ELSEVIER

Catalysis Today 37 (1997) 1–14

CATALYSIS TODAY

Development of active oxide catalysts for the direct oxidation of methane to formaldehyde

Richard G. Herman*, Qun Sun[1], Chunlei Shi, Kamil Klier, Chuan-Bao Wang, Hangchun Hu, Israel E. Wachs, Madan M. Bhasin[2]

Zettlemoyer Center for Surface Studies, Sinclair Laboratory, 7 Asa Drive Lehigh University, Bethlehem, PA 18015, USA

Abstract

Formaldehyde is currently produced from methane by a three-step process involving H_2/CO synthesis gas and methanol as intermediates, and development of a single-step process would have great economic incentive for producing this commodity chemical. A historical perspective is presented here in regard to the research carried out with heterogeneous metal oxide catalysts in attempts to achieve selective oxidative conversion of methane to formaldehyde. The concepts employed, both chemical and engineering, are described, and these include dual redox promoters and double-bed catalysts. More recent work in this laboratory has found V_2O_5/SiO_2 catalysts to be very active partial oxidation catalysts. The space–time yield of and selectivity toward formaldehyde are improved by the presence of steam in the methane/air reactant mixture, and an attractive feature of the product mixture is the low quantity of carbon dioxide produced. Space–time yields of >1.2 kg CH_2O/kg catalyst per h have been achieved.

Keywords: Formaldehyde; Methane oxidation; Vanadate catalyst; Cab-O-Sil

1. Introduction

The direct and selective oxidation of methane to formaldehyde has been of great interest from a long time, and there has been an extensive research effort during the last 25 years to develop such a process. A driving force for this effort has been the recognition that the current technology for producing formaldehyde consists of a multi-step process, schematically represented by Eq. (1), where the final step is the conversion of methanol to formaldehyde. In the three-step process, methanol is the formaldehyde precursor, and approximately 60% of the cost of this precursor arises from the high temperature steam reforming of methane to produce synthesis gas (step 1). Thus, there is a significant economic incentive to develop a one-step direct conversion of methane to formaldehyde (and/or methanol) that would by-pass methane reforming (step 1).

$$CH_4 \overset{1}{\Rightarrow} CO/H_2 \overset{2}{\Rightarrow} CH_3OH \overset{3}{\Rightarrow} CH_2O \qquad (1)$$

The primary oxidative conversion processes that methane undergoes are shown in Eqs. (2)–(6). All of

---

*Corresponding author.

[1] Present address: DuPont Central Research and Development, Experimental Station, P.O. Box 80356, Wilmington, DE 19880-0356, USA.

[2] Present address: Union Carbide Corporation, Industrial Chemicals Group, Technical Center, P.O. Box 8361, South Charleston, WV 25303, USA.

PII S0920-5861(96)00256-8

these reactions are thermodynamically favorable, but reaction (2) is the most favored of these oxidation processes. Thus, selective formation of formaldehyde (and methanol) can be viewed as a problem in controlling the kinetics of these reactions. The approach taken here is centered upon developing a selective oxide catalyst that is active at moderate reaction temperatures.

$$CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O \quad (2)$$

$$CH_4 + 0.5O_2 \Rightarrow CO + H_2 \quad (3)$$

$$2CH_4 + 0.5O_2 \Rightarrow C_2H_6 + H_2O \quad (4)$$

$$CH_4 + 0.5O_2 \Rightarrow CH_3OH \quad (5)$$

$$CH_4 + O_2 \Rightarrow CH_2O + H_2O \quad (6)$$

Intimately involved with selective formation of formaldehyde and methanol is the suppression of secondary reaction processes. At high temperatures, secondary reactions readily occur, especially those involving further reaction with free radicals. In the case of formaldehyde, direct oxidation to form CO can also occur, as represented by Eq. (7). To prevent reactions such as this from occurring, moderate temperatures and quick removal of reaction products from the synthesis zone of the reactor, i.e., short residence times, should be maintained.

$$CH_2O + 0.5O_2 \Rightarrow CO + H_2O \quad (7)$$

This report provides a perspective on the development of oxide catalyst for the selective oxidation of methane to formaldehyde. The emphasis is placed on the space–time yields of formaldehyde achieved in continuous flow reactors over heterogeneous catalysts, not on the %yields. There are many publications in this area of research, and those quoted here are principally those reporting significant increases in the productivity of formaldehyde synthesis directly from methane.

1.1. Progress before 1986

It had been reported that during World War II, formaldehyde was industrially produced from methane in Eastern Europe. In one process carried out in Copsa Mica, Romania [1], the reaction utilized a trace amount of NO as 'catalyst' and produced CH_2O from methane/air=1.0:3.7 mixtures (with recycle) at 400–600°C and atmospheric pressure in a silica/alumina ceramic-lined furnace. With four furnaces at the plant, 18 metric tons/month of formaldehyde (100% basis) were produced during World War II and at least until 1947. A small amount of methanol was formed as a side product.

Toward the end of World War II, a catalytic process was being developed by Germany at the Hibernia Stickstoffwerke at Herne using 0.5 wt% Ag_2O/BaO_2 supported on unglazed porcelain clips (10/90 wt%) [1], where the reactant mixture consisted of 30 vol% ozonized oxygen and 70 vol% dry coke oven gas, which resulted in ≈49% CH_4 in the final mixture. Demonstration runs of up to six weeks were made using typical catalyst volumes of 242 l, and it was reported that up to ≈30 g CH_2O/l catal per h, corresponding to ≈25% conversion of methane to formaldehyde with total gas hourly space velocity (GHSV)=100 l/l catal per h) could be produced at 80–120°C with the non-uniformly heated catalyst bed [1]. However, the typical flow rate employed was 8 l/l catal per h which resulted in a productivity of ≈1.2 g CH_2O/l catal per h.

Little further research was carried out on the direct synthesis of formaldehyde until 1970, when insight into the selective oxidation of methane to formaldehyde was provided by Cullis et al. [2] who were investigating metal catalysts dispersed on oxide supports. It was found that the product selectivity was switched from deep oxidation products toward formaldehyde by addition of pulses of chloromethane and dichloromethane to the methane/oxygen reactant mixture over a Pd/ThO_2 catalyst. Mann and Dosi observed similar behavior upon injection of halomethanes, especially with dichloromethane, into the reactant stream over Pd/Al_2O_3 catalysts [3]. Although the halogens exhibited a significant promotional effect, the productivity of formaldehyde over both catalysts was low.

In the early 1970s, two patents claimed high space–time yields of oxygenates over MoO_3-containing catalysts. In 1971, Dowden and Walker [4] reported very significant space–time yields of methanol and formaldehyde over a catalyst consisting of 5% $(MoO_3)_3{\cdot}Fe_2O_3$ supported on Al_2O_3/SiO_2=25:75 that had been sintered at 1000°C to obtain a surface area of 0.1 $m^2\,g^{-1}$. With a CH_4/O_2=96.9/3.1 vol% reactant mixture at 439°C and 5.3 MPa with GHSV of

46 000 h^{-1}, the methane conversion level was 2.1% and the observed productivities of formaldehyde and methanol were 100 and 869 g/kg catal per h, respectively. It was reported that these productivities were achieved by quenching the products just below the catalyst bed to <200°C by injection of water.

In 1975, it was disclosed by Stroud [5] that adding a small quantity of ethane to methane reactant was beneficial for oxygenate production over a $CuO{\cdot}MoO_3$ catalyst but at the same time, the oxygen conversion must be <75%. For example, with a reactant stream consisting of $CH_4/C_2H_6/O_2/N_2 \approx 89.5{:}5.9{:}3.3{:}1.3\%$ at 485°C, 2 MPa, and with GHSV=46 700 h^{-1}, 109.4 and 356.5 g/kg catal per h of formaldehyde and methanol were produced, respectively, corresponding to molar selectivities of 13.1 and 10.0%. Other products included some C_2 oxygenates, C_2H_4, CO and CO_2 [5].

In the early 1980s, it was found that silica (Cab-O-Sil) supported MoO_3 catalysts produced formaldehyde, methanol, and CO (with little or no CO_2) at 550–600°C and <0.1 MPa from $CH_4/N_2O/H_2O$ mixtures (typically ≈ 0.20–$0.25{:}1{:}1$) [6–9]. For example, Liu et al. [8] showed that with a $CH_4/N_2O/H_2O$ reactant mixture with partial pressures of 75/280/260 torr, respectively, at 594°C with GHSV=4387 l/kg catal per h, 17.44 g/kg catal per h of formaldehyde with 49.5% selectivity (6.0% CH_4 conversion) along with 2.93 g/kg catal per h of methanol (plus CO and CO_2) were produced over a MoO_3/Cab-O-Sil catalyst. Using O_2 as an oxidant in CH_4-rich reactant gas mixtures containing 3.11 mol% H_2O over a 5 wt% $MoO_3/SiO_2{\cdot}Al_2O_3$ catalyst, Pitchai and Klier obtained a similar space–time yield of CH_2O ($\approx$9 g/kg catal per h) at 600°C but no methanol [10]. A comparison of the formaldehyde productivities achieved in these quoted studies is shown in Fig. 1.

Liu et al. [8] provided particular insight into the mechanism of the activation of methane and conversion to oxygenates by proposing a mechanism, based on catalytic results (with N_2O as the oxidant in the presence of steam), electron spin resonance, and infrared spectroscopic evidence obtained with MoO_3/SiO_2 catalysts, in which $^{\bullet}CH_3$ reacted with the surface $Mo^{5+}O^{2-}$ moiety to form surface CH_3O^- species, as shown in Eqs. (8)–(12).

$$Mo^{5+} + N_2O \Rightarrow Mo^{6+}O^- + N_2 \quad (8)$$

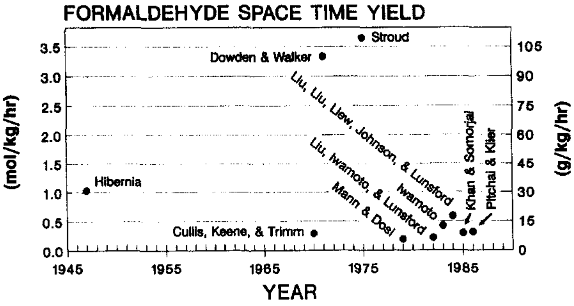

Fig. 1. Space–time yields reported up to 1986 for the direct synthesis of formaldehyde via methane oxidation over heterogeneous catalysts in continuous flow reactors.

$$Mo^{6+}O^- + CH_4 \Rightarrow Mo^{6+}OH^- + ^{\bullet}CH_3 \quad (9)$$

$$Mo^{6+}O^{2-} + ^{\bullet}CH_3 \Rightarrow Mo^{5+}OCH_3^- \quad (10)$$

$$Mo^{5+}OCH_3^- + Mo^{6+}O^{2-} \Rightarrow Mo^{4+} + Mo^{5+}OH^- + CH_2O \quad (11)$$

$$Mo^{6+}OH + Mo^{5+}OH^- \Rightarrow Mo^{5+} + Mo^{6+}O^{2-} + H_2O \quad (12)$$

As indicated, it was proposed that O^- was the reactive form of oxygen that abstracted a hydrogen from CH_4 to yield a methyl radical that subsequently formed the methoxide species. It was pointed out that reaction of the methoxide species with water in the reactant stream should yield methanol, although some studies did not detect methanol among the products formed [10]. Comparative studies of methane oxidation over MoO_3-based catalysts using N_2O and O_2 as oxidizing agents indicated that the partial oxidation products were favored by high CH_4/O_2 molar ratios but low CH_4/N_2O molar ratios [10]. The literature on selective oxidation of methane was reviewed up to 1985 by Pitchai and Klier [10], and mechanistic schemes proposed by others were also discussed.

1.2. *Progress after 1986*

1.2.1. *MoO_3/SiO_2 catalysts*

Significant improvements in the productivity of direct formaldehyde synthesis from methane were made after 1986. Much of the research effort continued with MoO_3-containing catalysts, but vanadium-based catalysts were also explored. The usual support for these catalysts was high surface area Cab-O-Sil, which is a silica that is particularly free of impurities, but other supports were investigated as well.

Using a $CH_4/O_2=9/1$ reactant mixture at 0.1 MPa and 650°C over Na-free MoO_3/SiO_2 catalysts (e.g., Cab-O-Sil or acid-washed (to remove alkali impurities) silica gel containing 1.8 wt% Mo), Spencer [11] obtained space–time yields of formaldehyde as high as 95.4 mol/kg catal per h (with GHSV=5000 h^{-1}, 6.9% CH_4 conversion was achieved with 25% selectivity to CH_2O). It was shown that as the methane conversion level was increased, e.g., by increasing temperature and/or decreasing GHSV, the formaldehyde selectivity decreased but the CO selectivity increased and CO_2 remained approximately 10% of the product slate. It was demonstrated that small quantities of sodium tended to poison the promotional behavior of Mo on the silica support and suppressed methane conversion and formaldehyde selectivity. The experimental data fit the model in which sodium inhibited the direct oxidation of methane to formaldehyde but promoted the oxidation of formaldehyde to carbon monoxide [12]. This inhibiting effect of sodium on a 7 wt% MoO_3/Cab-O-Sil catalyst was confirmed under low methane conversion conditions (<0.13%) by Kennedy et al. [13] when O_2 ($CH_4/O_2=28:1$) was used as the oxidant at 550°C. From the experimental data, Spencer [11] proposed that CO_2 and CH_2O were formed by parallel pathways over the Na-free MoO_3-promoted catalysts.

The structure of the molecularly dispersed surface molybdenum oxide species on SiO_2 has recently been determined by the application of several in situ spectroscopic methods. At elevated temperatures and in the presence of oxygen, in situ X-ray absorption near-edge spectroscopy (XANES) measurements revealed that the surface molybdenum oxide species on SiO_2 possess a coordination that is between tetrahedral and octahedral [14]. Corresponding in situ Raman and extended X-ray absorption fine structure (EXAFS) spectroscopy measurements demonstrated that the surface molybdenum oxide species on SiO_2 was present as an isolated species [14,15]. In situ infrared studies employing ^{18}O-labeling further showed that the surface molybdenum oxide species on SiO_2 possesses only one terminal Mo=O bond [16].

The preparation method and the nature of the silica support were shown to have no affect on the molecular structure of the isolated surface molybdenum oxide species on SiO_2 [17]. However, the presence of alkali impurities decreased the number of isolated surface molybdenum oxide species and formed new alkali molybdate compounds [18]. Corresponding temperature programmed reduction studies showed that alkali molybdate compounds generally decreased the amount of reducible oxygen available in the catalysts. The methane oxidation reactivity was found to correlate with the isolated surface molybdenum oxide species that did not form alkali molybdate compounds, which revealed that the oxygen associated with the alkali molybdate compounds was not readily available for methane oxidation.

In situ Raman studies of the MoO_3/SiO_2 catalysts under methane oxidation reaction conditions were also obtained in order to determine the influence of the reaction environment on the surface molybdenum oxide species. These studies demonstrated that the isolated surface molybdenum oxide species was essentially unchanged by the methane oxidation reaction environment [18]. There was no direct evidence for the formation of a $Mo–OCH_3$ species that may have been present in trace quantities, and consequently not detected. The $Mo–OCH_3$ species also could not be directly detected with in situ Raman spectroscopy during methanol oxidation [17]. However, the isolated surface molybdenum oxide species was not stable during methanol oxidation, and this resulted in the formation of microcrystalline MoO_3 particles that aggregated, perhaps due to the formation of $Mo–OCH_3$, i.e., the formation of mobile $Mo–OCH_3$ species might induce the agglomeration of surface molybdenum oxide species and crystallization of MoO_3 on SiO_2. The relative stability of isolated surface molybdenum oxide species on SiO_2 during methane oxidation suggests that such intermediate species are less stable during this reaction. It has also been proposed that the active state of the molybdenum oxide species in MoO_3/SiO_2 catalysts employed for methane oxidation may be in the form of silicomolybdic acid species, $H_4SiMo_{12}O_{40}$ [19]. Recent in situ Raman studies by Banares et al. [20] showed that this species can be formed by exposing the MoO_3/SiO_2 catalyst to water-saturated air at room temperature for an extended period of time, but it was shown that this species was not stable above 300°C and decomposed to form isolated surface molybdenum oxide species. The decomposition of bulk silicomolybdic acid species at 300°C has also been reported by Rocchiccioli-Deltcheff et al. [21]. Thus, silicomolybdic acid species are not stable at the much higher temperatures employed for methane oxidation, i.e., $\geq$500°C.

1.2.2. V_2O_5/SiO_2 catalysts

In contrast to the proposal that CO_2 and CH_2O were formed by parallel pathways from CH_4/O_2 over MoO_3-based catalysts [11], Spencer and Pereira [22] proposed that over V_2O_5/SiO_2 catalysts the following sequential pathway leads to CO_2 formation, i.e.,

$$CH_4 \Rightarrow CH_2O \Rightarrow CO \Rightarrow CO_2 \qquad (13)$$

The V_2O_5/SiO_2 (Cab-O-Sil) catalyst appeared to be more active than the corresponding MoO_3/SiO_2 catalyst, although the extrapolated data for the two catalysts at 575°C were similar, e.g., 32.5% CH_2O selectivity at 3% methane conversion. The sequential pathway over the V_2O_5/SiO_2 catalyst was consistent with the very low selectivities for CO_2 at low methane conversion levels and higher CO_2 selectivities at high CH_4 conversions observed over this catalyst.

Iwamoto, using N_2O in the presence of water as the oxidant instead of oxygen, also found that 2% V_2O_5/SiO_2 was a more active catalyst than 2% MoO_3/SiO_2 for oxidation of methane, and at 450°C a 92.7% selectivity to CH_2O was observed (0.5% CH_4 conversion to yield 1.12 g CH_2O/kg catal per h) [23]. However, upon increasing the temperature to 550°C with the $CH_4/N_2O/H_2O/He=1/2/4.7/2.3$ reactant mixture at GHSV=1800 l/kg catal per h, the activity of the catalyst increased to 11.2% CH_4 conversion, but the selectivity toward CH_2O decreased to 12.7% (but with a higher CH_2O productivity of 3.4 g/kg catal per h) because of the formation of methanol.

During this same period of time, Lee and Ng [24] also investigated methane oxidation over 2 wt% vanadia-promoted SiO_2, $TiSiO_2$, and TiO_2 catalysts. The V_2O_5/SiO_2 catalyst was the most active of those investigated and gave the highest selectivity and productivity for formaldehyde. It was observed that N_2O was a much better oxidant than O_2, in terms of both activity and CH_2O selectivity, under the reaction conditions employed. With a reactant mixture of $CH_4/N_2O/He=1/4/2$ with GHSV=4800 l/kg catal per h over a 2 wt% V_2O_5/SiO_2 catalyst, a high space–time yield of 132.2 g CH_2O/kg catal per h was obtained at 600°C and 0.1 MPa. This productivity occurred with a high methane conversion level of 31.5% and a formaldehyde selectivity of 51.0% (plus 35.4% CO and 13.6% CO_2). However, upon increasing the reaction temperature to 650°C, the CH_2O productivity dropped to zero. Under similar reaction conditions (600°C), a 1.7 wt% MoO_3/SiO_2 catalyst was appreciably less active (7.5% CH_4 conversion) and selective (42.7% CH_2O) than the corresponding vanadium catalyst, yielding 20.1 g of CH_2O/kg catal per h [24].

Recently, the molecular structure of the vanadium oxide species on the surface of 1–10 wt% V_2O_5/SiO_2 catalysts has been determined by in situ solid state ^{51}V NMR, Raman spectroscopy, and EXAFS/XANES studies. Comparison of the ^{51}V NMR spectra of the V_2O_5/SiO_2 catalysts to reference compounds with well-defined structures demonstrated that the surface vanadium oxide species possessing a tetrahedral structure contained one terminal V=O bond and three bridging V–O–Si bonds [25]. Similar conclusions were obtained from EXAFS/XANES measurements [26]. Raman studies were consistent with the above structure and also showed that the surface vanadium oxide species on SiO_2 were present as isolated moieties [25,27].

In situ Raman studies of the V_2O_5/SiO_2 catalysts were also utilized to monitor the influence of the methane oxidation reaction conditions on the isolated surface vanadium oxide species. It was shown that during methane oxidation at 500°C, the isolated surface vanadium oxide species were not altered by the reaction environment (neither shift nor diminution in the intensity of the 1034 cm^{-1} V=O line) and no V–OCH_3 species were directly detected [28]. However, surface V–OCH_3 species were readily detected during methanol oxidation over these catalysts [29]. Unlike the MoO_3/SiO_2 catalytic system, the active component in the V_2O_5/SiO_2 catalysts did not agglomerate, i.e., no microcrystalline V_2O_5 particles were formed, but a small amount of the vanadium oxide did volatilize during the reaction. Thus, it may be possible that trace quantities of V–OCH_3 species are present during the methane oxidation-to-formaldehyde reaction, but the small number of these surface species would be below Raman detectibility. It is more likely that such species are present under conditions that generate methanol during selective methane oxidation.

1.2.3. *Double redox catalysts*

A different approach to catalyst development was taken wherein double redox cations, e.g., Cu/Fe, were doped into high surface area [30] and low surface area supports [31,32]. For example, Anderson and Tsai synthesized a lattice-substituted Fe-ZSM-5 zeolite that was ion exchanged with Cu^{2+} and carried out methane oxidation studies with N_2O as the oxidant [30]. With $CH_4/N_2O=80/20$ at 342°C and GHSV=431 000 h^{-1}, 6.2 C% of the product was CH_2O (at 1.12% CH_4 conversion). However, it was reported [30] that 50 C% of the product was CH_3OH, with the remainder being CO_2 (35%) and CO (8.5%). Decreasing the GHSV led to a slightly higher methane conversion but lower selectivity toward CH_2O and CH_3OH.

Sojka et al. [31,32] also utilized redox couples as methane oxidation catalysts, where low surface area ZnO (e.g., 0.5 m^2/g) was employed as the support and air was used as the oxidant. The concept was to predominantly activate oxygen on one reactive center, e.g., $Cu^{1+/2+}$, while the second center would activate methane to form stabilized methyl radicals, e.g., on $Fe^{3+/2+}$ or $Sn^{4+/2+}$. Of those investigated, the best catalyst consisted of $Cu^{1+}/Fe^{3+}/ZnO=1/1/98$. As the reaction temperature was increased with this catalyst, the conversion of methane increased while the formaldehyde selectivity decreased. An optimum temperature of 750°C was observed for the formation of CH_2O in terms of productivity. At this temperature and at 0.1 MPa, a CH_4/air=1/1 reactant mixture with GHSV=70 000 l/kg catal per h produced 76 g of CH_2O/kg catal per h [32]. The methane conversion was low (2.5%), as was the formaldehyde selectivity (10%). The cationic dopants were found to be surface-enriched as Coulombic pairs and to function by switching the selectivity toward CH_2O and away from CO_2 at lower temperatures (<700°C) and away from C_2 hydrocarbons at higher temperatures (>700°C). A schematic model of the catalyst is shown in Fig. 2.

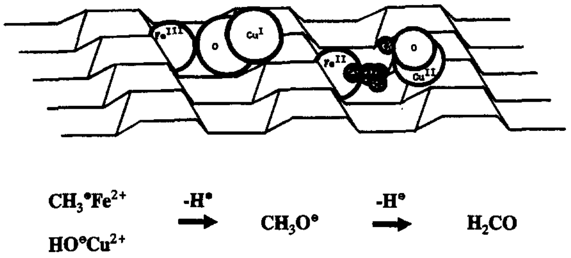

Fig. 2. Schematic of the active ZnO surface containing Cu^{1+}/Fe^{3+} Coulombic redox pairs doped into the ZnO matrix.

While undoped ZnO exhibited only low activity, Hargreaves et al. [33] demonstrated that a low surface area (≈3 m^2/g) unpromoted C_2 coupling catalyst, i.e., MgO prepared by calcination of magnesium hydroxycarbonate, could be induced to produce formaldehyde as the principal product by controlling the reaction conditions. With a CH_4/O_2/diluent=6:1:6 reactant mixture at 850°C and 0.1 MPa, the oxygen consumption was controlled by varying the flow rate in the range of GHSV=1000–48 000 h^{-1}. At high O_2 conversion (>70%), CO_2 was the dominant product, while in the range of about 10–70% O_2 conversion, CO was the principal product formed. However, at low levels of O_2 conversion in the range of 3–5%, formaldehyde was formed with ≈60% selectivity, with $CO \approx CO_2 \approx 20\%$. Hargreaves et al. [33] proposed that the product selectivity for the partial oxidation of methane was controlled by the balance between methyl radical coupling and oxidation, which was guided by the abundance of O_2 through the reaction zone. It was subsequently pointed out that the maximum in the CH_2O selectivity pattern shown [33] corresponded to a formaldehyde productivity of 9 mol (270 g)/l catal per h [34] (bulk density of the catalysts was not given).

1.2.4. *Double-bed catalysts*

Another reaction engineering approach to produce high space-time yields of CH_2O was taken by Sun et al. [35], where a double catalyst bed was utilized to enhance the productivity of CH_2O. The concept of this experiment is shown in Fig. 3, where the first catalyst consisted of 1 wt% SrO/La_2O_3, a very active methyl radical generator that oxidatively produces C_2 hydrocarbons from methane [36–39], while the second bed consisted of 2 wt% MoO_3/SiO_2 that is envisioned to trap the $C^\bullet H_3$ species long enough for reaction with activated oxygen on the surface of the catalyst, see Eqs. (8)–(11). Indeed, by using the dual-bed configuration, CH_4 conversion was increased by two orders of magnitude at 630°C, while CH_2O space–time yield was tripled, as shown in Table 1 [35].

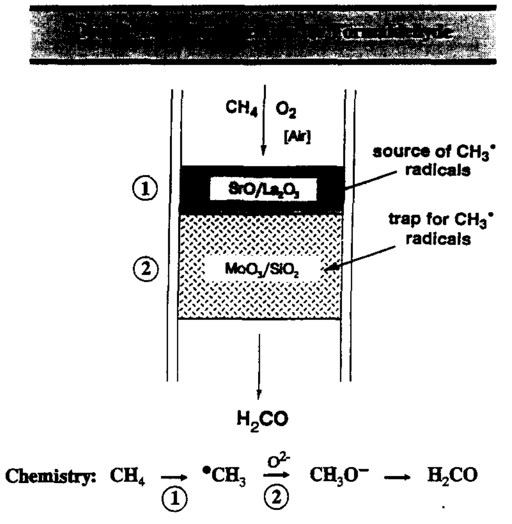

Fig. 3. Schematic drawing of the double-bed catalyst configuration for the oxidative conversion of methane to formaldehyde.

It is clear from the data in Table 1 that a small amount of the SrO/La_2O_3 catalyst activated a large quantity of methane, and, indeed, the available oxygen was almost completely consumed and converted to products. Formation of C_2 hydrocarbons was observed, and the quantity of and selectivity to these increased with temperature. At the same time, the CO_2 selectivity progressively decreased. A mechanically mixed bed of the two catalysts produced almost no formaldehyde, which appeared to be converted to CO, in contrast to the double-bed configuration.

1.2.5. SiO_2 as a catalyst

As previously pointed out, most of the catalysts investigated for the conversion of methane to formaldehyde have been silica-supported catalysts. It has been shown that at least some silicas can activate methane and under some reaction conditions, formaldehyde is observed as a product [11,40–45]. Various forms of SiO_2 are available, and as pointed out earlier, the fumed silica Cab-O-Sil is a common form utilized as a catalyst support because it is of rather high purity. A comparison of Cab-O-Sil with a silica gel (Grace 636 gel) in terms of methane conversion and product selectivity has been carried out at 730°C [46], and the experimental results are shown in Table 2. Blank reactor runs with no catalyst showed negligible conversion of methane.

The data in Table 2 show that the silica gel was much more active than the Cab-O-Sil, although both were high surface area materials, i.e., 385 and 480 m^2/g, respectively. Both silicas produced significant quantities of formaldehyde, but both also formed C_2 hydrocarbons. Over metal oxide promoted silicas, methyl radicals are stabilized long enough to react with activated oxygen to form oxygenates so that hydrocarbon synthesis is minimal or even eliminated. Lowering the reaction temperature to 630°C led to 100% formaldehyde selectivity (0.05 mol% CH_4 conversion) over the Cab-O-Sil catalyst, yielding 24.3 g of CH_2O/kg catal per h [28].

As the above discussion shows, between 1986 and 1992 progress was made in increasing the space–time yield of formaldehyde formed directly from methane

Table 1
Methane conversion, formaldehyde space–time yield (STY), and formaldehyde selectivity from CH_4/air=1.5:1.0 at ambient pressure and with GHSV=70 000 l/kg catal per h over a single-bed 2 wt% MoO_3/SiO_2 catalyst and a double-bed consisting of 1 wt% SrO/La_2O_3||2 wt% MoO_3/SiO_2 catalysts [35]

Temperature (°C)	CH_4 conversion (mol%)	H_2CO STY (g/kg catal per h)	H_2CO selectivity (C atom%)
(a) MoO_3/SiO_2 (0.100 g)			
595	0.02	10.8	100
630	0.08	37.9	100
665	0.24	39.7	31.5
(b) SrO/La_2O_3||MoO_3/SiO_2 (0.025 g/0.100 g)			
525	0.4	2.3	1.0
560	3.1	18.8	1.3
595	5.4	62.1	2.4
630	8.2	129.0	3.3
665	11.3	52.4	1.0

Table 2
Methane conversion, formaldehyde space–time yield (STY), and product selectivities from CH_4/air=1.5:1.0 at ambient pressure and 730°C with GHSV=70 000 l/kg catal per h over Cab-O-Sil (EH-5) and silica gel (Grace 636) catalysts [46]

Silica	CH_4 conversion	H_2CO STY	Selectivity (C mol%)			
	(mol%)	(g/kg per h)	CH_2O	C_2HC	CO	CO_2
Cab-O-Sil	0.31	75.7	46.0	39.1	–	14.9
Gel	1.36	267.0	38.8	11.4	41.8	8.0

over oxide catalysts, and a comparison of these results is shown in Fig. 4. It is noted that the latter investigations utilized air or oxygen as the oxidizing component of the reactant mixture.

There are a number of ways to manipulate reaction conditions so that high %yields, e.g., elevated temperatures with very small catalyst beds, or space–time yields, e.g., by employing high GHSV, are obtained. For example, it was shown that a silica gel catalyst was more active than Cab-O-Sil (Table 2), and to increase the space–time yield of formaldehyde even more over the silica gel catalyst, the reaction temperature was increased to 780°C and the reactant gas flow was increased stepwise to GHSV=560 000 l/kg catal per h [46]. Under these conditions, only 0.68 mol% CH_4 conversion was obtained, but the space–time yield of 812.8 g CH_2O/kg catal per h was achieved. The observed product selectivity (C atom%) was 28.0% CH_2O, 7.2% ethene, 31.6% ethane, 30.0% CO, and 3.2% CO_2.

Our more recent research has compared a variety of unsupported and supported, i.e., on SiO_2, TiO_2, and SnO_2, metal oxides in controlling the activity and selectivity of catalytic methane conversion [28]. It was confirmed that silica-supported V_2O_5 and MoO_3 catalysts showed the highest selectivity toward partial oxidation products, and these catalysts have now been investigated further. It is shown that the V_2O_5-based catalyst exhibits the highest observed productivity of formaldehyde and that progress is being made in increasing the selectivity to formaldehyde synthesis at appreciable methane conversion levels.

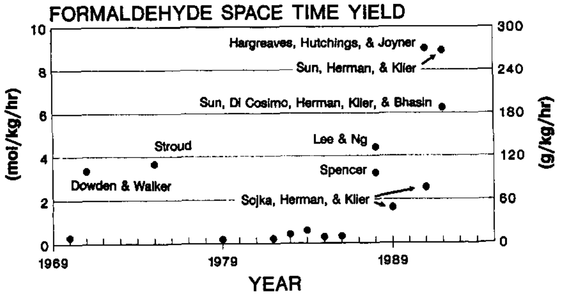

Fig. 4. Comparison of space–time yields of formaldehyde achieved recently by direct methane oxidation over heterogeneous catalysts in continuous flow reactors.

2. Experimental

Amorphous SiO_2 (Cab-O-Sil EH-5, surface area=380 m^2/g) was utilized as the catalyst support, and incipient-wetness impregnation with solutions of different precursors, i.e., $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, NH_4VO_3, and $VO(i\text{-}OC_3H_7)_3$ under N_2 was the general method used to prepare V_2O_5/SiO_2 and MoO_3/SiO_2 catalysts. Prior to impregnation, the Cab-O-Sil was slurried with water, filtered, dried at 120°C overnight, and calcined at 500°C for 24 h. Unless stated otherwise, each catalyst was dried at ambient temperature, heated at 120°C overnight, and then calcined at 500°C for 4 h in flowing air.

Catalytic testing was carried out in a fixed-bed continuous-flow 9 mm o.d. (7 mm i.d.) quartz reactor, typically using 0.100 g of catalyst [46]. The reactor narrowed to 5 mm i.d. below the catalyst bed to speed the removal of reaction products from the hot reactor zone. The testing system had two independently controlled inlet gas lines. A standard reactant mixture of CH_4/air=1.5/1.0 was used at 0.1 MPa pressure. Methane was ultra-high purity grade from Air Products and Chemicals. The N_2/O_2=80/20 vol% was a synthetic air mixture prepared by Air Products and Chemicals.

Each catalytic test was typically carried out for 2–4 h under steady-state reaction conditions and reactant conversions. The principal products analyzed by automated on-line sampling using gas chromatography were CO_2, CO, C_2 hydrocarbons (C_2H_6 and C_2H_4), and H_2O. Condensable products were collected from the exit stream with dual water scrubbers in series, usually with the first at ambient temperature and the second at ≈0°C, and CH_3OH was analyzed by GC/MS, while CH_2O was quantitatively determined by iodometric titration [47]. The carbon mass balance was always better than 90%, and usually better than 95%.

3. Results and discussion

3.1. Comparison of Cab-O-Sil-supported MoO_3 and V_2O_5

In screening the V_2O_5/SiO_2 and MoO_3/SiO_2 catalysts, it was observed that lower reaction temperatures tended to result in little or no formation of C_2 hydrocarbon products, which are formed by gas phase free radical reactions. Therefore, to minimize gas phase reactions, the temperature of 630°C was utilized as a standard temperature for catalyst comparisons. The catalytic results obtained with Mo- and V-containing Cab-O-Sil catalysts are shown in Table 3, and it is evident that 2 wt% MoO_3/Cab-O-Sil catalyst was only slightly more active than the support alone. In contrast, the V_2O_5/SiO_2 catalyst was very active under the reaction conditions employed. It is also shown that adding MoO_3 to the V_2O_5/SiO_2 catalyst hardly affected the catalytic behavior of the catalyst. Thus, the surface dispersed V_2O_5 is the active component of the catalyst. For the V_2O_5-containing catalysts, the CH_2O productivity was maintained at 680±5 g/kg catal per h.

The results shown in Table 3 are in qualitative agreement with batch reactor studies carried out by Parmaliana et al. [48,49], in which the reactants ($CH_4/O_2=2/1$, generally in N_2/He) at 0.17 MPa were recycled and condensable oxygenated products were trapped at −15°C. It was found that a 2.0% V_2O_5/Cab-O-Sil catalyst was an order of magnitude more active than a 2.0% MoO_3/Cab-O-Sil catalyst [48], and a space–time yield of up to 320 g CH_2O/kg catal per h was obtained at 600°C. It was also observed [48] that an updoped precipitated silica was much more active for methane conversion than was the Cab-O-Sil and could produce up to 303 g CH_2O/kg catal per h at 650°C by itself, confirmation of the continuous flow results reported in Table 2[46]. (It is noted again that precipitated silica often contains impurities that contribute to the catalytic behavior of the silica.) It was later reported that a 2.2% V_2O_5/Cab-O-Sil catalyst could produce up to 704 g CH_2O/kg catal per h in the batch reactor at 650°C [49], while a 5% V_2O_5/SiO_2 produced 819 g CH_2O/kg catal per h under the same conditions (with 0.078% CH_4 conversion per pass) [48]. A comparison experiment with the same catalyst in a conventional continuous flow reactor produced 760 g CH_2O/kg catal per h from $CH_4/O_2/N_2/H_e$ ≈2:1:2:6 (GHSV=60 000 l/kg catal per h) at 0.17 MPa and 650°C with 13.5 mol% CH_4 conversion [50].

Table 3
Methane conversion, formaldehyde productivity (STY: space–time yield, and product selectivity for methane oxidation by air (CH_4/air=1.5:1.0) over Cab-O-Sil (C) and Cab-O-Sil-supported metal oxide catalysts (0.100 g) at 630°C and 0.1 MPa with GHSV=70 000 l/kg catal per h

Catalyst	CH_4 conversion	CH_2O STY	Selectivity (C mol%)			
	(mol%)	(g/kg per h)	CH_2O	C_2HC	CO	CO_2
SiO_2=(C)	0.05	24.3	100	–	–	–
2% MoO_3/(C) [a]	0.08	37.9	100	–	–	–
1% V_2O_5/(C) [b]	9.52	685	15.7	1.7	76.4	6.3
1% V_2O_5/3%MoO_3/(C) [c]	8.47	675	16.6	2.0	73.5	7.9

[a] $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was used to impregnate the Cab-O-Sil.

[b] $VO[i\text{-}OC_3H_7]_3$ was used to impregnate the Cab-O-Sil. After drying, the catalysts were calcined under N_2 and then in flowing air at 500°C for 4 h.

[c] Prepared by first impregnating the Cab-O-Sil with the Mo salt and then the V salt.

Table 4
The space–time yields of products formed at 0.1 MPa over the double catalyst bed, where the first bed contained the $SO_4^{2-}/SrO/La_2O_3$ catalyst and the second bed consisted of 1 wt% V_2O_5/SiO_2. The bed of each catalyst was 0.100 g and the reactant mixture was water-free CH_4/air ≈1.5:1 with GHSV=141 000 l/kg catal per h relative to each catalyst and 70 500 l/kg catal per h for the double-catalyst bed

Temperature (°C)	Conversion (mol%)	Space–time yield (g/kg catal per h)				
		C_2HC	CH_2O	CH_3OH	CO	CO_2
550	13.8	1575	167	17	2980	11275
575	14.5	1946	247	21	3586	10100
600	15.2	2720	434	39	3951	8165
625	15.5	3025	746	40	4232	6895
650	15.1	3577	940	48	4234	4491

3.2. *Vanadium-based catalysts*

Table 3 indicates that the vanadium-containing catalyst was more active than the molybdena-doped Cab-O-Sil catalyst. The double-bed reactor configuration was again employed with this catalyst, but sulfated SrO/La_2O_3 was utilized as the top bed instead of the basic 1 wt% SrO/La_2O_3 catalyst because it has been shown that a 1 wt% SO_4^{2-}/1 wt% SrO/La_2O_3 catalyst is appreciably more active than the non-sulfated doped catalyst [38,39]. Using equal quantities of the $SO_4^{2-}/SrO/La_2O_3$ and 1 wt% V_2O_5/SiO_2 catalysts, the data in Table 4 were obtained. While a larger mass of the first catalyst was employed here, comparison of these data with those given in Table 1 indicates that higher CH_4 conversion and higher productivity of CH_2O were obtained with the vanadium catalyst system. In addition, an appreciable space–time yield of CH_3OH was also observed.

This $SO_4^{2-}/SrO/La_2O_3\|V_2O_5/SiO_2$ catalyst system was very active and the oxygen conversion level increased from ≈67% to ≈88% as the reaction temperature was increased. At the same time, the productivity and selectivity of CO_2 decreased while those of all other products increased with increasing reaction temperature. At 650°C, nearly 1 kg of formaldehyde/kg catal per h was formed using this catalyst configuration. The C_2 hydrocarbon productivity (with ethane as the dominant C_2 hydrocarbon) was significant, and further studies should decrease the mass of the first catalyst bed (the $SO_4^{2-}/SrO/La_2O_3$ free-radical generating catalyst) to determine the optimum ratio of the two catalyst beds for producing CH_2O and CH_3OH at high rates while minimizing the formation rates of the other products, principally the C_2 hydrocarbons.

3.3. *Addition of steam to the reactant mixture*

The concept of using steam in the reactant stream to enhance the selectivity of oxygenates was explored in the 1980s [7–10] utilizing N_2O [7–9] or O_2 [10] as the oxidant. The current investigations have employed air as the oxidizing component in the CH_4/air=1.5/1.0 reactant mixture (CH_4/O_2 molar ratio=7.5). It has been demonstrated that the presence of steam in this CH_4/air reaction mixture over the double-bed catalyst shifted the selectivity toward the formation of formaldehyde and methanol [51]. An example of this is shown in Table 5, where the productivities of the oxygenates can be directly compared with those obtained (Table 4) when the reactant mixture did not contain steam.

It is evident that the presence of a small quantity of steam significantly enhanced the productivity of CH_2O and CH_3OH, while slightly inhibiting the formation of CO and CO_2 (compare Table 5 with Table 4). At the same time, the productivity of the C_2 hydrocarbons was less at lower temperatures but was slightly higher at higher reaction temperatures when steam was present. At 600°C, the productivity of methanol was over 100 g/kg catal per h, while at higher temperatures the productivity of formaldehyde was >1 kg/kg catal per h (with a HCHO selectivity of 7.6 C mol%). It can also be seen that the presence of steam in the reactant mixture ($CH_4/N_2/O_2/H_2O$ = 1.5/0.8/0.2/0.2) only slightly depressed the methane conversion level.

Table 5
The conversion of methane and the space–time yields of products formed over double-bed catalysts, where the first bed contained $SO_4^{2-}/SrO/La_2/O_3$ catalyst and the second bed consisted of 1 wt% V_2O_5/Cab-O-Sil. The bed of each catalyst was 0.100 g and and the reactant stream was CH_4/air/steam=1.5:1.0:0.2, with GHSV=153 000 l/kg catal per h relative to each catalyst bed and 76 500 l/kg catal per h for the double catalyst bed

Temperature	Conversion	Space–time yield (g/kg catal per h)				
(°C)	(mol%)	C_2HC	CH_2O	CH_3OH	CO	CO_2
550	11.1	1438	210	31	2574	8136
575	11.9	1782	576	70	3228	6661
600	12.8	2690	739	104	3537	4687
625	15.3	3303	1082	86	3815	5842
650	14.8	3614	1248	89	3876	3967

The effect of steam on the formation rate of each of the products in this reactor configuration can be more clearly seen by tabulation of a performance index (PI(1)), defined as the space–time yields of products in the presence of steam relative to the space–time yields of products in the absence of steam. The calculated performance indices are tabulated in Table 6. Since the GHSV was slightly lowered (7.8% lower) for the steam-free testing, the %CH_4 conversion was slightly higher than for the testing carried out in the presence of steam, which resulted in slightly more CH_4 converted to products in the absence of steam. Therefore, if steam played no role in the methane conversion process, PI(1) values slightly less than 1.00 would be expected. As shown in Table 6, the PI(1) for CO showed no significant variation with temperature. Therefore, the presence or absence of steam did not affect the CO productivity. The PI(1) of C_2HC increased slightly, perhaps indicating that the inhibiting effect of steam was decreased at higher reaction temperatures. The PI(1) for CO_2 showed that the presence of steam tended to inhibit the formation of this product at lower reaction temperatures, especially at 600°C. In contrast, the presence of steam significantly enhanced the formation of both formaldehyde and methanol. Over the temperature range studied, the presence of steam increased the formation rate of formaldehyde by factors of $\approx$1.3 to $\approx$2.3, at the same time methanol productivity was increased by factors ranging from $\approx$1.8 to $\approx$3.3, with a maximum at 575°C. This illustrates the important role of steam in forming the oxygenates directly from methane.

It was earlier proposed that a role of steam during partial oxidation reactions with methane should be to react with surface methoxide species to form methanol [8,10]. The results shown here with the double-bed catalyst configuration are consistent with this, where the first catalyst generates methyl radicals and the second catalyst bed acts as the methyl radical trapping

Table 6
The performance index (PI(1)), that is the ratio of space–time yields of products formed with the double-bed catalyst system in the presence of steam relative to the space–time yields of products observed in the absence of steam in the reactant mixture. The first bed contained the $SO_4^{2-}/SrO/La_2O_3$ catalyst and the second bed consisted of 1 wt% V_2O_5/SiO_2. The bed of each catalyst was 0.10 g and the reactant mixture was CH_4/air/(steam)=1.5:1:(0.2) with total GHSV=76 500 l/kg catal per h in the presence of steam and 70 500 l/kg catal per h in the absence of steam

Temperature	PI(1)				
(°C)	C_2HC	CH_2O	CH_3OH	CO	CO_2
550	0.91	1.26	1.87	0.86	0.72
575	0.92	2.33	3.28	0.90	0.66
600	0.99	1.70	2.69	0.90	0.57
625	1.09	1.45	2.19	0.90	0.85
650	1.01	1.33	1.81	0.92	0.88

and oxygenate-forming catalyst. The additional H_2O present over the second catalyst bed, because of the injected steam, enhances the productivity of methanol. The principal reactions are schematically illustrated [51] by Eqs. (14)–(19), where $\square_o$ represents an oxygen vacancy and reactions (16) and (19) occur in parallel.

$$2CH_4 + 0.5O_2 \rightarrow {}^{\bullet}CH_3 + H_2O \qquad (14)$$

$$2{}^{\bullet}CH_3 + 2M^{(n+1)+}O^{2-} \rightarrow 2M^{n+}(OCH_3)^- \qquad (15)$$

$$2M^{n+}(OCH_3)^- + 2H_2O \rightarrow 2M^{n+}(OH)^- + 2CH_3OH \qquad (16)$$

$$2M^{n+}(OH)^- \rightarrow M^{n+}O^{2-} + M^{n+}\square_o + H_2O \qquad (17)$$

$$M^{n+}O^{2-} + M^{n+}\square_o + 0.5O_2 \rightarrow 2M^{(n+1)+}O^{2-} \qquad (18)$$

$$2M^{n+}(OCH_3)^- + 1.5O_2 \rightarrow 2M^{(n+1)+}O^{2-} + 2HCHO + H_2O \qquad (19)$$

Eq. (14) is for the first catalyst layer, while Eqs. (15)–(19) are for the second catalyst layer.

Further optimization of the vanadia-based catalysts can be carried out, and this might lead to both high activity and selectivity so that a single-bed catalyst can match the performance of the double-bed catalyst configuration. Research in this direction has been initiated, and the data in Table 7 show the trends in productivities and selectivities from a CH_4/air/steam=4/1/1 reactant mixture as the vanadium content of the catalysts was increased from 0.5 to 2.0 wt% V_2O_3. With this single-bed catalyst, no C_2 hydrocarbons were observed in the product mixture. While CO was the principal product formed under these reaction conditions, significant productivity and selectivity toward formaldehyde were obtained and both increased as the vanadium content of the catalyst was increased from 0.5 to 2.0 wt%. In addition, methanol was also formed, and its trends in productivity and selectivity followed those observed with CH_2O. The selectivity toward CO_2 was desirably low. It is pointed out that the high GHSV of 144 000 l/kg/h (Table 7) was utilized to approximate the gas flow rate over the V_2O_5/SiO_2 portion of the dual-bed reactor configuration that was employed to obtain the experimental data reported in Tables 4 and 5.

A further direction for optimization is illustrated in Table 8. In this experiment, the quantity of water injected into the reactant steam was greatly increased such that the methane and steam contents were nearly the same and the steam/O_2 ratio was 8.5. The presence of steam slightly inhibited the activation of methane, but it also significantly enhanced the selectivity to and productivity of formaldehyde.

Table 7

Methane conversions, space–time yields, and product selectivities obtained by air oxidation (CH_4/air/steam=4:1:1) over V_2O_5/Cab-O-Sil catalysts (0.100 g) at 600°C and 0.1 MPa with GHSV=144 000 l/kg catal per h

Vanadium loading	CH_4 conversion	Space–time yields (g/kg catal per h) (selectivities, mol%)				
(wt%)	(mol%)	C_2HC	CH_2O	CH_3OH	CO	CO_2
0.5 [a]	4.3	0	542	81	3850	380
		(0)	(10.8)	(1.5)	(82.2)	(5.2)
1.0 [a]	5.7	0	735	122	4989	639
		(0)	(11.1)	(1.7)	(80.6)	(6.6)
1.0 [b]	5.9	0	751	117	5112	771
		(0)	(10.9)	(1.6)	(79.8)	(7.7)
1.5 [a]	6.0	0	890	161	5150	617
		(0)	(12.8)	(2.2)	(79.1)	(6.0)
2.0 [a]	5.8	0	1028	181	4752	671
		(0)	(15.2)	(2.5)	(75.5)	(6.8)
2.0 [b]	6.2	0	1179	189	4930	842
		(0)	(16.3)	(2.5)	(73.2)	(8.0)

[a] This catalyst was prepared by mixing Cab-O-Sil with an aqueous solution of NH_4VO_3 in air. The mixture was stirred at 60°C for 10–15 h, which resulted in a thick paste. The paste was dried at 140°C overnight and then calcined in air at 600°C for 6 h.

[b] This catalyst was prepared by mixing Cab-O-Sil with a methanolic solution of $VO(i\text{-}OC_3H_7)_3$ under a N_2 atmosphere. The mixture was then processed as described in footnote a.

Table 8
Methane conversion, space–time yields, and product selectivities obtained over a 2 wt% V_2O_5/SiO_2 catalyst (0.100 g) by air oxidation (CH_4/air/steam=1.5:1.0:1.7) at 625°C and 0.1 MPa with GHSV=237 000 l/kg per h

CH_4 conversion (mol%)	Space–time yields (g/kg catal per h) (selectivities, mol%)				
	C_2HC	CH_2O	CH_3OH	CO	CO_2
4.4 [a]	0 (0)	1282 (30.3)	276 (6.1)	2166 (54.9)	539 (8.7)

[a] Prepared by mixing Cab-O-Sil with a methanolic solution of $VO(i\text{-}OC_3H_7)_3$ under a N_2 atmosphere. See Table 7 for the calcination procedure.

4. Conclusions

Significant progress has been made toward the goal of selectively oxidizing methane directly to formaldehyde, thereby by-passing the high-temperature steam reforming and methanol synthesis steps that are part of the current technology of producing formaldehyde. This is demonstrated in Fig. 5, where the productivities obtained with the SiO_2 and V_2O_5/SiO_2 catalysts are compared with those given in other reports. Over the silica-supported vanadium catalysts, formaldehyde productivities of >1.2 kg/kg catal per h have been achieved, but higher selectivities are needed. Significant progress has been made in the further challenging task of directly synthesizing methanol from methane.

Acknowledgements

This research was supported in part by the U.S. Department of Energy-METC (Contract No. DE-FG21-92MC29228), the National Science Foundation (Grant No. CTS-9417981), and the AMOCO Corporation. Equipment provided by Union Carbide is gratefully acknowledged.

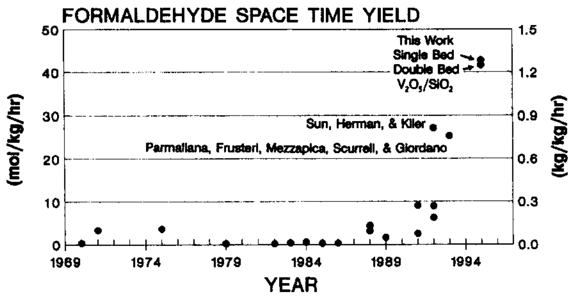

Fig. 5. Comparisons of the space–time yields of formaldehyde achieved recently by direct methane oxidation over SiO_2 and V_2O_5/SiO_2 catalysts in continuous flow reactors with the formaldehyde productivities reported earlier (see also Figs. 1 and 4).

References

[1] M.M. Holm and E.H. Reichl, Fiat Report No. 1085, U.S. Office of Miliary Government for Germany, March 31, 1947.
[2] C.F. Cullis, D.E. Keene and D.L. Trimm, J. Catal., 19 (1970) 378.
[3] R.S. Mann and M.K. Dosi, J. Chem. Technol. Biotechnol., 29 (1979) 467.
[4] D.A. Dowden and G.T. Walker (assigned to ICI, England), U.K. Patent No. 1 244 001, Aug. 25, 1971.
[5] H.J.F. Stroud (assigned to British Gas Corp.), U.K. Patent NO. 1 398 385, June 18, 1975.
[6] R.-S. Liu, M. Iwamoto and J.H. Lunsford, J. Chem. Soc., Chem. Commun., (1982) 78.
[7] M. Iwamoto, Japan. Kokai Tokkyo Koho, 5 892 629, June 2, 1983.
[8] H.-F. Liu, R.-S. Liu, K.Y. Liew, R.E. Johnson and J.H. Lunsford, J. Am. Chem. Soc., 106 (1984) 4117.
[9] M.M. Khan and G.A. Somorjai, J. Catal., 91 (1985) 263.
[10] R. Pitchai and K. Klier, Catal. Rev.-Sci. Eng., 28 (1986) 13.
[11] N.D. Spencer, J. Catal., 109 (1988) 187.
[12] N.D. Spencer, C.J. Pereira and R.K. Grasselli, J. Catal., 126 (1990) 546.
[13] M. Kennedy, A. Sexton, B. Kartheuser, E. Mac Giolla Coda, J.B. McMonagle and B.K. Hodnett, Catal. Today, 13 (1992) 447.
[14] H. Hu, I.E. Wachs and S.R. Bare, J. Phys. Chem., 99 (1995) 10897.
[15] M. de Boer, A.J. van Dillen, D.C. Koningsberger, J.W. Geus, M.A. Vuurman and I.E. Wachs, Catal. Lett., 11 (1991) 227.
[16] M. Cornac, A. Janin and J.C. Lavalley, Polyhedron, 5 (1986) 183.
[17] M.A. Banares, H. Hu and I.E. Wachs, J. Catal., 150 (1994) 407.

[18] M.A. Banares, N.D. Spencer, M.D. Jones and I.E. Wachs, J. Catal., 146 (1994) 204.

[19] S. Kasztelan, E. Payen and J.B. Moffat, J. Catal., 112 (1988) 320.

[20] M.A. Banares, H. Hu and I.E. Wachs, J. Catal., 155 (1995) 249.

[21] C. Rocchiccioli-Deltcheff, M. Amirouche, M. Che, J.M. Tatibouet and M. Fournier, J. Catal., 125 (1990) 2892.

[22] N.D. Spencer and C.J. Pereira, J. Catal., 116 (1989) 399.

[23] M. Iwamoto, Japan. Kokai Tokkyo Koho, 5 892 630, June 2, 1983.

[24] I. Lee and K.Y.S. Ng, Preprints, Div. Fuel Chem., ACS, 33(3) (1988) 403.

[25] N. Das, H. Eckert, H. Hu, I.E. Wachs, J.F. Walzer and F.J. Feher, J. Phys. Chem., 97 (1993) 8240.

[26] S. Yoshida, U. Tanaka, Y. Nishimura, H. Mizutani and T. Funabiki, in Proceedings of 9th International Congress Catalysis, 3, 1988, p. 1473.

[27] T. Oyama, G.T. Went, K.B. Lewis, A.T. Bell and G.A. Somorjai, J. Phys. Chem., 93 (1989) 6786.

[28] Q. Sun, J.-M. Jehng, H. Hu, R.G. Herman, I.E. Wachs and K. Klier, in M.M. Bhasin and D.N. Slocum, (Eds.), Methane and Alkane Conversion Chemistry, Plenum Press, New York, NY, 1995, p. 219.

[29] J.-M. Jehng, H. Hu, X. Gao and I.E. Wachs, Catal. Today, 28 (1996) 335.

[30] J.R. Anderson and P. Tsai, J. Chem. Soc., Chem. Commun., (1987) 1435.

[31] Z. Sojka, R.G. Herman and K. Klier, in Preprints Supplement, Symposium on Methane Activation, Conversion, and Utilization, PACIFICHEM'89, Intern. Chem. Congr. of Pacific Basin Societies, Honolulu, HI, 1989, p. 7.

[32] Z. Sojka, R.G. Herman and K. Klier, J. Chem. Soc., Chem. Commun., (1991) 185.

[33] J.S.J. Hargreaves, G.J. Hutchings and R.W. Joyner, Nature, 348 (1990) 428.

[34] J.S.J. Hargreaves, G.J. Hutchings and R.W. Joyner, Appl. Catal., 77 (1991) N18.

[35] Q. Sun, J.I. Di Cosimo, R.G. Herman, K. Klier and M.M. Bhasin, Catal. Lett., 15 (1992) 371.

[36] J.M. DeBoy and R.G. Hicks, Ind. Eng. Chem. Res., 27 (1988) 1577.

[37] J.M. DeBoy and R.G. Hicks, J. Catal., 113 (1988) 517.

[38] J. Sárkány, Q. Sun, R.G. Herman and K. Klier, Preprints, Div. Pet. Chem., ACS, 39 (1994) 226.

[39] J. Sárkány, Q. Sun, J.I. Di Cosimo, R.G. Herman and K. Klier, in M.M. Bhasin and D.N. Slocum (Eds.), Methane and Alkane Conversion Chemistry, Plenum Press, New York, NY, 1995, p. 31.

[40] S. Kasztelan and J.B. Moffat, J. Chem. Soc., Chem. Commun., (1987) 1663.

[41] G.N. Kastansa, G.A. Tsigdinos and J. Schwank, Appl. Catal., 44 (1988) 33.

[42] G.N. Kastansa, G.A. Tsigdinos and J. Schwank, J. Chem. Soc., Chem. Commun., (1988) 1298.

[43] S. Ahmed and J.B. Moffat, Appl. Catal., 58 (1990) 83.

[44] A. Parmaliana, F. Frusteri, D. Miceli, A. Mezzapica, M.S. Scurrell and N. Giordano, Appl. Catal., 78 (1991) L7.

[45] Y. Matsumura, K. Hashimoto and J.B. Moffat, Catal. Lett., 13 (1992) 283.

[46] Q. Sun, R.G. Herman and K. Klier, Catal. Lett., 16 (1992) 251.

[47] J.F. Walker, Formaldehyde, Reinhold, New York, NY, 1964, p. 489.

[48] A. Parmaliana, F. Frusteri, A. Mezzapica, D. Miceli, M.S. Scurrell and N. Giordano, J. Catal., 143 (1993) 262.

[49] A. Parmaliana, F. Arena, F. Frusteri, D. Miceli and V. Sokolovskii, Catal. Today, 24 (1995) 231.

[50] A. Parmaliana, F. Frusteri, A. Mezzapica, M.S. Scurrell and N. Giordano, J. Chem. Soc., Chem. Commun., (1993) 751.

[51] C. Shi, Q. Sun, H. Hu, R.G. Herman, K. Klier and I.E. Wachs, J. Chem. Soc., Chem. Commun., (1996) 663.