COMMENTS

Comment on "Thermal Conversion of Methoxy Species on Dimethyl Ether Adsorbed CeO$_2$"

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We comment on a recent paper in this journal by Hara et al.[1] Because of the important role of ceria in three-way catalysts (TWC),[2] the study of the ceria surface properties has become the subject of increased attention. Another challenge is the production of hydrocarbons from CO−H$_2$ reaction on metal oxides. Such a reaction has been investigated using ceria which selectively produced useful branched hydrocarbons, such as isobutene at 623 K or higher.[3] To understand the mechanism of the involved reaction, Hara et al. recently published an IR and TPD study of species resulting from dimethyl ether (DME) adsorption on CeO$_2$.[1] By comparison of IR bands characterizing methoxy species on this oxide, they concluded that (i) DME adsorption on ceria leads to facile formation of two methoxy species (terminal and bridged species) by dissociative adsorption at 300 K and (ii) the two methoxy species are mobile and recombine, giving back to DME which desorbs at higher temperature.

In previous papers, we reported the IR spectra of methoxy species formed from dissociative adsorption of methanol on CeO$_2$;[4−7] these spectra are in accordance with other literature results.[8] The wavenumber of the ν(OC) band was found to be 1108 and 1065 cm^{-1} for terminal and doubly-bridging methoxy species, respectively, adsorbed on unreduced ceria.[4] Therefore, among the bands observed at 1158 and 1070 cm^{-1} from DME adsorption,[1] only the last one matches that observed at 1065 cm^{-1} for methoxy species. Moreover, the appearance of another band at 1250 cm^{-1}, assigned to a methoxy rocking CH$_3$ band in ref 1, is not in agreement with the absence of any band in this frequency range when methanol is introduced.[4,8] Finally, the dissociative adsorption of DME at room temperature (rt) is quite unexpected. It is the reason why we have reundertaken the infrared (IR) study of DME adsorption on CeO$_2$ at rt, and herein we report the results.

CeO$_2$ (Rhône-Poulenc) has a specific surface area of 120 m^2 g^{-1}. For the IR study, it was pressed into self-supporting disks of 15 mg cm^{-2}. The called *unreduced* ceria sample was calcined with O$_2$ (13 kPa) at 723 K, then evacuated, and cooled to room temperature for adsorption measurements. The *reduced* ceria sample was obtained by a further reduction by H$_2$ (40 kPa H$_2$) at 823 K followed by evacuation at 723 K.

The spectra of the unreduced and reduced ceria samples exposed to 0.3 kPa of DME at rt are qualitatively the same as the one presented in Figure 1 of ref 1 in the 4000−1000 cm^{-1} range. For clarity we report in Figure 1 only the more informative spectral range (below 1500 cm^{-1}), the spectra shown being obtained after the subtraction of that of the activated catalyst, e.g., before DME adsorption. As in ref 1, bands at ca. 1250, 1156, and 1076 cm^{-1} are observed, but a strong band also occurs at 912 cm^{-1}. The behavior of this band, when introducing increasing doses of DME or when evacuating the sample, correlates well with that of the other bands observed
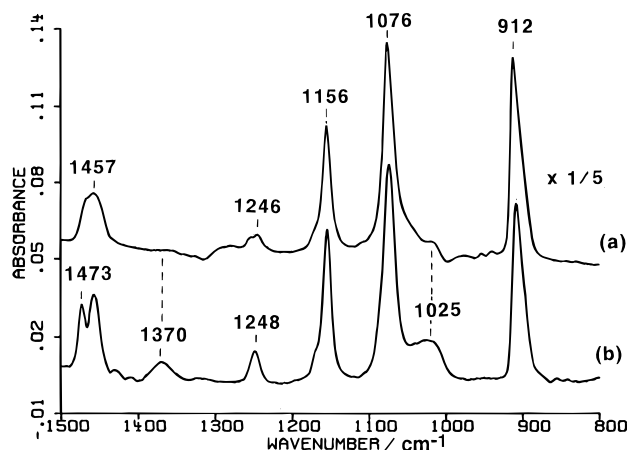

Figure 1. FTIR spectra for dimethyl ether (0.3 kPa) adsorbed at room temperature (a) on unreduced ceria and (b) on H$_2$-reduced ceria at 823 K. The absorbance of spectrum a has been divided by 5.

TABLE 1: Dimethyl Ether (DME) Fundamental Vibrations As Observed in CCl$_4$ Solutions[9] or Adsorbed on Ceria Either Unreduced or Reduced (This Work)

	wavenumbers/cm^{-1}		
		adsorbed on ceria	
assignments[9] (C_{2v} symmetry)	solution in CCl$_4$	unreduced	reduced
ν_s(COC)	922.5	912	908
ν_a(COC) and r$_{\parallel}$(CH$_3$)(B$_1$)	1095.5	1076	1074
ν_a(COC), r$_{\parallel}$(CH$_3$) (A$_2$) and r$_{\perp}$(CH$_3$) (B$_2$)	1168	1156	1155
r$_{\parallel}$(CH$_3$) (A$_1$)	1238	1246	1248
δ(CH$_3$)	1455	\}1457^a	1457
δ(CH$_3$)	1472.5		1473
ν_s(CH$_3$) (A$_1$ and B$_1$)	2812	2831	2827
ν_a(CH$_3$) (B$_2$)	2916	\}2932^b	\}2942^b
ν'_s(CH$_3$) (A$_1$ and B$_1$)	2986		

^{a} Unresolved bands. ^{b} Unlifted degeneracy.

in spectrum a (Figure 1), suggesting that it characterizes the same species. Such a band (912 cm^{-1}) never appeared when adsorbing methanol on ceria.[4,5,8] Moreover, Figure 1 shows that the spectrum of the main species formed from DME adsorption does not depend upon the state, oxidized or reduced, of ceria. By contrast, we previously reported that terminal methoxy species are not observed on reduced ceria[4−6] whereas the ν(OC) band characterizing doubly-bridging species is slightly shifted (ca. 10 cm^{-1}) toward higher wavenumbers when the sample is reduced.[4] This makes the transformation of DME into methoxy species, postulated in ref 1, questionable.

We propose here another assignment which better accounts for the observed bands, involving the occurrence of DME species not dissociatively chemisorbed. Indeed, comparison of wavenumbers of the main bands observed to those characterizing DME in carbon tetrachloride solution (Table 1) shows a nice agreement. It explains the presence of the 1246 cm^{-1} band in Figure 1 [r(CH$_3$) rocking mode] and that at 912 cm^{-1} [ν_s(COC)]. As for those at 1156 and 1076 cm^{-1}, they correspond to the r(CH$_3$) and ν_a(COC) modes of DME, strongly coupled. We note, by comparison with the fundamentals reported for the CCl$_4$ solution (Table 1), a downward shift of ca. −10 to −20 cm^{-1} of the bands involving the ν_s(COC) and ν_a(COC) modes. A similar shift has been reported when DME, acting as an electron donor, is H-bonded to HCl.[10] A more important shift occurs

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when DME is coordinatively bonded to strong Lewis acids like BF$_3$.[11,12] Since ceria does not present residual acidic OH groups, we conclude that DME is coordinatively adsorbed on unsaturated surface cerium cations, appearing to present a rather low acidity as previously shown using pyridine as a probe molecule.[13] Such an assignment also explains the upward shift of ca. +20 cm^{-1} of the $\nu_s(CH_3)$ mode (Table 1). The results do not depend on the oxidized or reduced state of ceria, its Lewis acidic properties being almost unaffected upon reduction.

The adsorption of undissociated species by introduction of DME on ceria well explains the linear part of the correlation between desorbed DME as a function of DME exposure reported in ref 1 (Figure 4).

Another point reported in ref 1 is the appearance of a new band at 1025 cm^{-1} when the DME-adsorbed CeO$_2$ temperature is increased to 530−570 K. It was assigned to a multiple coordination (possibly 4) of μ-OCH$_3$ species in ref 1. It is difficult to imagine a so high coordination, even on the (110) surface, since in the fluorite structure the oxygen ions are bound to four Ce^{4+} ions and that, to form a methoxy species, a coordinative unsaturation is needed which requires that the maximum of coordination of methoxy species be three. In our experiment (Figure 1) a band is also noted at 1025 cm^{-1}, with another one at 1370 cm^{-1}, mainly when ceria is reduced (spectrum b). These bands accompanied by a wide less intense one at 1550 cm^{-1} persist after a prolonged evacuation (6 × 10^{-4} Pa) of the reduced sample at rt, whereas no ν(CH) band is noticeable. This suggests that the 1370 and 1025 cm^{-1} bands observed in Figure 1b result from some carbonaceous more or less oxygenated species arising from some DME decomposition. Although this species is much less evident for unreduced ceria (Figure 1a), this makes also questionable the assignment of the 1025 cm^{-1} band in ref 1 to methoxy species.

In conclusion, there is no clear evidence of formation of methoxy species from DME adsorption on ceria at rt. Therefore, the mechanisms proposed in Figure 10 of ref 1 are not supported by the IR study and are only speculative.

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