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Manganese oxide catalyzed methane partial oxidation in trifluoroacetic acid: Catalysis and kinetic analysis

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ABSTRACT

Direct oxidation of methane to methanol has been studied for decades, and has yet to be commercialized. Three years ago, UOP LLC, a Honeywell Company, started a government co-sponsored project (NIST/ATP Award 70NANB4H3041) for selective liquid phase oxidation of methane to methanol. Recently we have discovered an efficient methane oxidation by manganese oxide. When used as stoichiometric oxidant, quantitative metal oxide-based yield was observed for methane oxidation. The spent catalyst activity can be 100% regenerated with air under basic conditions. A high methane-based yield (36%) with high selectivity (>95%) was achieved when manganese oxide was used in catalytic amount in the presence of air for methane oxidation. Our online GC analysis showed that catalytic methane oxidation occurs with two-stage reaction kinetics with constant reaction rate at the active stage, which can be explained by a low steady-state active catalyst concentration as observed by in situ UV–vis spectrometer.

1. Introduction

Methanol, one of the top 25 chemicals, is currently manufactured from natural gas through an energy intensive, two-step process. Methane reforming step for the current process is a highly endothermic and thermodynamically equilibrated process operated at high temperature (850 °C). The direct methane to methanol oxidation process at low temperature continues to be an interesting alternative to the current process [1]. If successful, this new process could lead to a decrease of methanol price in the current methanol market, as well as opening of new methanol markets in methanol-to-chemical and methanol-to-fuel areas.

Three years ago UOP LLC, a Honeywell Company, started a government co-sponsored project to convert methane to methanol selectively through direct liquid phase oxidation. When hydrogen peroxide was used as the oxidant, two catalytic systems were investigated including nonheme iron complex system and copper/palladium system. For nonheme iron complex system, we were the first to report the successful oxidation of methane to methanol under mild conditions. The conversion and selectivity were too low to pursue further in this direction [2]. For copper/palladium catalyzed methane oxidation in trifluoroacetic acid, we were able to improve the catalysis results to meet our project targets with hydrogen peroxide as the oxidant. However, the reactivity decreased dramatically when economically feasible oxidants such as alkyl hydroperoxide or air were used [3].

It was reported in the literature that some high valent transition metal salts were able to oxidize methane stoichiometrically in trifluoroacetic acid with high efficiency [4]. In the presence of air, the reaction became catalytic with respect to the transition metal salt for methane oxidation. This paper details our own investigation in this research area.

2. Experimental

2.1. Typical stoichiometric methane oxidation procedure

To an 80-ml reactor was added 10 ml trifluoroacetic acid and manganese oxide (Mn_2O_3, 300 mg, 99.999%, from Aldrich). The reactor was assembled and pressurized with methane to 600 psi. The reactor was heated to 180 °C for 3 h. The liquid sample was analyzed by GCMS or 1H NMR and the gas sample analyzed by GC equipped with FID, TCD and MS detectors. The estimated methane-based yield was calculated based on methanol product (isolated as methyl trifluoroacetate (MTFA)) divided by methane introduced into the system. Amount of methanol product formed was calculated based on GCMS and 1H NMR analysis, and the amount of methane introduced into the system was based on the weight difference before and after the introduction of methane gas and ideal gas law occasionally.

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2.2. Typical catalytic methane oxidation procedure

To a 300 cm^3 Parr reactor equipped with gas entrainment impeller were added 150 ml of trifluoroacetic acid and 150 mg of Mn_2O_3. The reactor was assembled and pressurized first with methane to 100 psig, then with 8% oxygen in nitrogen to 600 psig. The reactor was heated at 180 °C for 3 h. The liquid and gas samples were analyzed by the same methods as in stoichiometric methane oxidation.

2.3. Spent catalyst regeneration

To a solution of 5.0 g of anhydrous manganese(II) trifluoroacetate powder dissolved in 25 ml water was added sodium hydroxide (1.43 g) in the presence of air. Some brown solid precipitated out of clear solution immediately. After filtration, air drying of the precipitate led to the isolation of a black solid (1.4 g, 100% based on Mn_2O_3 composition) which was used for methane oxidation without any further purification. This black solid was characterized by XRD analysis.

2.4. Kinetic analysis

A Hastelloy process flow cell constructed by Custom Sensors & Technology (Fenton, MO) with fused silica optics, sapphire process windows, and chemraz seals was connected to a 300 cm^3 Hastelloy autoclave via Hastelloy tubing. An HPLC pump (Alcott Chromatography model 765) was attached to the cell so as to pump liquid sample continuously during analysis. A Deuterium Tungsten Halogen Light Source (Mikropack DH-2000-BAL) was attached to one end of the cell while a spectrometer (Ocean Optics USB2000) was attached to the other end. Also the system was constructed to allow for periodic analysis of liquid sample by online GC.

2.5. Material characterization

Single crystal X-ray analysis: A colorless plate crystal having approximate dimensions of 0.43 mm × 0.40 mm × 0.16 mm was mounted using oil on a glass fiber. All measurements were made on a Bruker SMART CCD area detector with graphite monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection corresponded to a triclinic cell, P-1, with dimensions: $a = 10.488(3)$ Å, $b = 13.614(3)$ Å, $c = 13.993(4)$ Å, $\alpha = 104.76(2)^\circ$, $\beta = 111.62(2)^\circ$, $\gamma = 107.33(2)^\circ$, and $V = 1616.5(7)$ Å^3. The structure was solved by direct methods and expanded using Fourier techniques. All calculations were performed using the Bruker SHELXTL3 crystallographic software package.

XRD analysis: XRD spectra were measured on a Kristalloflex Siemens D-5000 diffractometer using the Cu Kα radiation. Samples were analyzed after deposition on a quartz mono-crystal sample holder (Siemens). The measurements were made in the 2θ range 5–80° by steps of 0.02°, with a time per step equal to 2 s. The crystalline phases were identified by reference to the powder diffraction data files (JCPDS-ICDD).

3. Results and discussion

3.1. Stoichiometric methane oxidation

High valent transition metal oxides were screened as well as metal trifluoroacetates. In order to avoid possible interference of our desired reaction, transition metal salts with organic counter-ions were not considered here. Most of the transition metal oxides screened are commercially available with high purity, which can be handled conveniently to ensure reproducible results. When metal oxide dissolves in trifluoroacetic acid, the following reaction takes place:

$$M_2O_x + 2xCF_3COOH \rightarrow 2M(OCOCF_3)_x + xH_2O$$

Assuming water is not detrimental to methane oxidation under this condition, metal oxides can be viewed as equivalent to the corresponding metal trifluoroacetate salt as reported in the literature [4].

In addition to high valent transition metal oxides and metal trifluoroacetates, other transition metals such as Pd, Pt, and Cu known for liquid phase methane oxidation in the literature were screened here, too [5]. The results in terms of relative amount of MTFA formed per metal base used were summarized in Fig. 1. The conditions were optimized for each material screened.

First, transition metals known to catalyze direction methane oxidation to methanol such as palladium, copper, or platinum did not perform very well under these testing conditions. They showed minimal or essentially no activity toward methane oxidation. Sen et al. reported that $Pd(OAc)_2$ can oxidize methane in trifluoroacetic acid with 60% oxidant-based yield [6]. Other research groups were having trouble with reproducing that work [4,7]. We were also unable to reproduce the claimed 60% yield. Some MTFA product might come from the oxidation of the acetate group of $Pd(OAc)_2$ oxidant used in the literature.

Second, in direct comparison, transition metals with high reduction potentials such as manganese, cobalt, lead, and silver showed much higher activity toward methane oxidation. For metal catalysts with high reduction potentials, cobalt oxide (Co_3O_4) did not perform well here in terms of metal-based yield. Literature claimed that cobalt trifluoroacetate achieved 90% metal-based yield for methane oxidation. Solubility of Co_3O_4 in trifluoroacetic acid might be responsible for this apparent reactivity difference, although Periana claimed that they were unable to reproduce Moiseev's work because Co(III) did not react with methane [7].

Third, even though manganese(III) trifluoroacetate was a modest oxidant (~30% metal-based yield) for methane oxidation, the corresponding metal oxide, Mn_2O_3, gave essentially quantitative metal-based yield when reaction was oxidant limited. A 15% methane-based yield was achieved when reaction was performed with equivalent methane and metal oxide added inside a reactor. The likely reason for apparent difference between our work and literature one could be attributed to impure manganese(III) trifluoroacetate used in the literature.

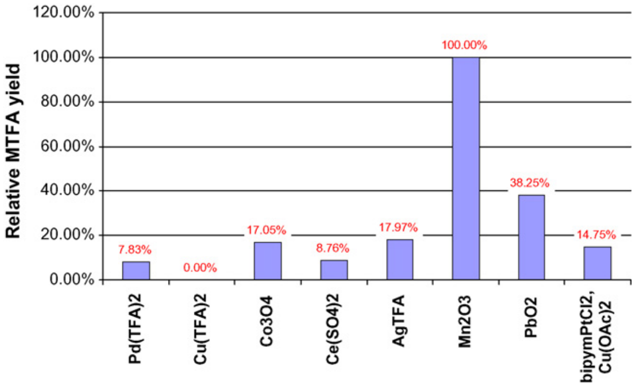

Fig. 1. Stoichiometric oxidation of methane: screening results. *Note*: air was not rigorously removed from the system during stoichiometric methane oxidation.

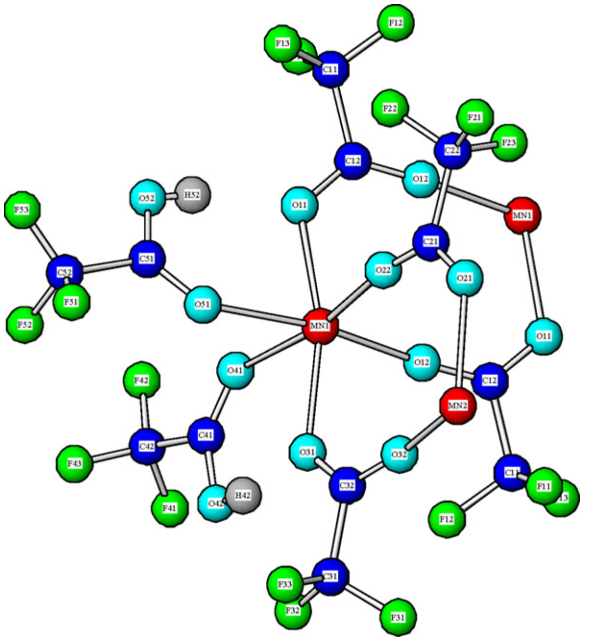

Fig. 2. Single X-ray crystal structure of Mn(TFA)$_2$-2TFAH.

Based on literature work, the following general reaction scheme has been proposed to account for manganese oxide-based stoichiometric methane oxidation in trifluoroacetic acid:

$$Mn_2O_3 + 6CF_3COOH \rightarrow 2Mn(OCOCF_3)_3 + 3H_2O \tag{1}$$

$$2Mn(OCOCF_3)_3 + CH_4 \rightarrow 2Mn(OCOCF_3)_2 + CF_3COOH + CF_3COOCH_3 \tag{2}$$

In accordance with the proposed mechanism, the spent oxidant, manganese(II) trifluoroacetate was characterized by single crystal X-ray (Fig. 2).

3.2. Catalyst regeneration and catalytic methane oxidation

In the above section we demonstrated a successful methane oxidation with manganese oxide as a stoichiometric oxidant. This process would be economically feasible on an industrial scale if active manganese catalyst can be regenerated with air or other feasible oxidants. A higher valent manganese species can be readily obtained from manganese(II) species with air under basic conditions [8]. When we treated the isolated reduced manganese(II) trifluoroacetate dissolved in water with sodium hydroxide in the presence of air, a dark color high valent manganese species was formed immediately (Fig. 3). The isolated sample was characterized by XRD and XANES analysis to reveal a mixture of Mn(II), Mn(III), and Mn(IV) oxides.

The ex situ regenerated catalyst gave essentially the same activity as commercial manganese(III) oxide, that is, quantitative manganese-based yield (Fig. 4). Mn(II), Mn(III), and Mn(IV) might interconvert under methane oxidation conditions to account for this apparent high oxidation efficiency of the regenerated spent catalyst.

The ex situ manganese regeneration requires an acid–base swing process for methane oxidation and catalyst regeneration which is still not economically feasible. It is desirable to combine these two separate processes into one single catalytic methane oxidation process.

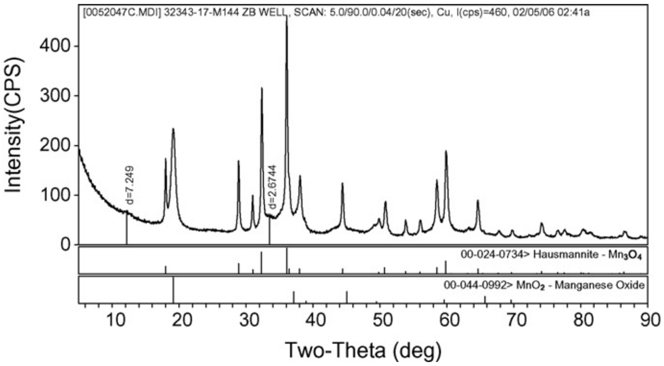

Fig. 3. XRD analysis of regenerated Mn material from Mn(TFA)$_2$.

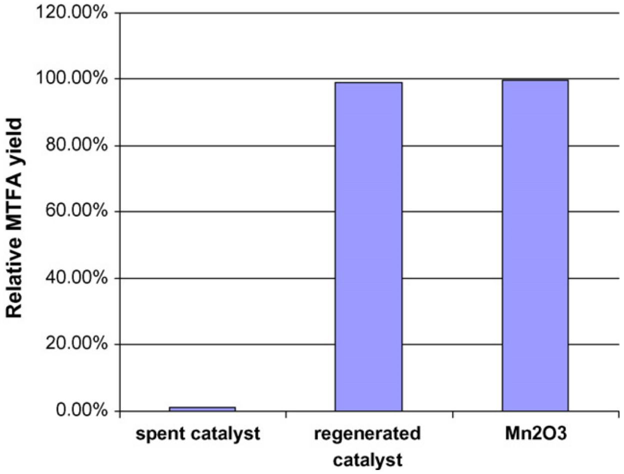

Fig. 4. Test of regenerated manganese material on stoichiometric methane oxidation.

When air was co-fed with methane (outside of methane explosion region in the gas phase) in trifluoroacetic acid with manganese oxide inside, dramatic increase of MTFA yield was observed compared with stoichiometric methane oxidation (Fig. 5). Without the presence of manganese catalyst, there was essentially no methane oxidation in the presence of air. This catalytic methane oxidation system was further optimized to give

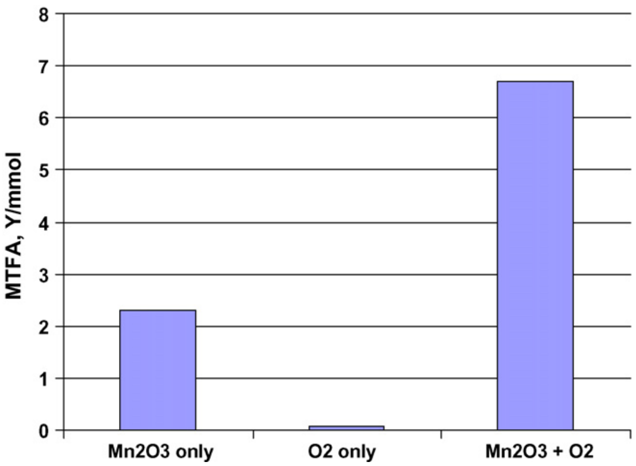

Fig. 5. Catalytic methane oxidation by air.

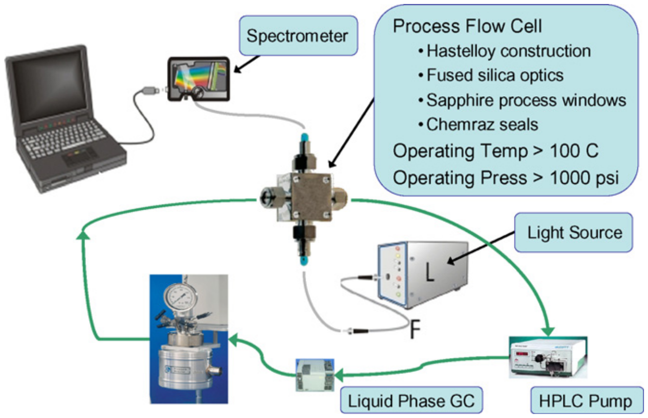

Fig. 6. In situ UV–vis and online GC analysis for catalytic methane oxidation.

36% methane-based yield with a catalytic turnover about 8.5, and more than 95% selectivity to MTFA.

3.3. Kinetic analysis

Under optimized reaction conditions, product yield stopped increasing after several catalyst turnovers, even in the presence of large excess of methane and air. In order to further understand this reaction system, an in situ UV–vis and GC analysis was set up for this high temperature, high pressure system with corrosive solvent inside (Fig. 6).

Our online GC analysis showed a rather unexpected kinetic behavior for catalytic methane oxidation system. For all catalytic methane oxidation reactions, the reaction takes place in two distinctive stages: active stage and inactive stage. In the active stage, all methane oxidation occurs with a constant reaction rate (Fig. 7). The reaction rate was the same for all reactions at the same temperature. For reactions at 180 °C, the reaction rate was 0.24 mmol/min under our testing conditions.

Based on reaction (2), the following product formation rate equation can be expressed:

$$\frac{d[\mathrm{MTFA}]}{dt} = k[\mathrm{Mn(TFA)_3}]^2[\mathrm{CH_4}] \qquad (3)$$

If we assume that methane concentration in liquid phase was constant under our kinetic analysis conditions (most time less than 10% methane conversion), a constant manganese(III) trifluoroacetate concentration is required for a constant MTFA formation rate based on the rate equation above. For a sharp transition from active stage to inactive stage to occur, a low steady-state concentration is necessary so that most time such a low concentration can be kept constant before suddenly all Mn_2O_3 precursor is consumed for a sharp drop of reactivity to occur.

In order to confirm the proposed low steady-state concentration of manganese(III) trifluoroacetate in trifluoroacetic acid spectroscopically, an in situ UV–vis analysis was developed. UV–vis analysis of reference manganese(III) species in trifluoroacetic acid showed that this species absorbs at both visible and ultraviolet region with much stronger absorption at the short wavelength region. The short wavelength region without interference with other species under reaction conditions was used for this analysis. The spectra of this absorption and MTFA concentration in the liquid phase were co-plotted below. Initially when $\mathrm{Mn(TFA)_3}$ concentration was zero (background), no reaction took place. When $\mathrm{Mn(TFA)_3}$ reached a steady-state concentration, the reaction occurred with a constant reaction rate. When all of the $\mathrm{Mn(TFA)_3}$ was consumed, the reaction stopped completely (Fig. 8). Similarly, a low steady-state Co(III) concentration in acetic acid was observed for commercial air oxidation of para-xylene to terephthalic acid [9].

The loss of reactivity at the inactive stage was caused by catalyst de-activation, rather than product decomposition. In the literature for cobalt trifluoroacetate catalyzed catalytic methane oxidation system, precipitation of cobalt difluoride was responsible for gradual de-activation of catalyst [4]. In our case precipitated manganese difluoride was isolated for catalytic methane oxidation. The precipitated manganese difluoride did not catalyze methane oxidation by air under reaction conditions. On the other hand, manganese difluoride was not observed when manganese oxide was used for stoichiometric methane oxidation and the catalyst activity was 100% regenerated.

In summary, the observed two-stage reactivity was caused by a low steady-state concentration of active catalyst under reaction conditions. The catalyst concentration was controlled by the rate of manganese oxide dissolution in trifluoroacetic acid, methane oxidation, manganese(II) trifluoroacetate reoxidation by air, and catalyst decomposition to un-reactive manganese difluoride. Staged reactivity was occasionally reported in the literature [10]. This is the first time in the literature a staged reactivity was observed in a liquid phase catalytic methane oxidation.

Reaction productivity can be improved dramatically upon the addition of silica gel. Fig. 9 shows that silica gel improved the

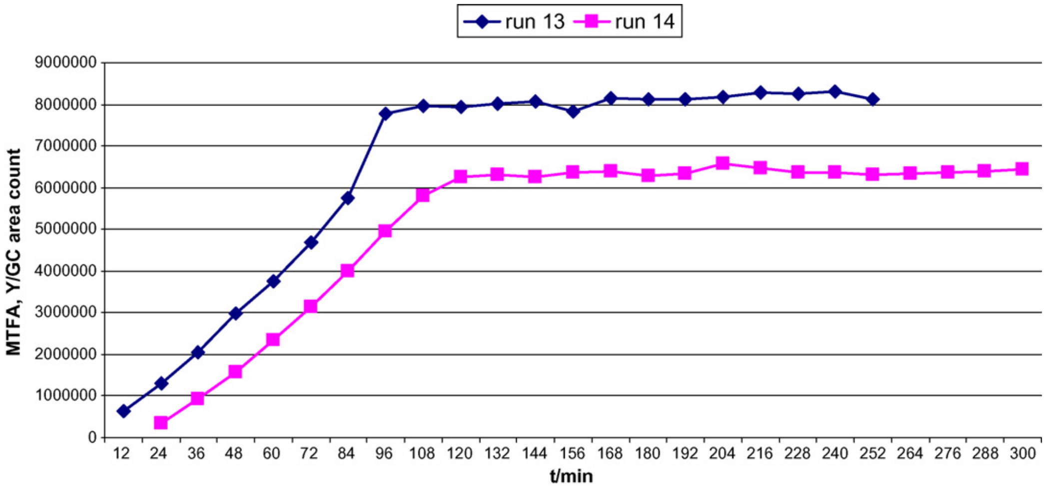

Fig. 7. Reaction kinetics for catalytic methane oxidation.

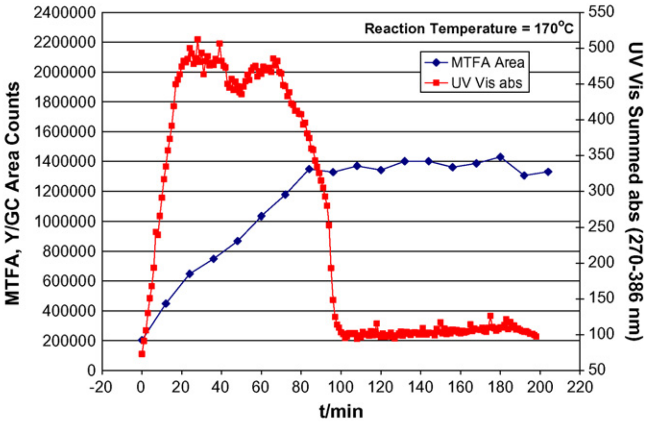

Fig. 8. In situ UV–vis and online GC analysis of catalytic methane oxidation.

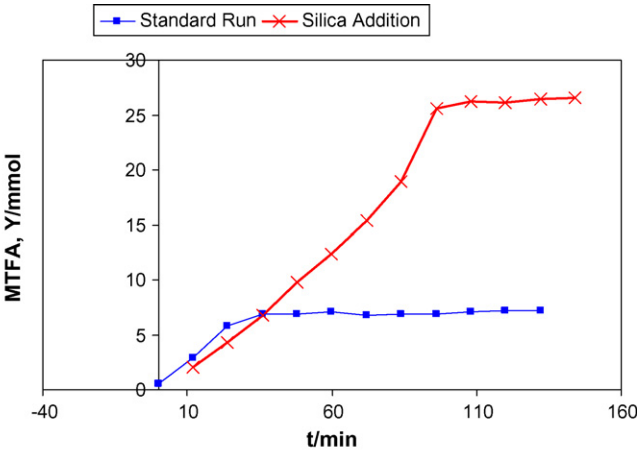

Fig. 9. Effects of silica on catalytic methane oxidation.

product yield by the increase of catalyst life. The reaction occurred at the same rate as reference reaction without silica gel at the same temperature. The enhanced catalyst life might be caused by the competing reaction between silica gel and fluoride to slow down the catalyst de-activation.

The apparent activation energy for catalytic methane oxidation was also calculated (201.0 kJ/mol) here based on our online GC analysis.

4. Conclusion

Metal oxide-based methane oxidation in trifluoroacetic acid was investigated. Manganese oxide was identified as the most promising material to work with when used as stoichiometric oxidant for methane oxidation. Oxidant-based yield approaches quantitative compared with literature reported 30% yield when manganese(III) trifluoroacetate salt was used as the oxidant. Under the reaction conditions manganese oxide reacts with trifluoroacetic acid to give manganese(III) trifluoroacetate which functions as a real oxidant to oxidize methane to methanol. Manganese(III) trifluoroacetate was reduced to manganese(II) trifluoroacetate, which was characterized by single crystal X-ray analysis.

The reduced manganese(II) trifluoroacetate can be oxidized back to high valent manganese species under basic conditions by air. This regenerated material gave the same methane oxidation efficiency as commercial manganese oxide. When air was co-fed with methane in trifluoroacetic acid, the reaction became catalytic with multiple turnover numbers with respect to manganese oxide. A process of methane to methanol conversion with high conversion (36%) and high selectivity (>95%) was achieved under optimized reaction conditions.

A novel system for in situ UV and GC analysis was set up to study the reaction mechanism. A low steady-state active manganese catalyst concentration was observed by the instrument which corresponded very well with the observed staged reactivity. In the active stage, the oxidation occurred with constant reaction rate until all of the high valent manganese catalyst was consumed and the reaction rate dropped to zero. The catalyst de-activates by manganese difluoride precipitation which can be inhibited by silica addition into the system. Additionally, the apparent activation energy was calculated (201.0 kJ/mol) for this system.

Acknowledgements

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