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Isotopic $^{18}O/^{16}O$ Substitution Study on the Direct Partial Oxidation of CH_4 to Dimethyl Ether over a Pt/Y_2O_3 Catalyst Using NO/O_2 as an Oxidant

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1. Experimental

The Pt/Y_2O_3 catalyst was prepared by incipient wetness impregnation of an aqueous solution of hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Wako, 98.5%) on yttrium (III) oxide (Y_2O_3, Nippon Yttrium, 99.9%). Quantities of reagents were used to give a loading of 2 wt% Pt/Y_2O_3, corresponding to a Pt concentration of 0.10 mmol g^{-1} Y_2O_3. The sample was dried at 110 °C for 12 h and calcined at 400 °C for 3 h in an open air furnace. The catalyst was reduced at 400 °C for 2 h in flowing H_2 and passivated at room temperature for 2 h under 0.2% O_2/He before BET surface area analysis (using a Micromeritics ASAP 2020 micropore size analyzer at 77 K) and TEM measurement (using a Topcon EM-002B high-resolution analytical electron microscope operated at 120 kV). The sample was reduced in the same manner prior to total dynamic CO uptake measurement (performed by passing pulses of 3% CO in He over the sample at 50 °C using a TPD-1-AT BEL instrument and monitoring the mass signal (m/z = 28) by a quadrupole mass spectrometer).

Isotopic substitution pulse measurements were conducted on the Pt/Y_2O_3 catalyst using a catalyst analyzer (BELCAT II, MicrotracBEL Corp) equipped with a quadrupole mass spectrometer (BELMASS). The gases used were methane (99.999%), 5% nitric oxide in helium (certified mixture), helium (99.998%), hydrogen (99.999%), oxygen (>99.99%), and isotopically labeled oxygen-18 (>99 at%). Gases were purchased from Tokyo Koatsu Yamazaki Co. Ltd, except $^{18}O_2$ which was obtained from Isotec® (Sigma Aldrich). Prior to the measurement, the catalyst (100 mg) was treated at 400 °C for 2 h in H_2 flow (100 cm^3 min^{-1} or 68 μmol s^{-1}), cooled to 325 °C in He flow (30 cm^3 min^{-1} or 20 μmol s^{-1}), and then held at 325 °C for 30 min. A reaction gas mixture (20% CH_4, 1% NO, 1% O_2 and 78% He), which was previously used for steady-state reactivity studies[1], was then introduced at a total flow rate of 100 cm^3 min^{-1} or 68 μmol s^{-1}. After 2 h of stabilization under this condition the O_2 flow was replaced with He, and the system was maintained until the mass spectrometer (MS) signals of the effluent streams were stable. Then, $^{16}O_2$ was premixed with He and 36 μmol pulses of the mixture (5% $^{16}O_2$/He) were injected at 6 min intervals until no changes in the effluent streams were observed. The sample loop was then purged by flushing with pulses of He for 20 min. This sequence was then repeated with pulses of $^{18}O_2$ premixed with He (5% $^{18}O_2$/He) and then with the 5% $^{16}O_2$/He. The areas for the MS peaks of the observed products were compared with the areas from calibrated pulses of CO_2 and DME.

2. Estimation of metal dispersion and particle size

The metal dispersion (*D*) is defined as the fraction of total Pt atoms at the surface. It is calculated from CO chemisorption measurements by assuming an adsorption stoichiometry of CO/Pt = 1 using eqn. 1:

$$D = \frac{N_{CO} \times n}{\frac{M_L}{MW_{Pt}}} \tag{1}$$

In this equation, N_{CO} is the CO uptake after accounting for CO uptake on bare Y_2O_3 (2 μmol g^{-1}), *n* is the chemisorption stoichiometry (assumed to be 1), M_L is the metal loading (2 g Pt per $g_{catalyst}$), and MW_{Pt} is the atomic weight of Pt (195.08 g mol^{-1}).

$$D = \frac{(96\ \mu mol/g) \times 1}{\frac{2}{(195.08\ g/mol)}} = 94\%$$

The particle size (D_p) was also calculated from the CO uptake value by assuming uniform spherical particles using eqn. 2:

$$D_p(nm) = \frac{6 \times 10^{23} \times n_s \times M_L}{\rho \times N_A \times n \times N_{CO}} \tag{2}$$

In this equation, n_s is the surface metal atom density (Pt = 1.2×10^{15} atoms per cm^2), ρ is the density of bulk metal (Pt = 21.4 g cm^{-3}), and N_A is Avogadro's number (6.02×10^{23} atoms mol^{-1}).

$$D_p = \frac{6 \times 10^{23} \times (1.2 \times 10^{15}) \times 2}{21.4 \times 6.02 \times 10^{23} \times 1 \times 96}$$

$$D_p = 1.2\,nm$$

3. Steady-state DME productivity

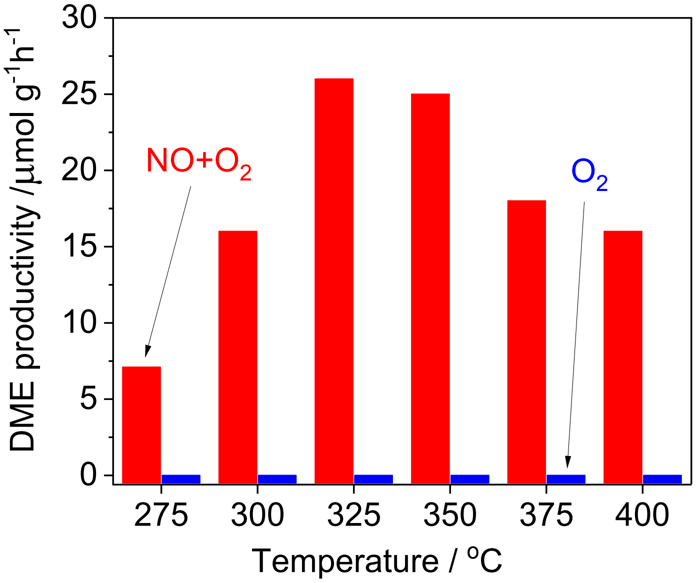


Fig. S1. DME production rate as a function of temperature with and without NO during CH_4 partial oxidation by $NO+O_2$. The y-axis is displaced to more clearly show zero DME formation with only O_2. Conditions: 100 mg of catalyst with NO/O_2 (CH_4:NO:O_2:inert = 20:1:1:78) and O_2 (CH_4:O_2:inert = 20:1:79) as oxidants at 0.1 MPa.

Fig. S1 shows the DME production rate as a function of temperature with and without NO. The measurements were conducted in a tubular quartz reactor at atmospheric pressure, a GHSV of 1200 h^{-1}, and temperatures of 275 °C to 400 °C. The DME production rate went through a maximum at 325 °C and decreased at higher temperatures, which was attributed to overoxidation.

4. Gas phase oxidation of NO to NO_2

The oxidation of NO to NO_2 in the gas phase has been reported to follow mainly two mechanisms. The first involves the formation of an NO dimer intermediate:[2-4]

$$2NO \leftrightarrows (NO)_2 \tag{3}$$

$$(NO)_2 + O_2 \rightarrow 2NO_2 \tag{4}$$

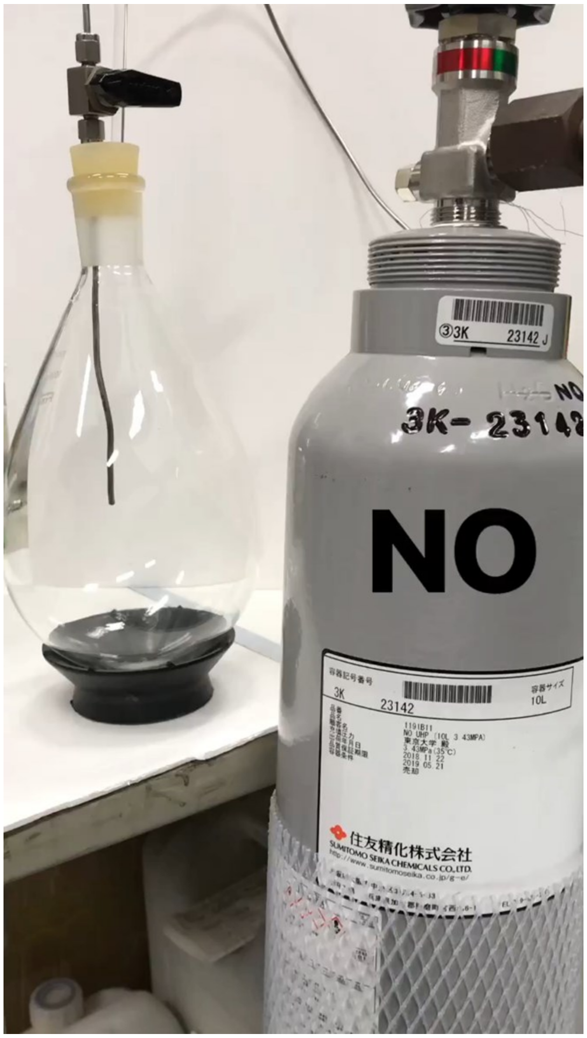
The second is with NO_3 and N_2O_4 as intermediates:

$$NO + O_2 \rightleftarrows NO_3 \tag{5}$$

$$NO_3 + NO \rightleftarrows N_2O_4 \tag{6}$$

$$N_2O_4 \rightarrow 2NO_2 \tag{7}$$

The video below demonstrates the rapid transformation of NO to NO_2 upon exposure to air at room temperature.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Media1.mov

5. A single oxygen transfer system

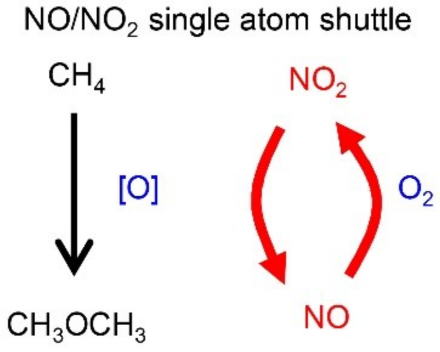

Fig. S2. Schematic of DME formation during CH_4 partial oxidation by NO+O_2

The steady-state DME productivity with NO + O_2 shown earlier (Fig. S1) was achieved without reduction of NO/NO_2 to N_2. This means that NO/NO_2 acted as an oxygen atom shuttle to oxidize methane using a single atom of oxygen [O] derived from O_2, as illustrated in Fig. S2. The single oxygen atom is subsequently transferred during the partial oxidation.

6. Thermodynamics

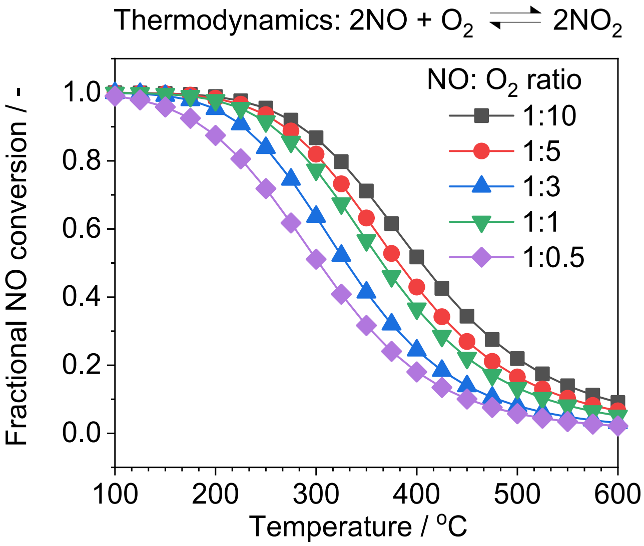

Figure S3. NO conversion as a function of temperature for different mixture ratios of NO and O_2 at 0.1 MPa.

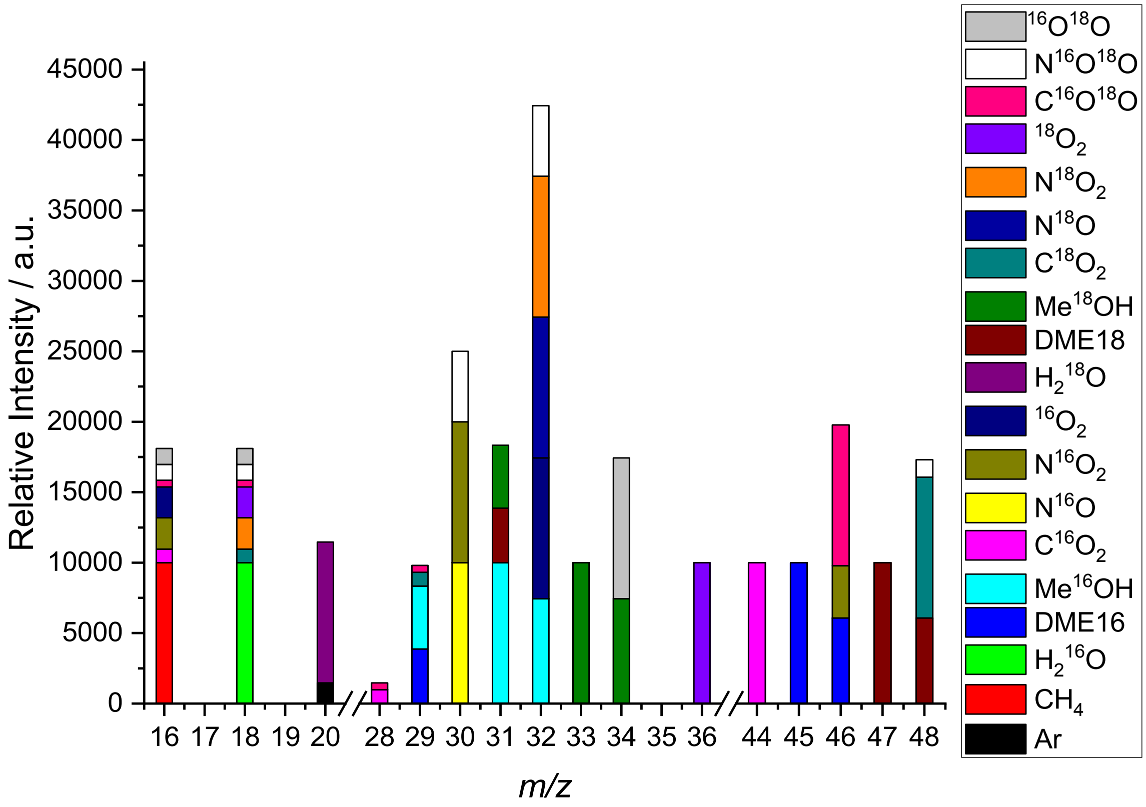

Figure S4. Expected contributions to each peak intensity in the MS signals (N_2, N_2O, HCHO and CO have been omitted).

7. Derivation of kinetic isotope effect

The relative rate for the reaction of isotopes was derived from the partition functions and statistical mechanics. The rate constants are given by eqn. 8:

$$k = \frac{k_b T}{h}\frac{Q^{\#}}{Q} e^{-E/RT} \tag{8}$$

Here, k_bT/h is the universal frequency, $Q^{\#}$ is the partition function of the activated complex, Q is the partition function of the reactant, and E is the activation energy.

For oxygen isotopes the difference in the zero-point energies is very small, so the activation energies are nearly equal. This means that only the difference in the partition functions is relevant. Assuming a simple representation of only the movement along the reaction coordinate, a one-dimensional translational partition function is used. This results in eqn. 9 expression:

$$\frac{Q^{\#}}{Q} = \frac{1}{\sqrt{2\pi M k_b T}} \tag{9}$$

where M is the mass of the molecule. The only difference in the partition functions of oxygen isotopes is the mass, resulting in an inverse square root dependence on mass of the isotope:

$$\frac{k_{18}}{k_{16}} = \sqrt{\frac{M_{16}}{M_{18}}} \tag{10}$$

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