IR study on migration of $^{18}OCH_3$ species on ZrO_2

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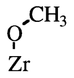
The migration of methoxy groups on ZrO_2 was studied by using ^{18}O-labelling and IR spectroscopy. The C–O bond of the methoxy group was found to remain intact during the migration of the bridged species to the vacant terminal sites on ZrO_2.

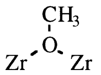
Keywords: methoxy groups, ZrO_2, IR spectroscopy

1. Introduction

ZrO_2 catalysts have been known to show a high selectivity for the hydrogenation of CO to methanol or isobutene [1]. Methoxy (CH_3O) species were found to be formed on ZrO_2 during the reaction [1,2], and were regarded as possible intermediates for the reaction [2–5]. The knowledge of properties of the species is essential for understanding the reaction mechanism. In our previous study of the H/D isotope exchange reactions of methoxy and formate (HCO_2) species on ZrO_2 [6], the hydrogen in the methoxy species was found to exchange with that of a surface OD group without gaseous D_2, while the isotope exchange reaction of the formate species did not proceed with the OD group but occurred only in the presence of D_2(g). Hence, the methoxy species were speculated to be movable on the catalyst surface during the reaction at 523–623 K [6]. Two types of methoxy species on ZrO_2 were identified by IR bands of C–O stretching mode (ν(CO)) at 1154 and 1052 cm^{-1} and ascribed to terminal (*t*-) and bridging (*b*-) methoxy groups, respectively [7,8]:

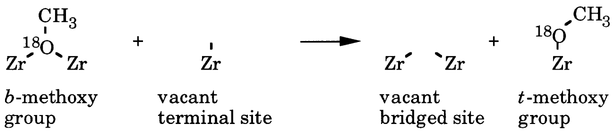


t-methoxy group



b-methoxy group

The intensity of the ν(CO) band of the *t*-methoxy group appeared larger than that of the *b*-methoxy group when only methoxy groups were formed from CH_3OH or CH_3OCH_3 on the ZrO_2 surface [6–9]. The intensity ratio of the ν(CO) bands of both methoxy groups was kept almost constant at various temperatures and regardless of the type of the precursors (CH_3OH and CH_3OCH_3). On the other hand, when formate species co-existed, the ν(CO) band of the *b*-methoxy group became larger than that of the *t*-methoxy group [9]. This indicates the occupation of the adsorption sites for *t*-methoxy groups by formate species. By thermal decomposition of the formate species on ZrO_2 covered with formate and methoxy groups, the site conversion of some *b*- to *t*-methoxy groups occurred [9]. It was confirmed by IR that the site conversion occurred by the migration of the *b*-methoxy groups to the vacant *t*-sites generated by decomposition of co-adsorbed formate species on ZrO_2 at 573 K [9]. Considering the similar reactivities of the *t*- and *b*-methoxy groups for the H/D isotope exchange reaction with surface OD groups, the *t*-methoxy group was also suggested to be movable [9]. However, it is not yet clear whether the C–O bonds of methoxy groups are maintained or cleaved during the migration. Methanol is selectively produced from CO hydrogenation on ZrO_2 at 573 K [1] where the site conversion of methoxy groups was observed [9]. Therefore, the C–O bond of methoxy groups is expected to be maintained during migration.



On the other hand, the cleavage of the C–O bond of methoxy groups and the resulting methyl formation are speculated to occur at higher temperatures where isobutene is selectively formed on ZrO_2 (673 K) [1]. In order to clarify the migration unit of methoxy groups at 573 K, we use $CH_3{}^{18}OH$ for observing the migration of methoxy groups in this work.

2. Experimental

The preparation of ZrO_2 has been fully described in the previous report [2]. After having been treated by 100 Torr (1 Torr = 133.3 Pa) of O_2 at 803 K for 2 h, the ZrO_2 was degassed at 773 K. HCO_2H (99%) was purified by water-free $CuSO_4$ to remove H_2O. $CH_3{}^{18}OH$ (97.4 atom% ^{18}O) was used as received. IR spectra were

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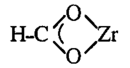
recorded on a Jasco 7300 FT-IR with a MCT detector at 4 cm^{-1} resolution, and 64 scans were collected for each spectrum.

3. Results and discussion

Adsorption of $CH_3{}^{18}O$ species was performed by introduction of 6 Torr of $CH_3{}^{18}OH$ on the ZrO_2 where formate species had been adsorbed by introduction of 4 Torr of HCO_2H at 523 K followed by evacuation at the same temperature. Then the ZrO_2 covered with formate and methoxy species was heated to 573 K under evacuation. At 573 K, formate species decompose under evacuation, while thermal decomposition of methoxy species is negligible for hours [6,9]. Figure 1 (a) shows the IR spectrum of methoxy and formate species co-adsorbed on the ZrO_2 surface under evacuation soon after the temperature reached 573 K. IR bands of the formate and methoxy species were observed in the ν(CH) (2800–3000 cm^{-1}) and ν(CO) (1600–1000 cm^{-1}) regions. The IR spectrum of the $CH_3{}^{16}O$ groups is shown in figure 1 (d) as a reference. Comparing with the bands of ν(CO) of $CH_3{}^{16}O$ groups (1154 and 1052 cm^{-1} in figure 1 (d)), the ν(CO) bands in figure 1 (a) shifted by 47 and 37 cm^{-1} toward the lower frequency side, and they are assigned to $\nu(C^{18}O)$ of *t*- and *b*-$CH_3{}^{18}O$ groups, respectively. This indicates that *t*- and *b*-$CH_3{}^{18}O$ groups were formed by cleaving the O–H bond of methanol and that the lattice O atoms are not involved in the methoxy groups [7]. On the other hand, adsorption of formic acid produced bidentate formate species coordinating to a single Zr ion, showing a strong ν_{as}(OCO) band at 1568 cm^{-1} [10]:



bidentate formate species

It is noticed that the intensity of the $\nu(C^{18}O)$ band at 1015 cm^{-1} due to *b*-$CH_3{}^{18}O$ groups was stronger than that at 1107 cm^{-1} due to *t*-$CH_3{}^{18}O$ groups when the formate species co-existed on ZrO_2 (figure 1 (a)).

The formate species are known to decompose by heating to 573 K [6]. Figure 1 (b) shows the IR spectrum after decomposition of formate species by maintaining the sample at 573 K for 30 min. The subtracted spectrum of (a) from (b) is presented in figure 1 (c) which shows the decrease of the intensity of $\nu(C^{18}O)$ due to *b*-$CH_3{}^{18}O$ groups and the increase of it due to *t*-$CH_3{}^{18}O$ groups accompanied by the decomposition of the formate species. Note that the *t*-methoxy groups converted from the *b*-methoxy groups show the upward ν(CO) band corresponding to the C–^{18}O bond in figure 1 (c). No increase of the ν(CO) band corresponding to the C– ^{16}O bond was observed, which evidences the absence of the formation of $CH_3{}^{16}O$ groups upon the migration of *b*-$CH_3{}^{18}O$ species.

The dependences of integrated intensities of bands at 1107 (*t*-$CH_3{}^{18}O$) and 1015 cm^{-1} (*b*-$CH_3{}^{18}O$) on that at 1568 cm^{-1} (formate) measured during thermal decomposition of the formate species are shown in figure 2. The integrated intensity of the $\nu(C^{18}O)$ band due to *t*-$CH_3{}^{18}O$ increased linearly with the linear decease of that due to *b*-$CH_3{}^{18}O$. This confirms that the migration of the *b*-$CH_3{}^{18}O$ groups to the vacant *t*-

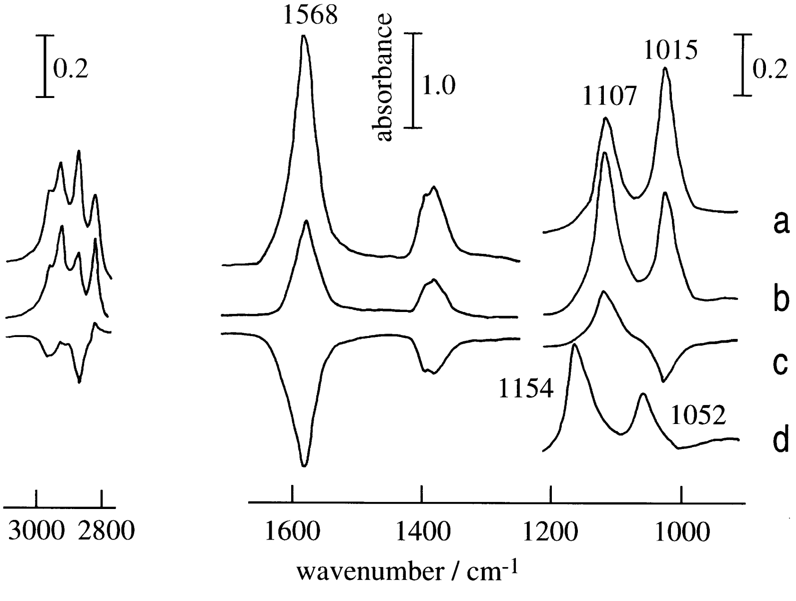


Figure 1. IR spectra of ZrO_2 co-adsorbed formate and ^{18}O-labelled methoxy species: (a) soon after the temperature was increased to 573 K under evacuation, (b) after 30 min at 573 K, (c) subtracted spectrum of (a) from (b). The co-adsorption was performed by pre-adsorption of formic acid (4 Torr) and evacuation at 523 K followed by introduction of 6 Torr of methanol and evacuation at 523 K. (d) A reference IR spectrum of $^{16}OCH_3$ adsorbed on ZrO_2.

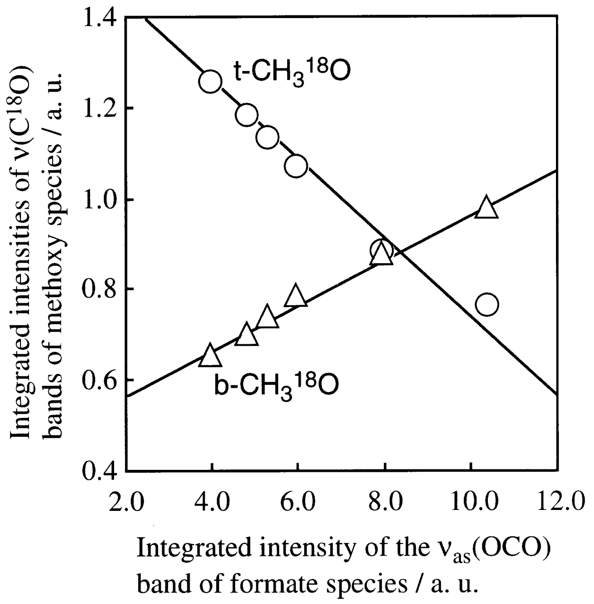


Figure 2. Dependence of relative integrated intensities of ν(CO) bands due to *t*- and *b*-methoxy species on that of ν_{as}(OCO) due to formate species on ZrO_2 at 573 K.

sites formed by the decomposition of the formate species took place to form the *t*-$CH_3{}^{18}O$ groups on the ZrO_2 surface as observed for the *b*-$CH_3{}^{16}O$ groups [9].

At higher temperature than 573 K, the disappearance of both *t*- and *b*-methoxy groups from the ZrO_2 surface was observed [6,10]. It is recalled that dimethyl ether and isobutene are produced from methoxy-covered ZrO_2 in the presence of CO and H_2 at the temperature range [1]. Therefore, C–O bond cleavage and methyl formation which result in immediate production of dimethyl ether and isobutene, and their desorption would occur at higher temperature than the present observation, although they were not observed at 573 K.

4. Conclusion

The C–O bond of methoxy groups was found to be maintained during migration on ZrO_2 at 573 K.

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