

Bifunctional pathways mediated by Pt clusters and Al₂O₃ in the catalytic combustion of dimethyl ether†

Akio Ishikawa and Enrique Iglesia*

Received (in Berkeley, CA, USA) 21st February 2007, Accepted 26th April 2007

First published as an Advance Article on the web 11th May 2007

DOI: 10.1039/b702693e

Mixtures of Pt clusters dispersed on γ -Al₂O₃ and additional γ -Al₂O₃ led to much higher DME combustion turnover rates than on the individual components or on Pt clusters supported on non-acidic oxides.

The physical properties of dimethyl ether (DME) resemble those of liquefied petroleum gas (LPG), making it an attractive energy carrier within developing economies.^{1–4} The emergence of DME as a low-cost commodity chemical could also provide opportunities for its use in space and water heating and in distributed power generation with small turbines or fuel cells.^{5–7} We have recently examined the catalytic combustion of DME on Pt clusters and found that reaction rates are controlled by the activation of C–H bonds in methyl groups within molecularly adsorbed DME on sites consisting of vacancy-oxygen pairs at Pt surfaces.⁸ A parallel study of the effects of Pt cluster dispersion (0.02–0.99 dispersion) detected significant effects of γ -Al₂O₃ and ZrO₂ supports on DME combustion turnover rates.

The combination of acid sites on various oxides and metal sites provides bifunctional alkane isomerization pathways,^{9–11} but it has not been reported previously for combustion reactions. We provide evidence here for bifunctional pathways in catalytic DME combustion when Al₂O₃ is present, either as a support for Pt clusters or as an added material present as a physical mixture with Pt-based catalysts. These bifunctional pathways lead to the exclusive formation of CO₂ and H₂O and to reaction rates more than ten-fold higher than for monofunctional Pt-catalyzed combustion reactions. These pathways involve the hydrolysis of DME with H₂O formed in incipient combustion reactions to give methanol, which combusts on Pt clusters much more rapidly than DME.

The γ -Al₂O₃ (193 m² g⁻¹) and SiO₂ (280 m² g⁻¹) samples were prepared by treatment of Al₂O₃ (Sasol North America Inc., Lot# C1643) and SiO₂ (Chromatographic Silica Media, CAS# 112926-00-8) in flowing dry air at 923 K for 5 h before use. ZrO₂ was prepared as previously described.⁸ Pt/Al₂O₃ and Pt/ZrO₂ were prepared by incipient wetness impregnation of γ -Al₂O₃ or ZrO₂ with aqueous H₂PtCl₆·6H₂O solutions and subsequent treatment in flowing dry air at 823–1023 K for 5 h. These samples were then treated in pure H₂ at 723–1023 K for 2 h. These treatments led to catalysts with a wide range of Pt dispersion (0.02–0.81). Pt dispersions were measured using volumetric methods from the uptake of strongly chemisorbed H₂ at 313 K. Reactant and

product concentrations were measured using gas chromatography (Agilent 6890). Catalyst samples (2–5 mg) were diluted with SiO₂ or γ -Al₂O₃ supports within pellets (250–450 μ m). Liquids (HCHO, CH₃OH, CH₃OCHO, H₂O) were introduced with a syringe pump and immediately vaporized into a reactant stream at 373–403 K. Homogeneous DME reactions did not contribute to the DME combustion rates measured below 523 K.⁸

Fig. 1 shows an Arrhenius plot for DME combustion on 0.9% wt Pt/Al₂O₃ (2 mg, 0.75 dispersion) diluted with SiO₂ or Al₂O₃. No effects from SiO₂ were observed at either 50 : 1 or 75 : 1 dilution ratios. In contrast, Al₂O₃ diluents increased DME combustion rates monotonically with increasing dilution ratio. Only CO₂ and H₂O were detected in these experiments. DME reaction rates were measured on Pt-free Al₂O₃ and SiO₂ samples with and without added 2 kPa H₂O (supplementary information†). DME conversion to CO₂ and CH₃OH (HCHO, CH₃OCHO in traces) was observed on Al₂O₃ above 473 K in the presence of H₂O, while no products were detected below 523 K without added H₂O. No products were observed on SiO₂ below 523 K with or without H₂O addition.

In these experiments, methanol formed *via* DME hydrolysis on acid sites on Al₂O₃,² while other products formed *via* CH₃OH oxidation reactions. DME reactions with water occur on Al₂O₃ above 473 K to form H₂–CO mixtures,² but neither product was observed on Al₂O₃ without Pt clusters in our study, apparently because CO and H₂ products were rapidly converted to CO₂ and H₂O in the presence of O₂ co-reactants.

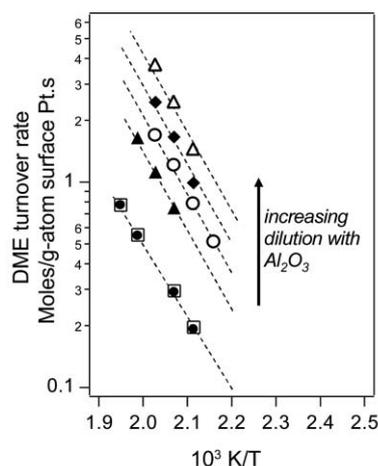
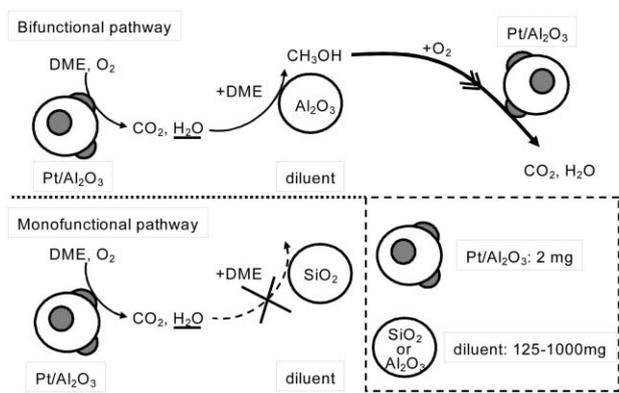


Fig. 1 DME combustion turnover rates (moles per g-atom surface Pt per s) on 1.0% wt Pt/Al₂O₃ as a function of temperature. [2 mg, 0.68 dispersion, 250–450 μ m, SiO₂ dilution: (□) 75 : 1, (●) 50 : 1; γ -Al₂O₃ dilution: (▲) 25 : 1, (○) 50 : 1, (◆) 100 : 1, (△) 200 : 1].

Department of Chemical Engineering, University of California, Berkeley, CA 94720, USA. E-mail: iglesias@berkeley.edu; Fax: +1 510 642 4778; Tel: +1 510 642 9673

† Electronic supplementary information (ESI) available: DME reaction rates on Pt-free Al₂O₃ and SiO₂. See DOI: 10.1039/b702693e



Scheme 1 Bifunctional pathways mediated by Pt clusters and Al₂O₃, and monofunctional pathways on supported Pt clusters.

DME reactions with O₂ on Al₂O₃ and SiO₂ without added H₂O became detectable only above 523 K. On SiO₂, the products formed reflect homogeneous DME pyrolysis and oxidation reactions *via* radical chain reactions, which become important above 523 K⁸ and form predominantly CO, CH₄, HCHO, HCOOH, and H₂O. The higher DME combustion rates on Al₂O₃ compared with SiO₂ are consistent with parallel contributions from DME reactions with H₂O molecules formed in homogeneous DME reactions, which formed more reactive CH₃OH molecules.

These results led us to propose the pathways depicted in Scheme 1 to account for the effects of Al₂O₃ on DME combustion rates on Pt-based catalysts (Fig. 1). DME combustion on supported Pt clusters forms CO₂ and H₂O, and the H₂O products then react with DME on Al₂O₃ to form CH₃OH. These CH₃OH molecules rapidly oxidize on Pt clusters to form CO₂ and H₂O. Only CO₂ and H₂O products were detected in all cases. The rapid combustion of CH₃OH on Pt clusters was confirmed from its complete oxidation to CO₂ and H₂O at temperatures (423 K, 2 kPa CH₃OH, 20 kPa O₂) well below those required for even modest DME conversions (473 K). In contrast, SiO₂, as a support or a diluent, did not influence DME combustion rates because DME reacts only on Pt clusters *via* slower monofunctional pathways. Bifunctional pathways do not require atomic proximity between Pt and γ -Al₂O₃ functions and they can be implemented even as physical mixtures of Al₂O₃ with Pt/Al₂O₃ (1.0% wt, 0.68 dispersion; 200 : 1 dilution ratio), which led to apparent turnover rates about ten-fold higher than on the Pt/Al₂O₃ sample used undiluted or diluted with SiO₂ (Fig. 1).

Our previous parallel study showed that DME turnover rates increase with increasing Pt cluster size because of concomitant changes in the number and stability of vacancy sites on the Pt surface, which are required for activating C–H bonds in DME.⁸ We extend here these Pt cluster size effects on DME combustion rates to a broader range of Pt dispersion (0.02–0.81) and show the consequences of the support on turnover rates.

Fig. 2 shows DME combustion rates (per mass of the supported Pt catalyst) as a function of Pt cluster size (from dispersion values assuming spherical clusters). On small and less reactive Pt clusters (<3 nm), DME combustion rates did not depend on the identity of the support because the H₂O concentrations prevalent at the low DME conversions achieved on these catalysts led to negligible contributions from bifunctional pathways on Al₂O₃ supports.

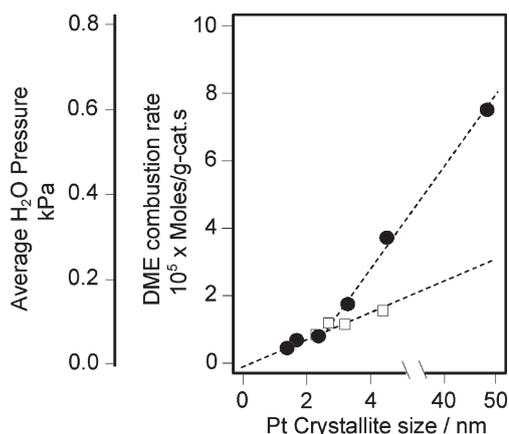


Fig. 2 DME combustion turnover rates (moles per g-cat per s) and average H₂O partial pressure as functions of Pt cluster sizes for ZrO₂ and γ -Al₂O₃ supports [473 K, 2 kPa DME, 20 kPa O₂, balance He, (□) 1.0% wt Pt/ZrO₂, (●) 0.9% wt Pt/Al₂O₃, catalysts (5 mg) diluted with SiO₂ within pellets (50 : 1), 250–450 μ m].

Larger and more reactive clusters led to higher DME conversions and H₂O concentrations; as a result, DME hydrolysis reactions on Al₂O₃ formed methanol, which converted to CO₂ and H₂O on Pt clusters much more rapidly than DME. Methanol was not detected (<50 ppm) among reaction products in any reaction conditions because of its rapid combustion. As a result, Pt/Al₂O₃ gave much higher DME combustion rates than Pt/ZrO₂ on samples with Pt clusters larger than \sim 3 nm (Fig. 2).

We provide evidence here for bifunctional pathways in the combustion of DME on Pt clusters supported on Al₂O₃. These bifunctional effects arise from DME reactions with H₂O (formed in combustion reactions or added to DME–O₂ reactants) on Al₂O₃ acid sites. Methanol molecules thus formed react on Pt clusters much faster than DME. These bifunctional pathways occur also on physical mixtures of Al₂O₃ with Pt-based catalysts and allow the design and use of catalysts with much lower Pt contents to achieve practical DME catalytic combustion rates.

This study was supported by BP as part of the Methane Conversion Cooperative Research Program at the University of California at Berkeley.

Notes and references

- V. V. Galvita, G. L. Semin, V. D. Belyaev, T. M. Yurieva and V. A. Sobyenin, *Appl. Catal., A*, 2001, **216**, 85.
- K. Takeishi and H. Suzuki, *Appl. Catal., A*, 2004, **260**, 111.
- T. Nishiguchi, K. Oka, T. Matsumoto, H. Kanai, K. Utani and S. Imamura, *Appl. Catal., A*, 2006, **301**, 66.
- K. Faungnawakij, Y. Tanaka, N. Shimoda, T. Fukunaga, S. Kawashima, R. Kikuchi and K. Eguchi, *Appl. Catal., A*, 2006, **304**, 40.
- J.-L. Li, X.-G. Zhang and T. Inui, *Appl. Catal., A*, 1996, **147**, 23.
- T. H. Fleisch, A. Basu, M. J. Gradassi and J. G. Masin, *Stud. Surf. Sci. Catal.*, 1997, **107**, 117.
- T. H. Fleisch and R. A. Sills, *Stud. Surf. Sci. Catal.*, 2004, **147**, 31.
- A. Ishikawa, M. Neurock and E. Iglesia, manuscript in preparation.
- H. Liu, V. Adeeva, G. D. Lei and W. M. H. Sachtler, *J. Mol. Catal. A: Chem.*, 1995, **100**, 35.
- K. Na, T. Iizaki, T. Okuhara and M. Misono, *J. Mol. Catal. A: Chem.*, 1997, **115**, 449.
- G. Onyestyak, G. Pal-Borbely and H. K. Beyer, *Appl. Catal., A*, 2002, **229**, 65.