Oxidative Coupling of CH₄ over Molybdates: Catalyst Performance and Characterization

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To effect oxidative coupling of methane, a variety of molybdates were used as catalysts with sustained activity for more than 280 h. The reaction was studied by cofeeding methane and oxygen at atmospheric pressure, through continuous conventional flow reactors containing the catalyst. The effects of operating conditions were studied and the optimum reactor temperature to achieve high yields of ethane and ethylene was ca. 700–780 °C, depending on the reactor dimensions. The influence of reactor dimensions on the distribution of products is also reported. Molybdate catalysts are active and yet resistant to deactivation and sintering. Selectivities $X(C_2)$ % and yields $Y(C_2)$ % up to 20.0 and 7.0% were observed, respectively. The reactor feed had a CH₄ to O₂ ratio of ca. 1.1. Our results present the effects of varying several operating conditions and the significant gas-phase products observed were H₂, C₂H₄, C₂H₆, C₃H₆, H₂O, and traces of HCHO and CH₃OH. C₂H₂ formation was not observed. The main oxidation products were CO₂ and CO. Structural characterization of the molybdates was carried out by elemental analysis, infrared spectroscopy (IR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).

Introduction

During the past few years, oxidative dimerization of CH₄ has become an important area of catalytic research. After Keller and Bhasin's initial work,¹ other catalysts, such as alkali metal oxides,²⁻⁴ transition metal oxides,^{5,6} pyrochlores,^{7,8} heteropolyoxometalates,⁹ and oxychlorides,¹⁰ were discovered. These initial studies have recently been reviewed by Hutchings et al.¹¹ and Anderson.¹²

The present study is motivated by previous work carried out in our laboratory involving methane activation.¹³⁻¹⁶ Preliminary results with molybdate catalysts, showing much higher selectivities and conversions into C_2^+ products than found in refs 13–16, have been reported recently by our group.¹⁷ This paper presents the effect of operating conditions on the catalytic reaction as well as on the structure of the molybdate catalysts used. It was also our objective to look into the possibility of obtaining high yields of unsaturated hydrocarbons since ethylene is more valuble than ethane.^{18,19}

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Experimental Section

Molybdate compounds were purchased and used as such. Molybdates of Na and K (p.a. grade) were supplied by Fluka, Switzerland, and those of Li, Mg, Ba, Fe, Cu, Zn, and Ni were obtained from Alfa Ventron. $MnMoO_4$ (Cerac, USA) and Co- MoO_4 (K&K Labs, USA) were also of the highest available purity (>99% p.a.).

The reactor was made of quartz U-tube. Two types of reactors were used: a long reactor with 560 mm length with 8 mm i.d., and a short reactor with 350 mm length and 6.5 mm i.d. The catalyst was used in the form of a bed, fixed into position with quartz wool plugs. The reactor was operated in the single-pass mode. The first and the last 7 cm of the longer reactor were outside the furnace, with 42 cm inside the furnace. The catalyst was situated in the second half of the U-tube. With 1 g of catalyst, the free volume of the cell (on the average) was 24.9 cm³. For the short reactor, the first and last 6 cm were outside the furance resulting in a free volume of 6.5 cm^3 , when loaded with 1 g of catalyst. Always "new" quartz reactors were used for the empty reactor runs.

Product analysis was performed by gas chromatography (GC) using a thermal conductivity detector. The major products C_2H_4 , C_2H_6 , C_3H_6 , and CO_2 were detected on a Porapak QS column at 60 °C using He as a carrier gas in a Carlo Erba HRGC 5300 Mega Series gas chromatograph. For CO analysis, a molecular sieve 5Å column at 40 °C was used. The absence of C_2H_2 in the product stream was confirmed chromatographically by using a Porasil-B column. H₂ was analyzed on a molecular sieve 5Å column, using Ar as the carrier gas. Water produced during the reaction was trapped at the reactor exit. C_3H_6 was detected in the gas phase as well as in the liquid H₂O collected in the trap, in a dissolved form. Small quantities of HCHO and CH₃OH were also observed (as reaction products) in both phases. Inlet gas flows were measured by calibrated flow meters. The activity of the catalyst is defined by the % conversion of CH₄ into all products. The selectivity X(i)% to product i is defined as the percentage amount of product i/amount of total reaction products.

Elemental analysis was carried out to determine the level of C before and after reaction by means of an elemental analysis unit (Perkin Elmer Model 240) with a lower detection limit of 10^{-7} mol C in 20 mg of sample. The XPS-measurements were performed, using a Leybold surface analyzer, equipped with a separate gas reaction cell attached to the spectrometer chamber.

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TABLE I: CH₄ Conversion (%), Product Selectivities (X%), C₂ Yields, and C₂H₄/C₂H₆ Ratios for Various Molybdates as Catalysts for CH₄ **Dimerization Reaction**

| catalyst | <i>T</i> , ⁰C | CH₄ conv, % | <i>X</i> (H ₂) | $X(C_2H_4)$ | $X(C_2H_6)$ | $X(C_3H_6)$ | X(CO) | X(CO ₂) | ratio C ₂ =/C ₂ | $X(C_2)\%$ selectivity | Y(C₂)% yield |
|-------------------------------------|---------------|----------------|----------------------------|-------------|-------------|-------------|-------|---------------------|--|---------------------------|-----------------|
| Na ₂ MoO ₄ | 726 | 74 | 0.7 | 8.7 | 2.7 | 0.6 | 66.0 | 17.4 | 3.3 | 12.0 | 8.9 |
| Li₂MoO₄ | 720 | 63 | 0.7 | 5.8 | 1.8 | 0.6 | 63.6 | 21.5 | 3.1 | 8.2 | 5.2 |
| K ₂ MoO ₄ | 722 | 57 | 1.7 | 5.9 | 2.0 | 0.3 | 54.7 | 30.2 | 2.9 | 8.2 | 4.7 |
| MgMoÕ₄ | 728 | 57 | 0.9 | 8.2 | 2.5 | 0.5 | 58.2 | 24.8 | 3.3 | 11.0 | 6.3 |
| BaMoO ₄ | 720 | 54 | 0.5 | 7.4 | 1.8 | 0.5 | 65.0 | 20.0 | 3.9 | 9.7 | 5.2 |
| MnMoO | 729 | 60 | 0.7 | 6.5 | 2.0 | 0.5 | 66.0 | 21.5 | 3.4 | 9.0 | 5.4 |
| CoMoO | 720 | 63 | 0.5 | 7.1 | 2.4 | 0.6 | 31.0 | 54.0 | 3.0 | 10.1 | 6.3 |
| Fe ₂ (MoO ₄) | 724 | 53 | 0.5 | 8.8 | 2.7 | 0.5 | 60.1 | 27.3 | 3.2 | 12.0 | 6.3 |
| CuMoO ₄ | 728 | 51 | 1.8 | 8.6 | 2.3 | 0.6 | 58.5 | 27.5 | 3.7 | 11.5 | 5.8 |
| ZnMoO | 728 | 45 | 0.7 | 9.4 | 3.8 | 0.7 | 54.0 | 30.0 | 2.5 | 13.9 | 6.2 |
| NiMoO | 728 | | | | | | | | | | |
| Na ₂ WO ₄ | 720 | 51 | 0.7 | 7.5 | 2.2 | 0.5 | 70.0 | 14.7 | 3.4 | 10.2 | 5.2 |

The base pressure of the spectrometer was 2×10^{-10} mbar and during the measurements 8×10^{-9} mbar. The XPS spectra were recorded using a twin-anode X-ray gun (Mg K α /Al K α) at a power of 200 and 250 W, respectively, and a hemispherical energy analyzer (Leybold EA11/100). The spectrometer calibration was repeatedly performed, following^{20,21} and referencing to the Au $4f_{7/2}$ signal at 84.0 eV.

Infrared spectral studies between 4000 and 200 cm⁻¹ were carried out on Na₂MoO₄ wafer disks made up with 4 mg of Na₂MoO₄ and 86 mg of KBr. The wafer of the finely ground powder was made by pressing up to 10 kbar in a hardened steel die. The spectra obtained were recorded in a Perkin-Elmer 684 infrared spectrophotometer. X-ray powder diffraction patterns were recorded from 0 to 90° (20) using a Hijaku diffractometer. A relatively large X-ray beam, 5 mm in diameter, permitted analysis of large quantities of powder, providing structural information on the main phases of each sample.

Results and Discussion

During this study, it was found that the noncatalyzed homogeneous thermal reaction in an empty reactor is relatively important at temperatures where the catalyst is active (>600 °C). Therefore, in the overall mechanism, both homogeneous and heterogeneous reaction steps are important. Recent literature evidences amply demonstrate this point.²²⁻²⁷

Figure 1 displays the variation in C_2H_4 and total C_2 (C_2H_4 + C_2H_6) product formation rate with change in temperature in a long reactor. The trends show improved C_2 selectivity with increasing temperature.^{6,11,18,19} A substantial gain in C_2 product formation was observed between 600 and 700 °C. Experiments, when carried out at higher temperatures,^{11,19} produce more methyl radicals which are favorable for the C_2 formation. For Na₂MoO₄, at temperatures above 690 °C the catalyst appeared to enter into a molten phase (687 °C). Diffusion of ions to the surface occurs more readily under such conditions. This is similar to that of LiCl/MgO catalyst, where the molten state of the catalyst intervenes in CH₄ dimerization.²

Figure 2 shows that, in a long reactor, the homogeneous reaction significantly contributes to the conversion of CH_4 to C_2H_6 and C_2H_4 (C_2 products). At 720 °C the reaction leading to C_2 products is purely homogeneous to the extent of $73 \pm 3\%$ and heterogeneously catalytic to the extent of $27 \pm 3\%$. Yates and Zlotin^{24,27} reported at 720 °C 26.8% CH₄ conversion in an empty reactor, and 39.2% in a reactor containing Li⁺/MgO, confirming this observation.

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Figure 1. Change in the amount of C₂ products as a function of reaction temperature, with a reaction mixture containing 8.5 mL/min of CH₄ and 7.5 mL/min of O₂, for an empty long reactor and a reactor loaded with 1 g of Na₂MoO₄.



Figure 2. Temperature effects on C_2H_4 and C_2H_6 product selectivities in a long reactor with and without 1 g of Na₂MoO₄ catalyst. Other conditions as stated in Figure 1.

The ratio of CH_4 to O_2 was found to be critical in the gas-phase conversion of methane. The highest selectivity toward C2 products

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was observed when 8.5 mL/min of CH₄ was used in conjunction with a flux of 7.5 mL/min of O₂ at 726 °C. Under these conditions both the C₂ selectivity and the CH₄ conversion with Na₂MoO₄ catalyst were generally high. A selectivity of 12% was achieved at 74% CH₄ conversion level, for Na₂MoO₄ (see Table I). The reaction was carried out in the region where the system has enough O₂ to attain the optimum performance.

For the homogeneous catalytic process in the absence of the catalyst, $\sim 80\%$ of O₂ in the feed stream gets consumed at 720 °C. When the reactor contains 1 g of catalyst, $\sim 90\%$ O₂ is consumed, confirming the increase in (heterogeneous) catalytic contribution.

Since the sampling point was after the cold trap, a considerable reduction in volume was noticed during the reaction. The degree of reduction in volume has been determined experimentally by measuring the outlet flows for each of the reaction conditions. Accordingly the values for conversion and selectivity have been normalized.

The contact time is defined as the volume of catalyst²⁸ divided by the flow rate of gases (CH₄ + O₂) adjusted to standard conditions. In Table I, where 1 g of catalyst was used each time with a gas flow of 8.5 mL/min of CH₄ and 7.5 mL/min of O₂, the contact time would be about 1.2 s (density of Na₂MoO₄ = 3.28 g/cm³). We will report residence and contact times separately, since residence time is only applicable to the free volume in the reactor.²⁶⁻²⁸ For the long reactor, residence time is approximately 93 s.

Figure 2 shows that C_2H_6 selectivity decreases with rise in temperature while C_2H_4 increases. This would suggest that some of the ethylene is produced from the oxidative dehydrogeneration of ethane. Both homogeneous and heterogeneous reactions extensively produce C_2 -products.

Table I presents the results obtained when a mixture of CH₄ (8.5 mL/min) and O₂ (7.5 mL/min) were continuously co-fed through the quartz reactor (long) loaded with 1 g of different catalysts at atmospheric pressure. Table I displays the results obtained at a temperature that appeared to be optimum for high ethane and ethylene selectivities of ca. 720-730 °C. The reaction under study also produced small amounts of HCHO and CH₃OH. These products, in most runs, comprised less than 3% of the total reaction products. Both were detected in gas and liquid phases. But the concentration of HCHO was particularly difficult to be quantified, because with temperature and time it polymerizes as well as decomposes. The product selectivities reported in Table I adds up to 94-98%, the remainder being HCHO and CH₃OH. CO is the most abundant product of the reaction with selectivities reaching up to 70%. This partial oxidation product formed in our reaction is valuable since it could be used to produce synthesis gas.⁶ The hydrogen product needs a few hours to attain steady-state values reported in Table I. This is probably due to the secondary reactions involving the dehydrogenation of HCHO and CH₁OH.

Additional experiments were carried out in a short reactor with and without the catalyst. Figure 3 displays the influence of temperature on C_2H_4 and C_2H_6 product formation. A contact time of 1.2 s for the catalyst and a residence time of 24 s for the free volume were attained. Consequently, at 760 °C in the presence of a catalyst, the homogeneous contribution to C_2H_4 formation was only 23% of the total C_2H_4 produced. This is reported in Figure 4. This is considerably lower than the 66% homogeneous contribution observed in the longer reactor, in the presence of the catalyst (Figures 1 and 2). The temperature onset for C_2H_6 generation is found to be 50 °C lower (in Figure 4) when Na_2MoO_4 was present. Comparing Figures 2 and 4, it is readily seen that the selectivities for C_2 products are significantly different as a function of temperature, for long and short reactors. This shows the importance of reactor dimensions in the study of oxidative dimerization of CH₄. Three different catalysts, namely, molybdates of Na, Mn, and Cu, have been used in the short



Figure 3. Amounts of C_2 products as a function of reaction temperature when a short reactor was used for the reaction, with and without 1 g of Na₂MoO₄ catalyst. Other conditions are similar to that of Figure 1.



Figure 4. Selectivity of products in an empty and loaded short reactor. Other details as in Figure 3.

reactors. Methane conversion and C_2^+ selectivities were 30-35% and 20%, respectively, at 760 °C. Compared to the results presented in Table I for experiments using long reactors, the C_2^+ selectivities were higher for short reactors. Owing to smaller contributions from homogeneous reactions, the methane conversion remained lower in the short tubes.

Figure 5 presents the C₂ yield $Y(C_2)$ and selectivity $X(C_2)$ as a function of time, when 8.5 mL of CH₄ and 7.5 mL of O₂ are continuously fed over 1 g of Na₂MoO₄ catalyst in a short reactor. As seen from Figure 5, deactivation of these materials with time did not take place. One of the problems of the Li⁺/MgO catalyst is their relative short life.^{2,29} The longest-lived catalyst for CH₄ dimerization up to now has been reported to be active over 120

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TABLE II: XPS Results Showing Surface Concentrations of Various Elements (in Atomic Percent) Present in Molybdates

| | 11 | la ₂ Mo | 04 | | | MnMoO ₄ | | | | MgMoO ₄ | | | |
|--------------------------------------|----------|----------------------------|-----------------|---|------------------|--------------------|--------------------------|---|--------------------------------------|---|-----------------------------|--|--|
| before reaction | | 710 °C (12 h) | | before reaction | 765 °C (12 h) | before reaction | | 710 °C (10 h) | | | | | |
| Na 1s | a 1s 9.3 | | 8.5 | Mn 2p _{3/2} | | 3.3 | 2.1 | Na 1s | | 0.4 | | | |
| F 1s 2.5 | | 6.2 | 6.2 4.6 O la | | 47.3 | 24.0 | F 1s 1.9 1. | | | | | | |
| O Is 32.9 | | 34.0 | | | 42.5 | 54.9 A7 7 | | 31.0 49 1 | 31.9 47.1 | | | | |
| C IS 45.0 Mo 3d 8.8 | | 88 | Mo 3d | | 10.6 | 71 | Mo 3d | 57 | 5.9 | | | | |
| Si 2p | 0.9 | | 4.0 Si 2p | | 2.4 | 8.7 | Si 2p | 5.9 | 10.7 | | | | |
| • | | | | | | | | | Mg 2s | 7.4 | 2.7 | | |
| | | | | CoMoO ₄ (before reaction) | | | (7 | CoMoO ₄ (after reaction, 735 °C (29 h)) | | CoMoO ₄ (after reaction, 740 °C (3 h)) | | | |
| Na 1s | | | | | | | | 0.8 | · · · · · | 1.9 | | | |
| Co 2p | | | 9.1 | | | | 10.4 5.8 | | | | | | |
| F 1s O 1s Mo 3p _{3/2} | | 1.9 47.0 0.7 41.2 | | | | 3.8 4.9 | | | | | | | |
| | | | | | 36.7 | | | 39.1 | | | | | |
| | | | | | | 4.5 | 4.8 | 4.8 | | | | | |
| | Si 2s | | | | 71.4 | | | 2.4 | | 3.6 | | | |
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| | | L | | <u>.</u> | I | | Figu C ₂ H | re 6. Arrhenius 6 and C ₂ H ₄ . Th | relationship for the rates deterr | or oxidative meth nined after 1 h r | ane converse eaction are | | |

Figure 5. C_2 yield and selectivity as a function of reaction time at 790 °C. Other details as in Figure 3.

h.³⁰ During our experiments, both Na_2MoO_4 and $MnMoO_4$ catalysts remained active throughout the run time (200 and 280 h).¹⁷ The C content was $\sim 0.08\%$ for both catalysts before reaction and 0.03% after reaction. These data have been obtained via elemental analysis. Carbonates and coke have been reported to be formed³¹ when Na₂MoO₄ was used as a methanol dehydrogenation catalyst leading to its deactivation. This did not occur in our case since the system was markedly different from that of methanol dehydrogenation reaction. $MnMoO_4$ has also been used as a catalyst in the present study. This substance was previously reported as a selective oxidation catalyst for the conversion of 1-butene to maleic anhydride, adsorbing oxygen from the gas phase and using it to regenerate the active surface site depleted during the oxidation process.32

Our results (obtained using both short and long reactors) reveal only slight variations for the overall product selectivity, conversion, and yield irrespective of the nature of molybdates used: for example, alkali or alkaline earth (Na, Li, K, Mg, and Ba) or transition metal containing (Mn, Co, Fe, Cu, Zn, and Ni). It is clear that the redox nature of the cation involved in each case does not play a significant role in the observed catalysis. The structure



of molybdate ion seems to be responsible for the favorable catalytic effect observed. Molybdates possess intermediate metal oxygen bond strengths⁶ which play positive role in the catalysis. The M=O bonds were identified as the sites of selective oxidation. These M-O orbitals³³ influence hydrogen atom (H[•]) abstraction and the formation of surface bound CH₃ radicals.⁶ This latter radical has been substantiated by ESR studies.³⁴ Subsequently Mo^{6+} is reduced to Mo^{5+} . A light grey color appears on the molybdate catalyst (Na₂MoO₄) during reaction. This color disappears on cooling, after the reaction. The M-O⁻ color center on molybdate was reported to be responsible for CH_4 activation via hydrogen atom abstraction to form methyl radicals.¹¹,¹⁹ Our experiments have also confirmed the inability of molybdates to evolve C_2 products in the absence of gas-phase oxygen. This suggests an active surface oxygen species generated only in the presence of O₂, affecting methane coupling. Further studies using Na polytungstates as catalysts are shown in the lower column in Table I. It shows that other heteropolyanions of this type are also active in CH₄ activation. In summary, Table I shows that reductive or oxidative pathways originating from molybdates with multivalent cations can be excluded in CH_4 activation.

Figure 6 presents the activation energy (E_a) observed for C₂H₆ and C₂H₄ formation at temperatures between 848 (575 °C) and 885 K (612 °C). An Arrhenius plot for the formation of these gases is plotted at 1 h reaction time. We found E_a values of 80

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Figure 7. XPS spectra of the Si 2p region for Na₂MoO₄ fresh and reacted (12 h at 710 °C) sample. The spectra reported have not been corrected for electrostatic charging of the samples.

kcal/mol for C_2H_4 and 64 kcal/mol for C_2H_6 production. At conversion below 10%, as it was in our case, it has been reported that E_a for methane conversion to ethane is in the range of 57–60 kcal/mol,³⁵⁻³⁷ which is close to our value. This value of E_a has been attributed to the following reaction

$$CH_4 + O_2 \rightarrow CH_3 + HO_2$$
(1)

Essentially, this is the E_a for C_2H_6 formation, because the coupling of CH₃ does not require any additional activation. The activation energy for the formation of C_2H_4 from C_2H_6 has been reported to be in the order of $\sim 10 \text{ kcal/mol.}^{38}$

IR spectra have been recorded for both fresh and spent Na₂- MoO_4 catalyst samples. The IR bands for molybdate have been observed at 1700 and 800 cm^{-1,31,39,40} HCHO formation was verified by the appearance of bands at 1700 and 850 cm⁻¹ and in the 1100-cm⁻¹ region. Carbonate and bicarbonate show bands around 1580 and 1320 cm^{-1,31,40} Neither of these bands was observed in the spent catalyst.

X-ray photoelectron (XPS) measurements were carried out for the surface concentrations of various elements in Na₂MoO₄, MnMoO₄, MgMoO₄, and CoMoO₄, before and after the oxidative coupling. The results of these experimental observations as well as the details of these measurements are reported in Table II. The spectra has been referenced as follows: from the experimental measurements, subtraction of the X-ray satellite peaks and polynominal fit (second order) was carried out according to ref 41. The quantitative determination of the elements as shown in Table II were carried out according to literature.⁴²⁻⁴⁵ The determination of the electrostatic charging of the catalyst samples was done by internal referencing to the contaminating aliphatic surface carbon at 284.6 eV, by cross checking the peak distances between C 1s, O 1s, Mo $3d_{5/2}$, and Mo $3p_{3/2}$ signals for the fresh and the reacted specimens, relative to pure standard samples of MoO₃, and by evaporating traces of gold onto the catalyst specimens and

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Figure 8. XPS spectra of the Mo 3d doublet region for (1) CoMoO₄ 710 Č, 3 h; (2) CoMoO₄ 735 °C, 24 h; (3) Na₂MoO₄ 710 °C, 12 h; (4) Mn₂MoO₄ reacted at 765 °C, 12 h.

measuring the position of the Au signals.

A quantitative evaluation of the surface concentrations for the diverse elements in Table II reveal that, for Na_2MoO_4 , Si gets enriched by a factor >4 on the catalyst after the reaction (CH_4) + O_2 for 12 h at 710 °C) as compared to that of a fresh catalyst. This catalyst has been pretreated at 300 °C in a mixture of gases CH_4 (56%) and O_2 (44%). The percentage amounts of Na, O, and Mo on the catalyst surface have not changed to any considerable extent due to catalysis. This is readily seen from the data presented in Table II. The uncorrected 2p signals of Si are shown in Figure 7. The surface enrichment of Si on the catalyst observed after the reaction is due to the contamination occurring from the walls of the quartz reactor. Table II shows the corrected values. With the corrected values for Si 2p at the surface, we observe the same trend for $MnMoO_4$ as seen for Na_2MoO_4 . The surface concentration of C before and after the reaction were nearly the same. These catalysts are long-lived and, since they do not change permanently in color after reaction, no coking has taken place. Since the elemental analysis of the catalyst showed only 0.08% C before use and 0.02% after reaction, it is concluded from XPS data that a major portion of the C is present in the surface, and this seems to have mostly derived out of absorption

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from the atmosphere. XPS results confirm the findings reported in Figure 3, that there is no C enrichment in the catalyst due to the reaction.

Figure 8 presents the XPS peaks in the Mo 3d region for (1) CoMoO₄ reacted 740 °C, 3h; (2) reacted 735 °C, 24 h; (3) Na_2MoO_4 reacted 710 °C, 12 h; (4) MnMoO₄ reacted 765 °C, 12 h. The peaks for Na_2MoO_4 and $MnMoO_4$ are well defined and show a doublet Mo $3d_{5/2}$. These narrow well-defined peaks are indicative of one chemical state for the Mo. The $CoMoO_4$ spectra in Figure 8 show broader peaks which could be ascribed to a superposition of two different chemical species, e.g., CoMoO₄ and MoO_3 . The energy values used to reference Figures 7 and 8 are found in refs 20, 21 and 43-45. Partly, the different binding energies and structures shown by the CoMoO₄ spectra are due to the fact that the O 1s signal in $CoMoO_4$ has a different binding energy (530.9 eV) than the O 1s state in MoO_3 (531.3 eV).^{20,21} It is seen from Table II that Mo in CoMoO₄ shows a marked surface enrichment during the reaction. In effect, this value increases from 0.7% in a fresh catalyst to 4.5 and 4.8% in $CoMoO_4$ reacted under the conditions of Table II. This effect was not present in the case of Na₂MoO₄ and MgMoO₄ and less pronounced in the case of $MnMoO_4$ (see Table II).

X-ray diffraction pattern for Na₂MoO₄ of the nonreacted material shows peaks characteristic of Na₂MoO₄ anhydrous material.⁴⁶ Also up to 10% oxide-hydrate was found in the unreacted sample and 1-3% of the same oxide-hydrate with 2%additional phases were detected in the reacted material under the conditions of experiments presented in Table II. Therefore, the

(46) Powder Diffraction File; International Center for Diffraction Data: Swarthmore, PA, 1978.

oxidative coupling does not introduce additional phases in Na₂- MoO_4 . This is a further proof that the catalyst is not affected during long-term catalysis.

Conclusion

This report helps in understanding the nature of involvement of molybdate catalysts in the oxidative coupling of methane. The effect of several operating variables was studied to derive an optimum set of conditions suitable to achieve reasonably high yields of C_2H_4 and C_2H_6 . C_2H_4 generation is favored at higher temperatures, indicating that C_2H_4 is produced additionally by a secondary reaction of C_2H_6 . CO and CO₂ are the main oxidation products. The dimensions of the reactor were found to influence significantly the product distribution. The CO and H₂ produced could be used for "synthesis gas" and is therefore useful. The separation of CO and H_2 from other products is not a serious problem, as technologies are available for its economic recovery.^{11,12}

Further studies involving molybdates are warranted in order to understand the mechanism taking place on the catalyst surface and to precisely characterize the active sites. In this way higher selectivities and C_2 yields could be achieved than those observed in this study. Such studies are currently in progress in our laboratory.

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Registry No. CH₄, 74-82-8; C₂H₄, 74-85-1; C₂H₆, 74-84-0; O₂, 7782-44-7; Na2MoO4, 7631-95-0; Li2MoO4, 13568-40-6; K2MoO4, 13446-49-6; MgMoO₄, 13767-03-8; BaMoO₄, 7787-37-3; MnMoO₄, 14013-15-1; CoMoO₄, 13762-14-6; Fe₂(MoO₄)₃, 13769-81-8; CuMoO₄, 13767-34-5; ZnMoO₄, 13767-32-3; NiMoO₄, 14177-55-0; CO, 630-08-0; H₂, 1333-74-0.

CO-Induced Changes in Structure of Supported Rhenium

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The interaction of CO with highly reduced Re/Al₂O₃ was investigated at 100-673 K by means of infrared spectroscopy. The adsorption of CO at 100 K produced absorption bands characteristic of linearly and bridge bonded CO. At 200-300 K well-observable spectral changes were experienced, their extent depending on the temperature and adsorption time. The absorption bands formed suggest the occurrence of CO-induced structural changes in the Re crystallites and the formation of Re carbonyls with higher CO/Re ratio, most probably Re2(CO)10. Further spectral changes occurred at 373-473 K, indicating the transformation of the more complex Re carbonyl into Re tricarbonyl. This transformation was promoted by H_2O . The formation of Re tricarbonyl from Re_x-CO species was found to be very limited.

1. Introduction

Study of the properties of supported rhenium is justified for at least two reasons: rhenium-containing supported catalysts are currently used in the reforming of petroleum feedstocks,¹ and Re seems to exhibit oxygen storage properties in automotive three-way catalysts.² The primary aim of this work is to explore whether the adsorption of CO on supported Re induces any morphological changes detectable by means of infrared (IR) spectroscopy.

Whereas the characterization of supported Re catalyst has been the subject of several detailed studies,³⁻¹¹ little information is to be found in the literature with regard to the IR spectrum of CO adsorbed on supported Re. Guerra and Schulman¹² in their classical paper reported the IR spectrum of CO adsorbed on 9% Re/SiO_2 (reduction temperature, R_T , of 648 K). They obtained a very broad absorption, consisting of several bands at 1950,

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