

Partial Oxidation of Methane to Formaldehyde by Means of Molecular Oxygen

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The partial oxidation of methane to formaldehyde by molecular oxygen has been studied, with molybdenum(VI) oxide-silica and related catalysts. Although HCHO selectivities in excess of 85% could be obtained at very low conversions, sodium contamination as low as 300 ppm Na was found to lower both activity and selectivity to formaldehyde. On Na-free MoO₃-SiO₂ catalysts, methane was shown to be oxidized, in parallel, to HCHO and CO₂ via a common activation step. CO was produced via HCHO, and became the dominant oxidation product at high conversions. Methanol was detected in trace quantities, and is presumed to be an intermediate in formaldehyde formation. Reagent MoO₃, and MoO₃ in excess of ~0.1 monolayers on silica did not catalyze the oxidation of methane significantly. Molybdenum(VI) oxide appears to promote the catalytic activity already present on the bare silica. © 1988 Academic Press, Inc.

INTRODUCTION

Methane is a highly abundant, low-cost carbon source. It is the principal component of natural gas and a by-product of oil production and refinery operations. Currently, methane is converted to formaldehyde by being steam-reformed over a nickel catalyst to a mixture of CO and H₂ (syngas) (1). This can then be converted to methanol over a copper-zinc catalyst (2). Formaldehyde is subsequently produced by oxidizing methanol with air, either over silver or "iron molybdate" (3).

The overall reactions of oxygen with methane to produce methanol or formaldehyde are exothermic, although the initial steam-reforming step is endothermic. Clearly a direct oxidative route from methane to these chemicals would be highly attractive. The thermodynamics are such that methanol and formaldehyde are present only in trace amounts when a mixture of methane and oxygen is heated above 700 K and allowed to come to equilibrium (Fig. 1). Therefore a catalyst that facilitates the formation of formaldehyde without catalyzing its further oxidation to carbon oxides is required.

There are numerous patents covering

partial air-oxidation of methane or natural gas, and several of these employ molybdenum oxide-containing catalysts (4-6). Very little fundamental work has been reported in this area, however (7). On the other hand, several papers concerning the MoO₃-SiO₂ catalyzed oxidation of methane using nitrous oxide have appeared in recent years. This reaction produces formaldehyde and methanol with selectivities as high as 80 and 20%, respectively. However, N₂O is too expensive to be used industrially for this purpose.

This paper presents results showing that MoO₃-SiO₂ is a highly selective catalyst for the partial oxidation of methane to formaldehyde with dioxygen. It also shows that sodium is a poison of this system, reducing both activity and selectivity to formaldehyde. Although formaldehyde is further oxidized to carbon monoxide with this catalyst, carbon dioxide appears to be formed directly from methane.

EXPERIMENTAL

Catalyst Preparation

The MoO₃-SiO₂ catalysts were generally prepared from ammonium paramolybdate and silica. The silica sources were either

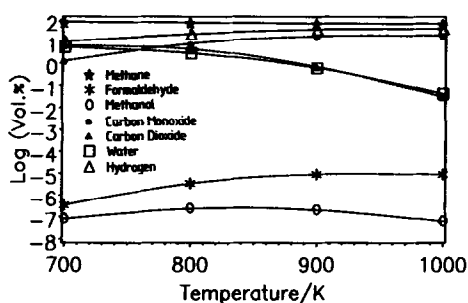


Fig. 1. Equilibrium concentrations obtained after the reaction of a gas mixture containing 90 vol% methane and 10 vol% oxygen at 1 atm.

Cabosil M5 (a fumed silica manufactured by Cabot Corporation) or "ID" silica gel (Davison Chemical Division of W.R. Grace & Co.). The latter was used either "as received" or washed in a stream of dilute sulfuric acid ($\text{pH} = 3$) at 373 K in order to reduce the sodium level. When it was washed for several days the sodium level in the silica was reduced to 10 ppm, and this material is referred to as "acid-washed silica gel" (AWSG). Silica gel with an intermediate degree of sodium removal (300 ppm) was also prepared, and is referred to as "partially acid-washed silica gel" (PAWSG). MoO_3 -silica gel catalysts were prepared by slurring the gel with ammonium paramolybdate solution and evaporating the mixture to dryness. MoO_3 -Cabosil catalysts were prepared by incipient wetness impregnation.

A catalyst with a deliberately high concentration of sodium was prepared by washing Cabosil with very dilute sodium hydroxide solution, drying it, and then calcining it at 673 K prior to molybdenum impregnation as described above.

A catalyst was prepared anaerobically from AWSG and molybdenum pentachloride. The silica was dehydrated in a vacuum oven overnight at 483 K and then, without being exposed to air, slurred with cyclohexane in the flask of a Soxhlet extraction apparatus. MoCl_5 had previously been placed in the thimble of the extractor. The extraction process was then carried out for ~15 h in a helium atmosphere. The result-

ing impregnated silica was washed with cyclohexane, dried, washed with water, and then dried again and calcined at 873 K.

A physically mixed MoO_3 - SiO_2 catalyst was prepared from reagent MoO_3 and Cabosil by ball-milling them together overnight.

A MoO_3 - Al_2O_3 catalyst was prepared by impregnation of pseudo-Boehmite (Davison Chemical Division of W.R. Grace & Co.) with ammonium paramolybdate dissolved in very dilute hydrogen peroxide solution. The resulting paste was extruded, dried overnight at 383 K, and calcined for 3 h at 483 K.

Prior to use, the catalysts made from Cabosil were compressed and crushed, and all catalysts were screened to a particle size of 0.5–0.7 mm. Catalyst properties are summarized in Table 1.

Apparatus and Methods

A 0.2-g sample of catalyst (screened to 0.5–0.7-mm particle size) was loaded into a reactor consisting of a quartz frit within a 9.5-mm-diameter quartz tube (Fig. 2). The

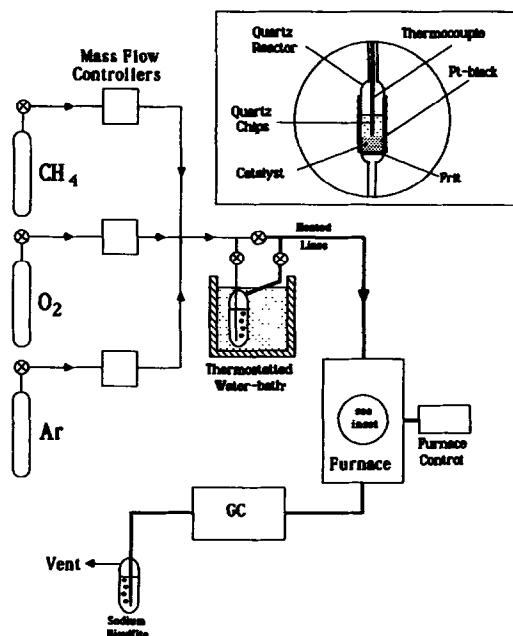


FIG. 2. Apparatus for methane partial oxidation studies.

TABLE I
Properties of Catalysts Used in the Present Study

Description	Wt% Mo	BET surface area (m ² g ⁻¹)	ppm Na
MoO ₃ -silica gel (as received)	9.7	282	520
MoO ₃ -PAWSG	9.8	280 ^a	300
MoO ₃ -AWSG	1.8	277	10
MoO ₃ -AWSG (anaerobic)	0.5	270	10
MoO ₃ -Cabosil (impregnated)	1.8	195	<4
MoO ₃ -Cabosil (impregnated)	9.8	210	<4
MoO ₃ -Cabosil (physical mixture)	2.0	205 ^a	<4
MoO ₃ -Cabosil (Na-treated)	9.4	180	3600
MoO ₃ reagent	67	4	<4 ^a
Cabosil	0	212	<4
AWSG	0	277	10
Silica gel (as received)	0	272	520
MoO ₃ -Al ₂ O ₃	11.8	180	290

^a Estimated.

catalyst was covered with an equal volume of quartz chips, screened to the same size, which formed a preheating zone. A stainless-steel-clad type-K thermocouple was positioned with its tip at the junction of the two layers. The reactor was placed on the axis of a radiant heating chamber (Research, Inc.) and painted with platinum black so as to maximize heating efficiency and eliminate radiation-induced artifacts.

Methane oxidation experiments were carried out by passing a mixture of methane and oxygen at 1 atm over the heated catalyst. The reactor effluent flowed through heat-traced lines to two GC sample valves in series; one was connected to a Poropak T column for formaldehyde, methanol, and water analysis; the other was connected to a Carbosphere column for the analysis of methane, oxygen, hydrogen, carbon monoxide, and carbon dioxide. Argon was used as a carrier gas in both columns. A thermal conductivity detector (TCD) was connected to the Carbosphere column. The Poropak T column was either connected to a TCD, a photoionization detector (11.7 eV), or a flame ionization detector preceded by a methanator. The presence of formaldehyde in the effluent was confirmed and the detectors were calibrated by means of a chromatropic acid assay (10) of the

sodium bisulfite solution in the final bubbler.

Formaldehyde and methanol oxidation experiments were carried out by passing an argon-oxygen (10% O₂) mixture through a thermostated bubbler containing paraformaldehyde or methanol, respectively. In this way, steady-state gas-phase concentrations of a few vol% could be fed readily to the reactor.

Molybdenum and sodium analyses of the catalysts were carried out by atomic absorption spectroscopy using a mixture of perchloric and hydrofluoric acids for the initial catalyst digestion. X-ray diffraction was carried out with a Phillips powder diffractometer and copper K α radiation.

RESULTS AND DISCUSSION

Molybdena on Sodium-Free Silica (1.8 wt% Mo) in Steady State

A 9:1 methane:oxygen mixture was passed at 1 atm over a MoO₃-AWSG catalyst at gas hourly space velocities ranging from 2500 to 10000 h⁻¹ (at NTP). The temperature was varied from 848 to 923 K and the effluent was analyzed by gas chromatography. The methane was oxidized principally to formaldehyde, carbon monoxide, carbon dioxide, and water. Methanol

and hydrogen were detected in trace quantities. The selectivities (based on converted methane) to HCHO, CO, and CO₂ are displayed as a function of methane conversion in Figs. 3a–3c. Very similar behavior was observed with the MoO₃–Cabosil and MoO₃–AWSG catalysts of the same loading.

At the zero conversion limit, the selectivities to formaldehyde, carbon monoxide, and carbon dioxide were ~90, 0, and ~10%, respectively. This implies that formaldehyde and carbon dioxide are primary products of methane oxidation, while carbon monoxide is a secondary product, formed from the further oxidation of formaldehyde. A surprising feature of these data was that they apparently lay on a single curve when plotted as shown in Figs. 3a–3c. HCHO selectivity appeared to depend solely on conversion, being independent of the temperature–space velocity combination that was used to achieve that conversion. As will be shown later, HCHO selectivity is, in fact, slightly dependent on

temperature. However, over the temperature range studied, this effect was sufficiently small that a simple, visual inspection of the HCHO selectivity–conversion “curve” was a very useful monitor of catalyst performance.

The oxygen concentration in the reaction mixture was varied from 2.5 to 10%, and no significant difference was observed in the rate of reaction. It appears, therefore, that the partial oxidation of methane over MoO₃–SiO₂ is zero-order in oxygen under the conditions studied, as is the case with several other hydrocarbon partial oxidation processes (11, 12). The kinetic order in methane was investigated by dilution of the system with helium while it was maintained at constant pressure. At a reactants : helium dilution factor of 1 : 1, the methane conversion had changed by less than 10%, implying that the reaction approximates first-order in methane.

To determine kinetic parameters and confirm the reaction pathways discussed above, formaldehyde vapor was passed

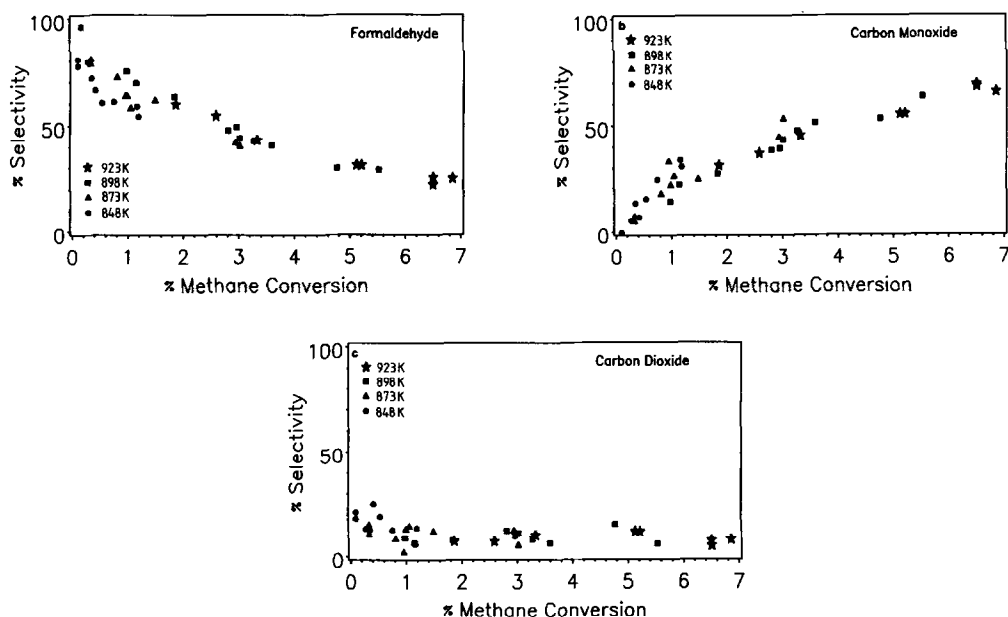


FIG. 3. Selectivity vs methane conversion curves for (a) formaldehyde, (b) carbon monoxide, and (c) carbon dioxide. Space velocity range: 2500–10000 h⁻¹ (GHSV, NTP), reactants: 9 : 1, CH₄ : O₂, 1 atm, MoO₃–AWSG catalyst (1.8 wt% Mo).

over the $\text{MoO}_3\text{-SiO}_2$ at 1.2 vol% in an argon stream containing 10 vol% oxygen. The GHSV was maintained at 5000 h^{-1} (NTP), and the temperature varied between 648 and 923 K. Figure 4 shows the composition of the effluent gas. Carbon monoxide is the principal product of HCHO oxidation under these conditions, although some carbon dioxide is formed at higher temperatures.

Since methanol was detected in trace amounts during CH_4 oxidation and was suspected of being an intermediate in formaldehyde formation, its behavior when fed to the catalyst in the absence of methane was investigated. Methanol oxidation over $\text{MoO}_3\text{-SiO}_2$ has been studied extensively at temperatures below 673 K (13), since this is the region where industrial formaldehyde reactors operate. However, few data are available for methanol oxidation at 848 K and above. Figure 5 shows the composition of the effluent gases during methanol oxidation. Formaldehyde is observed at temperatures as low as 520 K, with the onset of carbon monoxide formation occurring some 100 K higher. Carbon dioxide, as in the case of formaldehyde oxidation, is only a minor oxidation product. Methanol was found to produce dimethyl ether (DME) under these conditions, although DME was not detected during methane oxidation. This does not, however, rule out methanol as an intermediate; since DME formation

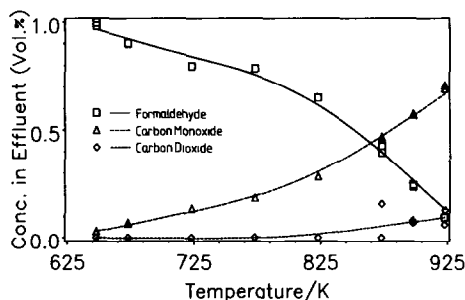


FIG. 4. Product gas distribution during oxidation of 1 vol% HCHO entrained in a 9:1 argon: oxygen mixture, 5000 h^{-1} (GHSV,NTP), 1 atm, $\text{MoO}_3\text{-AWSG}$ catalyst (1.8 wt% Mo).

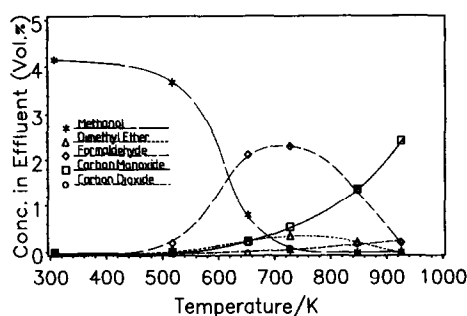
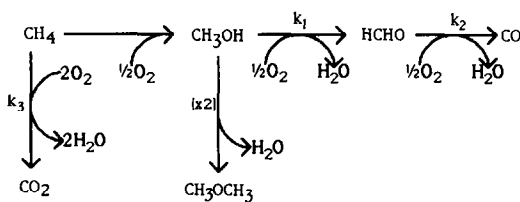


FIG. 5. Product gas distribution during oxidation of 4.2 vol% CH_3OH entrained in a 9:1 argon: oxygen mixture, 5000 h^{-1} (GHSV,NTP), 1 atm, $\text{MoO}_3\text{-AWSG}$ catalyst (1.8 wt% Mo).

requires the interaction of two methanol molecules, the disparity can be explained by the low steady-state methanol concentrations under CH_4 oxidation conditions.

Kinetic parameters were determined from the HCHO and CH_4 oxidation data by first-order rate equations under the assumption that formaldehyde and carbon dioxide were primary products. The results are summarized in Fig. 6. A kinetic model (described in detail elsewhere (14) was constructed from these parameters and the predicted selectivity-conversion curves are shown (compared with the actual data) in Figs. 7a-7c. Predictions are in good agreement with the experimental data, the



Summary of Rate Constants and Activation Energies

Index, i	k_i (at 923 K)	E_i (kJ mol $^{-1}$)
1	695	189
2	34300	134
3	86	189

FIG. 6. Kinetic pathways and parameters for methanol oxidation by molecular oxygen over $\text{MoO}_3\text{-AWSG}$ and $\text{MoO}_3\text{-Cabosil}$ catalysts (1.8 wt% Mo).

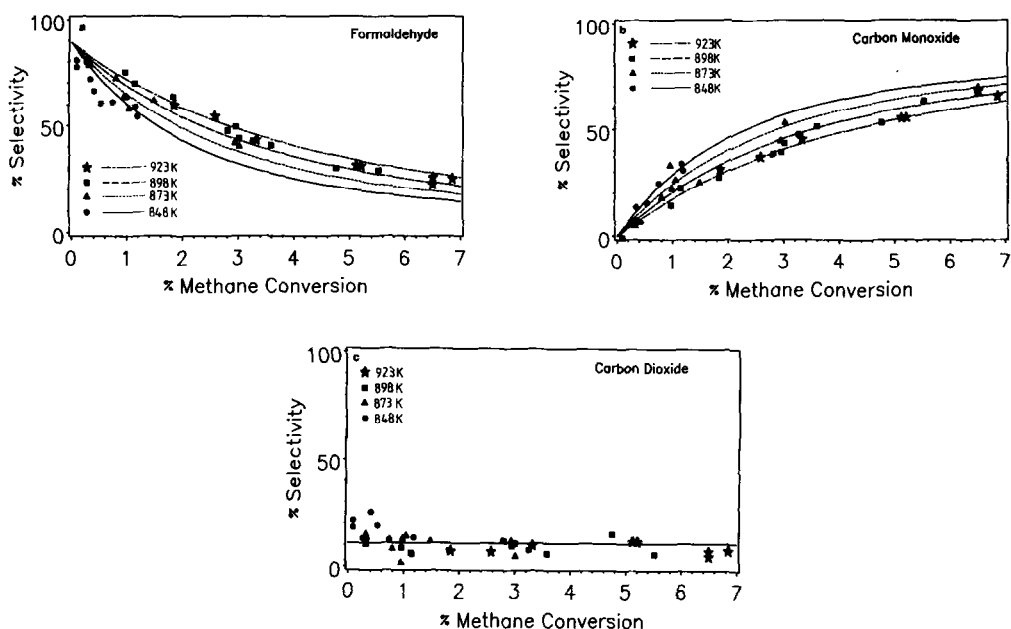


FIG. 7. Comparison of model (lines) and experimental (points) data in selectivity vs methane conversion curves for (a) formaldehyde, (b) carbon monoxide, and (c) carbon dioxide. Space velocity range: 2500–10000 h^{-1} (GHSV,NTP), reactants: 9: 1, CH_4 : O_2 , 1 atm, MoO_3 -AWSG catalyst (1.8 wt% Mo).

maximum discrepancies occurring at low conversions because of experimental difficulties in measuring product concentrations. It is notable that the activation energies for k_1 and k_3 appear to be identical. This suggests that CO_2 and HCHO formation are alternative pathways following a common rate-determining methane activation step. A small temperature effect can be seen in the HCHO and CO selectivity vs conversion curves (Figs. 7a, 7b). This follows from the activation energy difference between k_1 and k_2 . However, further experiments showed that HCHO selectivity increased less markedly at temperatures higher than 923 K, presumably because of the onset of gas-phase HCHO oxidation and the breakdown of the model as it is shown in Fig. 6.

Influence of Catalyst Preparation Method

A sample of MoO_3 -Cabosil (9.8 wt% Mo) was tested in our reactor at 873 K and 9766 h^{-1} (GHSV,NTP) using 19: 1 CH_4 : O_2 at 1

atm for a period of 75 h. After the test, a considerable amount of MoO_3 was found to have sublimed from the catalyst, forming needle-shaped crystals below the frit (i.e., in a cooler zone). To determine the extent of molybdena loss, the reactor was removed from the furnace and filled with warm agarose. The reactor was then refrigerated, fractured with a hammer, and the molybdena-containing agarose was sectioned and analyzed by atomic absorption spectroscopy. A large amount of molybdena had diffused into the quartz preheater section, but only 25% of the original molybdena was found to remain above the frit. The remainder had sublimed into the cooler zones below. However, during the 75-h experiment, the activity and HCHO selectivity had not changed noticeably, suggesting that the sublimed MoO_3 had not contributed to the catalyst's activity.

When a MoO_3 -Cabosil catalyst containing 1.8 wt% Mo was subjected to more severe conditions (898 K, 4883 h^{-1}

GHSV, NTP for 144 h), 87% of the molybdena remained on the catalyst at the end of the experiment. The activity and selectivity were again found to remain fairly constant over the duration of the test. It seems, therefore, that ~ 1.6 wt% Mo on Cabosil forms a tightly bound active layer, less volatile than bulk MoO_3 . X-ray powder diffraction patterns of different loadings of MoO_3 on Cabosil are shown in Fig. 8. The broad feature corresponds to "amorphous" silica, and the sharp peaks, visible at 5.16 wt% Mo and above, correspond to crystallites of MoO_3 that are ~ 50 Å or more in diameter. Since a monolayer of MoO_3 on Cabosil corresponds to ~ 19 wt% Mo, it appears that the molybdena is already forming 50-Å crystallites at coverages as low as $\sim 1/4$ monolayer, and presumably it starts forming three-dimensional structures at much lower coverages. This is consistent with the work of Jeziorowski *et al.* (15); using Raman spectroscopy, they were able to detect bulk MoO_3 in a MoO_3 - SiO_2 system of similar surface area at ~ 4.5 wt% Mo but not at 1.9 wt% Mo. This behavior is markedly different from that of the well-studied MoO_3 - Al_2O_3 system, where MoO_3 forms a monolayer before the onset of crystallite formation (16). It seems likely that the transition to three-dimensional structures in MoO_3 - SiO_2 corresponds to

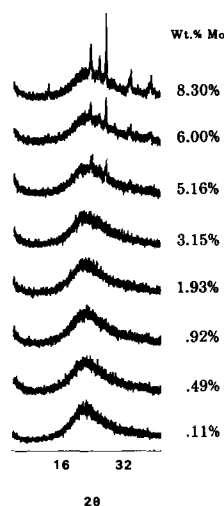


FIG. 8. Powder X-ray diffraction patterns for MoO_3 -Cabosil catalysts of different Mo loadings.

the change in MoO_3 volatility at ~ 1.6 wt% Mo (~ 0.1 monolayers). At this coverage, all sites where MoO_3 can bond strongly to the SiO_2 surface have presumably been saturated, and higher loadings form loosely bound crystallites, which may even block active sites, lowering the overall activity of the catalyst. This latter effect can be seen in the MoO_3 -Cabosil system (Table 2), where the 9.8 wt% Mo catalyst has less than half the CH_4 conversion activity of the 1.8 wt% Mo version.

Since the loss of bulk MoO_3 from the

TABLE 2

Catalyst Behavior at 923 K, 5000 h^{-1} (GHSV, NTP), 1 atm, 9 : 1, $\text{CH}_4 : \text{O}_2$

Catalyst	CH_4 (% conversion)	Selectivity (%)			Yield (%) HCHO
		HCHO	CO	CO_2	
MoO_3 -AWSG	6.9	25	65	9	1.72
MoO_3 -AWSG (anaerobic)	0.86	56	38	6	0.47
MoO_3 -Cabosil (impreg. 1.8% Mo)	5.3	32	56	12	1.70
MoO_3 -Cabosil (impreg. 9.8% Mo)	2.0	43	45	12	0.86
MoO_3 -Cabosil (physical mixture)	1.0	71	28	1	0.71
MoO_3 reagent	0.05	76	23	1	0.04
Cabosil	0.7	46	20	34	0.32
AWSG	1.2	50	42	8	0.6
MoO_3 - Al_2O_3	3.5	0	80	20	0

MoO₃-SiO₂ catalyst did not appear to affect the catalyst's performance, it may be deduced that crystalline MoO₃ is either inactive or much less active than MoO₃-SiO₂. Indeed, the methane conversion obtained over a sample of reagent MoO₃ (BET surface area = 4 m² g⁻¹) at 923 K and 5000 h⁻¹ (GHSV, NTP) was ~0.05%, compared to a value for MoO₃-Cabosil (1.8 wt% Mo, BET surface area = 195 m² g⁻¹, MoO₃ coverage ~0.1 monolayers) of ~6% under similar conditions. Normalized for MoO₃ surface area, reagent MoO₃ is about 25 times less active than MoO₃-Cabosil.

A most surprising observation was that silica itself is an active catalyst for methane partial oxidation to formaldehyde. Several forms of silica were tested, including Cabosil and silica gel, and all were found to catalyze the reaction. Figure 9 shows a HCHO selectivity-CH₄ conversion curve obtained with an AWSG catalyst. Although it displays the same general HCHO selectivity vs CH₄ conversion curve shape as seen (Fig. 3) for the MoO₃-AWSG catalyst, the conversion is lower by nearly a factor of six, and selectivity to HCHO drops somewhat more rapidly with increasing conversion. It seems, therefore, that the characteristic selectivity behavior is a property imparted by the silica, the activity being dramatically increased by the addition of ~0.1 monolayers of MoO₃, which itself is not an active catalyst for the reaction.

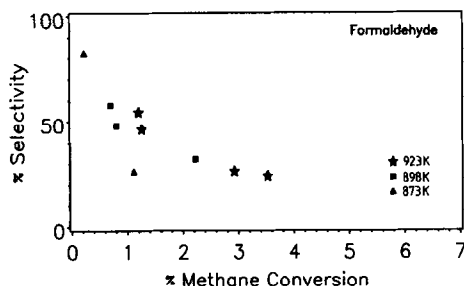


Fig. 9. HCHO selectivity vs methane conversion curve for AWSG. Space velocity range: 1000-5000 h⁻¹ (GHSV, NTP), reactants: 9: 1, CH₄: O₂, 1 atm.

The method by which MoO₃ was deposited onto the silica appeared to be unimportant. Aqueous impregnation of the silica by ammonium paramolybdate, anaerobic Soxhlet extraction of MoCl₅ with cyclohexane into silica, and physical mixing of silica with MoO₃ all produced catalysts that behaved similarly once they had been calcined in air at 873 K. The high vapor pressure of bulk MoO₃ at this temperature (~10 Torr) presumably leads to facile re-dispersion of molybdena onto the active silica sites.

No detectable formaldehyde was produced when molybdena-alumina was used as a catalyst, although CH₄ was readily oxidized to CO and CO₂ (see Table 2). Subsequent dual-bed experiments, with a bed of pure alumina following a bed of molybdena-silica in the reactor also produced carbon oxides as the sole methane oxidation products, suggesting that the formaldehyde produced by the MoO₃-SiO₂ bed was subsequently oxidized by the alumina under these conditions.

Effects of Sodium on Catalyst Behavior

Molybdena supported on "as received" commercially available silica gel was found to display lower activity and selectivity to formaldehyde than the corresponding MoO₃-Cabosil catalysts. Since silica gel is commercially produced by the acidification of sodium silicate, it often contains residual sodium concentrations of 500 ppm or higher. By acid-washing of the silica gel, the sodium concentration could be lowered below 10 ppm. Several MoO₃-SiO₂ gel catalysts with different sodium levels were tested under a range of conditions for HCHO selectivity during CH₄ oxidation. The results are summarized in Fig. 10 and Table 3 and compared with data obtained with an MoO₃-Cabosil catalyst, where the Cabosil had been deliberately doped to 3600 ppm with sodium. At any given conversion, the presence of sodium appears to suppress HCHO selectivity, and under a

TABLE 3

Catalyst	[Na] (ppm)	CH ₄ (% conversion)	Selectivity (%)			Yield (%) HCHO
			HCHO	CO	CO ₂	
			MoO ₃ -Silica gel (as received)	520	2.2	
MoO ₃ -AWSG	10	6.9	25	65	9	1.72
MoO ₃ -PAWSG	300	2.3	35	50	15	0.81
MoO ₃ -Cabosil (Na-treated)	3600	1.9	13	35	52	0.25
AWSG	10	1.2	50	42	8	0.6
Silica gel (as received)	520	0.85	69	25	6	0.59

given set of conditions, sodium reduces HCHO selectivity, CH₄ conversion and, therefore, HCHO yield. At a given conversion, the deliberately sodium-doped MoO₃-Cabosil has the lowest HCHO selectivity and the acid-washed silica gel with 10 ppm sodium has the highest. The ratio k_1/k_3 (based on extrapolated HCHO and CO₂ selectivities at zero conversion) seems little affected by the sodium content (17), so the decrease in CH₄ conversion and HCHO selectivity would appear to be caused by a decrease in the (common) CH₄ activation step rate.

The effect of sodium concentration on HCHO selectivity and CH₄ conversion with molybdena-free silica catalysts was also examined. Sodium was found to have no

noticeable effect on HCHO selectivity at any given conversion. Activity was found to be slightly suppressed by the residual sodium but much less so than in the case of MoO₃-SiO₂ catalysts (Table 3, Fig. 11).

It seems, therefore, that sodium is acting to poison the MoO₃ promotion function rather than the active sites on the silica. This is supported by the fact that 300 ppm sodium was found to suppress CH₄ conversion on MoO₃-SiO₂ by approximately 65% (see Table 2). Assuming that all sodium atoms were present on the surface of the catalyst, 300 ppm corresponds to a coverage of $\sim 3 \times 10^{16}$ sodium atoms m⁻² silica. The molybdenum coverage at 1.8 wt% Mo corresponds to $\sim 4.5 \times 10^{17}$ molybdenum

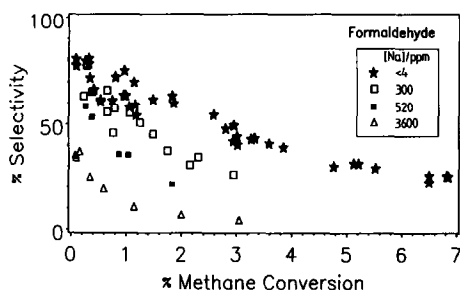


FIG. 10. HCHO selectivity vs methane conversion curve for MoO₃-silica, with various sodium concentrations. Space velocity range: 2500–10000 h⁻¹ (GHSV,NTP), reactants: 9:1, CH₄:O₂, 1 atm, 848–923 K.

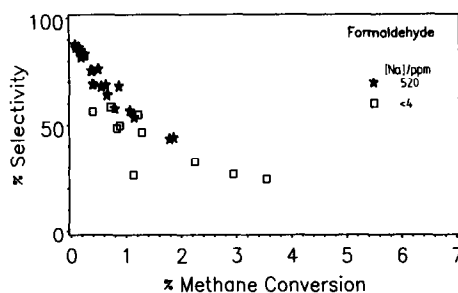


FIG. 11. HCHO selectivity vs methane conversion curve for "as received" (520 ppm Na) and acid-treated (<4 ppm Na) silica gel. Conditions for 520 ppm Na-silica: 2500–10000 h⁻¹ (GHSV,NTP), 848–923 K. Conditions for <4 ppm Na-silica: 1000–5000 h⁻¹ (GHSV,NTP), 873–923 K. Reactants: 9:1, CH₄:O₂, 1 atm.

atoms m^{-2} silica, and the silica surface concentration (based on quartz) is $\sim 9 \times 10^{18} m^{-2}$. Thus, on the surface, the Na:Mo:Si ratio is 1:15:300, for 300 ppm Na, 1.8 wt% Mo on $250 m^2 g^{-1}$ silica. A 65% reduction in activity therefore suggests that approximately 10 MoO_3 units are being deactivated by each sodium atom.

Long-range through-substrate interactions of the type observed in alkali metal-CO coadsorption on metals (18) seem unlikely to be occurring on silica. There is some evidence in the literature (15, 19, 20) that molybdena does form a polymeric species at low loadings on silica and also that the conjoint reduction of linked MoO_3 units occurs by the formation of shear structures (21). A possible poisoning mechanism may be that a sodium atom reacts with a MoO_3 unit, preventing reduction of the Mo(VI) by inhibiting the elimination of water. Other molybdena units may be linked together on the surface in groups, and the reaction of any one of the group with sodium could form a species that not only resists reduction to Mo(IV) itself, but also, by blocking the shearing mechanism, inhibits all the other units connected in the group from being reduced. It would seem reasonable to assume that the Mo(VI)-Mo(IV) redox system is involved in the operation of MoO_3 as a promoter. Therefore, blocking of the shearing reduction mechanism by sodium in this way could prevent the promotion mechanism, thereby lowering catalyst activity.

CONCLUSIONS

MoO_3-SiO_2 is a selective catalyst for the partial oxidation of methane to formaldehyde at low conversions. As methane conversion increases, HCHO selectivity decreases. Slight increase in selectivity (at any given conversion) can be obtained by increasing reactor temperature.

The active site for this partial oxidation reaction seems to exist on pure silica, although molybdenum oxide has a strong

promoting effect, increasing activity by roughly one order of magnitude. While promoting the silica catalyst, the molybdena is bonded to the silica in such a way that it is far less volatile than bulk MoO_3 .

Molybdena in excess of approximately 1/10 monolayers appears not to interact with the silica in this way, eventually volatilizing from the catalyst under reaction conditions and playing no part in catalyzing the CH_4 oxidation reaction.

Sodium in very low concentrations poisons the promoting effect of the molybdena, but has little effect on the intrinsic properties of the silica.

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