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Formation of chlorine species over magnesium oxide in the oxidative coupling of methane in the presence of carbon tetrachloride

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The oxidative coupling of methane on magnesium oxide (MgO) has been studied in the presence of carbon tetrachloride (TCM) as a gas-phase additive. Addition of a small amount of TCM to the reactant stream improves the selectivity to C_2H_4, while the conversion of methane is not influenced by the additive. X-ray photoelectron spectra of the used MgO reveal the formation of chlorine species on the catalyst surface in quantities up to 0.20 of Cl/Mg (atomic ratio), although X-ray diffraction spectra of the catalyst show MgO only and the content of the chlorine species in the bulk phase estimated by X-ray fluorescence analysis is very low. It is concluded that the enhancement of the selectivity to C_2H_4 primarily results from the presence of surface chlorine species. The chlorinated species on the catalyst has been identified as $MgCl_2$.

Keywords: methane; carbon tetrachloride; magnesium oxide; magnesium chloride; oxidative coupling

1. Introduction

The oxidative coupling of methane to C_{2+} hydrocarbons, especially to ethylene, is, in principle, one of the most important routes for the utilization of natural gas through the production of useful chemicals and fuels. Although a wide variety of catalysts has been examined for this process during the last decade, the conversion of methane and selectivity to ethylene remain less than desirable for an economic-

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ally practical process [1–4]. Work in one of our laboratories has shown that the introduction of a small quantity of carbon tetrachloride (TCM) to the feedstream often results in enhanced conversion of methane and increased selectivity to C_{2+} compounds, especially to ethylene [5,6]. Burch and co-workers have also studied the effect of the introduction of gaseous chlorine-containing compounds in the oxidative coupling of methane [7]. Although participation of TCM in the gas-phase reaction cannot be excluded [8] experimental observations show that the chlorine species interacts with and alters the surface of the catalyst. However, the source of the advantageous effect of the introduction of chlorine is not yet clear.

Publications from one of our laboratories have shown that oxychlorides are formed in the presence of TCM over lanthanide oxides and that the beneficial effects of TCM with these catalysts are primarily due to the formation of the oxychlorides [9,10]. In contrast, work in our laboratories has shown that chloride is formed on alkali sulphate in the presence of TCM and that the reaction behaviour is strongly influenced by the chloride [11]. These results reveal that the source of the effect of the introduction of TCM strongly depends on the nature of the catalyst and more work is required to clarify the role of TCM. In recent work, the oxidative coupling of methane over salts of magnesium doped by alkali carbonates has been studied and it is concluded that the influence of TCM on the methane conversion process appears to result primarily from the interaction of TCM with the anions of the magnesium compounds [12].

The present paper describes studies of the oxidative coupling of methane on magnesium oxide and the application of powder X-ray diffraction, X-ray photoelectron spectroscopy and X-ray fluorescence analyses to clarify the nature and source of the effect of the introduction of TCM into the methane conversion feedstream. While the present work was in progress, studies of the effect of dichloromethane on magnesia in the conversion of methane have shown that chlorine species are present on the surface of the catalyst, but the chlorinated species on the catalyst was not identified [7].

2. Experimental

2.1. CATALYST

Magnesia (MgO) was purchased from Wako Pure Chemicals as special grade and used as supplied. The oxide was kneaded for 1 h with a given amount of water. The paste was dried overnight at 353 K and calcined at 1048 K for 5 h. Particles of 1.70–0.85 mm were employed in the present work.

2.2. APPARATUS AND PROCEDURE

The catalytic experiments were performed in a fixed-bed continuous flow quartz reactor operated at atmospheric pressure. Details of the reactor design and catalyst packing procedures have been described elsewhere [11,13]. Prior to reaction the catalyst was calcined in situ in an oxygen flow (12.5 ml/min) at 1048 K for 1 h. The reaction conditions were as follows: $W = 0.7$ g, $F = 15$ ml/min, $T = 1048$ or 1123 K, $P(CH_4) = 28.7$ kPa, $P(O_4) = 4.05$ kPa, and $P(\mathrm{TCM}) = 0$, 1.73 or 6.93 hPa (1 hPa = 0.1 kPa); balance to the atmosphere was provided by helium.

2.3. ANALYSIS AND CHARACTERIZATION

The reactants and products were analyzed with a Shimadzu GC-8APT gas chromatograph with a TC detector and integrator (Shimadzu C-R6A). Two columns, one Porapak N (6 m × 3 mm, programmed 318–423 K), the other Molecular Sieve 5A (20 cm × 3 mm, 318 K) were employed in the analyses. The conversion of methane was calculated from the products and the methane introduced into the feed. The selectivities were calculated from the conversion of methane to each product on a carbon base.

The surface areas of the catalysts were measured with a conventional BET nitrogen adsorption apparatus (Shibata P-700). Powder X-ray diffraction (XRD) (MXP-18, MAC Science Co.) employed monochromatized Cu Kα radiation. Patterns were recorded over the range $2\theta = 5$–$90°$. X-ray photoelectron spectroscopy (XPS) (Shimadzu ESCA-1000AX) used unmonochromatized Mg Kα radiation. The binding energies were corrected using 285 eV for the C 1s level, resulting from contaminant carbon, as an internal standard. Argon-ion etching measurement of the catalyst was carried out at 2 kV for 0.5 min with a rate of the sputtering estimated as ca. 2 nm/min for SiO_2. The X-ray fluorescence analysis (XRF) was measured with a Rigaku 3370 X-ray spectrometer.

3. Results and discussion

In all catalytic experiments, the products were CO, CO_2, C_2H_4 and C_2H_6 together with unconverted CH_4 and O_2. Water and hydrogen were also produced but are not reported here. In some experiments, C_2H_2 and C_3 species were detected. Chloromethanes such as CH_3Cl were detected, but precise quantitative analyses could not be done due to overlapping with the GC H_2O peak. Carbon balances of $100 \pm 5\%$ were obtained in each experiment. The conversion of oxygen was virtually constant between 96 and 99% in each run. The BET surface area of MgO was 12 m^2/g.

3.1. ACTIVITY AND SELECTIVITY IN MgO IN THE PRESENCE AND ABSENCE OF TCM

The conversions, selectivities and yields on MgO in the absence and presence of

TCM are summarized in fig. 1. After 0.5 h on-stream under the standard conditions of $T = 1048$ K and P(TCM) = 0 or 1.73 hPa, the conversion of methane was little affected by the introduction of TCM while the selectivity to C_2H_4 was increased by a factor of approximately two. A similar enhancement by TCM has been reported on silica-supported magnesia catalyst [14]. However, deactivation was observed in the presence of TCM at 1.73 hPa during 6 h on-stream. Increase of the partial pressure of TCM (6.93 hPa) resulted in a decrease in the selectivity to C_2H_6, while the conversion and remaining selectivities are relatively stable up to 30 h on-stream (fig. 2). However, at a higher reaction temperature of 1123 K, evidence for deactivation was again obtained (fig. 1).

3.2. EXAMINATION OF THE USED CATALYSTS BY X-RAY ANALYSES

In order to study the interaction between TCM and MgO, X-ray analyses have been carried out and the results are summarized in table 1. No chlorinated species were detected in the XRD patterns of each used catalyst, in contrast with those of alkali sulphate [11] and lanthanide oxides [9,10] treated with the same procedures as employed in the present work. However, chlorine species were detected in XPS analysis by Burch and co-workers [7]. These observations suggest that the chlorinated species exist on the catalyst surface and/or in amorphous form in both the

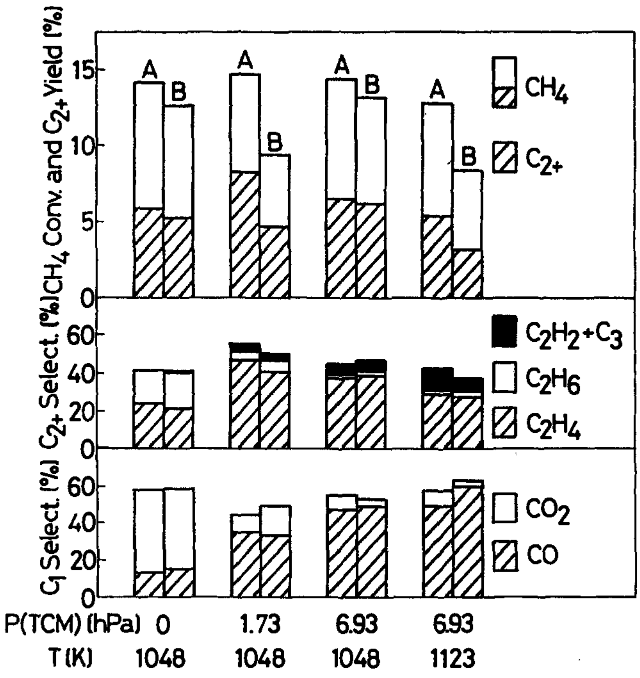

Fig. 1. Methane conversion on MgO in the presence and absence of TCM. (A) 0.5 h on-stream, (B) 6 h on-stream.

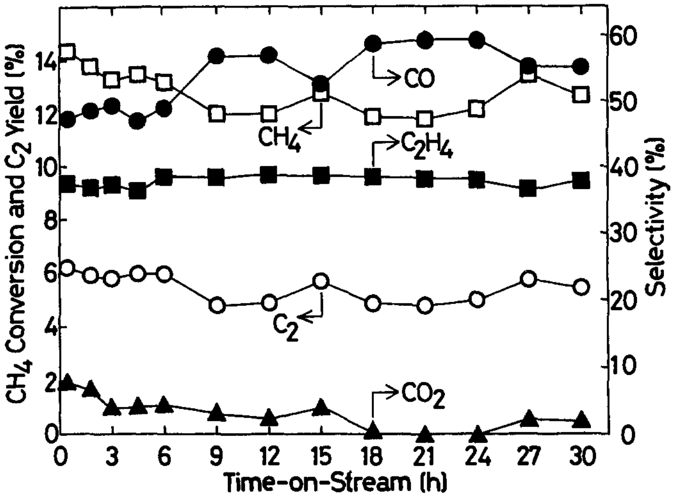

Fig. 2. Extended time-on-stream effects in the conversion of CH_4 on MgO at 1048 K in the presence of TCM (6.93 hPa).

surface and bulk structure. Quantitative analysis with XRF showed that the atomic ratio of Cl/Mg in the bulk phase was quite small. Therefore it is concluded that the chlorinated species are formed only on the catalyst surface, at least under the conditions employed in the present work, and the improvement by the addition of TCM may be attributed directly or indirectly to the presence of these species on the surface. The formation of the surface chlorinated species is further supported by argon-ion etching experiments of the used catalyst (fig. 3), for which the Cl/Mg ratio gradually decreased with increase in the sputtering time. Unfortunately, the identification of the chlorinated species by X-ray diffraction analyses could not be made due to their small quantities. The Cl/Mg ratio was strongly influenced by the reaction temperature, but the ratio did not depend on the partial pressure of TCM and time-on-stream as shown in table 1.

Table 1
Characterization of used MgO catalysts

Run No.	Reaction TCM[a]	Conditions T[b]	Phase (XRD)	Cl/Mg (XPS)	Cl/Mg (XRF)
1[c]	0	1048	MgO	0	–[e]
2[c]	1.73	1048	MgO	0.06_5	–[e]
3[d]	6.93	1048	MgO	0.04_5	0.001_6
4[c]	6.93	1123	MgO	0.21	–[e]

[a] Partial pressure of TCM (hPa).
[b] Reaction temperature (K).
[c] After 6 h on-stream.
[d] After 30 h on-stream.
[e] Not analyzed.

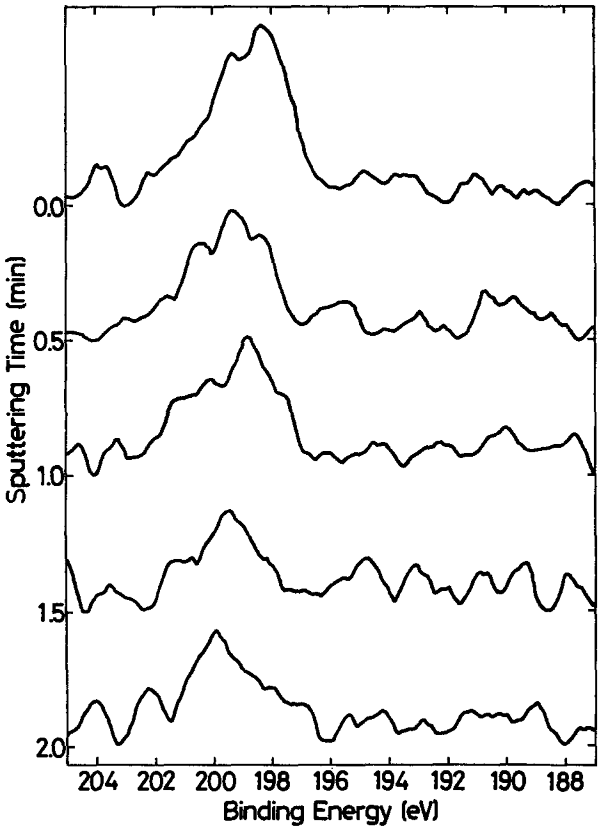

Fig. 3. Depth profile of chlorine species on used MgO in the presence of TCM. Sample: same as that of run 3 in table 1.

The results show that formation of an excess of chlorinated species on the catalyst surface leads to deactivation, possible due to the blockage of oxygen sites of MgO. In order to obtain the beneficial effects from the addition of TCM under stable conditions it is evident that the formation of a sufficient but not excess quantity of the corresponding chloride is needed together with the continuous introduction of a small but significant partial pressure of TCM (6.93 hPa). These observations demonstrate that the catalytic activity and stability in the presence of TCM depend on a balance of the chlorinated species on the catalyst surface and the contribution of gas-phase TCM to the catalyst surface.

3.3. IDENTIFICATION OF CHLORINATED SPECIES ON MgO

Although the identification of the chlorinated species on the catalyst by X-ray analyses is difficult due to the limited quantities of the species, the formation of chloride ($MgCl_2$) or oxychloride ($Mg(ClO_4)_2$ or $Mg(ClO_3)_2$) might be expected, based on our results from the oxidation on alkali sulphates [11] or lanthanide oxides [9,10]. However, the oxychlorides of magnesium decompose at 524 or 393 K, respectively [15] and thus are unstable under our reaction conditions. Therefore the formation of $MgCl_2$, which melts at 987 K but is stable as a molten salt up to 1710 K (boiling point) [15] appears to be more probable. $MgCl_2$ is very hygroscopic and converts to the hydrate ($MgCl_2 \cdot 6H_2O$), both of which are highly deliquescent. Therefore, if $MgCl_2$ forms on the catalyst under the present reaction conditions, the chloride would be expected to be converted to the hexahydrate under ambient conditions. The hexahydrate does not return to the anhydrous chloride by heating, but decomposes to MgO at around 503 K as shown in reactions (1)–(8) [16]:

$$\text{368–388 K} \quad MgCl_2 \cdot 6H_2O \rightarrow MgCl_2 \cdot 4H_2O + 2H_2O\,, \tag{1}$$

$$MgCl_2 \cdot 4H_2O \rightarrow MgCl_2 \cdot 2H_2O + 2H_2O\,, \tag{2}$$

$$\text{408–453 K} \quad MgCl_2 \cdot 4H_2O \rightarrow Mg(OH)Cl + HCl + 3H_2O\,, \tag{3}$$

$$MgCl_2 \cdot 2H_2O \rightarrow MgCl_2 \cdot H_2O + H_2O\,, \tag{4}$$

$$\text{458–503 K} \quad MgCl_2 \cdot 2H_2O \rightarrow Mg(OH)Cl + HCl + H_2O\,, \tag{5}$$

$$\text{>503 K} \quad MgCl_2 \cdot H_2O \rightarrow MgCl_2 + H_2O\,, \tag{6}$$

$$MgCl_2 \cdot H_2O \rightarrow Mg(OH)Cl + HCl\,, \tag{7}$$

$$Mg(OH)Cl \rightarrow MgO + HCl\,. \tag{8}$$

Therefore it is expected that the intensity of the Cl XPS signal of the used catalyst would decrease by heating above 503 K. The atomic ratio of Cl/Mg on the surface of commercial $MgCl_2$ and $MgCl_2 \cdot 6H_2O$ decreased markedly by heating at 623 K for 1 h in air as shown in table 2. A similar observation was also found with the used MgO, which is the same sample as that of run 4 in table 1. These results suggest that the chlorinated species on the catalyst is $MgCl_2$ and the reaction behaviour in the presence of TCM on MgO is strongly influenced by the disappearance and regeneration of $MgCl_2$ on the catalyst surface under the reaction conditions. Furthermore, the formation of $MgCl_2$ would be also supported by the binding energy at approximately 199 eV (fig. 3) because XPS signals attributed to chlorine species in the gas phase and of oxychlorides have been detected at approximately 207 eV, while those of chlorides have been found at approximately 199 eV [17].

Table 2
The atomic ratio of Cl/Mg estimated by XPS

	$MgCl_2$	$MgCl_2 \cdot 6H_2O$	Used MgO [a]
before heating	1.04	–[b]	0.21
after heating [c]	0.49	0.55	0.13

[a] Same example as that of run 4 in table 1.

[b] Not analyzed.

[c] At 623 K for 1 h in air.

4. Conclusions

(1) The introduction of TCM to the reactant stream in the oxidative coupling of methane on MgO improves the selectivity to ethylene.

(2) A very small quantity of the chlorinated species is observed by XPS and XRF. The chlorinated species are present mainly on the catalyst surface, suggesting that the reaction behaviour is strongly influenced by the surface chlorinated species, although gas phase participation cannot be excluded.

(3) Thermal decomposition of the used catalyst suggests that the chlorinated species is $MgCl_2$, based on the comparison with a similar treatment of the commercial samples.

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