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New progress in R&D of lower olefin synthesis

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Abstract

This paper gives a brief review of R&D researches for light olefin synthesis directly and indirectly from synthesis gas in the Dalian Institute of Chemical Physics (DICP). The first pilot plant test was on methanol to olefin (MTO) reaction and was finished in 1993, which was based on ZSM-5-type catalyst and fixed bed reaction. In the meantime, a new indirect method designated as SDTO (syngas via dimethylether to olefin) was proposed. In this process, metal–acid bifunctional catalyst was applied for synthesis gas to dimethylether(DME) reaction, and modified SAPO-34 catalyst that was synthesized by a new low-cost method with optimal crystal size was used to convert DME to light olefin on a fluidized bed reactor. The pilot plant test on SDTO was performed and finished in 1995. Evaluation of the pilot plant data showed that 190–200 g of DME were yielded by single-pass for each standard cubic meter of synthesis gas. For the second reaction, 1.880 tons of DME or 2.615 tons of methanol produced 1 ton of light olefins, which constitutes of 0.533 ton of ethylene, 0.349 ton of propylene and 0.118 ton of butene. DICP also paid some attention on direct conversion of synthesis gas to light olefins. A semi-pilot plant test (catalyst 1.8 l) was finished in 1995 with a CO conversion > 70% and a $C_2=C_4$ olefin selectivity 71–74% in 1000 h. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Synthesis gas; Light olefin; MTO; Dimethylether; Catalysis; Molecular sieve; SAPO-34; ZSM-5

1. Introduction

Synthesis of light olefins from synthesis gas has attracted attention in the past two decades because it may provide a chance for the production of light olefins from natural gas other than from the conventional oil route. Direct conversion of synthesis gas to

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light olefins [1] is particularly expected. However, it is difficult since the reaction products are Schulz–Flory distributed. Many efforts have been focused on indirect methods [2–9]. In recent years, there have been remarkable advances both on methanol to olefin (MTO) process development and on the understanding of catalyst and reaction [10]. The indirect method is now on its way to be commercialized in local places with an economic advantage in comparison with other natural gas utilization technologies and conventional naphtha-cracking processes [11–13]. Dalian Institute of Chemical Physics (DICP) has dedicated many efforts on both direct and indirect synthesis of light olefin since the early 1980s. Most attention was paid to the methanol conversion to light olefin in the 1980s. A 300 t/year MTO pilot plant test, finished in 1993, was based on ZSM-5-type catalyst and fixed bed reaction. In the early 1990s, we proposed a new indirect method, designated as SDTO [14,15] (syngas via dimethylether to olefin), based on our understanding of GTO (natural gas to olefin) and MTO processes, that is, to convert synthesis gas to dimethylether (DME), and then to convert DME to light olefins. SDTO method may exhibit greater efficiency than the method using methanol, since it is well known that the reaction of synthesis gas to DME is far more favorable in thermodynamics than that of methanol synthesis. A pilot plant test of SDTO was finished in 1995 with fluidized bed reactor for the second reaction and modified SAPO-34 as the catalyst. For the direct conversion of synthesis gas to light olefins, efforts were made to catalyst development in DICP. The semi-pilot plant test was finished in 1995. The present paper summarizes the R&D researches in DICP, which focuses on the most promising SDTO process.

2. MTO pilot plant test (finished in 1993)

Based on successful bench-scale tests of MTO reaction, a 300 t/year methanol to light olefin pilot plant was built in the late 1980s and the test was finished in 1993. The catalyst was made from modified ZSM-5 zeolite with ~ 25 wt.% inert oxide as binder. The ZSM-5 zeolite was synthesized on a 1-m³ autoclave with commercial chemicals as starting materials. The reaction system contained two adiabatic fixed bed reactors (Fig. 1). The first one is for the dehydration of methanol to dimethylether (DME) by γ -Al₂O₃ at 250–280°C and 0.04–0.05 MPa. The second reactor is for the conversion of DME to

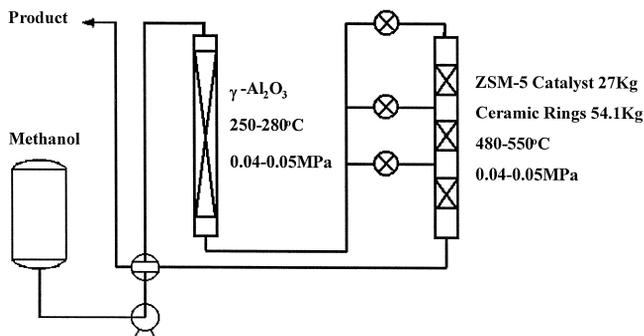


Fig. 1. The 300 t/a MTO pilot plant diagram.

Table 1
MTO reaction results from a 300 t/year pilot plant^a

No. of cycles	TOS (h) ^b	MeOH WHSV (h ⁻¹)	MeOH (wt.%)	Product distribution (wt.%)							C ₂ ⁼ –C ₄ ⁼ selectivity (wt.%) ^c
				CH ₄	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₂ ^o –C ₄ ^o	C ₅ ⁺	CO _x	
1	162	1.54	34.5	1.75	24.8	39.6	20.7	5.90	5.46	1.61	85.2
2	324	1.49	36.4	1.69	23.8	39.2	21.7	5.34	6.77	1.49	84.6
3	486	1.55	33.9	1.95	24.3	39.6	20.9	5.44	5.87	1.79	84.8
4	638	1.58	36.9	2.07	23.8	40.2	20.9	5.07	6.05	1.86	84.9
5	744	1.56	44.3	1.82	23.3	39.3	22.0	5.51	6.26	1.72	84.6
6	890	1.56	34.6	2.37	24.2	40.3	20.7	5.50	4.70	1.91	85.2
7	1022	1.52	34.5	2.04	23.3	40.0	21.3	5.38	6.24	1.59	84.6

^aReaction conditions: (1) first reactor (dehydration of MeOH to DME): temperature = 250–280°C, pressure = 0.04–0.05 MPa; (2) second reactor: temperature = 480–550°C, pressure = 0.04–0.05 MPa.

^bTOS: time on stream.

^cConversion = 100%.

light olefin by ZSM-5 at 480–550°C and 0.04–0.05 MPa. The ZSM-5 catalyst (27 kg) was diluted by ceramic rings (ϕ3 mm, 66.7 wt.%) and carefully loaded with three equal layers into the second reactor. For this fixed reaction, the addition of water to the reaction system was necessary to remove the reaction heat and to enhance light olefin selectivity. Thus, diluted methanol (~ 55–65 wt.% water) was used as feed in the pilot plant test. The WHSV of methanol is 1.49–1.58 h⁻¹. The reaction temperature was controlled by direct feeding of steam into the reactor when necessary. The methanol conversion was kept at 100%. When methanol conversion was lower than 100%, the catalyst needs to be regenerated by de-coking. The de-coking operation was carried out at 500–550°C, with a continuous increase in oxygen content of the nitrogen flow until final replacement of nitrogen by air. The long-term performance of the catalyst was tested up to 1022 h with seven cycles of regeneration. For every cycle, the reaction time was longer than 130 h. The 1022-h results are listed in Table 1. Under the reaction conditions shown on the table, the average selectivity of ethylene, propylene and C₂⁼–C₄⁼ olefin are 23.9%, 39.8% and 84.8%, respectively. The catalyst activity was found stable in the 1500-h test. Material balance results based on 20-h reaction showed that 2.85 tons of methanol can produce 1 ton of C₂⁼–C₄⁼ light olefin, in which ethylene, propylene and butene content are 31.0%, 46.2% and 22.8%, respectively.

3. SDTO process and pilot plant test

Compared with the above MTO process, SDTO directly converts synthesis gas to DME with high CO conversion, thus exhibiting greater efficiency than the MTO process. Other special features of the SDTO process include: (1) the development of a SAPO-34-type molecular sieve catalyst for the conversion of DME to lower olefins with an ethylene selectivity as high as 50–60%, which is remarkably higher than that by

employing the ZSM-5 type zeolites; (2) a fluidized bed reactor is utilized in the second stage for the conversion of DME to lower olefins, and no water addition is needed during the reaction, while smooth operation can be achieved.

3.1. Synthesis gas to DME

3.1.1. Catalyst

The first step of the SDTO process is the conversion of synthesis gas to DME. This stage can in fact be regarded as an independent process, since DME itself is a versatile chemical raw material, which is widely employed in the preparation of drugs, dyestuffs, pesticides, cosmetics, etc. Recently, it has been proposed that DME can be used as an environment-friendly fuel as a substitute for diesel fuels.

For synthesis gas to DME, metal–acid bifunctional catalyst was applied to the reaction [16–18]. The metallic component of the catalyst can be similar to that of methanol synthesis catalyst, while solid acids, such as zeolites, $\gamma\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-Al}_2\text{O}_3$, can be used as the acid component. The fundamental aspect about the incorporation between the two components has been studied. The effect of the acid component on the reaction is shown in Table 2. It has been found that when $\gamma\text{-Al}_2\text{O}_3$ is used as an acid component, the catalyst exhibits rather low DME selectivity and single-pass CO conversion, both around 70%. Furthermore, the initial reaction temperature is also rather high (250–270°C), which is unfavorable for the stability of the catalysts as well as for the thermodynamic equilibrium of the reaction, since this reaction is strongly exothermic, and CO conversion is diminished when the reaction temperatures are higher than 240°C. Zeolites that have much stronger acid strength than $\gamma\text{-Al}_2\text{O}_3$ can greatly enhance the activity and selectivity of the catalyst. Also, the Cu–Zn components of the conventional methanol synthesis catalysts were modified with transition metal promoters, so that the initial reaction temperature can be effectively lowered. Accordingly, three generations of the catalyst have been developed using Cu–Zn components and ZSM-5 zeolite [16–18]. Typical performance data of these catalysts are listed in Table 3. It is worth pointing out that besides their superior activity and selectivity, the SD219

Table 2

Effect of acid component of catalyst^a on the synthesis gas to DME reaction (P = 3.0 MPa; WHSV = 1000 h⁻¹; H₂: CO = 2:1)

Acidic component	Temperature (°C)	CO conversion	DME/DME + MeOH (wt.%)	CH ₄ selectivity (mol%)
$\gamma\text{-Al}_2\text{O}_3$	260	85.27	91.59	2.89
M- $\gamma\text{-Al}_2\text{O}_3^b$	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
HZSM-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).

^b Modified $\gamma\text{-Al}_2\text{O}_3$, HY, HMd or ZSM-5.

Table 3

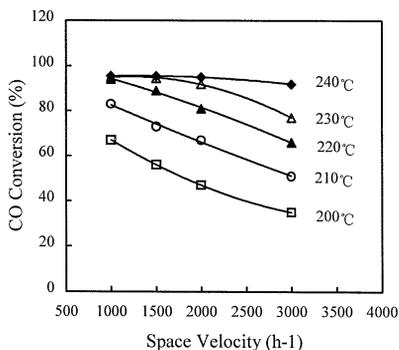
Properties of SD219 catalysts in synthesis gas to DME reaction ($\text{CO}/\text{H}_2 = 1/2$, $P = 3.0$ MPa)

Catalyst	Reaction temperature ($^{\circ}\text{C}$)	GHSV (h^{-1})	CO conversion (%)	DME selectivity (wt.%) ^a
SD219-1	240	1000	90.0	95.8
SD219-2	230	1000	95.1	93.8
SD219-3	220	1000	94.4	95.5
	240	1000	96.1	91.4
	240	3000	90.1	94.0

^aDME selectivity = $[\text{DME}/(\text{DME} + \text{MeOH})]$.

catalysts also show activities for the hydrogenation of CO_2 . As a result of this special feature of the SD219 catalysts, the carbon utilization efficiency (carbon selectivity) of the DME synthesis process in single-pass can exceed the theoretical value of 66.67%, when the feed gas contains CO_2 . The long-term (2200 h) test of 219-1 catalyst, under the conditions of 3.5 MPa and $\text{GHSV} = 1000 \text{ h}^{-1}$ ($\text{H}_2/\text{CO} = 2$), shows that the catalyst possesses good activity and stability (CO conversion > 75%).

Many factors such as reaction temperature, space velocity, reaction pressure and the content of CO_2 in the feed will influence the conversion and DME selectivity of the reaction. These reaction variables were investigated using SD219 catalyst. Fig. 2 shows the effects of space velocity and reaction temperature on the conversion. The CO conversion generally decreases with the increase of space velocity of synthesis gas. At a higher temperature, this decrease became insignificant. The CO conversion was still higher than 90% as the GHSV increased to 3000 h^{-1} , when the temperature was at 240°C , and the yield of DME was largely increased that figured out how to optimize the operating conditions. The influence of reaction pressure on CO conversion was similar to the change of thermodynamic equilibrium curve. Higher reaction pressure would be favorable for the reaction. When the pressure increased from ambient to 4.5 MPa, an increase of 15°C in the reaction temperature for reaching maximum CO conversion was observed. It was noted that the selectivity of DME was also enhanced with the increase of reaction pressure; in some cases at elevated pressure, the selectivity was even higher than equilibrium value, implying that CO_2 hydrogenation reaction became noticeable.

Fig. 2. Change of CO conversion versus GHSV of synthesis gas (catalyst: SD219-3, $P = 3.0$ MPa).

Studies on the effect of CO_2 on methanol synthesis suggested that a certain amount of CO_2 in the reaction system would be favorable for Cu-based catalysts to maintain their activity, but high CO_2 content would compete in adsorption with CO and decline the CO conversion. Thermodynamic calculation, on the other hand, shows that the equilibrium CO conversion is restrained by the existence of CO_2 . The results with 14.3% of CO_2 are shown in Fig. 3. At high reaction temperatures, the decrease in CO conversion was mainly caused by the restriction from thermodynamics and, at low temperatures, with the added effect of competitive adsorption. For different CO_2 content, the CO conversion went down as the CO_2 content increased, and the change in CO conversion with temperature was nearly parallel to the change of equilibrium values at relatively high temperatures. The maximum CO conversion was also achieved at 230°C. Above this temperature and with the $(\text{H}_2\text{-CO}_2)/(\text{CO} + \text{CO}_2)$ ratio higher than 1, the effect of CO_2 content became negligible. It can also be seen from Fig. 3 that the CO_2 in the reactant is favorable for obtaining a higher DME selectivity at high temperatures.

3.1.2. Pilot plant test of DME synthesis

The pilot plant test of synthesis gas to DME reaction was carried out on a $\phi 40 \times 4000$ -mm fixed bed reactor with catalyst SD219-2 (pellet size: $\phi 5 \times 6\text{--}7$ mm). Under reaction conditions of 3.4–3.7 MPa, $240 \pm 5^\circ\text{C}$, $\text{GHSV} = 1000 \text{ h}^{-1}$, and with semi water gas (H_2 42.43%, CO 23.21%, CO_2 11.59%, N_2 21.54%) as reaction feed, the pilot plant test operated continuously and smoothly for 1000 h, with a CO single-pass conversion of 75–78% and a DME selectivity of 95%. The changes of CO conversion and DME selectivity with reaction variables are similar to the results obtained from the laboratory. Fig. 4 gives an example on changing reaction pressure. Even though the feedstock from industrial sources contained high concentration of CO_2 and nitrogen, the high activity of catalyst was still satisfactorily exhibited and high CO conversion was obtained at a relatively low temperature. Fig. 5 shows the changes of CO conversion and DME content in the products during the 1000-h test. Apart from a characteristic initial decrease in activity, the CO conversion and DME content kept

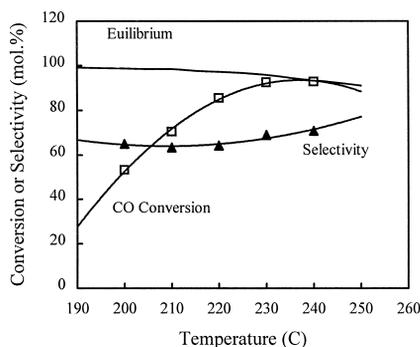


Fig. 3. Reaction results with CO_2 contained synthesis gas as reactant (catalyst: SD219-3, feed: $\text{H}_2\text{:CO:CO}_2 = 2\text{:}1\text{:}0.5$, $P = 3.0 \text{ MPa}$, $\text{GHSV} = 1000 \text{ h}^{-1}$).

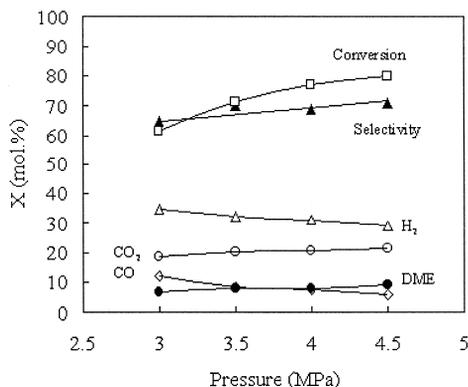


Fig. 4. Reaction results of the pilot plant (catalyst: SD219-2, 210°C, GHSV = 1000 h⁻¹).

stable without raising temperature. No evident decrease has been found for the activity and selectivity of the catalyst during the 1000-h tests. Evaluation of the pilot plant data showed that 190–200 g of DME were yielded by single pass of each standard cubic meter of synthesis gas (H₂/CO = 2). The results of the pilot plant tests proved that this process has shown a concrete potentiality for further scaling-up to become a commercial process.

3.2. DME to light olefins

3.2.1. DO123 catalyst

In the SDTO process, a type of SAPO-34 [19,20] catalyst, designated as DO123, has been developed for the conversion of DME to lower olefins with excellent performance in a fluidized-bed reactor system. One of the features of the DO123 catalyst lies in the fact that the molecular sieve is synthesized with a new method different from the conventional procedure. Usually, SAPO-34 molecular sieve is synthesized using tetraethyl-hydroxyl-amine (TEAOH) as the template agent [8,21]. However, TEAOH is an expensive reagent, and this will cause a high cost for the production of the catalysts.

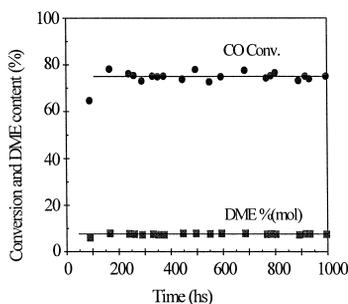


Fig. 5. Pilot plant performance over the SD219-2 catalyst for the direct synthesis of DME from synthesis gas. Regeneration time (minutes).

Table 4

Catalytic performance of modified SAPO-34 molecular sieves

Fixed bed reaction, 450°C, WHSV(MeOH) = 2.0 h⁻¹, with 60 ml/min nitrogen dilution, reaction time = 2 min, for all cases conversion = 100%.

M =	C ₂ H ₄	C ₃ H ₆	C ₃ H ₆ /C ₃ H ₈	C ₂ ⁼ –C ₄ ⁼
Mg	23.4–30.8	28.8–33.2	1.0–2.0	57.7–75.0
Ca	43.1–51.9	34.2–37.4	7.5–11.1	89.3–92.9
Sr	37.8–42.7	30.7–38.1	3.7–5.5	83.8–86.9
Ba	39.4–41.9	34.7–38.9	3.6–5.5	84.2–87.3
Fe	35.2–41.3	30.9–35.8	2.5–3.9	78.6–83.8
Co	29.9–43.5	33.9–35.8	2.5–7.1	78.6–86.4
Ni	37.5–43.5	32.1–35.7	2.8–8.6	78.7–90.2
Cu	35.3–52.2	31.7–34.9	3.1–4.5	79.0–87.7

Many efforts were paid to the synthesis of SAPO-34 to develop a cheap synthesis method. Triethylamine was successfully applied as template in the synthesis [22,23] instead of TEAOH. A dual-template method was invented to control the crystal size of the molecular sieve [24]. It has been estimated that the SAPO-type molecular sieve synthesized with templates of these cheap amines and with optional procedures can reduce the cost to 20% of the molecular sieve prepared with the TEAOH template.

In the synthesis of the SAPO-34 type molecular sieve, crystallization conditions were monitored by means of IR, NH₃-TPD, SEM and MASNMR techniques [25]. The properties of the catalysts, such as the number and strength of the acid sites, contents and distributions of the Si, Al and P elements, crystal size, pore size, etc., can be optimized to give the best performances of the catalysts for DME conversion to lower olefins. The addition of metals into the SAPO-34 molecular sieve was also found effective for enhancing light olefin selectivity (Table 4). Consequently, the selectivity for ethylene formation can be remarkably enhanced, and the formation of alkanes can be suppressed.

By incorporating appropriate binders to the SAPO-34 molecular sieve, the DO123 catalyst has been prepared by spray-drying method into micro-spheres with excellent

Table 5

Performance of the DO123 catalyst with different feed components in a fluid bed bench-scale reactor (550°C, reaction time = 10 min, conversion = 100%)

Feed	Products (wt.%)			
	C ₂ H ₄	C ₃ H ₆	C ₂ ⁼ –C ₃ ⁼	C ₂ ⁼ –C ₄ ⁼
Methanol ^a	62.79	22.34	85.13	89.57
DME + H ₂ O ^b	62.80	22.65	85.45	90.23
DME ^c	59.35	24.22	83.57	88.32

^aWHSV of methanol 6.45 h⁻¹, linear velocity of the reactants 15.21 cm/s.

^bWHSV of DME 4.64 h⁻¹, linear velocity of reactants 15.21 cm/s.

^cWHSV of DME 7.16 h⁻¹, linear velocity of reactants 11.75 cm/s.

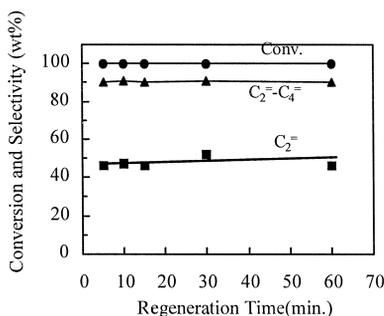


Fig. 6. Influence of regeneration time on DO123 catalyst performance (regeneration condition: 600°C in air; catalytic evaluation: fluidized reactor, 500°C, MeOH line velocity = 14.2 cm/s, reaction time = 2 min).

mechanical as well as abrasive-resistant properties. This catalyst was tested with a bench-scale fluidized-bed reactor with a size of $\phi 20 \times 500$ mm, and under the reaction conditions of ambient pressure, 550°C, WHSV of 5–7 h⁻¹, and linear velocity of 12–15 cm/s. The conversion of DME was 100%, and the selectivity to ethylene, C₂⁼–C₃⁼ olefins and C₂⁼–C₄⁼ olefins were 50–60%, 85% and 90%, respectively. Methanol was also used as the feedstock for the reaction test, and nearly identical results as the DME feedstock were obtained (Table 5). This implied that both DME and methanol could be used as the feedstock for the production of lower olefins over the DO123 catalyst. It has also been found from the bench-scale operations that coke depositions on the DO123 catalyst could be regenerated easily by burning in air at 600°C within 10 min (Fig. 6). More than 100 cycles of regeneration have been carried out on the catalyst during the bench-scale tests, and the reactivity of the catalyst did not change very obviously. Because large amounts of water exist in the products and the catalyst has to be regenerated frequently at high temperatures (> 550°C), high stability of the catalyst is important. The performance of the catalyst was also tested after thermal and hydrothermal treatments under severe conditions. The activity and selectivity of the catalyst were almost the same as those of the fresh catalyst after 300-h calcination in air or 80-h stream treatment at 800°C [15]. X-ray diffraction results show only a small decrease of the relative crystallinity of the treated samples compared to that of the fresh catalysts.

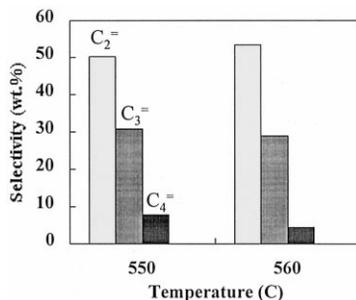


Fig. 7. Typical reaction results from pilot plant test of DME to light olefins.

Table 6

Typical reaction results of synthesis gas to light olefin reaction from semi-pilot plant tests

Reaction conditions: temperature = 307–367°C; pressure = 2.0 MPa; GHSV = 1000–1500 h⁻¹; H₂/CO = 2.

Time on stream (h)	40	100	200	300	400	500	600	700	800	900	1010
CO conversion (%)	95.4	88.6	86.0	85.4	78.1	78.6	77.6	78.9	78.4	78.2	78.6
C ₂ ⁼ –C ₄ ⁼ selectivity (wt.%)	71.4	72.8	72.4	72.2	72.1	71.6	72.1	72.5	71.7	72.2	72.0

All these results indicate that the DO123 catalyst does not only have very good activity and selectivity for the conversion of DME or methanol to lower olefins, but also the advantages of easy regeneration, excellent thermal and hydrothermal stability, and the absence of the need for water addition during the reaction operations.

3.2.2. Pilot plant test of DME to light olefins

The SAPO molecular sieve was then prepared in autoclaves of 1-m³ capacity under commercial production conditions, and the DO123 catalyst so produced was put into scale-up tests in a pilot plant fluidized reactor system that was connected in series with the “synthesis gas to DME” fixed-bed reactor mentioned above. Pilot plant test of DME to light olefin was carried out on a fluid bed reaction system (reactor ϕ 100 mm) with continuous regeneration of the catalyst. The fluidized bed reactor was an up-flow dense phase bed type, with a capacity of 15–25 t/year. The DME feed charge for the second stage reaction came from the concentrated product of the first stage, with a concentration of greater than 98%. The DO123 catalyst was operated in this pilot plant under different reaction conditions for process studies, and a total of 1500 cycles of regeneration was carried out on the same batch of catalyst. Characterization investigations have been done on the catalyst after the pilot plant operations, and no remarkable changes on its physical–chemical properties had been detected. Data from the pilot plant performances (Fig. 7) showed that there was a good duplication of the pilot plant results with that of the bench-scale tests. Estimations from material-balance data indicated that for the production of a ton of lower olefins (constituting 0.533 ton of ethylene, 0.349 ton

Table 7

Synthesis direct conversion — comparison of the results of bench-scale tests and semi-pilot plant test

Reactor diameter (mm)	13	20	26
Catalyst loaded (ml)	10	150	1800
Reaction conditions			
Reaction temperature (°C)	360–390	310–360	300–350
Reaction pressure (MPa)	2.0	2.0	2.0
H ₂ /CO	2.0	2.0	2.0
GHSV (h ⁻¹)	800–1100	800–1100	800–1500
CO conversion (%)	70–85	70–80	70–90
C ₂ ⁼ –C ₄ ⁼ olefin selectivity (%)	68–72	68–71	71–74
Catalyst life test (h)	> 1292	> 1620	> 1000

Table 8

Yield of $C_2=C_4$ olefin at different operation conditions by direct conversion method ($H_2/CO = 2$)

Operation condition		$C_2=C_4$ yield (g/m^3)	
CO conversion (%)	$C_2=C_4$ selectivity (wt.%)	Single pass	Recycle
78.6	71.6	68.1	86.6
92.1	69.5	77.5	84.1
45.3	76.2	41.8	92.2

of propylene and 0.118 ton of butene), 1.880 tons of DME or 2.615 tons of methanol have to be consumed.

4. Direct conversion of synthesis gas to light olefin

In DICP, efforts were also made to the direct conversion of synthesis gas to light olefin. K–Fe–MnO/Si-2 catalyst with good performance was developed [26–29]. After this catalyst was tested successfully on bench-scale, a semi-pilot plant with a tube reactor (id of $\phi 26$ mm) was constructed, which is capable of loading 1.8 l of catalyst ($\phi 1.5 \times \sim 5$ mm). Life test of the catalyst was carried out to examine the performance and its stability for olefin production via CO hydrogenation. The test was operated continuously in this fixed-bed reactor for more than 1000 h. Typical results are listed in Table 6. The comparison with the results of the bench-scale tests was listed in Table 7. It can be seen from Table 6 that the catalytic properties of Fe–MnO/Si-2 were quite stable during the 1000-h test. CO conversion and $C_2=C_4$ selectivity were a little higher than the bench-scale results. After the 1000-h reaction on semi-pilot plant, a regeneration experiment was carried out on the catalyst and then the activity and selectivity of the regenerated catalyst was tested. The results showed that the catalytic properties of the regenerated catalyst were nearly the same as the fresh catalyst.

Table 8 shows the yield of $C_2=C_4$ olefin at different operation conditions by direct conversion method. In comparison with the indirect method, it can be seen that the olefin yield of the bench-scale test was not high even taking into account the recycle operation. Under the conditions of high selectivity and low conversion, the yield can be enhanced. However, this yield is still lower than that of the SDTO method (single pass of synthesis, 100% conversion of DME, $C_2=C_4$ yield is $105 g/m^3$). Further work on the direct conversion of synthesis gas to light olefin is still undergoing development of a higher selective catalyst.

5. Conclusion

For the development of synthesis gas to light olefin process, DICP made a lot of effort both on direct and indirect conversion methods. Pilot plant tests were successfully finished on MTO and on the newly proposed SDTO process. The results show that the

SDTO method, in which metal–acid bifunctional catalyst was applied for synthesis gas to DME reaction, and modified SAPO-34 catalyst that was synthesized by a new method with optimal crystal size and low cost was used to convert DME to light olefin on a fluidized bed reactor, was the most attractive process at present stage. The single pass yield of DME for each standard cubic meter of synthesis gas was 190–200 g. For SDTO second reaction, 1.880 tons of DME or 2.615 tons of methanol can produce 1 ton of light olefins, which constitutes 0.533 ton of ethylene, 0.349 ton of propylene and 0.118 ton of butene. Direct conversion of synthesis gas to light olefin was mostly expected; however, its yield was lower than that of the indirect method. To enhance light olefin selectivity of the catalyst is the key step in future work on the direct conversion method.

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