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RESEARCH NOTE

Role of Tetrachloromethane as a Gas-Phase Additive in the Oxidative Dehydrogenation of Propane over Cerium Oxide

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In the absence of tetrachloromethane (TCM) carbon dioxide is the principal product formed in the oxidation of propane on ceria. The introduction of small partial pressures of TCM increases the conversion of propane with selectivities to propene up to 80%. Except under special circumstances no evidence of chlorinated species from TCM is found in the bulk structure while the surface region is shown to contain chlorine, although its form is not known. The enhancement of conversion and selectivity to propene is shown to be dependent upon the presence of chlorine, in whatever form, in the surface region of the catalyst. © 2000 Academic Press

Key Words: **cerium oxide; oxidative dehydrogenation; propane; tetrachloromethane.**

INTRODUCTION

Heterogeneous catalysts for the oxidative dehydrogenation of propane typically contain vanadium and magnesium as the critical elements (1–4). Relatively little work has been reported in which rare earth oxides are employed as catalysts in this reaction (5, 6) in spite of evidence of their activity in the oxidative dehydrogenation of methane (7–10) and ethane (11, 12). Both gas- and solid-phase additives have been examined for alkane oxidation processes, in particular those involving methane (13–19). Early studies on the oxidation of methane have shown that the introduction of a halomethane improves the selectivity to formaldehyde on supported palladium and platinum catalysts (13, 14) and higher selectivities to C_{2+} hydrocarbons have been reported on Na/Mn/SiO_2 catalysts in the presence of gaseous CH_3Cl or HCl (15). Work in one of our laboratories has found that the addition of tetrachloromethane (TCM) increases the yield of formaldehyde on heteropolyoxometalates in the partial oxidation of methane (16) and of C_2 hydrocarbons in the oxidative coupling of methane (OCM) on a variety of silica-supported oxides (17). With alkali metal-doped oxides as catalysts for the OCM process the introduction of the alkali metals by employing the corresponding chlorides led to increases in the selectivities to C_2 hydrocarbons (18, 19). Relatively little work has been reported on the use of gas-phase additives in the oxidative dehydrogenation of propane. More recently, the OCM process on Pr_6O_{11} (9, 10) and the oxidative dehydrogenation of ethane on CeO_2 (11) and Pr_6O_{11} (12) were shown to benefit from the addition of small partial pressures of tetrachloromethane to the feedstream. A preliminary study has shown that while the oxides of lanthanum, cerium, praseodymium, and samarium are active in the oxidative dehydrogenation of propane only that of cerium is substantially activated by the introduction of TCM (20).

The present work reports on the oxidative dehydrogenation of propane on cerium oxide and the effect of the introduction of TCM to the feedstream.

EXPERIMENTAL

The catalytic experiments were performed in a fixed-bed continuous-flow quartz reactor operated at atmospheric pressure. Details of the reactor design have been described elsewhere (20). In all experiments, the catalyst was heated to the reaction temperature while maintaining a continuous flow of helium and was held at this temperature under a 25 ml/min flow of oxygen for 1 h. No homogeneous oxidation of propane was observed at 723 K under the present conditions (20). Column systems and definitions of the conversion and selectivity have been reported previously (20). Blank experiments conducted with propane absent from the feed ($O_2 + TCM + He$) indicated that TCM is

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converted to HCl while producing carbon oxides. Although the quantities of carbon oxides produced in the latter experiments were small, all of the data reported were corrected by performing duplicate experiments with propane absent under otherwise identical values of the process variables. The carbon mass balances were 100 ± 5%. Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 2500 X, using monochromatized Cu*Kα* radiation. X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-1000AX) used Mg*Kα* radiation. The binding energies were corrected using 285 eV for C 1*s* as an internal standard.

RESULTS

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 pressure of O_2, while the conversion of propane, as expected, increased (Fig. 1A). Oxygen limiting conditions prevailed for all partial pressures of oxygen employed.

On addition of TCM at 0.17 kPa (Fig. 1B) the conversion of propane increased at all partial pressures of O_2,

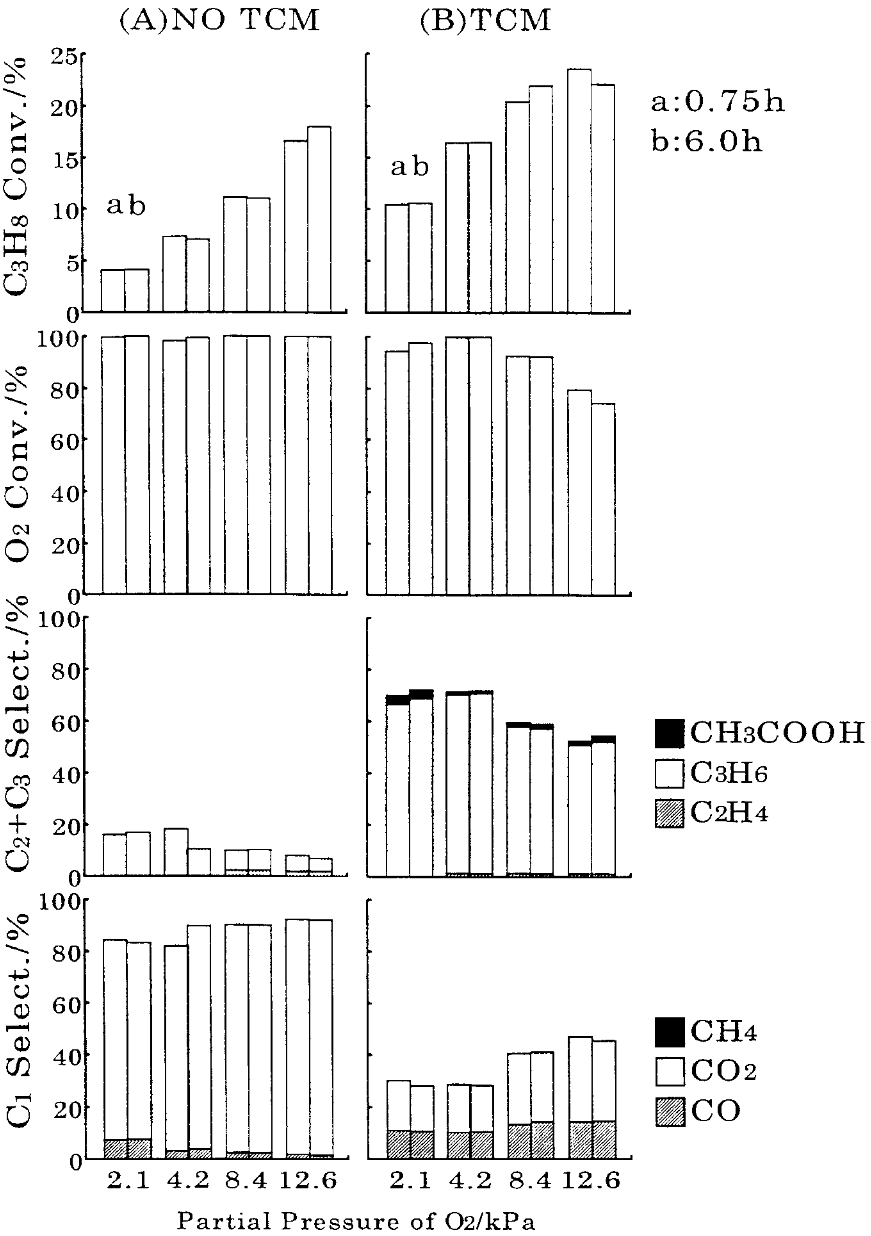

FIG. 1. Effect of the partial pressure of O_2 on propane oxidation in the absence (A) and presence (B) of TCM on CeO_2 at 723 K. Reaction conditions: $W = 0.5$ g, $F = 30$ ml/min, $P(C_3H_8) = 14.4$ kPa, $P(O_2)$ as shown, $P(\text{TCM}) = 0$ or 0.17 kPa diluted with He. Catalysts were pretreated with O_2 (25 ml/min) for 1 h at the reaction temperature.

although more substantially at the lower values of the latter. Concomitantly the selectivity to C_3H_6 was significantly increased. It should be noted that the conversion of O_2 decreased with increasing partial pressures of O_2.

To provide further information on the catalytic properties of CeO_2 experiments in the absence of O_2 were performed. With neither oxidant nor TCM present, no conversion of propane was observed. On introduction of TCM, 0.8% propane was converted and selectivities to C_3H_6, C_2H_4, and CO_2 of 71.0, 10.0, and 19.0%, respectively, were measured.

XRD patterns of CeO_2 after use in the oxidation of propane without and with TCM were essentially identical to that for fresh CeO_2 (JCPDS 34-0394) regardless of the partial pressure of O_2 employed (not shown).

The XP spectra of CeO_2 previously used in the oxidation with TCM contained peaks at 883 eV due to Ce $3d_{5/2}$, at 530 and 532 eV, ascribed to O1s, the former of which can be related to lattice oxygen (21), and at 199 eV due to Cl $2p$. The values of Cl/Ce on the surface of CeO_2 used at pressures of O_2 equal to 0, 2.1, 4.2, 8.4, and 12.6 kPa were 0.23, 0.31, 0.53, 0.31, and 0.25, respectively.

Although changes in the residence time (W/F) have little or no effect on the conversion and selectivities in the absence of TCM, with TCM present in the feedstream the conversion of C_3H_8 increases with W/F reaching a plateau at approximately 17% (not shown). Concomitantly the propane reaction rate decreased. The selectivity to C_3H_6 remains at approximately 70% for all W/F and small selectivities to acetic acid and ethylene are observed. Extension of the time-on-stream from 0.75 to 6 h produced little or no change in the conversions and selectivities at any residence time. XRD patterns of the catalysts after use for 6 h were identified as CeO_2 and no other species were detected. As before, in spite of the absence of detectable Cl in the bulk, the surface region indicated its presence in the aforementioned samples. Although no trend in the Cl/Ce values from XP spectra was discernable a maximum value of 1.1 was reached.

The addition of a partial pressure of TCM equal to 0.085 kPa produces a conversion approximately twice that observed in its absence and an increase in the $C_2 + C_3$ selectivity by more than a factor of three with concomitant decreases in the selectivities to carbon oxides (not shown). A value for Cl/Ce of nearly 2 was obtained under these conditions. A further increase of P(TCM) by a factor of two produces only relatively small increases in the conversion and $C_2 + C_3$ selectivities to approximately 17 and 75%, respectively. Additional increases in P(TCM) have little or no effect on either the conversions or the selectivities. Increases in the time-on-stream generally produced negligible observable changes in the reaction, although values of Cl/Ce in excess of 1 were measured.

To provide ancillary information on the role of TCM in the oxidation of propane the catalyst was exposed to a mixture of C_3H_8, O_2 and various partial pressures of TCM diluted with helium at 723 K for 6 h prior to the introduction of the reactant stream not containing TCM (Fig. 2). After pretreatment of the catalyst at the lowest P(TCM) the selectivities to C_3H_6 and CO were enhanced, while that to CO_2 decreased and the conversion of C_3H_8 and the selectivity to C_2H_4 increased slightly. However, for further increases in the partial pressure of TCM to which the catalyst was exposed during the pretreatment the changes in the aforementioned reaction variables were relatively small.

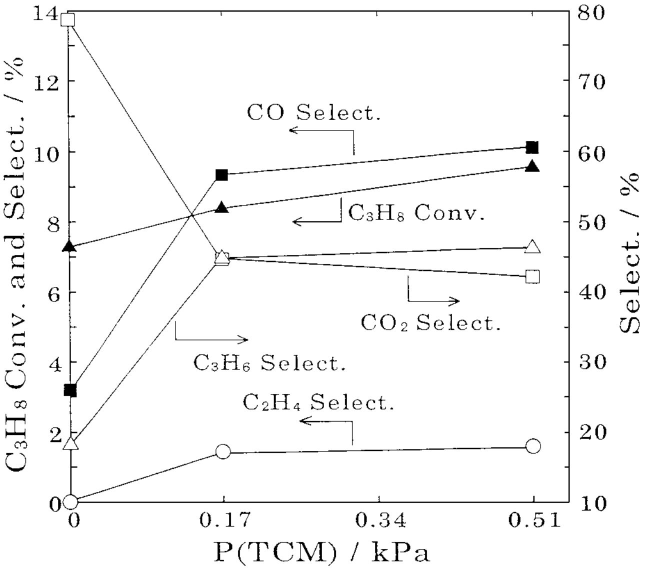

FIG. 2. Effects of pretreatment of CeO_2 (0.5 g) for 6 h at 723 K with a mixture of $P(C_3H_8) = 14.4$ kPa, $P(O_2) = 4.2$ kPa, and $P(TCM) = 0$, 0.17, or 0.51 kPa diluted with He (total flow rate, 30 ml/min), followed by the oxidation of propane in the absence of TCM at 723 K. Reaction conditions as in Fig. 1, except $P(O_2) = 4.2$ kPa. Data were collected at 0.75 h on-stream.

XPS analyses showed that the values of Cl/Ce on the pretreated catalysts where P(TCM) was 0.17 and 0.51 kPa were 0.89 and 0.66, respectively, again significantly smaller than expected for the formation of a stoichiometric chlorinated analog of CeO_2. XRD patterns of the catalyst pretreated at 0.51 kPa of TCM show the presence of a phase additional to CeO_2 at $2\theta = 25.4$, 34.2, and 30.9°. Although the XRD pattern for CeOCl is not available, these additional lines appear at 2θ values similar to those in the XRD patterns of the oxychlorides of various rare earth metals, for example, Sm, La, and Pr, and consequently may be indicative of the presence of the oxychloride of cerium.

DISCUSSION

The rare earth oxides of Sm, La, and Pr catalyze the conversion of methane to form C_{2+} hydrocarbons with significant selectivities (9, 10, 21). In contrast only the carbon oxides are produced from methane with cerium oxide. With the former three oxides, the introduction of TCM into the feedstream has a positive effect on both the conversions of methane and the selectivities to C_{2+} hydrocarbons while with cerium oxide no increase of conversions is observed and only carbon oxides are produced.

In contrast, in the oxidative dehydrogenation of propane, with which the earlier results for the oxides of Sm, La, and Pr showed that the introduction of TCM had little or no effect (20), the present work demonstrates that with CeO_2 substantial increases of both the conversion of propane and selectivity to C_3H_6 are observed on addition of TCM to the feedstream. While care must be taken in comparing selectivities at different conversions it is clear that both the conversion of C_3H_8 and the selectivity to C_3H_6 are increased on introduction of TCM. It must therefore be concluded that the beneficial effect of TCM in this instance is not a consequence of a reciprocal relationship between conversion and selectivity but results from concomitant increases in both conversion and selectivity to the desired product. To be noted is the relatively large depression in the selectivity to CO_2 on addition of TCM, while that to CO increases, although remaining relatively small. Therefore, contrary to observations with other catalytic systems with which the effect of the introduction of TCM was, at least in part, the suppression of the further oxidation of CO, with the present catalyst and reaction the further oxidation of propane to CO_2 appears to be suppressed (22, 23).

Other differences between the present and earlier systems are evident. After either partial oxidation or oxidative coupling of methane in the presence of TCM on a wide variety of catalysts, almost inevitably XRD showed that a chlorinated analog of the catalyst had been produced in the bulk structure, in contrast to the present results under which such species were not formed (23). However, as with previous studies chlorine, in whatever form, was found in the surface region after reaction in the presence of TCM.

The results of the experiments performed with neither O_2 nor TCM present suggest that lattice oxygen does not participate directly in the oxidation process. However, on introduction of TCM, propane was converted to the expected products with a relatively high selectivity to propene. Other workers have shown that adsorbed oxygen is responsible for the activation of propane (6). The observations obtained from the pretreated catalyst show that the enhancement of conversion and selectivity result from the modification of the catalyst by TCM, rather than a gas phase effect and further, together with the XPS and XRD data, show that a saturation with TCM is occurring in the surface, apparently forming the stoichiometric equivalent of CeOCl whose instability may preclude its formation throughout the bulk of the catalyst. It is important to emphasize, however, that little or no direct evidence is available for the formation of CeOCl from CeO_2 exposed to TCM. In this context it is worth noting that the heats of formation of the analogous oxychlorides from the oxides of La, Pr, Sm, and Ce and, hence, at least approximately, the free energies of formation, are negative but that for CeOCl is only −8.0 kcal/mol, a factor of 4–5 times smaller in magnitude than those for the remaining three rare earth oxychlorides. While this data is strictly applicable to 25°C, nevertheless the formation of the oxychloride of cerium is evidently the least thermodynamically favored.

The ability of some of the lanthanides to assume a valency of 4, in addition to their group valency of 3, is well known, particularly for cerium, which has a higher proclivity for the latter oxidation state than any of the remaining lanthanides. It is also well known that this serves as the basis for the use of ceria as an oxygen-storage compound in automobile exhaust catalysts:

$$Ce_2O_3 + 1/2\,O_2 \rightleftarrows 2CeO_2.$$

From the present results it is clear that the introduction of TCM into the feedstream is chlorinating the surface. While the values of Cl/Ce of one or less than one can be rationalized on the basis of the partial formation of the oxychloride the stoichiometric equivalent may not, of course, be generated.

Of some relevance are reports of studies involving the preparation of Rh/CeO_2 catalysts, of importance in "three-way catalysis," by conventional impregnation or by ionic exchange of metal complexes. A number of workers have shown that the use of a chlorinated precursor could lead to the formation of a CeOCl phase after reduction by H_2 (24–29).

A number of possibilities exist to account for the incorporation of TCM as chlorine into cerium oxide. Partial reduction of CeO_2 during the ODH of propane could produce anionic (oxygen) vacancies which become occupied by chlorine (26):

$$Ce^{4+}O^{2-}Ce^{4+} \rightarrow Ce^{3+}\square Ce^{3+} \rightarrow Ce^{3+}Cl^{-}Ce^{3+}.$$

Since the bulk of CeO_2 would be unlikely to be reduced during the ODH process, this may explain the absence of CeOCl from XRD patterns. On the other hand, the presence and consumption of gas phase oxygen would suggest that cerium is more likely to exist in its higher oxidation state. Alternatively, where cerium is found in the +4 oxidation state, the direct substitution of O^{2-} ions by chlorine,

$$Ce^{4+}O^{2-}O^{2-} \rightarrow Ce^{4+}O^{2-}Cl^{-}\square,$$

would lead to the formation of anionic vacancies which could, with gas phase oxygen, form O_2^-, a frequently proposed oxidant in hydrocarbon oxidation processes (27). The latter rationalization would be consistent with the observation that, in the absence of both TCM and oxygen no conversion of propane occurs, whereas with TCM in the feedstream but no oxidant the expected ODH products are observed. In view of the significant partial pressures of oxygen to which the catalyst is exposed during the ODH process it would not be surprising to find a significant portion of cerium in its higher oxidation state.

It is probable that both the aforementioned mechanisms are operative during the ODH process with propane. This would provide explanations for most of the observations from the present work, particularly those related to the apparent irregularity of chlorine concentrations in the surface region which may result from the presence of both oxidation states of cerium in the surface.

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