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Methane is oxidized directly to dimethylether (DME) on Pt/Y_2O_3 without the formation of methanol using the recycling of NO and NO₂ as an oxygen transfer system. There is no formation of N₂ and the ultimate oxidant is O₂.

Keywords

Methane partial oxidation; dimethyl ether; Pt/Y2O3; NO/O2 shuttle

The Direct Partial Oxidation of Methane to Dimethyl Ether over Pt/Y₂O₃ Catalysts Using an NO/O₂ Shuttle

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Abstract

Using a mixture of NO + O₂ as the oxidant enabled the direct selective oxidation of methane to dimethyl ether (DME) over Pt/Y₂O₃. The reaction was carried out in a fixed bed reactor at 0.1 MPa over a temperature range of 275-375 °C. During the activity tests, the only carbon-containing products were DME and CO₂. The DME productivity (μ mol g_{cat}⁻¹h⁻¹) was comparable to oxygenate productivities reported in the literature for strong oxidants (N₂O, H₂O₂, O₃). The NO + O₂ mixture formed NO₂ which acted as the oxygen atom carrier for the ultimate oxidant O₂. During the methane partial oxidation reaction, NO and NO₂ were not reduced to N₂. In situ FTIR showed the formation of surface nitrate species, that are considered to be key intermediate species for the selective oxidation.

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The direct conversion of methane to oxygenates such as methanol (MeOH) and formaldehyde (HCHO) has intrigued researchers around the globe for more than a century. Currently methanol is produced by an energy-intensive, two-stage process involving the initial disaggregation of methane to synthesis gas followed by its reassembly, while formaldehyde is obtained by the further oxidation of methanol. A substantial amount of work has been done on the direct partial oxidation of methane with activated oxidants such as H_2O_2 [1], N_2O [2] and O_3 [3] and much research have been carried out with the plain oxidant O_2 using oxide catalysts like ferric molybdate [4], MoO₃/SiO₂ [5] and V_2O_5/SiO_2 [6], as covered in recent reviews [7,8,9,10]. Other studies have reported the use of a chlorine dioxide radical for the partial oxidation of methane in a photocatalytic reaction [11], and the co-conversion of CH₄ and CO₂ to oxygenates over RhVO₃⁻ cluster anions [12]. Recent studies have tried to mimic the tri-copper and di-iron active sites in methanol producing natural enzymes [13,14] by using Fe- and Cu- exchanged zeolite catalysts [15,16]. But the difficulty in activating the strong C-H (440 kJ/mol) bond in CH₄ [17] has impeded the development of a viable selective oxidation system.

This study reports the direct partial oxidation of CH₄ over a Pt/Y₂O₃ catalyst using a novel oxidant consisting of an NO + O₂ mixture that results in the unprecedented formation of dimethyl ether (DME) as the sole partial oxidation product [18,19]. Though past studies have reported the formation of DME, it was always accompanied by the formation of methanol [20]. During the partial oxidation of CH₄ with the NO + O₂ mixture, the gas-phase reaction (NO + $\frac{1}{2}$ O₂ \rightarrow NO₂) [21] takes place to form the strong oxidant NO₂ which is used to oxidize the CH₄. The use of NO and O₂ in the presence of hydrocarbons, including methane, has been researched extensively in the past in connection with the treatment of automotive car emissions at high temperatures (> 700 °C). The objective was to reduce the NO to N₂ and simultaneously oxidize

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the hydrocarbons to CO_2 , not to carry out selective oxidation. Here the goal was to selectively oxidize CH_4 at moderate temperatures (< 400 °C) without reducing NO to N₂ or N₂O, with the NO transferring oxygen atoms from O₂. Tests with various supports such as CeO₂, TiO₂, and CaCO₃ (Fig. S1), showed that Y₂O₃ was uniquely effective in producing DME with a possible important property being the stabilization of Pt in an oxidic state.

The Pt/Y₂O₃ catalyst was prepared by incipient wetness impregnation of a commercial yttria support and had a loading of 2 wt% (0.10 mmol/g_{support}), a surface area of 41 m² g⁻¹ and a CO uptake of 27 μ mol g⁻¹. A transmission electron microscopy (TEM) image of a reduced and passivated Pt/Y₂O₃ sample showed the formation of highly dispersed Pt particles with particle size < 3 nm (Fig. S2).

X-ray absorption near-edge spectra (XANES) of reduced and calcined Pt/Y_2O_3 at in situ conditions are displayed in Fig. 1, along with the reference samples Pt foil and Pt oxide.



Figure 1. XANES spectra at Pt L_{III} edge; Conditions: Pt/Y_2O_3 after reduction at 400 °C in H₂, Pt/Y_2O_3 after calcination at 400 °C.

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The XANES showed that the calcined sample had similar white-line intensity, adsorption edge position (11563 eV), and spectral features as PtO_2 so was in a similar state of oxidation. The reduced Pt/Y_2O_3 had a slightly higher white-line intensity and adsorption edge postion (11562 eV) than the Pt foil, suggesting that the Pt was in a partially oxidized state. A linear combination fitting using the XANES spectra of Pt foil and PtO₂ indicated that Pt in reduced Pt/Y_2O_3 was 33 % in an oxidic state and 67 % in a metallic state. The partly oxidic state appears to be associated with DME formation, as the XANES results for Pt/CeO₂, Pt/TiO₂ and Pt/SiO₂ showed that the Pt was in a metallic state in these catalysts (Fig. S3), and the reactivity results showed that they were inactive for DME formation (Fig. S1).



Figure 2. DME production rate and CH₄ conversion over the Pt/Y_2O_3 catalyst. Conditions: 0.3 g of catalyst with NO + O₂ (CH₄:NO:O₂:inert = 20:1:1:78) as the oxidant at 0.1 MPa.

Fig. 2 shows the DME production rate and CH_4 conversion for the oxidation of methane (20 kPa) with a mixture of NO (1 kPa) and O₂ (1kPa) over the Pt/Y_2O_3 catalyst. The temperature

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was varied in the order: $375 \rightarrow 325 \rightarrow 275 \rightarrow 300 \rightarrow 350$ °C and the smooth conversion curve obtained gave evidence of catalyst stability in the course of the measurements. Note that the conversion is low and this is because of the use of excess methane (CH₄:O₂ = 20:1) to avoid the explosive region, which gives a maximum possible CH₄ conversion of 5%. During the activity test, the DME productivity increased with temperature to a maximum of 110 µmol g⁻¹h⁻¹ at 350 °C. A full mass balance in oxygen and nitrogen was achieved and it was confirmed that the only nitrogen compounds present were NO and NO₂. Oxygen conversion is reported in Fig S4. As the temperature increased the conversion of NO to NO₂ decreased (Fig. S4), as also expected thermodynamically, and may be one of the reasons for the decrease in DME selectivity with temperature (Table S1). The DME productivity was compared to literature values of MeOH, DME, and HCHO productivities from catalytic gas-phase methane partial oxidation with stronger oxidants such as N₂O [15,16,22,23,24], H₂O₂ [1] and O₃ [3] at low temperatures (Table 1). The DME productivity (µmol g_{cat}⁻¹h⁻¹) and turnover frequencies (TOFs) from this study were comparable to reported values at similar conditions of temperature, pressure and space velocity.

$$TOF(mol/mol_{surf} s) = \frac{Production rate(\mu mol/g_{cat} s)}{Surface site concentration(\mu mol/g_{cat})}$$
(1)

. The TOF over Pt/Y_2O_3 compared favorably to results reported with N₂O over Fe and Cu based catalysts and was comparable to that using H₂O₂ over a FeCu/ZSM-5 catalyst [25]. In contrast, the TOF was substantially lower than that using O₃ over Li/MgO [3] and this was because of substantial contributions from gas-phase reactions in the latter. Hence, the present studies show

that the production rate of oxygenates on Pt/Y_2O_3 is comparable to other reported catalysts, except that the ultimate oxidant is O_2 , and not activated oxygen sources like N_2O , H_2O_2 , and O_3 .

Catalyst				SV ^a /	TT b		Productivity		
	Т	P	CH ₄ :Oxidant:	h ⁻¹	X_{CH_4}	So ^c			Ref
	°C	atm	H ₂ O:inert	Lkg ⁻¹ h ⁻¹	%	%	μmol	TOF mol	
							g _{cat} ⁻¹ h ⁻¹	mol ⁻¹ s ⁻¹	
Fe-ZSM-5	300	1	$1:0.1(N_2O):0:3.9$	3600	0.2	14	19	1.5×10-5	22
						(MeOH)	(MeOH)	(MeOH)	
						4.6	7	5.4×10-0	
						(DME)	(DME)	(DME)	
Fe-ZSM-5	300	1	$1:0.1(N_2O):0:3.9$	5000	3.6	1.9	19	5.6×10-5	15
						(MeOH)	(MeOH)	(MeOH)	\mathbf{O}
H-Cu-SSZ-	300	1	$1:1(N_2O):0.1:1.2$	24000	0.75	2.3	55	3.1×10 ⁻⁵	15
13						(MeOH)	(MeOH)	(MeOH)	
						0.1	1.1	6.1×10 ⁻⁷	
						(HCHO)	(HCHO)	(HCHO)	
FePO ₄	400	1	$1:1(N_2O):0:1$	7200	0.87	35	300	1.7×10-5	22
						(MeOH)	(MeOH)	(MeOH)	
						23	200	1.1×10-5	
						(HCHO)	(HCHO)	(HCHO)	
						34	300	1.7×10-5	
						(DME)	(DME)	(DME)	
FePO ₄ /MCM	400	1	$1:1(N_2O):0:1$	18000	0.98	24	570	3.1×10 ⁻⁵	23
-41						(MeOH)	(MeOH)	(MeOH)	
						48	1200	2.4×10 ⁻³	
						(HCHO)	(HCHO)	(HCHO)	
						25	600	3.2×10-5	
						(DME)	(DME)	(DME)	
Fe	280	1	$1:0.4(N_2O):0:0.07$	12000	0.93	20	610	2.9×10 ⁻⁵	21
/Ferrierite						(MeOH)	(MeOH)	(MeOH)	\bigcirc
						28	870	4.1×10^{-3}	()
						(DME)	(DME)	(DME)	
FeCu/ZSM-5	50	20	$1:0.025(H_2O_2/H_2O)$	410	0.5	92	76	3.9×10 ⁻⁶	25
						(MeOH)	(MeOH)	(MeOH)	
Li/MgO	377	1	$1:0.5(O_2):0.009(O_3):8.4$	360000	4.0	90	60000	0.3	3
						(HCHO)	(HCHO)		
Pt/Y_2O_3	350	1	$1:0.05(O_2):0.05(NO):3.$	6000	0.54	11	110	1.1×10 ⁻⁴	This
			9			(DME)	(DME)	(DME)	work

Table 1. St	ummary of	catalytic m	ethane partial	oxidation at le	ow temperatures	(≤400 °C)
	2	2	1		1	(-	

^a SV = Space velocity L kgcat⁻¹ h^{-1} , ^b X= Conversion, ^c S_o = Oxygenate selectivity

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Figure 3. (a) Turnover frequency and (b) DME selectivity. Conditions: 0.3 g of Pt/Y₂O₃ (CO uptake value based on the surface Pt atoms: 27 μ mol g⁻¹) with NO + O₂ (CH₄:NO:O₂:inert = 20:1:1:78), NO₂ (CH₄:NO₂:inert = 20:1:79) and O₂ (CH₄:O₂:inert = 20:1:79) as oxidant at 0.1 MPa.

In the activity test over the Pt/Y₂O₃ catalyst (Fig. 2), the NO and NO₂ were not reduced to form N₂. This indicates that NO was not participating in the direct oxidation of CH₄, otherwise it would have been reduced to form N₂ or N₂O. Hence, the possible oxidants for this catalytic system were NO₂ and O₂. To evaluate the role of NO₂, activity tests (Fig. 3(a)) were done using NO₂ (CH₄:NO₂:inert=20:1:79) and O₂ (CH₄:O₂:inert=20:1:79) over the Pt/Y₂O₃ catalyst. The activity results were compared using TOFs based on surface Pt atoms titrated by CO chemisorption and the total CH₄ reacted. The catalyst gave similar TOFs with NO + O₂ and NO₂, but the TOFs with O₂ were higher. However, the production of DME was observed only with NO + O₂ or NO₂, while only CO₂ was observed with O₂ (Fig. 3(b)). Hence, the DME formation and similar TOF values with NO + O₂ and NO₂, indicates that the NO₂ formed by the NO + O₂ mixture was acting as the oxygen atom carrier during the CH₄ partial oxidation reaction. Since NO₂ is produced from NO by oxidation by O₂, the ultimate oxidant was molecular oxygen. The lower activity of the Pt/Y₂O₃ catalyst with NO + O₂ and NO₂ compared

to O_2 suggests that the active sites responsible for the activation of O_2 were blocked by some adsorbed NO_x species. With $NO + O_2$ the selectivity was lower than with NO_2 because the O_2 contributed to complete oxidation. Evidence for these adsorbed NO_x species and their role in the reaction was found by in situ FTIR measurements.

The FTIR studies required surface sensitivity so a sample of Pt/Y_2O_3 with higher surface area was used. The sample was prepared in the same manner as before using incipient wetness impregnation with the same loading of 2 wt.%. The BET surface area was roughly double at 96 m^2g^{-1} and the CO uptake was 98 µmol g⁻¹.

First, the adsorption of NO + O₂ was studied on the Y₂O₃ support and the Pt/Y₂O₃ by in situ FTIR (Fig. S6). The Y₂O₃ support showed the formation of a monodentate nitrate species (1357 cm⁻¹), while the Pt/Y₂O₃ sample additionally displayed bands due to bidentate (1240 cm⁻¹) and bridged (1004 cm⁻¹) nitrate species [26,27,28]. The latter were indicated to be associated with the Pt. A CO₂-TPD profile of the Pt/Y₂O₃ sample indicated the presence of strong basic sites, which other inactive samples lacked (Fig. S7). The presence of these strong basic sites can facilitate the stable adsorption of nitrate species at reaction temperatures.

Following this, the behavior of CH₄ with the adsorbed nitrate species on Pt/Y₂O₃ was studied at two different temperatures, 250 °C and 300 °C. Again, the formation of monodentate (1357 cm⁻¹), bidentate (1240 cm⁻¹), and bridged (1004 cm⁻¹) nitrate species on the Pt/Y₂O₃ catalyst was observed at these temperatures (Fig. 4). At 250 °C, there were no changes in the spectra upon exposure to CH₄ (Fig. 4(a)) consistent with the lack of conversion (Fig. 3). However, at 300 °C, the band for the bridged (1004 cm⁻¹) nitrate species disappeared (Fig. 4(b) as indicated by the arrows) and this coincided with the start of reaction (Fig. 3). The panels labeled after NO +O₂ exposure (Fig. 4(a) and (b), were actually taken in He, indicating that the

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bridged nitrate species was stable. Additional control experiments confirmed that the bridged nitrate species in the absence of methane was stable and did not desorb even at 400 °C.



Figure 4. In situ FTIR spectroscopy spectra for the reaction of adsorbed NO_x species on Pt/Y₂O₃ with CH₄. Conditions: (a) 250 °C, (1) under flow of He (2) under He after flow of NO:O₂:He = 1:1:98 (100 ml min⁻¹), (3) under flow of 2 % CH₄ in He (50 ml min⁻¹) for 30 min, (4) under He after flow of CH₄ (b) 300 °C (1) under He after flow of NO:O₂:He = 1:1:98 (100 ml min⁻¹), (2) under flow of 2 % CH₄ in He (50 ml min⁻¹) for 30 min, (3) under He after flow of CH₄

Previous studies have reported that the synthesis of DME via methanol dehydration follows a dual-site mechanism, involving the reaction between surface methoxy and methyl species [29,30]. Other studies have reported the formation of methoxy radical (CH₃O•), as a key intermediate for the gas phase partial oxidation of CH₄ by NO + O₂ [18].

A possible reaction scheme involves the reaction of the bridging nitrate species with adsorbed methyl groups to form methoxide species (Fig. 5(a)), and then the reaction of the methoxide species with additional methyl groups to form DME (Fig. 5(b)). Thus, DME may be formed without the intermediacy of methanol.



Figure 5. A possible scheme for the partial oxidation of CH_4 to DME by NO + O₂ (a) Reaction between the adsorbed nitrate and methyl species to form methoxy species (b) Reaction between the adsorbed methoxy species and methyl species to form DME.

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Figure 6. Effect on the DME production rate (points are experimental results and curves are calculated fits) and TOF by varying the (a) CH₄ partial pressure, (b) O₂ partial pressure and (c) NO partial pressure. Conditions: 325 °C, 1.0 g of Pt/Y₂O₃ (CO uptake value: 98 μ mol g⁻¹). (a) under constant O₂ (1 kPa) and NO (1 kPa) partial pressure, (b) under constant CH₄ (20 kPa) and NO (1 kPa) partial pressure, and (c) under constant CH₄ (20 kPa) and O₂ (1 kPa) partial pressure

The effects of CH₄, NO, and O₂ partial pressures for the partial oxidation of CH₄ on the Pt/Y_2O_3 catalyst were determined at 325 °C (Fig. 6) With increase in CH₄ partial pressure the TOF of the reaction increased linearly and the DME productivity increased slightly (Fig. 6(a)). With increase in O₂ partial pressure, the TOF of the reaction remained almost constant (Fig. 6(b)), which indicates that O₂ was not participating directly in the CH₄ partial oxidation. The DME productivity decreased with O₂ partial pressure up to 1 kPa but did not change appreciably

above 1 kPa. With increase in NO, the TOF of the reaction increased up to 2 kPa NO partial pressure, but was almost constant above this pressure (Fig. 6(c)). The DME productivity decreased steadily below 2 kPa and remained almost constant above 2 kPa. Here, the 2 kPa NO partial pressure was the pressure required for the complete conversion of 1 kPa O₂ to form 2 kPa NO₂ (2NO + O₂ \rightarrow 2NO₂). With increase in NO partial pressure, the availability of NO₂ increased up to 2 kPa NO partial pressure but above this pressure, due to the limited O₂ (1 kPa) availability no more NO₂ was formed and hence the TOF of the reaction became almost constant. This indicates that NO₂ was directly participating in the partial oxidation of CH₄.

The partial pressure dependencies of the DME production rates can be described by a power-rate law expression:

$$DME \ rate = k P_{CH4}^{0.51} P_{O2}^{-0.30} P_{NO}^{-0.94} \tag{2}$$

The rate expression is consistent with a sequence of steps in which the adsorption of methane and the reaction of an adsorbed methyl species on Pt with a surface NO_2 species are irreversible (SI) and is consistent with the reaction scheme (Fig. 5). The DME production rate curves in Fig. 6 were obtained with this equation. Since the adsorption of methane is a rate-determining step, other steps are fast and species such as methyl or methoxide groups are not observed (Fig. S8 and discussion). The species are highly reactive and have low surface coverages.

In summary, the direct partial oxidation of CH₄ to dimethyl ether (DME) on Pt/Y₂O₃ was studied using a mixture of NO and O₂ as the oxidant. In the activity tests, Pt/Y₂O₃ gave the highest productivity for DME (110 μ mol g⁻¹h⁻¹) at 350 °C. The activity test results showed that NO₂ was acting as the oxygen atom carrier for the ultimate oxidant O₂, in the NO + O₂ mixture. The effect of O₂ partial pressure suggested that O₂ was not directly participating in the CH₄

partial oxidation, but only through the intermediacy of NO₂. In situ FTIR studies on the Pt/Y_2O_3 showed the formation of surface NO_x which were the likely reactive species.

Experimental section

The reactions were carried out in a fixed bed reactor after pretreating the catalysts at 400 °C under a flow of H₂. The products were analyzed by a combination of two gas chromatographs and one FTIR spectrometer connected in parallel (SI. 1.2), which allowed quantification of all products of reaction, including all relevant nitrogen species.

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