High Yields of Methanol from Methane by C–H Bond Activation at Low Temperatures

Dorit Wolf**

Despite intensive research, until now no process for the direct selective conversion of methane into liquid chemicals such as methanol, formaldehyde, higher paraffins, and olefins exists which is satisfying from a technical and economical point of view.[1] The first step of methane conversion is the scission of a C–H bond. The high energy of dissociation (435 kJ mol^{-1}) aggravates a selective reaction. One reason for the comparatively low yields obtained upon thermal or radical activation of methane is the high activation energy for C–H bond scission, which requires high reaction temperatures. The desired products (oxygenates or olefins) are unstable intermediates, which in the presence of oxygen suffer fast consecutive reactions to carbon oxides at the high reaction temperatures.[2] Therefore, low reaction temperatures are desired for a potential catalytic process. In this respect, the following reaction steps have to be considered simultaneously, regardless of whether they are catalyzed homogeneously or heterogeneously: I) C–H bond scission, II) oxidation, and III) functionalization (when oxygenates are desired).

The reaction temperature required is determined by the highest activation energy of those steps. To ensure a stationary catalytic process, the structure of the catalyst (solid phase or metal – ligand complex in a homogeneous solution) may not be destroyed by changes in the oxidation state of the catalytically active sites during steps I – III. Against this background, heterogeneously and homogeneously catalyzed processes for the oxidative conversion of methane are summarized in Table 1.

The high yield of methanol obtained in the presence of Pt complexes in fuming sulfuric acid during the catalytica process (Periana et al.[13]) is remarkable [Eqs. (a) – (d)].

$$CH_4 + H_2SO_4 + SO_3 \longrightarrow CH_3OSO_3H + H_2O + SO_2 \quad (a)$$

$$CH_3OSO_3H + H_2O \longrightarrow CH_3OH + H_2SO_4 \quad (b)$$

$$SO_2 + \tfrac{1}{2}O_2 \longrightarrow SO_3 \quad (c)$$

$$\text{net reaction:} \quad CH_4 + \tfrac{1}{2}O_2 \longrightarrow CH_3OH \quad (d)$$

Clearly this process, where methane is converted with 90 % conversion and 81 % selectivity into methyl bisulfate (methyl hydrogensulfate) in 102 % sulfuric acid at 220 °C, fulfills the requirements of C–H bond scission, oxidation, and functionalization in the best way so far.

C–H Bond Activation

The strong C–H bond is activated by interaction of the methane with the (η^2-2,2′-bipyrimidyl)platinum(II) complex **1**, which is dissolved in the sulfuric acid (Scheme 1). The choice of appropriate ligands for the platium(II) complex determines the activity, selectivity, and stability of the catalyst in hot, strongly acidic and oxidizing environment of the fuming sulfuric acid. Ligands containing nitrogen atoms combine high thermal stability with high activity and selectivity. The bidiazine ligand in **1** proves to be well suited owing to its high affinity for the Pt^{II} center. The complex remains stable for over 50 hours at 200 °C in oleum.

It is very likely that the initial step of C–H bond activation includes interaction of the methane with the Pt^{II} center. Accordingly, when a nonoxidizing, acidic deuterated solvent (CF_3SO_3D) is applied, a H/D exchange is only observed in the presence of Pt^{II}, but not of Pt^{IV} or platinum black. Although catalytic activity of dissolved Pt^0 species cannot be ruled out, there have been no indications for the reduction of the Pt^{II} complex during the reaction. The expected key intermediate **2** (Scheme 1) is not observed at a reaction temperature of 180 °C. The reason for this is the low acid resistance of this complex, which immediately forms methane in stoichiometric amounts upon contact with sulfuric acid. Therefore, the back reaction of methane activation is fast, and under stationary conditions the concentration of the CH_3 – Pt^{II} complex is probably low. At room temperature, decomposition of **2** is slow enough for the complex to be observed by ^{1}H NMR spectroscopy. At 180 °C methyl bisulfate is formed besides methane.

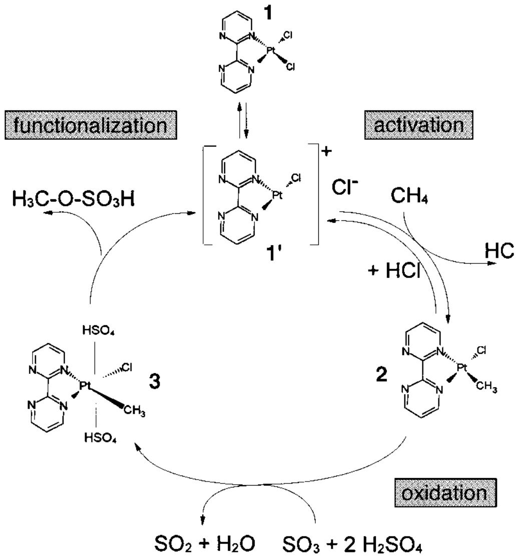
Concerning further improvement of the activity and selectivity of the catalyst, it is important to clarify whether the C–H bond activation is an oxidative addition with formation of a methylhydrido – Pt intermediate which loses one proton (as proposed by Shilov et al. for Pt^{II} centers[10a]), or whether it is an electrophilic substitution with formation of a

---

[*] Dr. D. Wolf
Institut für Angewandte Chemie Berlin-Adlershof
Rudower Chaussee 5, D-12484 Berlin (Germany)
Fax: (+49) 30-6392-4454
E-mail: dwolf@aca-berlin.de

Table 1. Processes for direct oxidative conversion of methane.

	C–H bond activation	Oxidation	Functionalization	Maximum yield so far
heterogeneously catalyzed processes:				
oxidative coupling of methane on basic oxide catalysts[3, 4] $CH_4 + n\,O_2 \rightarrow C_2H_6, C_2H_4$ (600–900 °C)	substitution of the C–H bond by the weaker O–H bond at electrophilic oxygen centers of oxides; methyl radicals are formed as primary gas-phase products	reduction of the catalyst surface; catalyst regeneration proceeds by readsorption of oxygen	ethane is formed by recombination of radicals in the gas phase; ethylene and C_{2+} are formed by consecutive reactions	20–25% ethane + ethylene
partial oxidation on transition metal oxides $CH_4 + n\,O_2 \rightarrow CH_3OH, HCHO$ (250–600 °C)[5, 6]	substitution of C–H bonds by the weaker O–H bond at electrophilic oxygen centers of oxidic surfaces of solids	reduction of the catalyst surface; catalyst regeneration proceeds by readsorption of oxygen	functionalization by gas-phase reactions of methyl, methyl peroxo, and methoxy radicals	catalytic: < 4% CH_3OH or HCHO (noncatalytic: up to 9%)
oxidation with *tert*-butyl hydroperoxide and O_2 at 270 °C on Fe–phtalocyanine complexes encapsulated in zeolites[7]		mechanism not yet clarified		< 5% CH_3OH + HCHO
homogeneously catalyzed processes:				
super acid catalyzed oxidation[8, 9]	protonation of methane to CH_5^+ and formation of CH_3^+ and H_2	oxidation with H_2O_2 or O_3	with H_2O_2 via $[HOOH_2]^+$ and formation of $[CH_3OH_2]^+$, with O_3 via $[OOOH]^+$ and formation of $[CH_3O]^+$	no information (selectivity towards CH_3OH + HCHO > 95%)
electrophilic substitution and conversion with nucleophiles on Pt or Pd complexes[10, 11]	substitution of the C–H bond by the weaker Me–C bond	oxidation by reduction of the metal cations, no efficient oxidants are used which can be recycled	conversion with nucleophiles (here trifluoroacetates)	stoichiometric conversion
methane oxidation in fuming sulfuric acid on Hg^{II} salts[12] or Pt^{II} complexes[13] (150–220 °C)	substitution of the C–H bond by the weaker Me–C bond	oxidation by SO_3 reduction	formation of methyl bisulfate, which is protected from consecutive reactions and which can be converted into methanol by hydrolysis	Hg^{II} salt: 43% CH_3OH Pt^{II} complex: 72% CH_3OH



Scheme 1. Reaction mechanism for the oxidation of methane to methyl bisulfate on the Pt-complex catalyst **1** in fuming sulfuric acid.

methane–metal complex which loses a proton (as proposed for the Hg^{II} system[12]). So far there has not been enough evidence to prove this unambiguously. However, according to Periana et al.[13] it is a process with a cationic, highly electrophilic 14-electron complex (**1′**, Scheme 1). This thesis is supported by experiments on H/D exchange for a solution of **1′** in D_2SO_4. Introduction of deuterium only occurs with methane. When methyl bisulfate is used instead of methane, no H/D exchange with the deuterated sulfuric acid is observed. Therefore, it appears that the electron-withdrawing bisulfate group inhibits the electrophilic reaction between the metal complex and the C–H bond.

Oxidation

The oxidation of **2** in the strongly oxidizing fuming sulfuric acid is the rate-determining step of the catalytic cycle. There exists a direct correlation between the rate of oxidation of different Pt complexes (oxidation of Pt^{II} to Pt^{IV}) and the effective reaction rate of the formation of methyl bisulfate. However, complexes like $[(NH_3)PtCl_3]$, which can be oxidized at a high rate, also have short live times.

Functionalization

The functionalization can be investigated at 150 °C. At this temperature, only the C–H bond activation, but no oxidation of **2**, takes place. When Pt^{IV} is applied as $[H_2Pt(OH)_6]$ together with oleum, methyl bisulfate is formed. The amount of methyl bisulfate produced correlates with the amount of Pt^{IV} used. Therefore, the functionalization proceeds at the Pt^{IV}

centers. As explained above, the dissociation of the bond between the η^2-2,2′-bipyrimidyl ligand and the Pt^{II} center is reversible. The question may be raised whether the ligands are bonded to the Pt center during the transition state. As metal salts also catalyze the reaction—however, with lower activity and selectivity—the ligands must be relevant for the selectivity of the reaction.

How is the high selectivity of the process achieved? According to Periana et al., the rate constant of the oxidation step of CH_4 to methyl bisulfate is 100 times higher than that of the further oxidation of methyl bisulfate.[13] Methanol can be trapped by esterification and thus be protected from nonselective consecutive reactions. Therefore, only low amounts of CO_2 and traces of methyl chloride are formed. This appears to be the key towards high selectivities. A similar concept also enables high selectivities when methane is activated by super acids (Table 1): The selective products are trapped after protonation as $[CH_3OH_2]^+$ or $[CH_3O]^+$.[9] With catalyst **1**, space time yields of $10^{-6}\,mol\,cm^{-3}\,s^{-1}$ (ca. $0.1\,t\,m^{-3}\,h^{-1}$) are obtained. This makes the process interesting from a technical point of view. Whether such a process can be applied technically depends on the long-term stability of the catalyst. From the given turnover numbers and frequencies, a time span of 14 hours can be calculated during which the catalyst is completely deactivated. This shows that further improvement is necessary. Furthermore, when evaluating the process efficiency, the necessary workup steps—hydrolysis of the ester, destillation of methanol, oxidation of the formed SO_2 to SO_3 (space time yield $0.2-0.2\,t\,m^{-3}\,h^{-1}$) for regeneration of sulfuric acid as oxidizing agent—have to be taken into account.

German version: *Angew. Chem.* **1998**, *110*, 3545–3547

Keywords: homogeneous catalysis · methane · methanol · N ligands · platinum

[1] a) L. Guczi, R. A. van Santen, K. V. Sarma, *Catal. Rev. Sci. Eng.* **1996**, *13*, 356; b) *Catal. Today* **1997**, *37*(1) (Ed.: J. B. Moffat).

[2] C. Batiot, B. K. Hodnett, *Appl. Catal. A* **1996**, *137*, 179.

[3] a) M. Baerns, J. R. H. Ross in *Perspectives in Catalysis* (Eds.: J. A. Thomas, K. I. Zamaraev), Blackwell, **1992**; b) A. M. Maitra, *Appl. Catal. A* **1993**, *104*, 11.

[4] O. Forlani, S. Rossini, *Materials Chemistry and Physics* **1992**, *31*, 155.

[5] *Direct Methane conversion by Oxidative Processes* (Ed.: E. E. Wolf), von Nostrand Reinhold, New York, **1993**.

[6] O. V. Krylov, *Catal. Today* **1993**, *18*(3).

[7] R. Raja, P. Ratnasamy, *Appl. Catal. A* **1997**, *158*, L7.

[8] G. A. Olah, R. Renner, P. Schilling, Y. K. Mo, *J. Am. Chem. Soc.* **1973**, *95*, 4952.

[9] G. A. Olah, *Acc. Chem. Res.* **1987**, *20*, 422.

[10] a) L. A. Kushck,V. V. Lavrushko, Y. S. Misharin, A. P. Maravsky, A. E. Shilov, *New J. Chem.* **1987**, *7*, 8109; b) A. E. Shilov, *Activation of Saturated Hydrocarbons by Transition Metal Complexes*, Reidel, Dordrecht, **1984**.

[11] E. Getz, T. F. Oliver, A. Sen, *J. Am. Chem. Soc.* **1987**, *109*, 8109.

[12] a) R. A. Periana, D. J. Taube, E. R. Evitt, D. G. Loffler, P. R. Wentrcek, T. Masuda, *Science* **1993**, *259*, 340; b) R. A. Periana, E. R. Evitt, H. Taube (Catalytica Inc.), US patent 5,233,113, **1993**; c) R. A. Periana, D. J. Taube, H. Taube, E. R. Evitt (Catalytica Inc., US patent 5,306,855, **1994**.

[13] R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560.

Large Molecules from the Virtual Bakery—Filling a Gap in Structure Research**

Peter Luger*

It is a common practice for preparative chemists to cook or bake their new compounds in hot ovens. By contrast, the determination of the structure of large molecules by "shake-and-bake" (or half-bake) in the gigabyte world of modern computers is a new, but very successful, method and fills a long-lamented gap in the otherwise very effective field of structure research by X-ray diffraction. When the Japanese group of Kondo et al.[1] solved the crystal structure of the deep-blue flower pigment commelinin six years ago, it caused such a sensation that this compound was featured on the cover of the first August issue of *Nature*. The group was also awarded the prize for the best poster contribution at the 16th International Crystallography Congress in Beijing in 1993.[2] The scientific community is used to the scientific literature being expanded through the addition of routine crystal structure solutions, so why was this particular one so special? One aspect may have been its aesthetic value, for the commelinin structure (Figure 1, top) is almost as beautiful as the flowers from which it is derived.

But there is more to its significance than just good looks. It contains 253 non-hydrogen atoms in the asymmetric unit and thus belongs to that group of middle-sized structures that were formidable tasks for crystallographers to solve in the early 1990s. The number of structures registered at the Cambridge Crystallographic Data Centre (CCDC) has increased almost exponentially for thirty years, with more than

---

[*] Prof. Dr. P. Luger
Institut für Kristallographie der Freien Universität
Takustrasse 6, D-14195 Berlin (Germany)
Fax: (+49) 30-838-3464
E-mail: luger@chemie.fu-berlin.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB312, Vectorial Membrane Processes) and the Fonds der Chemischen Industrie.