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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 SO_3/H_2SO_4, $K_2S_2O_8$, or H_2O_2 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 O_2 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 Pd^{2+} is able to oxidize methane selectively to methanol in CF_3COOH at 80 °C and 55 atm according to eq 1.[5]

$$CF_3COOH + CH_4 + Pd^{2+} \longrightarrow CF_3COOCH_3 + Pd^0 + 2H^+ \quad (1)$$

However, in that process Pd^{2+} does not act as a catalyst because it is stoichiometrically converted to Pd^0.[5] Therefore we have been looking for a route to regenerate Pd^0 to Pd^{2+} within the reaction system with O_2 and turn this reaction into a catalytic process.

In the Wacker process for the industrial aerobic oxidation of ethylene to acetaldehyde, the $CuCl_2/CuCl$ redox couple is used to regenerate the catalytically active Pd^{2+} 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/H_2Q) 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 Pd^{2+}/Pd^0, Q/H_2Q, and NO_2/NO in CF_3COOH, the selective oxidation of methane to methanol by dioxygen has been achieved at 80 °C.

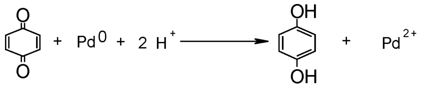
Table 1 lists a series of typical reaction results for the selective oxidation of methane in CF_3COOH in combination with palladium acetate $Pd(OAc)_2$ and Q at 80 °C.[8] Run 1 shows that the amount of the product CF_3COOCH_3 (9.5 μmol) in the absence of O_2 and Q is practically equivalent to the initial quantity of Pd^{2+} 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 Pd^{2+} remained in the liquid[9] indicating the stoichiometric consumption of Pd^{2+}, in agreement with eq 1 and the earlier work.[5]

Table 1. Typical Reaction Results[a]

run	Pd^{2+} (μmol)	Q (μmol)	$NaNO_2$ (μmol)	O_2 (atm)	CF_3COOCH_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

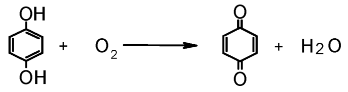
[a] Conditions: CF_3COOH, 3 mL (39 mmol); CH_4, 54 atm (114 mmol); O_2, 1 atm (2 mmol); 80 °C, 10 h. [b] Remaining Pd^{2+} after the reaction.[9]

With the addition of 20 μmol Q in run 2, the CF_3COOCH_3 yield increased to 30 μmol, which is equivalent to the sum of the Q and Pd^{2+} amounts. Obviously Q is a very effective oxidant to convert Pd^0 to Pd^{2+}. Q is reduced to H_2Q (eq 2) and Pd^{2+} is twice fully recycled before Pd^0 precipitates and reaction (1) comes to a standstill again. Accordingly there is almost no Pd^{2+} left in the liquid at the end of run 2. When Q is increased to 50 μmol, the product CF_3COOCH_3 consequentially increases to 55 μmol and again almost no Pd^{2+} remains in the liquid (run 3).



(2)

After the addition of O_2 in runs 4 and 5, the yields are slightly higher, and larger amounts of Pd^{2+} remain in solution than in runs 2 and 3, respectively. This indicates that H_2Q indeed can be regenerated by O_2 (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 Pd^0 at the Q concentrations used in our experiments. Therefore, another active component is necessary to speed up reaction 3.



(3)

Metal macrocycles such as cobalt porphyrin and iron phthalocyanine have been previously used for the reoxidation of H_2Q to Q by O_2.[10] However, the stability of these metal macrocyles is very poor in strongly acidic media such as CF_3COOH.[10] On the other hand, nitrogen oxides are efficient catalysts for the aerobic

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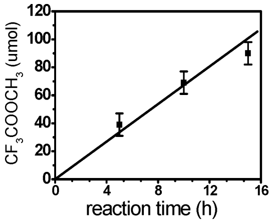
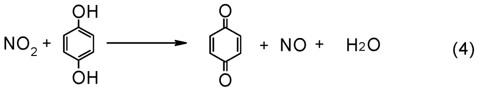


Figure 1. The yield of CF_3COOCH_3 versus the reaction time.

regeneration of Q but in CH_2Cl_2.[11] We tested the feasibility of this reaction (eq 4) in CF_3COOH by adding $NaNO_2$ to an air-stable white suspension of H_2Q in CF_3COOH. $NaNO_2$ is a convenient nitrogen oxide source because it decomposes to NO in CF_3COOH and then rapidly reacts with O_2 to form NO_2 (eq 5).[11] Once $NaNO_2$ was introduced, the suspension cleared into a yellow solution under air within 1 min and contained only Q as determined by NMR.



(4)

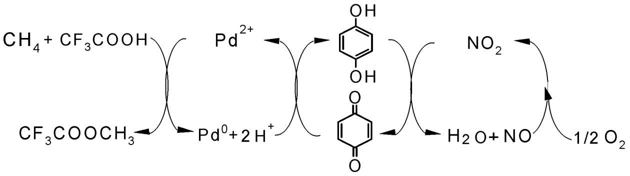
$$NO + 1/2O_2 \longrightarrow NO_2 \qquad (5)$$

When 20 μmol of each $NaNO_2$ and Q were added to our system in run 6, the yield doubled to 69 μmol CF_3COOCH_3 with respect to runs 2 and 4. The molar ratios of CF_3COOCH_3 to Pd^{2+}, Q, or $NaNO_2$ are clearly larger than 1. Moreover, all Pd^{2+} 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 Pd^{2+}, Q, $NaNO_2$, and O_2 in CF_3COOH. Note that Pd^0 can also be oxidized to Pd^{2+} directly by NO_2.[12] However, without Q the yield of CF_3COOCH_3 is ca. 25% lower even when 40 μmol $NaNO_2$ is used (see SI-2, Supporting Information). Run 7 shows that increasing the amounts of Q and $NaNO_2$ beyond twice the stoichiometric amount of Pd^{2+} 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 Pd^{2+}, 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 Pd^{2+} reported previously.[5] However, it is worthwhile to note that the regeneration of Pd^0 to Pd^{2+} by Q is not fast enough even in the presence of NO/NO_2 to prevent Pd^0 from precipitation when the ratio of Q/Pd^{2+} 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 CF_3COOCH_3 was confirmed by isotope experiments, replacing 14 out of 54 atm methane with $^{13}CH_4$ in the reaction. Indeed, GC−MS analysis showed that the ratio of the fragments $COO^{12}CH_3$ and $COO^{13}CH_3$ ($m/e = 59$ and 60, respectively) was very close to 3:1. By ^{13}C NMR, we also detected the formation of $CF_3COO^{13}CH_3$ (see SI-3). Therefore, the methyl group in CF_3COOCH_3 is derived unambiguously from methane. Note that we did not observe any other oxidation products of methane such as formaldehyde, formic acid, or CO_2.[8]

This oxidation process is described in Scheme 1. Pd^{2+} is the catalytically active center, oxidizing methane to CF_3COOCH_3 in CF_3COOH. The reduced Pd^0 (eq 1) is subsequently regenerated by Q, leading to Pd^{2+} and H_2Q (eq 2). Then NO_2 oxidizes H_2Q to Q and NO is produced (eq 4), which is finally reoxidized to NO_2 by O_2 (eq 5). Thus the net oxidation reaction can be described as in eq 6. Since CF_3COOCH_3 can be hydrolyzed to CH_3OH and CF_3COOH (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



$$CF_3COOH + CH_4 + 1/2\,O_2 \longrightarrow CF_3COOCH_3 + H_2O \qquad (6)$$

$$CF_3COOCH_3 + H_2O \longrightarrow CF_3COOH + CH_3OH \qquad (7)$$

$$\text{net reaction: } CH_4 + 1/2O_2 \longrightarrow CH_3OH \qquad (8)$$

In summary, with the combination of the three redox couples Pd^{2+}/Pd^0, Q/H_2Q, and NO_2/NO in CF_3COOH, we have developed a catalytic system for the one-pot aerobic oxidation of methane at 80 °C. The activation of methane with Pd^{2+} initiates an electron-transfer chain, which carries the electrons from methane to O_2, 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 Pd^{2+} can be found for reaction 1.

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Supporting Information Available: Gravimetric method for the determination of Pd^{2+} 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 CF_3COOH in air are between 3.8−21 v% and of CH_4 in O_2 between 5−61 v%. In a 50 ml autoclave, catalysts and 3 ml CF_3COOH were put in a glass liner with a Teflon-coated magnetic stirrer. The reactor was three times purged with 30 atm CH_4 and then pressurized with 54 atm CH_4 and 1 atm O_2. 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 CO_2 in all runs, but a control experiment with CF_3COOH pressurized with 1 atm O_2 and 54 atm N_2 yielded the same amount of CO_2 within the experimental error (5%) indicating that it is due to decomposition of CF_3COOH as reported in reference 3d.
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