

Combined Redox Couples for Catalytic Oxidation of Methane by Dioxygen at Low Temperatures

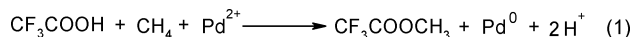
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The development of new paths for the selective conversion of methane to value-added chemicals is very important for the optimal utilization of abundant natural gas, which has methane as the main component. Current technologies for obtaining oxygenates from methane are mainly based on indirect routes via syngas.¹ Obviously a direct selective oxidation process is more attractive from an economic point of view. Gas-phase heterogeneous catalytic processes are usually operated at high temperatures (>600 °C), which result in low selectivities (typically <40%).² In contrast, homogeneous catalytic reactions in the liquid phase seem to be more promising, because they are generally run at moderate temperatures with a high selectivity. The most widely studied homogeneous catalytic systems for the direct synthesis of methanol from methane involve transition metals such as Pd, Hg, Pt, or Co.^{2,3} Those processes usually require strong oxidants such as SO₃/H₂SO₄, K₂S₂O₈, or H₂O₂ or temperatures up to 200 °C.^{2,3a–d} Dioxygen on the other hand is an attractive oxidant because it is inexpensive, readily available, and not harmful to the environment. However, the use of dioxygen for the selective oxidation of methane to methanol at low temperatures still remains a challenge.^{3e–g}

Some biological oxidation processes utilize chains of redox couples to transfer electrons from a substrate to O₂ in a highly efficient manner under mild conditions.⁴ We intend to build a similar electron-transfer chain to use dioxygen for the methane oxidation to methanol at low temperatures. The key to initiate this chain is the activation of the C–H bond of methane. An interesting starting point could be the work of Gretz et al., who have shown that Pd²⁺ is able to oxidize methane selectively to methanol in CF₃COOH at 80 °C and 55 atm according to eq 1.⁵



However, in that process Pd²⁺ does not act as a catalyst because it is stoichiometrically converted to Pd⁰.⁵ Therefore we have been looking for a route to regenerate Pd⁰ to Pd²⁺ within the reaction system with O₂ and turn this reaction into a catalytic process.

In the Wacker process for the industrial aerobic oxidation of ethylene to acetaldehyde, the CuCl₂/CuCl redox couple is used to regenerate the catalytically active Pd²⁺ in aqueous hydrochloric acid.⁶ However, the use of chloride has drawbacks with respect to corrosion and the environment. Therefore we tried the p-benzoquinone/hydrobenzoquinone (Q/H₂Q) redox couple as a mediator for the aerobic regeneration of Pd after methane activation, which had also been used in early studies of the Wacker process.⁷ By combining three redox couples Pd²⁺/Pd⁰, Q/H₂Q, and NO₂/NO in CF₃COOH, the selective oxidation of methane to methanol by dioxygen has been achieved at 80 °C.

Table 1 lists a series of typical reaction results for the selective oxidation of methane in CF₃COOH in combination with palladium acetate Pd(OAc)₂ and Q at 80 °C.⁸ Run 1 shows that the amount of the product CF₃COOCH₃ (9.5 μmol) in the absence of O₂ and

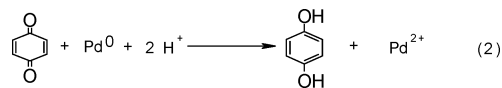
Table 1. Typical Reaction Results^a

run	Pd ²⁺ (μmol)	Q (μmol)	NaNO ₂ (μmol)	O ₂ (atm)	CF ₃ COOCH ₃ (μmol)	Pd ²⁺ (%) ^b
1	10	0	0	0	9.5	trace
2	10	20	0	0	30	trace
3	10	50	0	0	55	trace
4	10	20	0	1	34	15
5	10	50	0	1	67	27
6	10	20	20	1	69	98
7	10	50	100	1	70	95
8	5	20	20	1	32	95
9	20	20	20	1	106	54

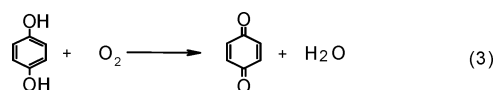
^a Conditions: CF₃COOH, 3 mL (39 mmol); CH₄, 54 atm (114 mmol); O₂, 1 atm (2 mmol); 80 °C, 10 h. ^b Remaining Pd²⁺ after the reaction.⁹

Q is practically equivalent to the initial quantity of Pd²⁺ in the liquid. After the termination of the reaction, we observed that a metallic film had formed on the glass liner and stirrer, and black precipitates were suspended in the liquid. Almost no Pd²⁺ remained in the liquid⁹ indicating the stoichiometric consumption of Pd²⁺, in agreement with eq 1 and the earlier work.⁵

With the addition of 20 μmol Q in run 2, the CF₃COOCH₃ yield increased to 30 μmol, which is equivalent to the sum of the Q and Pd²⁺ amounts. Obviously Q is a very effective oxidant to convert Pd⁰ to Pd²⁺. Q is reduced to H₂Q (eq 2) and Pd²⁺ is twice fully recycled before Pd⁰ precipitates and reaction (1) comes to a standstill again. Accordingly there is almost no Pd²⁺ left in the liquid at the end of run 2. When Q is increased to 50 μmol, the product CF₃COOCH₃ consequentially increases to 55 μmol and again almost no Pd²⁺ remains in the liquid (run 3).



After the addition of O₂ in runs 4 and 5, the yields are slightly higher, and larger amounts of Pd²⁺ remain in solution than in runs 2 and 3, respectively. This indicates that H₂Q indeed can be regenerated by O₂ (eq 3) but a large excess of Q would be required to make the system catalytic because reaction 3 is not sufficiently fast to prevent the eventual precipitation of Pd⁰ at the Q concentrations used in our experiments. Therefore, another active component is necessary to speed up reaction 3.



Metal macrocycles such as cobalt porphyrin and iron phthalocyanine have been previously used for the reoxidation of H₂Q to Q by O₂.¹⁰ However, the stability of these metal macrocycles is very poor in strongly acidic media such as CF₃COOH.¹⁰ On the other hand, nitrogen oxides are efficient catalysts for the aerobic

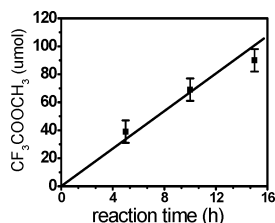
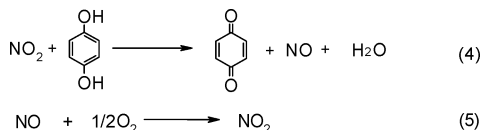


Figure 1. The yield of CF₃COOCH₃ versus the reaction time.

regeneration of Q but in CH₂Cl₂.¹¹ We tested the feasibility of this reaction (eq 4) in CF₃COOH by adding NaNO₂ to an air-stable white suspension of H₂Q in CF₃COOH. NaNO₂ is a convenient nitrogen oxide source because it decomposes to NO in CF₃COOH and then rapidly reacts with O₂ to form NO₂ (eq 5).¹¹ Once NaNO₂ was introduced, the suspension cleared into a yellow solution under air within 1 min and contained only Q as determined by NMR.

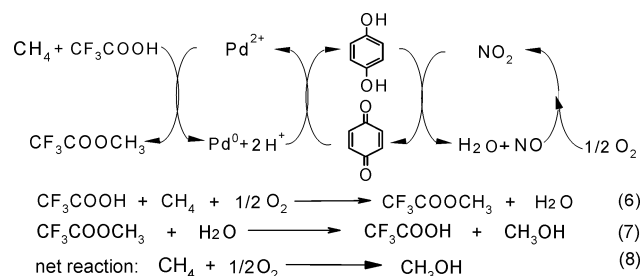


When 20 μmol of each NaNO₂ and Q were added to our system in run 6, the yield doubled to 69 μmol CF₃COOCH₃ with respect to runs 2 and 4. The molar ratios of CF₃COOCH₃ to Pd²⁺, Q, or NaNO₂ are clearly larger than 1. Moreover, all Pd²⁺ is practically retained in the active state after the reaction. Thus, it can be concluded that the selective oxidation of methane to methanol has become catalytic by coupling Pd²⁺, Q, NaNO₂, and O₂ in CF₃COOH. Note that Pd⁰ can also be oxidized to Pd²⁺ directly by NO₂.¹² However, without Q the yield of CF₃COOCH₃ is ca. 25% lower even when 40 μmol NaNO₂ is used (see SI-2, Supporting Information). Run 7 shows that increasing the amounts of Q and NaNO₂ beyond twice the stoichiometric amount of Pd²⁺ does not significantly promote the reaction further since the ester yield remains constant. Figure 1 displays a nearly linear dependence of the yield on the reaction time within 15 h under the conditions of run 6. Also, the yield increases nearly linearly with the amount of Pd²⁺, as seen in runs 6 and 8. This indicates that the turnover number (TON) is approximately 0.7 per hour, which is consistent with the yield of 60% methanol within 1 h on the basis of the Pd²⁺ reported previously.⁵ However, it is worthwhile to note that the regeneration of Pd⁰ to Pd²⁺ by Q is not fast enough even in the presence of NO/NO₂ to prevent Pd⁰ from precipitation when the ratio of Q/Pd²⁺ is too small as in run 9. Consequently the yield in run 9 is not exactly twice as high as in run 6, as could be expected.

The origin of the methyl group in CF₃COOCH₃ was confirmed by isotope experiments, replacing 14 out of 54 atm methane with ¹³CH₄ in the reaction. Indeed, GC–MS analysis showed that the ratio of the fragments COO¹²CH₃ and COO¹³CH₃ (*m/e* = 59 and 60, respectively) was very close to 3:1. By ¹³C NMR, we also detected the formation of CF₃COO¹³CH₃ (see SI-3). Therefore, the methyl group in CF₃COOCH₃ is derived unambiguously from methane. Note that we did not observe any other oxidation products of methane such as formaldehyde, formic acid, or CO₂.⁸

This oxidation process is described in Scheme 1. Pd²⁺ is the catalytically active center, oxidizing methane to CF₃COOCH₃ in CF₃COOH. The reduced Pd⁰ (eq 1) is subsequently regenerated by Q, leading to Pd²⁺ and H₂Q (eq 2). Then NO₂ oxidizes H₂Q to Q and NO is produced (eq 4), which is finally reoxidized to NO₂ by O₂ (eq 5). Thus the net oxidation reaction can be described as in eq 6. Since CF₃COOCH₃ can be hydrolyzed to CH₃OH and CF₃COOH (eq 7), the net reaction can be written as in eq 8.

Scheme 1. Catalytic Oxidation of Methane by Dioxygen through an Electron-Transfer Chain



In summary, with the combination of the three redox couples Pd²⁺/Pd⁰, Q/H₂Q, and NO₂/NO in CF₃COOH, we have developed a catalytic system for the one-pot aerobic oxidation of methane at 80 °C. The activation of methane with Pd²⁺ initiates an electron-transfer chain, which carries the electrons from methane to O₂, similar to the biological oxidation processes. This is the first example integrating an organic cocatalyst for the selective oxidation of methane, which significantly increases the catalytic efficiency of a transition metal. The TON of approximately 0.7 per hour is limited by the initial activation step. Further improvement of productivity could be possible if a more active catalyst than Pd²⁺ can be found for reaction 1.

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Supporting Information Available: Gravimetric method for the determination of Pd²⁺ left in the liquid after reaction; *p*-benzoquinone in the oxidation process; NMR analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) Care should be taken during the operations because of the danger of explosion. The explosion limits of CF₃COOH in air are between 3.8–21 v% and of CH₄ in O₂ between 5–61 v%. In a 50 ml autoclave, catalysts and 3 ml CF₃COOH were put in a glass liner with a Teflon-coated magnetic stirrer. The reactor was three times purged with 30 atm CH₄ and then pressurized with 54 atm CH₄ and 1 atm O₂. It was heated to 80 °C in an oil bath and kept for 10 h under stirring. After the reaction, the reactor was cooled to 3 °C in ice water, and the pressure was slowly reduced. The product was analyzed by GC–MS, NMR, and quantified by GC. In all runs, approximately 20 μmol acetic acid was detected, corresponding to the amount of the ligand of Pd(OAc)₂. In addition we found CO₂ in all runs, but a control experiment with CF₃COOH pressurized with 1 atm O₂ and 54 atm N₂ yielded the same amount of CO₂ within the experimental error (5%) indicating that it is due to decomposition of CF₃COOH as reported in reference 3d.
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