Effect of tetrachloromethane on redox behaviors of copper(II) oxide in the oxidative dehydrogenation of propane

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The oxidative dehydrogenation of propane on CuO has been investigated at 723 K in the presence and absence of tetrachloromethane (TCM). Under oxygen-limiting conditions, the conversion of propane and the selectivity to propylene were enhanced by the introduction of TCM. The catalyst converted to metallic Cu during the oxidation in the absence of TCM while no conversion of CuO was observed in the sample used in the presence of TCM. In contrast, the conversion of propane dramatically decreased upon addition of TCM into the feedstream for the oxidation of propane under the oxygen-excess conditions. The catalyst used under the oxygen-excess conditions was not reduced to metallic Cu, regardless of the addition of TCM. It is suggested that an abstraction of lattice oxygen from the catalyst is strongly influenced by the concentration of oxygen in the feed, resulting in the different effect of TCM on the oxidative dehydrogenation of propane.

KEY WORDS: oxidative dehydrogenation; propane; CuO; tetrachloromethane

1. Introduction

Since it was reported that catalysts containing vanadium [1–3] and molybdenum [4,5] species show considerable activity for oxidative dehydrogenation of propane (ODP), many researchers have focused on those catalysts undoped and doped with other solid-phase additives [6–8]. However, relatively little work has been reported in which gas-phase additives are employed to control catalytic activity for ODP although it has been reported that the oxidative coupling and partial oxidation of methane on various catalysts are enhanced upon addition of tetrachloromethane (TCM) into the feedstream [9]. It has been suggested that the formation of chlorinated species on the surface of the catalyst together with chlorine radicals in gas phase [10] directly contributes to the enhancement of the activity for methane oxidation [9,11]. The effect of TCM on control of the basic properties on the catalyst has been also reported [12]. In our laboratory, the effect of the introduction of TCM into ODP feedstream has been investigated on cerium oxide [13] and strontium hydroxyapatite ion exchanged with Cu^{2+} (Cu–SrHAp) [14], both of which have not been generally employed as the catalyst for ODP, together with α-magnesium pyrovanadate [15], which is known as one of the active and selective catalysts for ODP [1–3,5,6]. The conversion of propane and/or the selectivity to propylene on those catalysts have been enhanced by the introduction of TCM into the feedstream [13–15]. It has been suggested that the introduction of TCM appears to directly contribute to redox behaviours of those catalysts, resulting in the enhancement of the activity for ODP [13–15]. Particularly the activity for ODP on Cu–SrHAp has been improved by the addition of TCM, probably due to the suppression of the reduction of Cu^{2+} to metallic Cu [14]. However, since the nature of Cu species in Cu–SrHAp was not evident [14], we could not obtain definite information on redox behaviours of Cu species over the catalyst. Therefore, the effect of the introduction of TCM into the feedstream for ODP on well-defined Cu^{2+}-containing catalyst should be tested. To the best of our knowledge, there were few reports on the effect of TCM on the oxidation of alkanes on catalysts containing reducible cations such as transition metals. The present work reports on ODP on CuO and the effect of the introduction of TCM to the feedstream.

2. Experimental

Reagent CuO (99.9%) was purchased from Wako Pure Chemicals (Osaka) and used as received. The XRD pattern of the fresh catalyst matched that of CuO (JCPDS 45-0937). A particle size of 0.85–1.70 mm was employed as the catalyst. The surface area and apparent density of the catalyst were 2.1 m^2/g and 1.54 g/cm^3, respectively. The catalytic experiments were performed in a fixed-bed continuous-flow quartz reactor operated at atmospheric pressure. Details of the reactor design, the procedure of catalytic experiments and the calculation methods of the conversion and the selectivity have been described elsewhere [14]. No homogeneous oxidation of propane was observed at 723 K under the present reaction conditions. The carbon mass balances were 100 ± 5%. Turnover rate using the catalyst surface area was estimated as the rate ($r = FC_0X_A/W$, in which F, C_0, X_A and W were the flow rate, the initial concentration of C_3H_8, the conversion of C_3H_8 and the catalyst weight [16]) per catalyst surface area. Decomposition behaviours of TCM were examined using the same procedure described elsewhere [17]. In the absence of the catalyst, no

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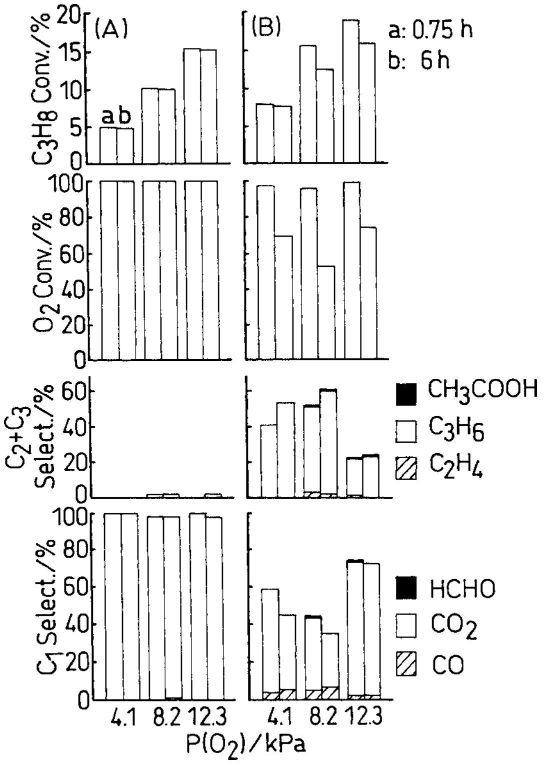

Figure 1. The oxidative dehydrogenation of propane on CuO (0.5 g) at 723 K in the absence (A) and presence (B) of TCM. Reaction conditions: $P(C_3H_8) = 14.4$ kPa, $P(\mathrm{TCM}) = 0.17$ kPa (when present) and $F = 30$ ml/min.

decomposition of TCM was observed under the present conditions. X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-1000AX) used Al Kα radiation [18]. The binding energies were corrected using 285 eV for C 1s as an internal standard. Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 2500X diffractometer, using monochromated Cu Kα radiation.

3. Results and discussion

The oxidative dehydrogenation of propane was examined at $W = 0.5$ g, $F = 30$ ml/min, $P(C_3H_8) = 14.4$ kPa and $P(O_2) = 4.1$, 8.2, and 12.3 kPa (figure 1). In the absence of TCM, CO_2 was the principal product from the oxidation of propane and the selectivity to this oxide remained relatively unchanged with increases in the partial pressures of oxygen, while the conversion of propane, as expected, increased (figure 1(A)). Oxygen-limiting conditions prevailed for all partial pressure of oxygen employed. On addition of TCM at 0.17 kPa (figure 1(B)) the conversion of propane increased at all partial pressures of oxygen although more substantially at the lower partial pressure of the oxidant. Concomitantly the selectivity to propylene was significantly increased. The turnover rates at 0.75 h on-stream using the catalyst surface area are summarized in table 1. To provide information on the decomposition of TCM, the conversion of TCM was examined at the identical reaction conditions as employed in obtaining the results shown in figure 1(B) but $P(\mathrm{TCM}) = 0.51$ kPa. The conversion of TCM was 92 and 61% at 0.75 and 6 h on-stream, respectively, and both $C_xH_yCl_z$ ($x = 1$, 2 and 3) and Cl_2 were not detected while the extensive formation of HCl was observed. Therefore, the formation of propylene may not be through those chlorinated organic species. XRD patterns of the catalysts previously employed in ODP at $P(O_2) = 4.1$ and 8.2 kPa showed that CuO was completely converted to metallic Cu (JCPDS 4-0836) (not shown). It is of interest to note that XRD shows that the inlet portion of the catalyst used at $P(O_2) = 12.3$ kPa in the absence of TCM consists of CuO, Cu_2O (JCPDS 5-0667) and metallic Cu (figure 2(A)) while the outlet portion is metallic Cu only (figure 2(B)), indicating that lattice oxygen of CuO would be abstracted more evidently from the outlet portion, at which there is no gaseous O_2 in the feed, than the inlet portion, at which gaseous O_2 is still present in the feed. It should be noted that the employment of the oxygen-limiting conditions could afford such an evident reduction behaviour of Cu species. However, the catalyst remained CuO structure after ODP in the presence of TCM under the present conditions (figure 2(C)). Therefore, it is evident that addition of TCM into the feedstream for ODP would directly contribute to redox behaviours of CuO catalyst, reflecting the activities in the presence of TCM. Peaks in the XPS spectra of the fresh and used catalysts were found at approximately 933 and 530 eV, which have been attributed to Cu $2p_{3/2}$ and O 1s. A peak at approximately 199 eV due to Cl 2p was also detected in the samples used in the presence of TCM. The Cl/Cu ratios on the surface of the catalysts previously employed in ODP with TCM at $P(O_2) = 4.1$, 8.2 and 12.3 kPa were 0.75, 0.20 and 0.20, suggesting that the formation of the chlorinated species on the surface of CuO prevents the catalysts from reducing.

Table 1
Turnover rate using the catalyst surface area obtained under various conditions at 0.75 h on-stream

W[a] (g)	F[b] (ml min^{-1})	$P(O_2)$[c] (kPa)	X_A[d]	P(TCM)[e] (kPa)	TOR[f] (mol min^{-1} m^{-2})
0.5	30	4.1	4.9	0	8.4×10^{-6}
0.5	30	8.2	9.3	0	15.9×10^{-6}
0.5	30	12.3	15.3	0	26.1×10^{-6}
0.5	30	4.1	7.8	0.17	13.3×10^{-6}
0.5	30	8.2	15.7	0.17	26.7×10^{-6}
0.5	30	12.3	18.9	0.17	32.3×10^{-6}
0.05	60	12.3	15.8	0	269.8×10^{-6}
0.05	60	12.3	1.7	0.085	28.8×10^{-6}
0.05	60	12.3	2.4	0.17	40.8×10^{-6}
0.03	60	12.3	14.9	0	424.3×10^{-6}
0.03	60	12.3	1.0	0.17	17.1×10^{-6}

[a] Catalyst weight.
[b] Flow rate.
[c] Partial pressure of O_2.
[d] Conversion of C_3H_8.
[e] Partial pressure of TCM.
[f] Turnover rate using the catalyst surface area.

In order to avoid the oxygen-limiting conditions, ODP was examined at $W = 0.05$ g, $F = 60$ ml/min, $P(C_3H_8) = 14.4$ kPa, $P(O_2) = 12.3$ kPa and $P(\mathrm{TCM}) = 0$, 0.085 and

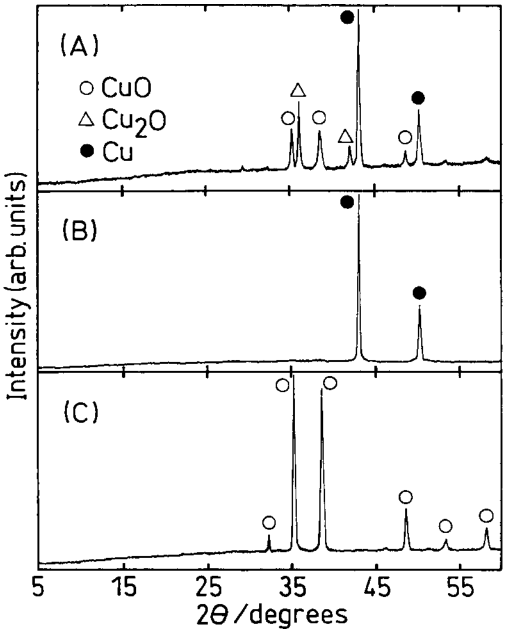

Figure 2. XRD patterns of the catalysts previously employed in obtaining the results shown in figure 1 but after 6 h on-stream. (A) Inlet portion of the catalysts used at $P(O_2) = 12.3$ kPa in the absence of TCM. (B) Outlet portion of the catalysts used at $P(O_2) = 12.3$ kPa in the absence of TCM. (C) Catalysts used at $P(O_2) = 4.1$, 8.2 and 12.3 kPa in the presence of TCM.

0.17 kPa (figure 3). In the absence of TCM, the high conversion of propane and the rather low selectivity to propylene were observed as expected. Upon addition of TCM, however, the enhancement of the conversion of propane, which was evidently detected under oxygen-limiting conditions, was not observed while the selectivity to propylene increased with increasing P(TCM). Similar effects of the introduction of TCM on the conversion and the selectivity were also observed under the same reaction conditions employed in figure 3 except $W = 0.03$ g. At $W = 0.03$ g in the absence of TCM, the conversions of C_3H_8 and O_2 were 14.9 and 89.7%, respectively, while the selectivities to CO, CO_2 and C_3H_6 were 1.7, 92.7 and 5.6%, respectively, at 0.75 h on-stream. Upon addition of TCM (0.17 kPa), the conversions of C_3H_8 and O_2 and the selectivity to CO_2 decreased to 1.0, 13.3 and 28.6%, respectively, while the selectivity to C_3H_6 increased to 71.4%. The high turnover rates observed at $W = 0.03$ and 0.05 g in the absence of TCM (table 1) show that such a small amount of the catalyst is sufficient to completely consume the oxygen in the feed. Those effects of TCM would be strongly influenced by redox behaviors of the catalyst. However, unfortunately, XRD patterns of those samples previously employed in obtaining the results using $W = 0.03$ and 0.05 g of the oxide could not be carried out due to the limiting amount. It is generally accepted that XPS signals due to Cu species are rather insensitive to the corresponding valences. It has been already reported that the distinction between CuO, Cu_2O and metallic Cu with XPS is possible in employing the combination of Cu $2p_{3/2}$ and Cu LMM Auger spectra [18]. In fact, as shown in figure 4, Cu $2p_{3/2}$ due to Cu^{2+} was detected together with satellite peak while the shape of Cu LMM due to metallic Cu is evidently different from those due to Cu^{2+} and Cu^{+} particularly after argon ion etching for 1 min, indicating that Cu^{+} can be also distinguished with XPS. Such distinguish-

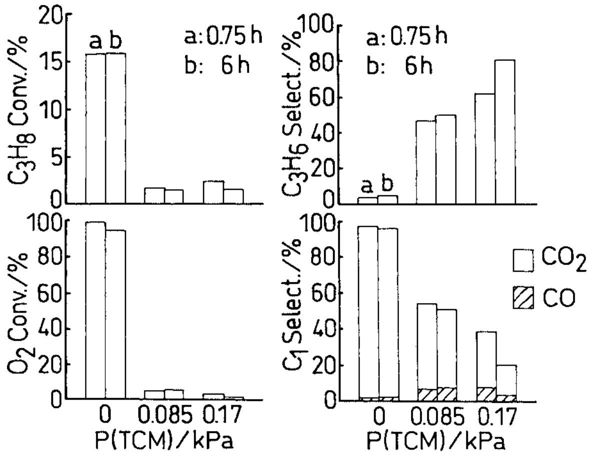

Figure 3. The oxidative dehydrogenation of propane on CuO (0.05 g) at 723 K in the presence and absence of TCM. Reaction conditions: $P(C_3H_8) = 14.4$ kPa, $P(O_2) = 12.3$ kPa and $F = 60$ ml/min.

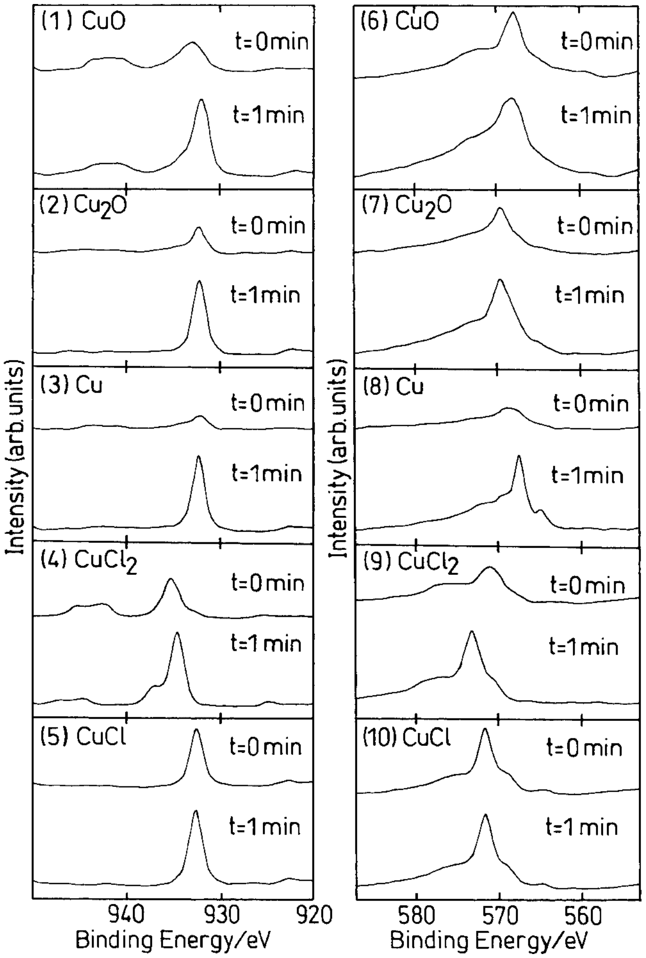

Figure 4. XPS spectra of CuO, Cu_2O and metallic Cu: Cu $2p_{3/2}$ of (1) CuO, (2) Cu_2O, (3) metallic Cu, (4) $CuCl_2$ and (5) CuCl; Cu LMM of (6) CuO, (7) Cu_2O, (8) metallic Cu, (9) $CuCl_2$ and (10) CuCl.

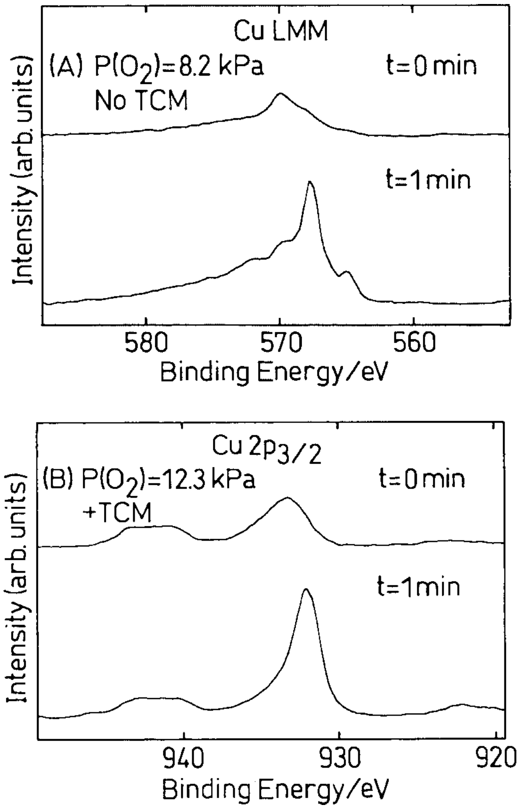

Figure 5. XPS spectra of the catalysts previously employed in obtaining the results shown in figure 1. (A) Cu LMM of the catalyst used at $P(O_2) = 8.2$ kPa in the absence of TCM. (B) Cu 2p$_{3/2}$ of the catalyst used at $P(O_2) = 12.3$ kPa in the presence of TCM.

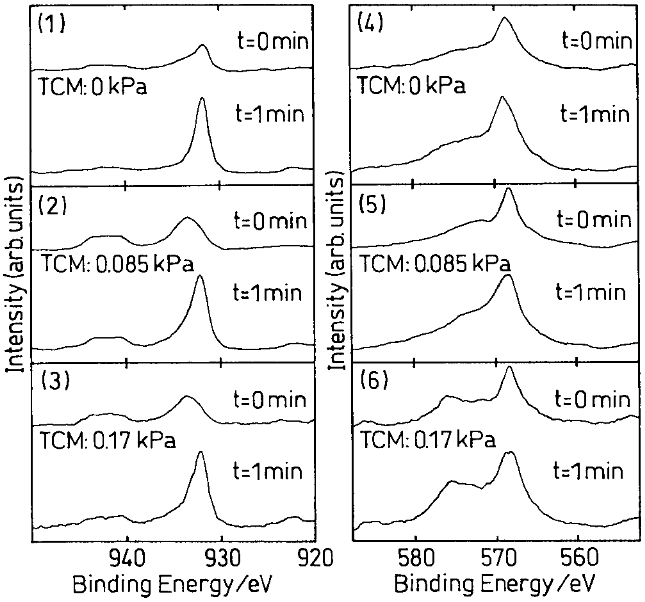

Figure 6. XPS spectra of the catalysts previously employed in obtaining the results shown in figure 3. Cu 2p$_{3/2}$ of the catalysts used at $P(\mathrm{TCM}) =$ (1) 0, (2) 0.085 and (3) 0.17 kPa, respectively; Cu LMM of the catalysts used at $P(\mathrm{TCM}) =$ (4) 0, (5) 0.085 and (6) 0.17 kPa, respectively.

able XPS and Auger peaks were also obtained from CuCl$_2$ and CuCl, although the Cu 2p$_{3/2}$ signal particularly from CuCl$_2$ was observed at a higher binding energy than those from the other three species [19]. In order to confirm the validity of XPS for distinction of valence of Cu, the catalysts previously employed in obtaining the results shown in figure 1 but at $P(O_2) = 8.2$ kPa in the absence of TCM and $P(O_2) = 12.3$ kPa in the presence of TCM, in the former of which metallic Cu was detected by XRD while in the latter CuO was detected, were analyzed by XPS. Figure 5(A) showed that the surface of the catalyst was metallic Cu while figure 5(B) showed CuO. Therefore, those identifications with XPS matched those with XRD. Figure 6 showed XPS results of the samples previously employed in obtaining the results shown in figure 3 but after 6 h on-stream, indicating that the catalyst used in the absence of TCM converted to Cu$_2$O while the catalysts used in the presence of TCM remained CuO structure. Since those catalysts were used under oxygen-excess conditions, reduction of CuO to metallic Cu appears to be rather suppressed even in the absence of TCM. Although the oxidation in the absence of TCM was performed under oxygen-excess conditions, it is reasonable to detect the reduction of CuO to Cu$_2$O since the conversion of O$_2$ was approximately 100%. The Cl/Cu ratios on those catalysts but employed at $P(\mathrm{TCM}) = 0.085$ and 0.17 kPa were 0.13 and 0.60, respectively, both of which were rather corresponding to those obtained from the catalysts used under oxygen-limiting conditions. Since the redox behaviours and chlorination of the surface of the catalysts are essentially identical between the catalysts used in the oxidation under oxygen-limiting and oxygen-excess conditions, it is rather strange that the effects of the introduction of TCM into the feedstream were quite reverse between them. It should be noted that the turnover rates estimated under the oxygen-excess conditions with TCM are rather similar as those under the oxygen-limiting conditions with TCM while the rate without TCM under the oxygen-excess conditions is evidently greater than that under the oxygen-limiting conditions (table 1).

Finally in order to examine the catalyst deactivation, ODP in the presence of TCM was examined under the same reaction conditions employed in obtaining the results shown in figure 1 but $P(O_2) = 4.1$ kPa by 48 h on-stream (figure 7). The conversions of propane and oxygen gradually decreased while the selectivity to propylene increased with time-on-stream. After the oxidation, the XRD pattern showed that a small amount of CuCl (JCPDS) 6-0344 was detected together with CuO (not shown). The surface analysis with XPS also showed an excess amount of chlorinated species on the used catalyst (Cl/Cu = 1.36). Therefore, it is evident that the formation of an excess amount of the chlorinated species in and on the surface results in the deactivation.

It should be noted that the effects of the addition of TCM observed in this study do not indicate that the catalytic activities of CuO for the oxidation of C$_3$H$_8$ can be improved by the additive. The oxidation of C$_3$H$_8$ in the absence of TCM at $W = 0.5$, 0.05 and 0.03 g shows that CuO is quite active particularly for the deep oxidation of C$_3$H$_8$ to CO$_2$. Since a contribution of lattice oxygen in CuO to the oxidation, that is, abstraction of lattice oxygen from the oxide, is

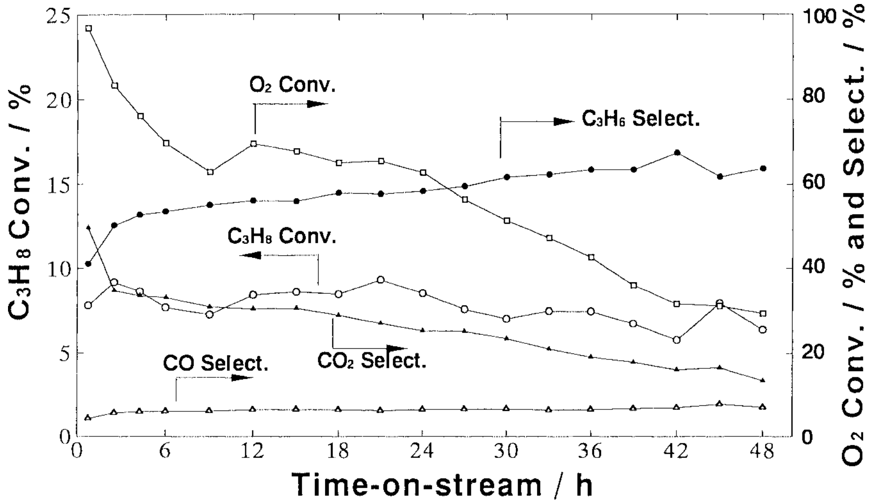

Figure 7. Extended time-on-stream effect over CuO (0.5 g) on the oxidative dehydrogenation of propane in the presence of TCM (0.17 kPa) at 723 K. Reaction conditions: $P(C_3H_8) = 14.4$ kPa, $P(O_2) = 4.1$ kPa and $F = 30$ ml/min.

evident, the great oxidation activity of lattice oxygen should be suppressed to obtain C_3H_6 more selectively. The surface chlorinated species on the catalyst used with TCM, which is detected by XPS, appears to contribute to the suppression of the activity of the lattice oxygen for the deep oxidation of C_3H_8 to CO_2. Since the amount of oxygen consumed in the deep oxidation of C_3H_8 to CO_2 is greater than that consumed in ODP to C_3H_6, the conversion of C_3H_8 under the oxygen-limiting conditions increases by the addition of TCM (figure 1). Under the oxygen-limiting conditions ($W = 0.5$ g), most of the lattice oxygen does not directly contribute to the oxidation since $W = 0.03$ g is sufficient for the oxidation in the absence of TCM. Therefore, rather great activities can be observed due to the synergistic contribution of gaseous oxygen and the excess lattice oxygen. If the consumption of the lattice oxygen in the catalyst used in the presence of TCM is not fully supplied with gaseous oxygen due to an excess formation of the surface chlorinated species, the gradual decrease of the activities shown in figure 7 is reasonable. Under the oxygen-excess conditions ($W = 0.03$ and 0.05 g), there is rather no excess lattice oxygen, resulting in the different effects of TCM from those observed under the oxygen-limiting conditions. The addition of TCM plays an important role for controlling the activity of the lattice oxygen in the oxide, which also depends on the partial pressure of oxygen. We believe that the employment of the evidently different reaction conditions could afford evident information on the effects of the addition of TCM on the redox in the oxidation of C_3H_8.

4. Conclusions

The activity of CuO for the oxidative dehydrogenation of propane to propylene was enhanced by the addition of TCM under the oxygen-limiting conditions. In contrast, the oxidation was suppressed by the addition of TCM under the oxygen-excess conditions. It is evident that the participation of TCM to redox of the catalyst plays an important role for the charge of the activities together with an oxygen abstraction from the catalyst, which depends on the concentration of oxygen in the feed. The formation of an excess amount of chlorinated species in and on CuO employed in the oxidation with TCM resulted in the decrease of the activity.

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