.12	2.65	0
C_{5+}	0	0	0	0	○0	0
$C_2^=-C_3^=$	72.36	80.74	83.83	83.18	76.16	94.71
$C_2^=-C_4^=$	84.51	85.68	89.95	90.56	85.94	95.64

[a] Fixed bed, reaction temperature: 450°C, WHSV (MeOH) = 2.0 h^{-1}, partial pressure of MeOH = 0.35 (balance N_2), reaction time = 30 min.
[b] $CO + CO_2$ less than 1% in total products.

SDTO method. Considerable research has been done on this subject. Pentasil-type zeolites and some narrow-pore zeolites such as chabazite and ZSM-34 have been found to be effective for this purpose [11–14]. Recently, silicoaluminophosphate SAPO-34 and modified SAPO-34 were found to exhibit good catalytic performance for methanol conversion to light alkenes [6,8,15]. In this work, SAPO-34 and modified SAPO-34 molecular sieve synthesized with triethylammonium as templating agent were used as the catalysts for the conversion. Because pure dimethyl ether is difficult to obtain in our laboratory, methanol was used as reactant in part of this study.

The modification effects on the catalytic behavior and acidic properties of the SAPO-34 molecular sieve by divalent metal ions are shown in Table 2 and Fig. 2, respectively. The amounts of metal ions introduced into the molecular sieve were kept at same atomic ratio. It is clear that the addition of metal ions results in a decrease of the acidity of the SAPO-34 catalyst. The activity of the modified SAPO-34 catalysts is lower than that of HSAPO-34. However, the selectivity for ethylene and $C_2^=-C_4^=$ can be enhanced. The formation of methane, which is commonly considered to be a product of strong acid sites, is also reduced. A moderate strength of the acid sites was considered sufficient for formation of ethylene. One example is SP05-58, which was modified so as to obtain a medium acidity character, and which exhibits a good light alkene selectivity.

The effects of diluting the feed with water were also investigated. The relevant results for the SAPO-34 catalyst for methanol conversion are listed in Table 3. As reported in the literature [16–19], the increased concentration of water due to dilution may result in an increase in light alkene selectivity and a reduction of the rate of coke formation. However, for low water content (<30%), the increase of ethylene selectivity is not obvious. The effective water content is >50%. The cause
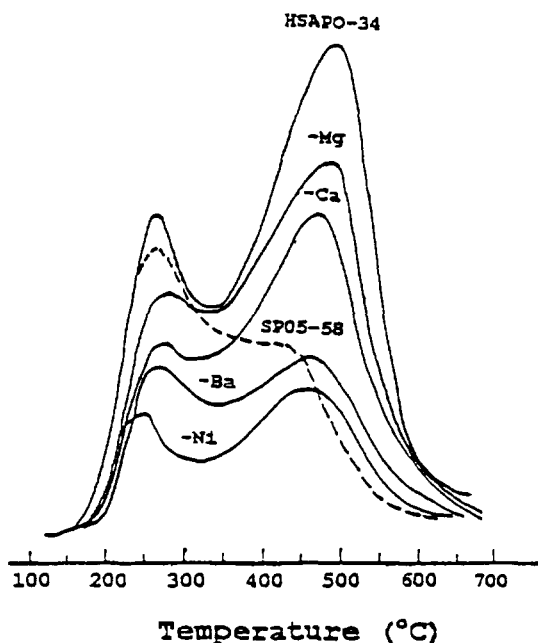
HSAPO-34

Fig. 2. NH₃-TPD profiles of modified SAPO-34 catalysts.

of the water effect may be that adsorbed water molecules can promote the desorption of the initially formed alkene and then inhibit the formation of larger molecules.

The results of on-stream testing in a fixed bed reactor shows that the activity of the SAPO-34 catalyst decreases within about 2 h under the reaction conditions of 450°C, WHSV(MeOH) = 2.0 h⁻¹. However the activity could be completely restored by heating the catalyst in a stream of air at 500–650°C. Coking is the main reason of the deactivation. Because repeated regeneration is necessary and large amounts of heat could be produced during the reaction and regeneration, a fluid bed reactor was considered suitable for this type of catalyst.

Table 3
Effect of water dilution on the conversion of methanol[a]

	MeOH	70% MeOH[b]	50% MeOH[b]	30% MeOH[b]
Methanol conv. (wt.-%)	100	100	99.68	97.88
Alkene selectivity (wt.-%)				
C_2H_4	42.00	43.17	52.69	56.10
C_3H_6	35.53	37.55	39.00	33.21
C_4H_8	9.40	8.60	3.15	6.09
$C_2^=-C_3^=$	77.53	80.72	91.69	89.31
$C_2^=-C_4^=$	86.93	88.60	94.84	95.40
Life time (min)	ca. 60	ca. 75	ca. 90	ca. 90

[a] Catalyst: SAPO-34; 450°C, WHSV (MeOH) = 2.0 h⁻¹ (no N₂ dilution), 60 min.
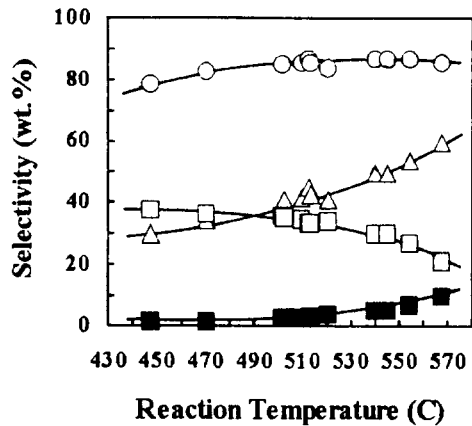[b] By weight.

Fig. 3. Influence of reaction temperature on the DME to alkene reaction (catalyst: modified SAPO-34 + binder, 10 g; WHSV(MeOH) = 5 h^{-1}, line velocity = 11.78 cm/s; conversion = 100%; regeneration 600°C, 30 min, in air flow) (○) $C_2^=$–$C_4^=$, (△) C_2H_4, (□) C_3H_6, (■) CH_4.

Variables influencing the reaction have been investigated using the fluid bed reactor. Temperature is one of the major factors affecting light alkene selectivity. A high reaction temperature could enhance the ethylene selectivity and promote the formation of the by-product methane (Fig. 3). A suitable temperature for the fluid bed reaction is 500–560°C, which is about 50°C higher than in the fixed bed reactor. Another major factor is the line velocity of the reactant. The influence of the line velocity on the catalytic reaction is shown in Fig. 4. With the increase of the line velocity or space velocity of methanol, the selectivity for ethylene increases notably, the total light alkene selectivity remains almost constant after some initial
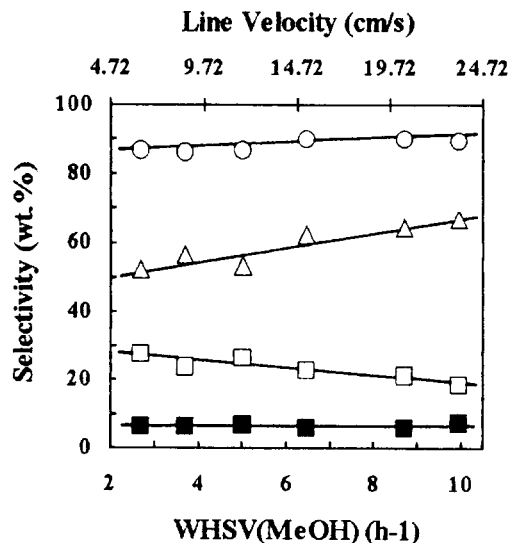

Fig. 4. Variation of selectivity with space velocity or line velocity in the fluid bed reactor (catalyst: modified SAPO-34 + binder, 10 g; reaction: 550°C, 10 min; conversion = 100%; regeneration: 600°C, 30 min, in air flow) (○) $C_2^=$–$C_4^=$, (△) C_2H_4, (□) C_3H_6, (■) CH_4.

Table 4
Reaction results in fluid bed reactor[a]

| Regeneration cycles | 0 | 10 | 30 | 60 | 80 | 100 | |
Reaction temp. (°C)	500	530	530	530	530	530	450[b]
Alkene selectivity (%)							
$C_2^=$	35.66	49.49	52.55	52.53	52.33	50.69	42.82
$C_3^=$	39.76	34.09	34.41	31.46	32.08	35.88	40.10
$C_2^=-C_4^=$	87.16	92.19	94.81	92.51	92.66	93.46	86.75

[a] Catalyst: modified SAPO-34, WHSV $(Me_2O) = 2.0 \ h^{-1}$ (no N_2 dilution), conversion = 100%.
[b] In fixed bed reactor.

increase. The selectivity for the by-product methane seems not to be influenced by line velocity.

The regeneration test of the modified SAPO-34 catalyst was carried out in the fluid bed reactor. The results of the investigation show that the temperature of the decoking reaction in air flow could be in the range of 550 to 650°C. If the temperature is 550°C, the regeneration is finished in 30 min, while when the temperature is kept above 600°C, the coke cloud be removed within 10 min. The results multiple regenerations on the catalytic behavior are listed in Table 4. The regeneration was carried out in the fluid bed reactor at 600°C and in air flow for 30 min. After regeneration for about 10 times, the selectivity for light alkenes tended to remain constant. In the steady state of the catalytic performance, the selectivity for ethylene was > 50%, $C_2^=-C_3^= > 80\%$ and $C_2^=-C_4^= > 90\%$.

Because large amounts of water exist in the products and the catalyst has to be regenerated frequently at high temperature (> 550°C), a high catalyst stability is needed. Severe conditions were selected under which the stability of the catalyst was tested. The results are shown in Figs. 5 and 6. The activity and selectivity of the catalyst are almost the same as those of the fresh catalysts after long time
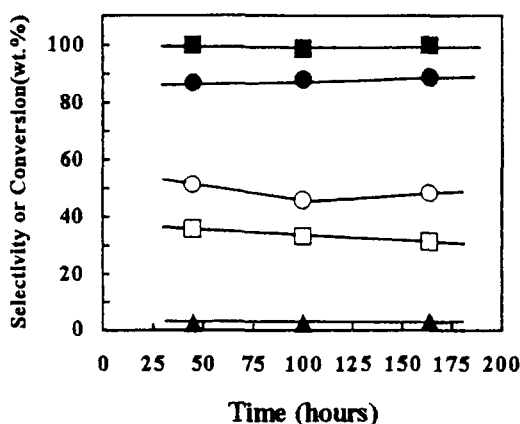

Fig. 5. Variation of conversion and selectivity with calcination time at 800°C of modified SAPO-34 catalyst (fixed bed reaction, 450°C, WHSV (MeOH) = 1.0 h^{-1}, reaction time = 60 min) (■) conversion, (●) $C_2^=-C_4^=$, (○) C_2H_4, (□) C_3H_6, (▲) CH_4.
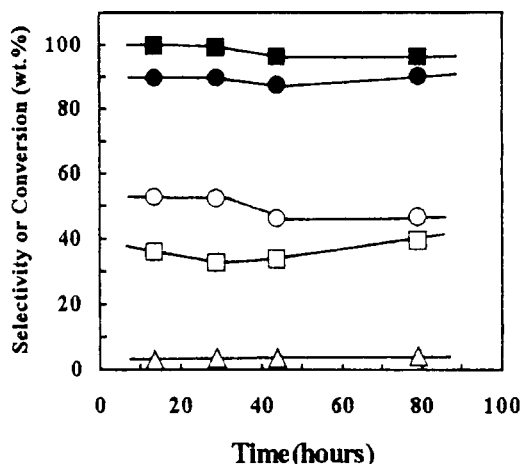
Fig. 6. Variation of conversion and selectivity with the time of steam treatment at 800°C of modified SAPO-34 catalyst (reaction condition as in Fig. 3) (■) conversion, (●) $C_2^=$–$C_4^=$, (○) C_2H_4, (□) C_3H_6, (△) CH_4.

treatment in steam or in air flow at 800°C. The X-ray diffraction results show only little decrease of the crystallinity of the treated samples, as compared with that of the fresh catalysts. It could be concluded that the developed SAPO-34 molecular sieve catalyst possesses not only a high light alkene selectivity but a high stability as well.

3.3. Serial connection of the two conversion steps

The test to connect the two reactions was carried out in a fixed bed reactor. The products of the conversion of syngas were used as the reactant of the second reaction without any separation. The results of the connected reactions are listed in Table 5. The selectivity for light alkenes of the second reaction is lower than that of the methanol conversion reaction. However, the yield of $C_2^=$–$C_4^=$ alkenes could still reach 100 g/(m³ syngas) per pass. The lack of water in the reaction system and the existence of carbon dioxide may be the main reasons of the decrease of light alkene selectivity. When the feed of the second reaction was diluted with water, the yield of light alkenes could be enhanced up to 110 g/(m³ syngas). A production of 110 g/(m³ syngas) of $C_2^=$–$C_4^=$ light alkenes is equivalent to a carbon utilization from synthesis gas (H_2:CO = 2:1) of about 52.8%, which, on a per pass basis, is much higher than that of the direct method and which is also much higher than that of the method via methanol.

4. Conclusion

A new route, named the SDTO method, for the synthesis of light alkenes from syngas is proposed. The method consists of the conversion of syngas to dimethyl

Table 5
Results of the two connected reactions

	The first reaction[a]	The second reaction	
Catalyst	Cu–Zn–Al + M–HMd	Modified SAPO-34	
React. temp. (°C)	265	450	
GHSV (h^{-1})	1000	2000	
Pressure (MPa)	4.0	normal pressure	
CO Conv. (%)	90.35		
DME + MeOH selectivity (%)	99.26		
DME + MeOH conv. (%)		100[b]	100[c]
Light alkenes (wt.-%)			
$C_2^=$		40.19	56.68
$C_3^=$		34.14	26.84
$C_4^=$		8.03	4.82
$C_2^=$–$C_4^=$		82.36	88.34
Yield of $C_2^=$–$C_4^=$[d]		103	110

[a] H_2:CO = 2:1;
[b] No water dilution in feed.
[c] Dilution by water, WHSV (H_2O) = 1.67 h^{-1}
[d] g/(m^3 syngas), calculated on the base of yield rate = 95% for both reactions.

ether, followed by the conversion of dimethyl ether to light alkenes. Catalysts for the two conversions have been developed. The serial connection of the two conversion steps without any separation results in a$C_2^=$–$C_4^=$ alkenes yield greater than 100 g/(m^3 syngas).

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