===== CHRONICLE =====

Catalytic Conversion of Natural Gas

(Summary of the Proceedings of "Natural Gas Conversion VII,"
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In June 2004, Dalian (China) welcomed the seventh meeting of the International Symposium on Natural Gas Conversion. This forum is summoned every three years and is always a very important event for gas chemists. The Dalian symposium gathered some 450 participants from 26 countries, including five scientists from Russia. There were 110 oral reports, including 40 from China, and 90 poster papers. The materials presented at the symposium demonstrated that gas conversion science has made rapid progress in recent years: new technologies and catalysts have been developed, and there has been growing aspiration to realize the industrial application of scientific achievements. Most of the present-day research is focused on the conversion of natural gas into liquid, easily transportable fuel.

PRODUCTION OF SYNTHESIS GAS

Most of the reports dealt with the production of synthesis gas from methane. This is explained by the fact that synthesis gas production is the first step in the most important industrial processes. Production of synthesis gas followed by hydrogen separation is very expensive, accounting for 60–80% of the cost of the final product (ammonia, methanol, etc.). Therefore, even a small reduction in the cost of synthesis gas might make the final product much cheaper.

Synthesis gas is produced using a variety of catalytic processes: steam methane conversion (SMC, $CH_4 + H_2O = CO + 3H_2$); partial methane oxidation (PMO, $2CH_4 + O_2 = 2CO + 4H_2$); carbon dioxide methane conversion (CDMC, $CH_4 + CO_2 = 2CO + 2H_2$); and autothermal reforming (ATR), which is a combination of the preceding processes. There were 23 reports on this problem, which covered all methods of synthesis gas production.

In his plenary lecture, Rostrup-Nielsen (Haldor Topsøe Co., Denmark, p. 121)[1] made an excursus into SMC history. SMC over nickel catalysts has been industrially used since 1966. Ever since, researchers have fought against the sulfur poisoning of catalysts

and coking and for reduction in reactor size. In the SPARG process, developed by Haldor Topsøe, sulfur poisoning of the catalyst is prevented either at a sacrifice in overall catalytic activity or by introducing a pre-converter. The highest activity is shown by base- promoted Ni and Co catalysts. At the moment, catalytic activity is not the limiting factor in the improvement of the SMC process. It is necessary to intensify heat and mass transfer and to minimize the reactor. New lines of research in this field deal with microtunnel ceramic reactors allowing short contact times and with membrane reactors. It is noteworthy that 95% of world synthesis gas is produced by SMC, although there have been advances in other synthesis gas technologies.

The mechanism of SMC was considered by Holmen (Trondheim University, Norway; p. 139). It was demonstrated that the low conversion is due to the low energy of the metal–carbon (M–C) bond. The optimum energy of the M–C bond lies between 160 and 169 kcal/mol; that of the M–H bond, between 64 and 67 kcal/mol. It was suggested that these data be used when selecting a promoter for Ni catalysts. According to Zhao (Süd Chemie, Louisville, the United States; p. 217), a good support for Ni and Rh catalysts is $CaAl_2O_4$. With $Ni/CaAl_2O_4$ and $Rh/CaAl_2O_4$, equilibrium conversion is reached at 400 and 480°C, respectively, and at a feed rate higher than that in conventional commercial reactors.

Most of the reports on synthesis gas production have been devoted to PMO. This method yields synthesis gas with $H_2 : CO = 2 : 1$, which is most appropriate for the Fischer–Tropsch synthesis. The main problems associated with this method are the need for an oxygen plant, explosion hazard, and great overheatings. Furthermore, the PMO process is difficult to commercialize because of the large reactor size.

Forzatti (Milan University, Italy), Mazanec (Velocise Co., the United States), Pavlova, Sadykov (both from the Institute of Catalysis, Siberian Division, Russian Academy of Sciences; p. 169), and some other reporters studied PMO on block catalysts with through channels ~1 mm in diameter at contact times of <10 ms. These contact times are short enough to reduce coking owing to the fact that coking takes more time than conversion. Tulenin *et al.* (Institute of Chemical Physics,

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[1] Hereafter, reports are referred to by indicating the name of the first or the major author and the starting page number in *Stud. Surf. Sci. Catal.*, 2004, vol. 147.

Russian Academy of Sciences; p. 151) discovered autooscillations and autowaves in PMO over nickel catalysts. The mechanism of PMO was investigated by Silva (National Institute of Technology, Rio de Janeiro; p. 157). It was demonstrated that the activity of the Pt/Al_2O_3, Pt/ZrO_2, and $Pt/Ce–ZrO_2$ catalysts is related to their oxygen capacity. Due to the capacity of CeO_x to store and release oxygen, carbon can be removed from the catalyst through a redox reaction. Cyclic PMO on $La_{1-x}Sr_xFeO_3$ perovskite catalysts was studied by I. Li (Nanking University, China; p. 199). In this process, a perovskite catalyst is circulated between two reactors at 800–900°C. In one reactor, methane is oxidized by lattice oxygen into synthesis gas; in the other, the perovskite is reoxidized with air. One cycle lasts for a few minutes. This process is explosion-proof and needs no oxygen plant. Sadykov *et al.* (Institute of Catalysis, Siberian Division, Russian Academy of Sciences; p. 241) studied a similar process catalyzed by Pt on Ce, Zr, La, and Sm oxides.

A membrane technology for PMO was reported by L. Chen (Air Products Co. and Chevron Co., the United States, in collaboration with the Ministry of Power of the United States; p. 55). Nonporous multicomponent catalysts exceptionally permeable for oxygen have been developed. These catalysts work at 600°C and a pressure of 28 atm, eliminating the need for an oxygen plant. The membranes are ion- and electron-conducting at the same time. They are based on $(La_xCe_{1-x})FeO_{3-y}$ perovskites with supported noble metals.

Carbon dioxide methane conversion takes place at a higher temperature (about 900°C) than SMC or PMO. It has been intensively studied in recent years, because it yields $CO : H_2 = 1 : 1$ synthesis gas, which is necessary for dimethyl ether (DME) synthesis. This process, like SMC and PMO, is catalyzed by supported Ni and Co.

Aika (Tokyo Institute of Technology; p. 187) demonstrated that the activity of the Co/TiO_2 catalyst depends strongly on the temperature at which the catalyst has been reduced. Only reduction at $T > 850°C$ affords an active and stable catalyst. Small amounts of Pt or Ru raise both the activity and stability of the catalyst. J. Ross (Limerick University, Ireland; p. 193) studied active carbide catalysts: Mo_2C/SiO_2, WC/SiO_2, Mo_2C/Al_2O_3, and Mo_2C/ZrO_2. The first turned out to be the most active in CDMC. Mo_2C conversion to MoO_2 deactivates the catalyst.

The outlook for ATR was analyzed by Dybkjaer (Haldor Topsøe, Denmark; p. 13). Membrane technology is very promising for this process: it allows oxygen to be replaced with air. However, present-day membranes are insufficiently strong and stable. According to the reporter, membrane technology will not find large-scale application in this process in the next 10 years.

The mechanism of ATR on the supported catalysts Pt/CeO_2, Pt/ZrO_2, and $Pt/CeZrO_2$ was reported by Schmal (University of Rio de Janeiro; p. 253). This mechanism is indirect: its first step is methane combustion; next, the unburnt methane undergoes steam and carbon dioxide conversion. The best catalyst for this process is $Pt/Ce_{0.18}Zr_{0.82}O_2$. Having a high oxygen capacity, it facilitates the redox reaction. Without CeO_2, the catalyst undergoes rapid deactivation.

The demands of hydrogen power engineering have stimulated interest in producing synthesis gas from other hydrocarbons. Kaiva (Helsinki University; p. 247) reported the steam conversion and ATR of *n*-heptane over the 15% Ni/Al_2O_3 catalyst at 700°C. At lower temperatures, the hydrocarbon undergoes thermal cracking. Vargas (Laboratory of Materials, Surface, and Catalysis, France; p. 115) introduced cobalt into a Cu–Zr fluorite catalyst to obtain an active and selective catalyst for steam ethane conversion into synthesis gas. Reduction of cobalt in this catalyst generates Co nanoparticles capable of reacting with oxides.

FISCHER–TROPSCH SYNTHESIS

Interest in the Fischer–Tropsch synthesis (FTS) has grown rapidly in recent years, because a number of gas-processing companies changed over to liquid products pipelined to other plants for further conversion. There were reports from companies that are going to use FTS as a method of synthesis gas conversion into a liquid.

On larger scales, FTS is being used by SASOL Co. (South Africa). Steinberg (SASOL, South Africa; p. 37) presented the newest achievements of this company, including a slurry reactor for diesel fuel production using a Co catalyst and a steam cracking process for converting liquid hydrocarbons into lower olefins. However, the company is changing over to synthesis gas conversion into liquid hydrocarbons for production of valuable chemicals rather than fuel. At its Sasolburg plants, SASOL is going to produce special-purpose wax, detergents, high-molecular-weight olefins, valuable solvents (with Co catalysts), and valuable pure C_6 and C_8 paraffins (with Fe catalysts).

According to Schanke (Norway; p. 43), Statoil Co. (Mosselbaai, South Africa) has constructed a semicommercial-scale FTS plant capable of producing up to 1000 barrels of liquid products a day. Iran participates in this project. A Co–Re catalyst is used in this process. Its selectivity is as high as 89% in a slurry reactor and 84% in a fixed-bed reactor.

Shell Co. was the second, after SASOL in South Africa, to commercialize FTS. It constructed an FTS plant in Bintulu (Malaysia) as early as the 1970s. Hoek (Shell, Amsterdam; p. 25) reported Shell's latest achievements: burners used at the first stage of the process (noncatalytic combustion) have been improved, new multifunction fixed-bed SFT reactors for synthesis of high-molecular-weight hydrocarbons have been designed, and the formation of methane and CO_2 has been diminished.

Gradassi (BP-America Co., the United States; p. 43) reported the design of a plant using the same process sequence as Shell: ATR, FTS, and steam cracking yielding diesel fuel.

More than 20 reports were devoted to cobalt FTS catalysts containing various promoters and supported on various materials. Iron catalysts were reported only by Shell. Bezemer (Utrecht University, the Netherlands; p. 259) reported cobalt catalysts on carbon nanotubes. In these catalysts, cobalt particles are situated both inside and on the outer surface of the nanotubes. The C_{5+} hydrocarbon selectivity of these catalysts is as high as 86%. According to Chen (Institute of Coal Chemistry, Taiyuan, China; p. 277) the selectivity of Co/ZrO_2 increases markedly with increasing degree of cobalt reduction. When the cobalt concentration is low, this catalyst is difficult to reduce and favors methane formation. Holmen (Trondheim University, Norway; p. 301) demonstrated that the selectivity of Co/Al_2O_3 catalysts rises with decreasing specific surface area of Al_2O_3. According to Li (Uhan University, China; p. 307), promotion of the Co/SiO_2 catalyst with Ce raises CO conversion. According to Conner (University of Kentucky, the United States; p. 331), CO conversion on Co/TiO_2 and Co/Al_2O_3 is reduced by water. Mendez (University of Rio de Janeiro; p. 361) studied the effect of pressure on the selectivity of FTS on Co/Nb_2O_5, $Co–Ru/Nb_2O_5$, and $Co–Re/Nb_2O_5$. The highest C_{5+} selectivity was observed at 2 MPa.

It is well known that FTS mainly yields linear hydrocarbons. Fujimoto (Kitakyushu University, Japan; p. 367) reported the possibility of obtaining isoparaffins from synthesis gas. Combining an FTS catalyst with hydrocracking and isomerization catalysts allowed selective production of $C_4–C_6$ isoparaffines. Selective synthesis was also carried out with hybrid catalysts containing Co/SiO_2 together with RuKY, SO_4^{2-}/ZrO_2, or Pd/zeolite β. In these hybrids, linear FTS hydrocarbons diffuse from the Co catalyst to the hydrocracking catalyst through the gas phase or on the surface.

SYNTHESIS GAS CONVERSION INTO OXYGEN-CONTAINING PRODUCTS AND OTHER VALUABLE CHEMICALS

Methanol remains the most important oxygen-containing commercial product of synthesis gas conversion. At present, annual methanol output is 35 million tons. It is not expected to grow until 2007, because the United States has abandoned methyl *tert*-butyl ether (MTBE). Furthermore, methanol is converted into DME, higher alcohols, etc. Strensen (Haldor Topsøe, Denmark; p. 7) presented a new conception combining methanol synthesis with natural gas ATR. The SMC process is suitable only for small-scale methanol production. For methanol production at a rate of 1500 to 7000 t per day, it is recommended to use the two-stage process including SMC and PMO. For production rates above 5000 t, ATR is favorable. A new gas–liquid process has been designed for methanol synthesis. Its first stage is conventional gas-phase methanol synthesis at an elevated pressure. Its second stage is low-temperature methanol synthesis below the dew point. Conducting the synthesis in the liquid phase enables one to circumvent thermodynamic limitations and raise the methanol yield.

In his plenary lecture, Fleisch (BP Technology Co., the United States; p. 31) considered the processes that were developed by BP Technology and some other companies for the synthesis of methanol, DME, and oxygen-containing products. The methanol plant Atlas, with an annual production capacity of 1.7 million tons, was constructed by BP in Trinidad. Within 5 years, its annual capacity will be increased to 4 million tons. The methanol produced will be used as a turbine fuel and as a raw material in olefin production by the methanol-to-olefins (MTO) method.

A rapidly increasing effort is being put into DME production. DME is a promising diesel fuel: it forms no soot owing to the absence of C–C bonds in its molecule. Its production in combination with methanol synthesis may turn out to be cheaper than methanol synthesis alone. However, DME as a motor fuel requires a new infrastructure to be created. It is also possible to use high-molecular DME analogues such as polyoxomethylene, $CH_3–(OCH_2)_n–OCH_3$. These polymers are produced from methanol, DME, and formaldehyde below 100°C using acid catalysts. An $n = 3–8$ product mixed with diesel fuel ensures the required boiling point without any modification of the engine. The $n > 8$ product is solid and is, therefore, unsuitable for motor fuel applications. DME can also be used in hydrogen production in fuel cells by the reaction $CH_3OCH_3 + 3H_2O = 2CO_2 + 6H_2$. This reaction is carried out below 350°C on clay-supported Ni–Cu–Zn catalysts.

A new low-temperature methanol synthesis process was presented by Reubrajkaroen (Toyama University, Japan; p. 409): 61% CO conversion and 98% CH_3OH selectivity were attained with a Cu/ZnO catalyst and a synthesis gas containing excess CO_2 at 170°C and 0.5 MPa. Earlier, the Brookhaven laboratory (the United States) developed a low-temperature process for methanol synthesis from CO and H_2 on a strong-base catalyst consisting of NaH, alcohols, and acetates. However, this catalyst is poisoned by CO_2 and H_2O. The Cu/ZnO catalyst does not react with acid impurities, so it is unnecessary to remove them.

Daly (Velocise, the United States; p. 415) reported application of microchanneled monoliths with a $Cu–ZnO/Al_2O_3$ catalyst. With this catalyst, equilibrium conversion at 250°C is reached at a contact time of 600 ms. The reactor used in this process is conveniently coupled with a microchanneled reactor for synthesis gas production.

The world leader in DME process design is Japan. Ogawa (National DME Initiative, Hokkaido, Japan; p. 379) summed up the operation of a pilot plant with a DME production capacity of 5 t per day in Kushiro, Hokkaido. In 2004, the company launched the project of a new plant with a production capacity of 100 t per day. This project is supported by the Japanese government. Synthesis gas will be produced by oxygen–carbon dioxide methane conversion:

$$2CH_4 + O_2 + CO_2 \longrightarrow 3CO + 3H_2 + H_2O.$$
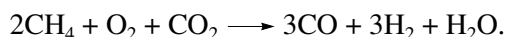
Next, DME is obtained using a slurry catalyst under conventional conditions of 260°C and 5 MPa:

$$2CO + 3H_2 \longrightarrow CH_3OCH_3 + H_2O.$$

The selectivity of this process, DME/(DME + CH$_3$OH), is 0.91, and the purity of DME is 99.9%.

Arena (Messina University, Italy; p. 385) carried out a two-step synthesis of DME. The first step is methanol production from CO_2 on a Cu/ZnO catalyst at 180–240°C and 0.9 MPa, and the second step is methanol dehydration into DME.

Li (Taiyuan Institute of Coal Chemistry, China; p. 391) reported alcohol synthesis using the desulfurization catalyst MoS_2 promoted with FTS catalysts: Ni, Co, and Fe. These admixtures raise the activity and selectivity of the catalyst in the synthesis of higher alcohols. The Ni/MoS$_2$ catalyst with Ni : Mo = 0.5 afforded a C$_2$H$_5$OH/CH$_3$OH ratio of 8.75, while, with Ni-free MoS$_2$, this ratio is 0.87. The promoted catalysts are resistant to sulfur poisoning.

Volkova, Plyasova, and their colleagues (Institute of Catalysis, Siberian Division, Russian Academy of Sciences; p. 403) employed solid superacids in the halogen-free synthesis of methyl acetate from DME at 200–250°C and 1 atm:

$$CH_3OCH_3 + CO = CH_3CO\text{–}O\text{–}CH_3.$$
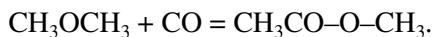
In this process, the Rh/Cs$_x$H$_{3-x}$PW$_{12}$O$_{40}$ catalyst was more active than Rh/SO$_4^{2-}$/ZrO$_2$ or Rh/WO$_x$-ZrO$_2$. An excellent correlation between catalytic activity and the number of proton sites was established.
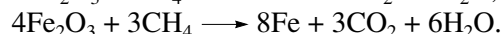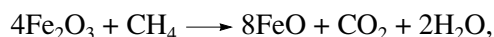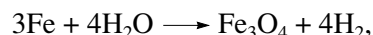
Asami (Kitakyushu University, Japan; p. 427) reported a selective synthesis of liquefied petroleum gas (LPG, C$_3$–C$_4$ hydrocarbons). Combining a methanol synthesis catalyst (Cu/ZnO) with a dehydration catalyst (β- or USY-zeolite) afforded LPG in high yield: at 225°C and 2.1 MPa, process selectivity and conversion were 75 and 70%, respectively. The reaction proceeds in three steps: CO $\longrightarrow$ CH$_3$OH $\longrightarrow$ DME $\longrightarrow$ C$_3$–C$_4$ hydrocarbons.

Wang (Curtin University, Australia; p. 439) reported the synthesis of gasoline additives from methanol and olefins on sulfated SiO$_2$. The commercial resin Amberlite 15 is nonselective in the conversion of the C$_3$H$_6$ + CH$_3$OH mixture into ether. Sulfated SiO$_2$ and montmorillonite afforded a higher ether yield. The resulting high-molecular gasoline additive is less water-soluble and has a lower vapor pressure than MTBE. The United States does not use MTBE any longer.

HYDROGEN PRODUCTION FROM METHANE, METHANOL, AND OTHER SOURCES

According to Sanfilippo (Snamprojetti Co, Italy; p. 91), uncontrolled energy consumption undermines the principle of sustainable development. The expensiveness of hydrogen from synthesis gas prompts researchers to seek new ways of producing hydrogen. Attention is again attracted by the old, iron–steam method of H$_2$ production. Of the oxide pairs considered for this process, iron oxide appears to be the best. Iron metal is oxidized by water vapor, and the resulting oxides are reduced by methane:

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2,$$
$$3FeO + H_2O \longrightarrow Fe_3O_4 + H_2,$$

$$4Fe_2O_3 + CH_4 \longrightarrow 8FeO + CO_2 + 2H_2O,$$
$$4Fe_2O_3 + 3CH_4 \longrightarrow 8Fe + 3CO_2 + 6H_2O.$$

This technology allows pure hydrogen to be obtained without producing synthesis gas as an intermediate product.

Otsuki (Tokyo Institute of Technology; p. 97) reported the modified oxides Cu–Cr–FeO$_x$ and Ni–Cu–FeO$_x$ as catalysts of the same process. The admixtures in iron oxide decrease the reduction temperature from 600–700 to 300–400°C and prevent iron agglomeration. Copper and nickel bring about active sites necessary for methane activation.

Hydrogen can also be obtained by direct decomposition of methane into carbon and hydrogen. Chen (Institute of Chemical Physics, Dalian, China; p. 97) studied the formation of hydrogen and carbon nanotubes on Al$_2$O$_3$-supported Fe, Co, and Ni. At 750°C, the activity order (Fe > Co > Ni) is opposite to the orders of metal melting points and deactivation onset temperatures. Doping the Ni/Al$_2$O$_3$ catalyst with copper increases its activity. With Co, this effect is not observed.

Mirodatos (Institute of Catalysis, Villeurbanne, France; p. 79) studied the two-stage cracking of CH$_4$ on Pt/CeO$_2$ at 400°C. Here, hydrogen formation is facilitated owing to the capacity of the CeO$_2$ surface to hold carbon. It was demonstrated by *in situ* IR spectroscopy that surface formates are intermediates in this process.

HYDROCARBON PRODUCTION METHODS

Along with FTS, other methods of hydrocarbon production from natural gas have been developed in recent years. Great advances have been made in the MTO method, in which methanol is converted into lower olefins on a zeolite catalyst. In a plenary report, Chen (UOP Co., Des Plaines, the United States, in collaboration with Norsk Hydro, Norway; p. 1) reported the improvement of the MTO process by UOP. With the

aluminum phosphate catalyst SAPO-34, this company achieved a $C_2H_4 + C_3H_6$ yield of about 80% and complete methanol conversion. Moreover, with new catalysts, the yield of these olefins was as high as 85–90%. This high selectivity is due to small pore size (4 Å in SAPO against 5.5 Å in HZSM-5). The propylene : ethylene ratio is 1.33. The company constructed a plant with an annual ethylene production capacity of 400 000 t.

Based on UOP–Norsk Hydro technology, Statoil, another Norwegian company, developed a project of a polyethylene and polypropylene plant with a production capacity of 10 000 t per day in Nigeria (see the report by Olsvik, Norway; p. 19). Thus, ethylene and propylene produced by the MTO method and their polymers are entering the world market.

There have been studies on the nonoxidative dehydroaromatization of methane into benzene and naphthalene (reactions discovered by Dalian researchers) on the Mo/HZSM-5 catalyst. Ichikawa (Catalysis Center, Sapporo, Japan; p. 553) demonstrated that adding CO_2 to methane increases the activity of Mo/HZSM-5 and Re/HZSM-5. Catalyst performance is also improved by periodically adding hydrogen to remove carbon, which is a catalyst-poisoning substance. Huang (Xiamen University, China; p. 565) studied CH_4 dehydroaromatization on HZSM-5- and HMCM-22- supported W–M (M = Mn, Zn, Ga, Mo, or Co) catalytic systems. The maximum benzene selectivity was 70% at a conversion of 17%. A deactivated W catalyst can be fully reactivated by reoxidation. Kang (Changchun University, China; p. 631) synthesized a new support (MCM-49) for the molybdenum catalyst for methane dehydroaromatization. With regularly shaped hexagonal MCM-49 particles, 300–500 nm in diameter and 25–50 nm in thickness, benzene forms in high yield and the catalyst lifetime is long. At 700–800°C, methane conversion was 10–12% and benzene selectivity was up to 90%.

Soimosi (Szeged University, Hungary; p. 559) studied reactions of ethane, propane, and n-butane on Re/ZSM-5. As in the case of methane, these reactions yield aromatic hydrocarbons.

Borko and Guczi (Institute of Isotopes, Hungarian Academy of Sciences, Budapest; p. 601) studied nonoxygen methane conversion into C_2 hydrocarbons on Pt–Co/Al$_2$O$_3$ and Pt–Co/zeolite NaY. In this process, raising the temperature and pressure reduces catalyst poisoning. However, the C_2 yield was low: at 750°C and 1.0 MPa, methane conversion was 0.24% and ethylene selectivity was 28%.

Kotel'nikov (Yarsintez Co., Yaroslavl, Russia, collaborating with Snaprojetti, Italy; p. 67) reported the large-scale production of light olefins (propylene, isobutylene, and isoamylenes) by alkane dehydrogenation. An Al–Cr catalyst, a fluidized-bed reactor, and a regenerator are used in this process.

CATALYTIC COMBUSTION

Several reports were devoted to the catalytic combustion of natural gas. This process was unrelated to the main problems discussed at the symposium. It was the subject of occasional reports made for the most part by Chinese participants.

Three reports dealt with catalytic combustion on Mn-substituted barium hexaaluminate, $BaMnAl_{12}O_{19}$. Richardson (Houston University, the United States; p. 457) demonstrated that, in high-temperature processes, foamy systems are superior to ceramic monoliths. They ensure perfect mixing of the reacting gases and have no hot spots. As a consequence, NO_x emission is reduced. Teng (Institute of Chemical Physics, Dalian, China; p. 493) synthesized $BaAl_{12}O_{19}$ nanoparticles using inverted nonionic emulsions. Depending on the emulsifier (polyoxyethylene, tridecyl ether, or n-hexyl ether), the resulting nanoparticles may have the shape of a sphere, cylinder, spindle, etc. In turn, gas combustion depends on particle shape. For example, gas ignition occurs at 700–770°C on $BaAl_{12}O_{19}$ needles and at a temperature 90°C higher on $BaAl_{12}O_{19}$ spheres.

OXIDATIVE TRANSFORMATIONS OF METHANE

Of the oxidative transformations of methane, only partial CH_4 oxidation into synthesis gas and CH_4 combustion have found industrial application. Much was expected of the oxidative condensation of methane (OCM) into C_2 hydrocarbons. At present, this project is no longer backed because of the low $C_2H_4 + C_2H_6$ yield (20–25% at best).

Simon (Laboratory of the Chemical Physics of Reactions, Nancy, France; p. 571) reported the detailed mechanism of OCM on La_2O_3 at 750–900°C. Kinetic calculations were based on 450 elementary homogeneous reactions and only six heterogeneous reactions. For the latter, k_0 values were set using absolute reaction rate theory and E was estimated by analogy with homogeneous reactions, According to the reporter, the rate-limiting step of this process is O_2 dissociation on the surface.

Green (Oxford University, England; p. 607), in collaboration with Ji (Xiamen University, China), studied the active catalyst M–Mn–WO$_4$/SiO$_2$ (M = Li, Na, K, Ca, Ba, Fe, Co, Ni, Ag), which had been developed by Chinese researchers. The highest activity is shown by catalysts containing W only as WO_4 tetrahedra (e.g., Na_2WO_4). The presence of WO_6 octahedra reduces the selectivity of the catalyst. The following results were obtained with Na_2WO_4, the most active catalyst, at 800°C: CH_4 conversion, 29.5%; C_2H_4 selectivity, 42.6%; C_2H_6 selectivity, 23.8%; and C_2 yield, 19.3%.

In the catalytic oxidation of methane into methanol or formaldehyde, the yield of the desired product was still lower (a few percent).

Zhang (Tsinhua University, Peking, China; p. 541) reported methane-to-methanol oxidation on the 7% MoO_3/La–CoO catalyst. At 420°C and a high pressure of 5 MPa, a high selectivity (60%) and a high CH_3OH yield were observed. Raising the O^-/O^{2-} ratio on the surface increases catalytic activity and CH_3OH selectivity.

Parmaliana (Messina University, Italy; p. 535) has continued to investigate the catalytic oxidation of CH_4 into formaldehyde. A new method for iron hydroxide precipitation has been developed to reduce Fe_2O_3 particle size and raise the activity of the Fe_2O_3/SiO_2 catalyst. With this catalyst, at 650°C, methane conversion is 2.2–5.4% and CH_2O selectivity is 52–84%.

Periana (University of Southern California, the United States; p. 493), who discovered the liquid-phase oxidation of methane into methanol in the presence of mercury salts and concentrated H_2SO_4, continues research in this field in cooperation with his Chinese colleagues. At the symposium, he reported CH_4 oxidation into CH_3OH in the presence of the Pt(II)– η-(2,2'-bipyridyl) complex in dry (102%) H_2SO_4. With this catalyst, CH_4 conversion into the $CH_3OSO_3H + CH_3OH$ mixture was 75%. The catalyst was received from Catalytica Co.

Bell et al. (University of California, Berkeley, the United States; p. 523) considered the direct synthesis of methanesulfonic acid from CH_4 and SO_3 in the presence of radical-reaction initiators: $K_2S_2O_8$, $K_4P_2O_8$, CaO_2, and BaO_2. The highest conversion (90%) was observed with CaO_2. Acetic acid was obtained by reacting CH_4 and CO_2 in fuming H_2SO_4 in the presence of $K_2S_2O_8$ and V(acac)$_2$. Methane conversion was 7%.

Maeda (University of Kanagawa, Japan; p. 583) reported the formation of acetaldehyde and acetonitrile from CH_4, CO, and NO on the 5% Rh/SiO_2 and 5% Ru/SiO_2 catalysts at 130°C. Acetaldehyde forms through the insertion of CO into surface CH_3 groups. Acetonitrile results from the association of CH_3 and CN groups, and the latter form by the reaction between CO and NO.

CONVERSION OF LIGHT HYDROCARBONS

A number of reports at the Dalian symposium dealt with oxidative transformations of ethane, propane, and butane. There has been rapid progress in the synthesis of valuable products from lower paraffins in the recent years. This technology is usually discussed at congresses on catalytic oxidation, and it was somewhat beyond the scope of the Dalian symposium.

The oxidative dehydrogenation of ethane into ethylene was the subject of several reports. This reaction was carried out in unconventional ways. Mirodatos (Institute of Catalysis, Villeurbanne, France; p. 655), in collaboration with Chinese researchers from the Dalian Institute of Chemical Physics, studied this reaction in a membrane reactor. Air was on one side of the membrane and ethane on the other. The membrane was made of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-x}$ and was both electron- and ion-conducting. At 800°C, the C_2H_4 yield was 68%. After Pd was supported, it reached a value of 76%.

Grasselli (Institute of Chemical Physics, Munich; p. 673) carried out oxidative dehydrogenation with a molten Li/DyMg/Cl catalyst containing a small amount of Cr. This reaction was reported to be due the O^- and $\cdot OCl$ free radicals resulting from the interaction between LiCl and CrO_x in the melt. A C_2H_4 yield of about 77% was attained with a catalyst containing 8% Cr.

Holmen (Trondheim University, Norway; p. 685) studied the same reaction in a monolithic reactor with a cordierite-supported Pt or Pt–Sn catalyst. A C_2H_4 yield of about 63% was reached at 580°C with the Pt–Sn catalyst in the presence of H_2.

The oxidative dehydrogenation of propane was reported by Trifiro (Bologna University, Italy; p. 649). This reaction was carried out in a flow reactor at 500°C with a V_2O_5/SiO_2 catalyst to attain a C_3H_6 selectivity of 13–25% at complete O_2 conversion. Conducting this process in the reduction–reoxidation cyclic mode raises both the C_3H_8 conversion and propylene selectivity to 50%.

The selective oxidation of propane into acrolein was carried out with catalysts containing molybdenum and vanadium oxides. Huang (Xiamen University, China; p. 661) studied this reaction on $MoV_{0.2}Te_{0.1}O_x$/SiO_2. The following results were obtained at 550°C: propane conversion, 25%; acrolein selectivity, 30.1%; and acrolein yield, 6.7%. With Al_2O_3, CaO, or ZrO_2 as the support, acrolein selectivity was much lower.