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Oxidative Coupling of Methane on MgO–$MgSO_4$ Catalysts in the Presence and Absence of Carbon Tetrachloride

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The effect of carbon tetrachloride (CCl_4) on the oxidative coupling of methane on binary catalysts containing MgO and $MgSO_4$ was studied at 1048 K. With no CCl_4 in the feedstream the conversion of methane increased with increasing content of MgO in the binary catalyst, but was even further enhanced by introducing a small partial pressure of CCl_4. The selectivity to ethylene increased upon the addition of CCl_4, but was not dependent on either the concentration of CCl_4 in the feedstream or the relative amounts of the two components in the catalyst. X-Ray photoelectron spectroscopic analyses of the used catalysts showed that the sulfate is partially transformed into the oxide as well as the formation of Cl species in the near-surface region of the catalysts during the methane conversion process. The addition of CCl_4 enhances the conversion of sulfate to oxide. The oxide formed by the decomposition of the sulfate and the chlorine species plays different roles in improving the catalytic activities by introducing CCl_4.

The anion effect in the oxidative dehydrogenation of methane[1—4] and ethane[5—7] on oxides, sulfates and phosphates of magnesium and of lanthanum in the presence of carbon tetrachloride (CCl_4) was studied in our laboratories. In the oxidative coupling of methane with and without CCl_4 the catalytic effects of the oxides and sulfates were found to be distinctly different. In the absence of CCl_4 in the feedstream, the conversion of methane on the oxide catalyst was larger than that on the sulfate catalysts. Since the C–H bond scission of methane is believed to occur on basic sites of the catalyst,[8] the low conversion of methane on the sulfates may be related to the presence of disadvantageous weakly acidic sites,[9,10] in contrast to that of basic sites of oxide catalysts. Upon introducing CCl_4 into the feedstream during the oxidative coupling of methane, a substantial improvement in the conversion of methane was observed on the sulfates, but not on the oxides, while the selectivity to ethylene and ethane increased and decreased, respectively, on both catalysts. These differing observations regarding the methane coupling process with the oxides and sulfates are not yet understood.

The oxidative dehydrogenation of ethane to ethylene has also been studied in the presence of CCl_4 on $MgSO_4$[6] and MgO.[7] Although the effects of introducing CCl_4 over a variety of catalysts have been attributed to the formation of the corresponding chlorides[3—7,11] and oxychlorides,[12,13] during the reaction the source of the enhancement is not yet fully understood.

In view of the substantial differences observed with $MgSO_4$ and MgO, that is, the relatively high activity of the oxides in the absence of CCl_4 and the noticeable improvement in the activities of the sulfates upon the addition of CCl_4, it is of interest to study binary catalysts containing the oxide and sulfate for the oxidative coupling of methane in the presence and absence of CCl_4. Although the activities found with the binary catalysts do not exceed those on MgO, with or without CCl_4, the significant enhancement of the conversion of methane on the binary catalysts and $MgSO_4$ upon the addition of CCl_4 may be primarily due to a transformation of the sulfate to MgO during the reaction, while the increase in the selectivity to ethylene, where CCl_4 is present, may be related to the formation of the Cl species on the surface of the catalyst.

Experimental

MgO and $MgSO_4$ reagents were purchased from Wako Pure Chemicals, Osaka, and were used as received. The MgO–$MgSO_4$ catalysts were prepared by adding an aqueous solution of $MgSO_4$ to an aqueous suspension of MgO, followed by evaporation of the water with vigorous stirring until a thick paste was formed. The paste was dried overnight at 353 K and calcined at 1048 K for 3 h. Particles of 1.70—0.85 mm were employed in the present work. The compositions of the binary catalysts are expressed as mol percent of MgO, and are denoted as $x\%$ MgO/$MgSO_4$. The surface areas calculated based on the nitrogen-adsorption isotherms obtained at 77 K and the apparent densities of the pure components and binary catalysts are summarized in Table 1.

The oxidative coupling of methane was performed in a conventional fixed-bed continuous-flow quartz reactor at atmospheric pressure.[11] In all experiments, the catalyst (0.7 g) was heated to 1048 K while maintaining a continuous flow of helium, and was then conditioned at this temperature under a 25 ml min^{-1} flow of oxygen

Table 1. Surface Areas and Apparent Densities of the Components and Binary Catalysts

Catalyst[a]	Surface area[b]	Apparent density[c]
MgO	11	0.55
90	25	0.25
75	11	0.41
50	6.4	0.49
25	2.7	0.45
MgSO$_4$	0.8	0.74

a) Numbers indicate mole percent of MgO in the binary catalyst.
b) m^2 g^{-1}. c) g cm^{-3}.

Table 2. Surface Properties of Fresh Catalysts

Catal.[a]	Time[b]	Binding energy/eV			Atomic ratio	
	min	Mg 2s	O 1s	S 2p	O/Mg	S/Mg
0%	0	89.8	532.5, —	169.3	3.01	1.02
	1	89.6	532.5, —	169.6	2.52	0.78
25%	0	89.4	532.9, —	169.5	2.73	0.69
	1	89.6	532.7, —	169.9	2.04	0.55
50%	0	87.8	532.1, 530.5 (1 : 0.27)[c]	169.1	1.43	0.35
	1	88.4	532.0, 530.5 (1 : 0.54)[c]	169.2	1.32	0.27
75%	0	88.1	532.0, 529.8 (1 : 1.1)[c]	169.1	1.17	0.14
	1	88.3	531.8, 530.2 (1 : 2.7)[c]	169.3	1.07	0.12
90%	0	88.0	531.9, 530.1 (1 : 2.7)[c]	169.0	0.72	0.08
	1	88.6	532.0, 530.4 (1 : 3.6)[c]	170.0	0.75	0.05
100%	0	88.4	532.4, 530.4 (1 : 2.7)[c]	—	1.02	—
	1	88.6	532.7, 530.5 (1 : 4.3)[c]	—	0.89	

a) Mole percent of MgO. b) Etching time. c) Ratio of intensities.

for 1 h. The reaction conditions were as follows: $T = 1048$ K, $F = 30$ ml min^{-1}, $P(CH_4) = 28.7$ kPa, $P(O_2) = 4.1$ kPa, and $P(CCl_4) = 0$, 0.17, and 0.34 kPa. The balance to the atmospheric pressure was provided by helium. Monitoring of the reaction was accomplished with an on-line Shimadzu GC-8APT gas chromatograph with a thermal-conductivity detector and integrator (Shimadzu C-R6A). The column packings used were: Molecular Sieve 5A (0.5 m×3 mm) for O_2, CH_4, and CO (318 K) and Porapak Q (6 m×3 mm) for CO_2, C_2H_6, C_2H_4, CH_3Cl, and C_3 species (363 K). 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. Blank experiments conducted with methane absent from the feed ($O_2 + CCl_4 + He$) indicated that CCl_4 undergoes oxidation while producing carbon monoxide and/or carbon dioxide. Although the quantities of these products relative to those from methane were small, all of the data reported were corrected by performing duplicate experiments with methane absent under otherwise identical values of the process variables.[11]

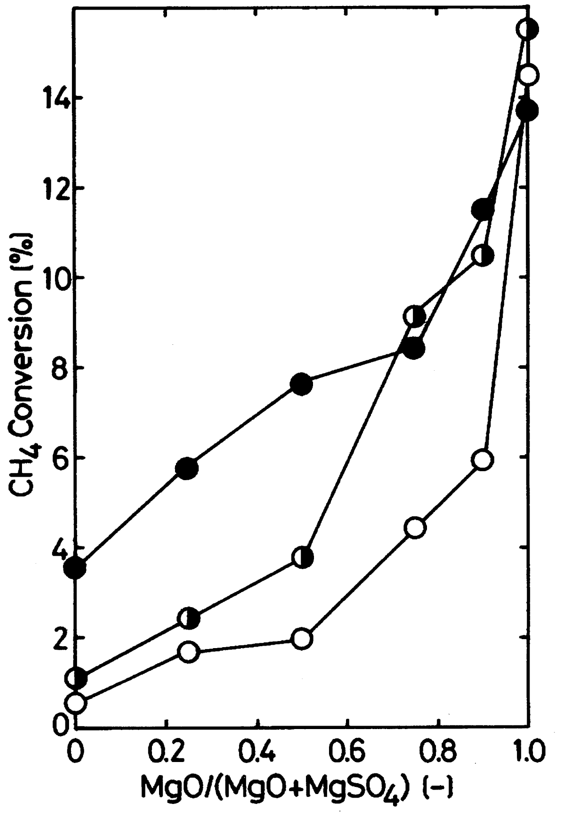

Fig. 1. The effect of CCl_4 on the conversion of methane on MgO–MgSO$_4$ catalysts at 1048 K. Reaction conditions: $CH_4 = 28.7$ kPa, $O_2 = 4.1$ kPa, and $CCl_4 = 0$, 0.17 or 0.34 kPa diluted with He. Total flow rate=30 ml min^{-1}. Weight of catalyst=0.7 g. Open symbols; $CCl_4 = 0$ kPa. Half-filled symbols; $CCl_4 = 0.17$ kPa. Filled symbols; $CCl_4 = 0.34$ kPa.

The X-ray photoelectron spectra (XPS) were measured using a Shimadzu ESCA-1000AX, and the observed binding energies were corrected using the 1s level (285.0 eV) for contaminant carbon as an internal standard. Argon-ion etching measurements of the catalyst were carried out (2 kV, 1 min), where the rate of the sputtering was estimated to be ca. 2 nm min^{-1} for pure SiO_2.

Results and Discussion

Surface Properties of Prepared Catalysts. The binding energies and atomic ratio of each component in the fresh catalyst analyzed by XPS are described in Table 2. No significant differences in the binding energies of Mg 2s and S 2p (when present) were observed for a fresh catalyst. There were two peaks at 531.8—532.9 and 529.8—530.5 eV in the spectrum for O 1s of 50—100% MgO/MgSO$_4$. In contrast, the only former peak was observed for 0 and 25% MgO/MgSO$_4$ catalysts. Since the intensities of the former peak decreased along with an increase in the MgO/MgSO$_4$ ratio until the latter peak became the principal signal in MgO, the former peak can be attributed to the lattice oxygen of the sulfate and the latter to that of the oxide. The ratios of the intensities of the latter peak to the former after argon ion-sputtering were approximately twice that found prior to the sputtering. Therefore, other oxygen-containing species, such as adsorbed CO_3^{2-} and SO_4^{2-}, appear to be included in the former peak. Since it is generally known that the O 1s peaks

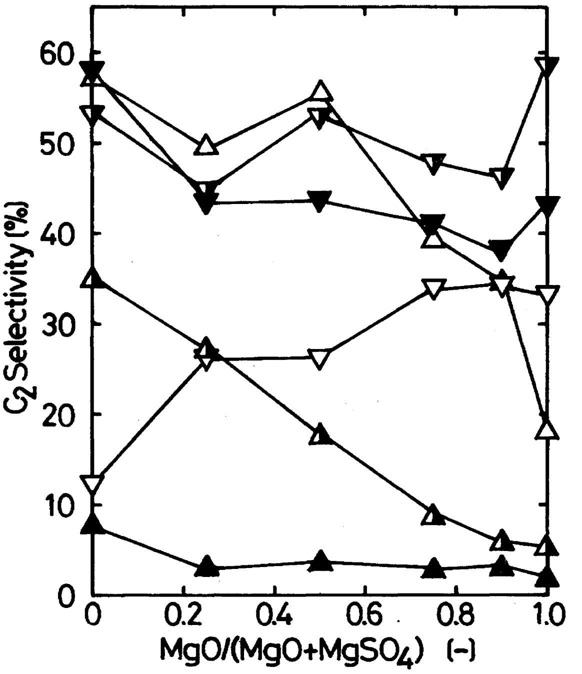

Fig. 2. The effect of CCl_4 on the selectivity to C_2H_6 and C_2H_4 on MgO–$MgSO_4$ catalysts at 1048 K. Reaction conditions: same as those in Fig. 1. Symbols: △ C_2H_6 selectivity. ▽ C_2H_4 selectivity. Others are same as those in Fig. 1.

found for a variety of oxygen species overlap at 532±2 eV,[14] the presence of the peak at 531.8—532.9 eV on MgO cannot be interpreted unambiguously as being indicative of the presence of the lattice oxygen of $MgSO_4$. The O/Mg and S/Mg atomic ratios with and without sputtering correlate with the composition of the bulk phase.

Effect of the Partial Pressure of CCl_4 on the Oxidative Coupling of Methane on MgO–$MgSO_4$. 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. Although water and H_2 were also produced, they are not reported here. The selectivities to the CH_3Cl and C_3 species were less than 1%, and are not reported. The measurements taken during 6 h on-stream in the absence of CCl_4 demonstrated the stability of the catalyst during this period of time, while those in the presence of CCl_4 changed with time-on-stream due, at least in part, to the formation of Cl species on the surface of the catalyst and the transformation of $MgSO_4$ to MgO (described below). In order to obtain information concerning the initial states of the catalysts, data collected at 0.5 h on-stream are described in the following section.

The conversion of methane obtained with the various binary catalysts in the presence and absence of CCl_4 is shown in Fig. 1. In the absence of CCl_4, the conversion increased along with an increase in the relative amount of basic MgO in the catalyst, in agreement with earlier suggestions that the activation of CH_4 occurs on basic sites of the catalyst,[8] but is suppressed on acidic $MgSO_4$.[9,10] Upon introducing 0.17 kPa CCl_4 into the feedstream, the conversions increased by a factor of two over those found in the absence of CCl_4, with the exception of those for MgO. Although an increase in the partial pressure of CCl_4 to 0.34 kPa resulted in a further improvement in the conversion on 0—50% MgO/$MgSO_4$, little effect was observed on 75—100% MgO/$MgSO_4$ catalysts.

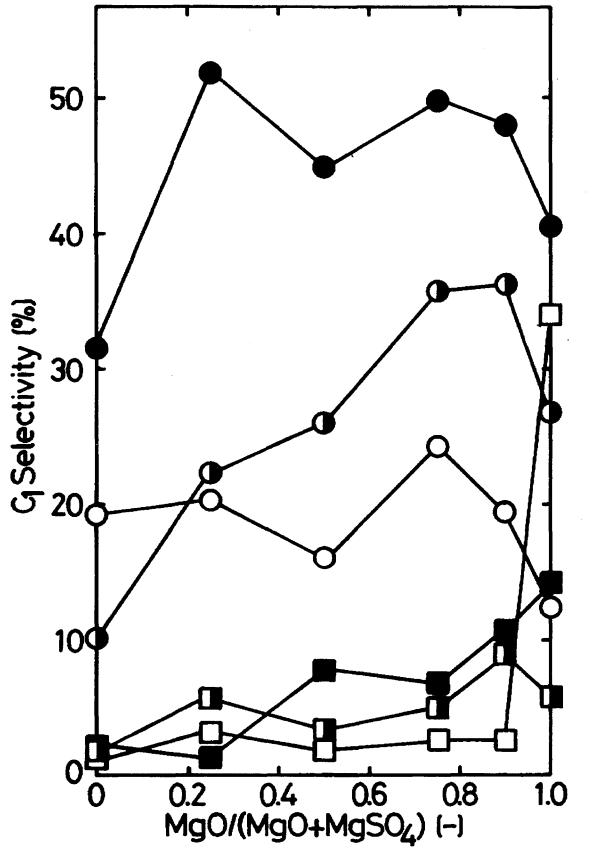

Fig. 3. The effect of CCl_4 on the selectivity to CO and CO_2 on MgO–$MgSO_4$ catalysts at 1048 K. Reaction conditions: same as those in Fig. 1. Symbols: ○ CO selectivity. □ CO_2 selectivity. Others are same as those in Fig. 1.

Figure 2 shows the effects of introducing CCl_4 on the selectivities to C_2H_6 and C_2H_4 on each catalyst. Along with an increase in the concentration of MgO in the binary catalyst, the selectivity to C_2H_4 in the absence of CCl_4 increased, while that to C_2H_6 decreased until the selectivity to C_2H_4 exceeded that to C_2H_6 on MgO. Upon the addition of 0.17 kPa of CCl_4 into the feedstream, the selectivity to C_2H_4 increased on all catalysts, but changed relatively little with the catalyst composition. In contrast, the selectivity to C_2H_6 decreased approximately linearly with increasing concentration of MgO. The selectivity to C_2H_4 was little influenced by increased partial pressures of CCl_4 up to 0.34 kPa, while that to C_2H_6 decreased to less than 10% and appeared to be relatively insensitive to the composition of the catalyst.

The selectivity to CO_2 was less than 10% for all catalyst compositions, except for MgO, in either the presence or absence of CCl_4, and showed a remarkable independence of the catalyst composition (Fig. 3). In contrast, the selectivities to CO increased markedly upon an increase in the partial pressure of CCl_4; at 0.34 kPa CCl_4 they were larger for the binary than for the one-component catalyst.

Table 3. Binding Energy and Ratio of Intensity of O 1s of Catalysts Used in the Absence and Presence of CCl$_4$

Catal.$^{a)}$	Time$^{b)}$	Binding energy/eV		
	min	0 kPa$^{c)}$	0.17 kPa$^{c)}$	0.34 kPa$^{c)}$
0%	0	532.9, —	532.5, —	532.6, —
	1	533.3, —	533.4, 530.7 (1 : 0.36)	532.9, —
25%	0	532.4, 530.4 (1 : 0.19)	532.6, 530.7 (1 : 0.22)	532.2, 530.1 (1 : 0.21)
	1	532.5 530.9 (1 : 0.19)	533.0, 531.0 (1 : 0.68)	532.1, 530.2 (1 : 0.18)
50%	0	532.4, 531.0 (1 : 0.33)	532.0, 530.1 (1 : 0.57)	531.8, 529.8 (1 : 3.3)
	1	532.4, 530.5 (1 : 0.33)	532.4, 530.7 (1 : 1.7)	532.3, 530.1 (1 : 4.0)
75%	0	532.2, 530.2 (1 : 1.8)	531.9, 530.1 (1 : 1.6)	532.6, 530.3 (1 : 3.2)
	1	532.2, 530.5 (1 : 4.9)	532.3, 530.4 (1 : 5.1)	532.4, 530.4 (1 : 6.1)
90%	0	531.8, 529.8 (1 : 2.4)	—, 530.4	532.3, 530.2 (1 : 2.7)
	1	532.0, 530.5 (1 : 4.3)	—, 530.8	532.7, 530.5 (1 : 3.4)
100%	0	531.3, 529.5 (1 : 2.6)	532.1, 529.9 (1 : 2.1)	532.0, 530.1 (1 : 3.5)
	1	531.1, 529.6 (1 : 4.3)	532.2, 530.1 (1 : 2.5)	532.3, 530.0 (1 : 3.9)

a) Mole percent of MgO. b) Etching time. c) Partial pressure of CCl$_4$ in the feedstream. Values in parentheses show ratio of intensities.

Table 4. Atomic Ratio of O/Mg, S/Mg and Cl/Mg in the Near-Surface Region of Catalysts Used in the Absence and Presence of CCl$_4$

Catal.$^{a)}$	Time$^{b)}$	0 kPa$^{c)}$		0.17 kPa$^{c)}$			0.34 kPa$^{c)}$		
	min	O/Mg	S/Mg	O/Mg	S/Mg	Cl/Mg	O/Mg	S/Mg	Cl/Mg
0%	0	2.76	0.97	2.30	0.88	—	2.88	0.96	—
	1	2.08	0.67	1.68	0.49	—	2.33	0.63	—
25%	0	1.77	0.40	1.52	0.45	0.09	1.81	0.50	0.10
	1	1.65	0.32	1.20	0.25	—	1.68	0.39	0.05
50%	0	1.51	0.29	1.29	0.24	0.05	0.85	—	0.12
	1	1.34	0.21	1.10	0.16	0.03	0.89	—	0.08
75%	0	1.02	0.11	0.92	0.03	0.10	0.90	0.06	0.09
	1	1.04	0.07	0.86	—	0.03	1.01	0.06	0.07
90%	0	0.85	—	0.74	—	0.09	0.93	0.03	0.11
	1	0.86	—	0.53	—	0.04	0.90	—	0.08
100%	0	1.06	—	0.85	—	0.09	0.91	—	0.12
	1	1.05	—	0.87	—	0.06	0.88	—	0.03

a) Mole percent of MgO. b) Etching time. c) Ratio of intensities. c) Partial pressure of CCl$_4$ in the feedstream.

Surface Properties of Catalysts after Use in a Reaction. The XPS analyses of catalysts previously used in methane conversion showed no peaks other than those detected on the fresh catalysts, except for that of Cl 2p at approximately 199 eV on 25—100% MgO/MgSO$_4$, which had been used in the presence of CCl$_4$. However, the relative intensities of the two peaks at ca. 532 and 530 eV for O 1s (Table 3) and the atomic ratio of O/Mg and S/Mg (Table 4) on each used catalyst were different from those on fresh catalysts. With the catalysts employed in the absence of CCl$_4$, the S 2p peak for 90% MgO/MgSO$_4$ was not detected (Table 4) and the O 1s peak due to lattice oxygen of MgO (Table 3), which was not detected for the fresh 25% MgO/MgSO$_4$ catalyst, is now evident (Table 2). Furthermore, the intensities of the signals of the lattice oxygen of MgO (Table 3) were stronger than those for the corresponding fresh catalyst (Table 2). These results, together with those showing decrease in the S/Mg and O/Mg ratios for the sulfate-containing catalysts, suggest that a partial decomposition of MgSO$_4$ to MgO occurs during the methane conversion reaction in the absence of CCl$_4$.

On catalysts which had been used in the presence of CCl_4 of 0.17 kPa, little or no peak for S 2p was observed for those containing less than 25% of $MgSO_4$ (Table 4). Furthermore, the peak of O 1s due to the lattice oxygen of MgO at approximately 530 eV was clearly evident, and the O/Mg atomic ratios were similar to that of MgO (Table 3). Similar results were obtained for catalysts containing less than 50% of $MgSO_4$, which had been used in a reaction with 0.34 kPa CCl_4. These observations provide strong evidence for promoting the decomposition of $MgSO_4$ to MgO by CCl_4 in the feedstream. The peak of Cl 2p was observed for each binary catalyst and MgO, but not for $MgSO_4$, on which the formation of very small quantities of the Cl species has been previously reported.[4] Compared with the intensity of the Cl 2p peak before argon-ion sputtering, the intensity after the sputtering decreased, demonstrating that the effect of adding CCl_4 is primarily related to changes in the properties of the surface, rather than those of the bulk.

Role of CCl_4 in the Reaction. The activities found with the binary catalysts were smaller than those on MgO, regardless of the presence of CCl_4. The addition of CCl_4 to the feedstream evidently enhances the conversion of methane on $MgSO_4$ and MgO–$MgSO_4$, while increases in the selectivity to ethylene were observed on all catalysts. In addition, the selectivities to each product in the presence of 0.34 kPa of CCl_4 were similar regardless of the catalyst composition. These observations suggest that different factors resulting from introducing CCl_4 play important roles in changes of the conversion and selectivity. As described above, the decomposition of $MgSO_4$ to form MgO on the surface of the binary catalysts and $MgSO_4$ is apparently influenced by the concentration of CCl_4 introduced, while the quantity of chlorinated species formed over each catalyst surface, except for that on $MgSO_4$, is virtually identical, regardless of the partial pressure of CCl_4.

The results obtained in the present work show that, in the absence of CCl_4, the conversions of methane obtained on MgO are considerably greater than those on $MgSO_4$ under otherwise identical conditions. Indeed, as the binary catalyst is varied from the latter to the former composition the conversion increases continuously. Upon the addition of CCl_4 to the feedstream, although the conversion of methane is increased on $MgSO_4$ and the binary catalysts containing MgO and $MgSO_4$, little or no beneficial effect is observed with MgO. In contrast, the selectivities to C_2H_4 are increased upon adding CCl_4 to the feedstream with all compositions, while that of C_2H_6 is decreased. These results suggest that, where the catalyst $MgSO_4$ or the binary compositions are inferior catalytically to MgO, although the addition of CCl_4 is advantageous for increasing the conversion, this is not true for MgO itself. Thus, it must be concluded that MgO, of the compositions examined in the present work, is the preferred catalyst for producing methyl radicals, possibly because of its inherently superior basicity.

In the absence of CCl_4 the selectivities to C_2H_4 and C_2H_6 on MgO are higher and lower, respectively, than that observed on the remaining binary compositions. In the presence of 0.34 kPa CCl_4, although the selectivity to C_2H_4 on MgO increased from that without CCl_4, the C_2H_4 selectivity on MgO is less than that obtained with $MgSO_4$ with CCl_4 present. The total C_2 selectivities on MgO in the absence and presence of CCl_4 (0.34 kPa) are 52 and 45%, respectively, while those on $MgSO_4$ are 70 and 66%, respectively. Thus, the principal effect of CCl_4 is seen in the increased selectivity to C_2H_4 with a concomitant decrease to that of C_2H_6.

The results shown in the present work suggest that two processes occur on and in the catalysts. $MgSO_4$ is converted to MgO at the temperature at which the coupling reaction occurs, either with or without CCl_4; however, in the presence of CCl_4 this process appears to occur more readily. Thus, since the formation of the basic MgO would be advantageous in the activation of methane, the conversion of methane in the presence of CCl_4 is enhanced on $MgSO_4$ and MgO–$MgSO_4$. In the presence of CCl_4, chlorine (presumably in the form of Cl^-) is chemisorbed on the catalyst. The surface chloride appears to be less able to form from the sulfate, and is only present after a portion of the sulfate on the surface has been converted to the oxide. Although the explanation of this observation involves a number of variables, the differing sizes of the sulfate and oxygen ions may play a role in facilitating the chloride ions to exchange with these species. Consequently, although the enhancement effects of CCl_4, particularly with respect to the selectivities in the methane coupling reaction, are seen with all compositions, the addition of CCl_4 is particularly beneficial in converting $MgSO_4$ and the binary sulphates into more active methyl radical generators while altering of C_2 selectivites in favor of the production of ethylene.

Conclusion

The enhancement of the conversion of methane and the selectivity to ethylene by the addition of CCl_4 into the feedstream was observed on $MgSO_4$ and the MgO–$MgSO_4$ binary catalysts, while only the selectivity, and not the conversion, increased on MgO when CCl_4 was present. The increase in the selectivity to C_2H_4 and in the conversion of methane appear to have resulted from the deposition of chlorine, in whatever form, and the formation of MgO (when the catalyst includes the sulfate) on the surface of catalysts during the reaction, respectively. Although the decomposition of $MgSO_4$ to MgO was promoted by introducing CCl_4, but the formation of the chlorided surface was little influenced by the concentration of CCl_4 in the feedstream.

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