

# Reply to Comment on "Thermal Conversion of Methoxy Species on Dimethyl Ether Adsorbed CeO<sub>2</sub>"

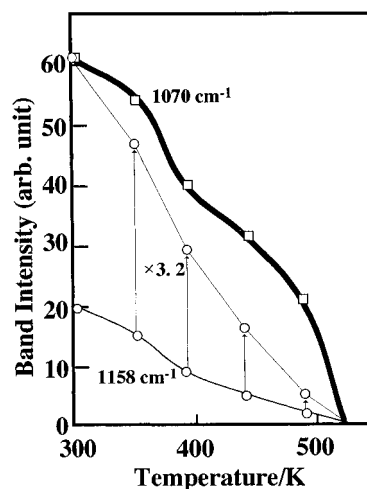
Michikazu Hara, Miyuki Kawamura, Junko N. Kondo, Kazunari Domen, and Ken-ichi Maruya\*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta Midori-ku, Yokohama 226, Japan

Received: November 19, 1996

We would like to thank Binet and Lavalley for giving us this opportunity to complement our shortcomings and short explanations in our recent paper.<sup>1</sup> Our conclusions in the paper that the methoxy species formed on CeO<sub>2</sub> surface by the dissociative adsorption of dimethyl ether (DME) at room temperature are converted into the new  $\mu$ -OCH<sub>3</sub> with increasing temperature are quite contrary to the comments summarized in "There is only molecular DME on the DME-adsorbed CeO<sub>2</sub>." It will be interesting and important for understanding the catalysis in metal oxide catalysts to consider the conflict carefully.

Binet and Lavalley have assigned the bands at 1156 and 1076 cm<sup>-1</sup> in the infrared (IR) spectra of the DME-adsorbed CeO<sub>2</sub> at 300 K to the C–O stretchings ( $\nu$ (CO)) of molecular DME adsorbed on to CeO<sub>2</sub>, while the two bands have been attributed to the  $\nu$ (CO) of the terminal- and bridged-OCH<sub>3</sub>, respectively, in ref 1. Although the bands were attributed to the  $\nu$ (CO) of molecular DME adsorbed onto CeO<sub>2</sub> as everyone initially thought, we could not identify these bands only by the IR study since the IR background of the CeO<sub>2</sub> disk below 950 cm<sup>-1</sup> was so large in our IR experiments that the  $\nu_s$ (COC) band (900 cm<sup>-1</sup>) to identify molecular DME could not be recognized in the noisy IR spectrum. For this reason, many experimental results in addition to the IR results were considered to identify the bands. We note here three bases for the surface methoxy species on the DME-adsorbed CeO<sub>2</sub>. The first basis is Figure 9 in ref 1 which shows the temperature dependence of the band intensities (area) at 1158 and 1070 cm<sup>-1</sup>. Figure 1 shows Figure 9 in ref 1 again. As shown in Figure 1, both bands at 1158 and 1060 cm<sup>-1</sup> decreased with increasing temperature (300–500 K), whereas the decrease of the band intensity at 1158 cm<sup>-1</sup> with temperature was certainly not in accord with that at 1070 cm<sup>-1</sup>. This implies that the bands are due to two kinds of surface species rather than a single adsorbate. Second, TPD results (ref 1, Figure 3) suggested methoxy species formed on the CeO<sub>2</sub> surface. There were three desorption peaks at 370–380, 470–500, and 570 K in the spectra of the DME-adsorbed CeO<sub>2</sub>, and all three desorption peaks were the desorption of DME.<sup>1,2</sup> The desorption peak at 470–500 K as a major peak increased in intensity, shifting to lower temperatures with increasing DME exposure.<sup>1,2</sup> Such a desorption is explained well in terms of second-order desorption.<sup>3</sup> The equation of Redhead for second-order desorption indicates that the increase of the amount of mobile adsorbate results in the recombination between adsorbates at lower temperature.<sup>4</sup> It is difficult to consider the physisorbed molecular DME obeying second-order desorption. On the other hand, the methoxy species formed on metal oxides by methanol adsorption desorb as DME by the recombination at relatively high temperature.<sup>5,6</sup> As a result, the major desorption peak at 470–500 K should be attributed to the recombination of surface methoxy species. As shown in Figure 3, the beginning temperature of the desorption decreased toward room temperature as the DME exposure approached the saturation coverage at which the IR spectra were observed. This



**Figure 1.** Temperature dependence of the IR band intensities (area) at 1158 and 1070 cm<sup>-1</sup> in the DME-adsorbed CeO<sub>2</sub>: ○, 1158 cm<sup>-1</sup>; □, 1070 cm<sup>-1</sup>.

suggests the surface methoxy species at room temperature. Third, a chemical analysis (chemical trapping) revealed the formation of methoxy species at room temperature. The amount of surface methoxy species can be estimated by determining the amount of methanol that is formed by the reaction of the methoxy species formed on metal oxide surfaces and the vapor of hydrochloric acid.<sup>7</sup> The details of chemical trapping have been described elsewhere.<sup>7</sup> From the chemical trapping for the DME-adsorbed CeO<sub>2</sub> catalyst (150 mg, powder) prepared in a similar manner as ref 1, the amount of methoxy species on the surface at the saturation coverage (300 K) was estimated at 0.39 molecule nm<sup>-2</sup>. This estimation is somewhat smaller than that by the volumetric experiments (0.58 molecule nm<sup>-2</sup>, ref 1),<sup>1</sup> whereas this indicates the formation of methoxy species on the DME-adsorbed CeO<sub>2</sub> surface at room temperature.

The comments with regard to the band at ca. 1025 cm<sup>-1</sup> also disagree with our conclusion. The IR and TPD results in ref 1 show that the band at 1025 cm<sup>-1</sup> appears above 490 K (Figures 5–7 in ref 1), and the behavior of the band intensity with temperature is in fair agreement with the DME desorption at 570 K as shown in Figures 3 and 9 (ref 1). As a result, it is only natural that the band at 1025 cm<sup>-1</sup> observed above 490 K is attributed to the  $\nu$ (CO) band of a methoxy species formed at relatively high temperature ( $\geq 490$  K) rather than "some carbonaceous more or less oxygenated species" since it is difficult to consider "some carbonaceous more or less oxygenated species" formed by the decomposition of DME to form DME at such a high temperature again. By the way, CeO<sub>2</sub> is subject to reduction, and Ce<sup>4+</sup> on the surface is easily reduced to Ce<sup>3+</sup> even by CO.<sup>8,9</sup> Hydrogen reduces CeO<sub>2</sub> at temperatures higher than 473 K and forms tridentate OH groups on the surface.<sup>9</sup> It is not so strange that the  $\mu$ -OCH<sub>3</sub> with a multiple coordination is formed on the CeO<sub>2</sub> surface above 490 K as tridentate OH groups. Taking into account the band positions of the  $\nu$ (CO) and  $\nu$ (CH) in addition to the above results and discussion, the band at 1025 cm<sup>-1</sup> is expected to be the  $\nu$ (CO) band of the  $\mu$ -OCH<sub>3</sub> as tridentate OH groups. The surface species giving the band at 1025 cm<sup>-1</sup> in the preceding Comment seems to be different from the  $\mu$ -OCH<sub>3</sub> since the band already appears at room temperature.

As mentioned above, there is no resemblance between the preceding Comment and our study except for investigating the DME-adsorbed CeO<sub>2</sub>. In many reasons for the difference, it may be worthwhile to compare the catalytic activities of the CeO<sub>2</sub> used in both studies. The CeO<sub>2</sub> catalyst prepared in our

study have been investigated for the isosynthesis in the CO hydrogenation and can directly synthesize isobutene from synthesis gas with high activity.<sup>7,10,11</sup> The aim in our study is to explore the surface methoxy species on such a catalyst. Regretfully, we cannot refer to the activity of the commercial CeO<sub>2</sub> in the preceding Comment since the method of preparation of the commercial CeO<sub>2</sub>, the CO hydrogenation over the CeO<sub>2</sub>, and the IR results for the DME-adsorbed CeO<sub>2</sub> above room temperature are not described in the Comment. The commercial CeO<sub>2</sub> has a large specific surface area (120 m<sup>2</sup> g<sup>-1</sup>), whereas the specific surface area is not expected to remain unchanged after the high-temperature pretreatment. Furthermore, surface area is not always an indication of the catalyst activity before pretreatment. The commercial metal oxides prepared by the methods as the pyrolysis of salts have often considerably lower activity than the metal oxide catalysts prepared by the coprecipitation method or the alkoxide method. Although we cannot discuss the activity of CeO<sub>2</sub> in both experiments now, this may result in the difference between both studies.

We hope that this reply will prove helpful.

## References and Notes

- (1) Hara, M.; Kawamura, M.; Kondo, J. N.; Domen, K.; Maruya, K. *J. Phys. Chem.* **1996**, *100*, 14462.
- (2) Hara, M.; Kawamura, M.; Maruya, K. *Langmuir*, submitted.
- (3) Menzel, D. *Topics in Applied Physics*; Springer: Berlin, 1975; Vol. 4.
- (4) Redhead, P. A. *Vacuum* **1962**, *12*, 203.
- (5) Montagne, X.; Lynch, J.; Freund, E.; Lamotte, J.; Lavalley, J.-C. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 1417.
- (6) Hussein, A. M.; Sheppard, N.; Zaki, M. I.; Fahim, R. B. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2655.
- (7) Maruya, K.; Takasawa, A.; Aikawa, M.; Haraoka, T.; Domen, K.; Onishi, T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 911.
- (8) Li, C.; Sakata, T.; Arai, T.; Domen, K.; Maruya, K.; Onishi, T. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1451.
- (9) Laachir, A.; Perrichon, V.; Badri, A.; Lamotte, J.; Catherine, E.; Lavalley, J.-C.; Fallah, E. G.; Hilaire, L.; Normand, F. I.; Quemere, E.; Sauvion, G. N.; Touret, O. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1601.
- (10) Maruya, K. The Japan Petroleum Institute, 1994, 37, 26.
- (11) Maruya, K.; Fujisawa, T.; Takasawa, A.; Domen, K.; Onishi, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 11.
- (12) Li, C.; Sakata, Y.; Arai, T.; Domen, K.; Maruya, K.; Onishi, T. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 929.