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Selective Methane Oxidation over Promoted Oxide Catalysts

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SUMMARY OF PROGRESS

In a systematic study with a CH_4/air reactant mixture at 600°C and 0.1 MPa, it is demonstrated that among eight Cab-O-Sil supported redox transition metal oxide catalysts, a V_2O_5/SiO_2 catalyst exhibited the highest productivities of formaldehyde and methanol. The effect of steam on enhancing the space time yields of the oxygenates was observed with the catalysts that were study with this third component in the reaction mixture. With the vanadia-containing catalyst, it was shown that a loading of 2 wt% of V_2O_5 on SiO_2 produced the highest conversion of methane from a CH_4/air/steam = 4/1/1 reactant mixture and the highest productivities of both CH_3OH and HCHO. It was also shown that increasing the reactant flow rate (thereby decreasing the contact time) increased the space time yield of methanol but decreased the overall methane conversion level.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

OBJECTIVES OF THE RESEARCH

The objective of this research is the selective oxidative coupling of methane to C_2H_4 hydrocarbons (Equations 1-3) and oxygenates, in particular formaldehyde and methanol as represented by Equations 4 and 5. Air, oxygen, or carbon dioxide, rather than nitrous oxide will be utilized as the oxidizing gas at high gas hourly space velocity, but mild reaction conditions (500-700 °C, 0.1 MPa total pressure). All the investigated processes are catalytic, aiming at minimizing gas phase reactions that are difficult to control.

$$2CH_4 + \tfrac{1}{2}O_2 \rightleftarrows C_2H_6 + H_2O \tag{1}$$

$$2CH_4 + O_2 \rightleftarrows C_2H_4 + 2H_2O \tag{2}$$

$$2CH_4 + 2CO_2 \rightleftarrows C_2H_4 + 2CO + 2H_2O \tag{3}$$

$$CH_4 + O_2 \rightleftarrows CH_2O + H_2O \tag{4}$$

$$CH_4 + \tfrac{1}{2}O_2 \rightleftarrows CH_3OH \tag{5}$$

Oxide catalysts have been chosen for this research that are surface doped with small amount of acidic dopants. It was thought that, for example, the very basic Sr/La_2O_3 catalyst which is active in the formation of methyl radicals and therefore C_2H_4 products, can be doped with some Lewis acidic oxides or other groups to increase further its activity and selectivity to C_2H_4 products.

The research to be carried out under U.S. DOE-METC contract is divided into the following three tasks:

Task 1.	Maximizing Selective Methane Oxidation to C_2H_4 Products Over Promoted Sr/La_2O_3 Catalysts.
Task 2.	Selective Methane Oxidation to Oxygenates.
Task 3.	Catalyst Characterization and Optimization.

Task 1 dealt with the preparation, testing, and optimization of acidic promoted lanthana-based catalysts for the synthesis of C_2H_4 hydrocarbons and is essentially completed. Task 2 aims at the formation and optimization of promoted catalysts for the synthesis of oxygenates, in particular formaldehyde and methanol. Task 3 involves characterization of the most promising catalysts so that optimization can be achieved under Task 2.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

RESEARCH PROGRESS

This research project is directed toward the direct selective oxidation of methane to oxygenates. Many supported metal oxides have been reported to exhibit some activity for the synthesis of oxygenates such as formaldehyde and methanol from methane, but most of these oxides produced oxygenates with only marginal yields and often required high pressure [1,2]. In the present work, a series of silica-supported transition metal oxides have been prepared and tested in a continuous flow reactor at atmospheric pressure for the selective oxidation of methane to methanol and formaldehyde. Further optimization experiments were carried out with the active V_2O_5/SiO_2 catalyst system.

Experimental

Catalysts consisting of silica-supported V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3, Cu_2O, MoO_3, WO_3, and Re_2O_7 were prepared by using an impregnation method. The amorphous silica (Cab-O-Sil EH-5 with a surface area of 380 m^2/g) that was used as the support was first mixed with deionized water, and then the mixture was stirred and dried at 140°C so that the density of the silica was increased. The V_2O_5/SiO_2 catalyst was typically prepared by aqueous impregnation of ammonium metavandate (NH_4VO_3 from Aldrich) into the amorphous silica. For preparing other catalysts, $Cr(NO_3)_3$, $Mn(NO_3)_4$, $Fe(NO_3)_3$, iron(II) acetate, copper(I) acetate, and ammonium heptamolybdate were used. The resulting mixtures were thoroughly mixed by vigorous stirring at 60°C on a magnetic hot plate for 10-15 hr until a think paste was formed. The paste was then dried at 140°C overnight and calcined in air at 600°C for six hr. Oxidation of the catalysts during this latter treatment was not monitored.

The catalytic testing experiments were carried out over in a quartz tubular reactor and the products were initially analyzed by gas chromatography, as described in our previous quarterly progress reports (for example, see [3-5]). In some cases, steam was added to the reactant mixture by injection of distilled water into the heated volume preceding the catalyst bed by means of an ISCO liquid metering pump (Model 314). Condensible products, trapped at 0°C, were also analyzed by GC/MS. The GC/MS formaldehyde analysis was calibrated by a series of standard solutions that were quantified by iodometric titration.

Results

The transition metal catalysts that were prepared are considered to be redox catalysts that are appropriate for methane partial oxidation. Table 1 compares the results obtained with the silica-supported catalysts using a CH_4/air = 1.5/1.0 reaction mixture at 600°C and with a relatively moderate hourly space velocity (GHSV). Also shown for comparison are the results obtained with the empty reactor and with the reactor containing only quartz wool or the Cab-O-Sil support.

TABLE 1. The conversion of methane, space time yield (STY) of oxygenates, and product selectivities observed the partial oxidation of methane over Cab-O-Sil supported transition metal oxide catalysts (0.10 g) at 600°C and 0.1 MPa with CH_4/air = 1.5/1.0 reactant mixture at GHSV = 144,000 ℓ/kg catal/hr.

Catalyst	CH_4 Conv. (mol%)	CH_2O STY (g/kg/hr)	CH_3OH STY (g/kg/hr)	Selectivity (C mol%)			
				CH_2O	CH_3OH	CO	CO_2
Blank	0.1	0.0	0.0	0.0	0.0	0.0	100
Wool	0.01	0.0	0.0	0.0	0.0	0.0	100
Cab-O-Sil	0.02	0.0	0.0	100	0.0	0.0	0.0
V_2O_5/SiO_2	7.9	481	49	5.2	0.5	84.5	9.7
Cr_2O_3/SiO_2	10.4	18.2	0.0	0.2	0.0	19.9	79.9
MnO_2/SiO_2	4.3	32.1	0.0	0.6	0.0	29.8	69.6
Fe_2O_3/SiO_2	1.5	278	19.6	15.9	1.1	50.4	32.6
Cu_2O/SiO_2	1.5	185	18.2	10.6	1.0	45.7	42.7
MoO_3/SiO_2	0.05	29.4	18.8	50.5	30.3	13.4	5.7
WO_3/SiO_2	0.2	11.6	0.0	5.0	0.0	26.7	68.3
Re_2O_7/SiO_2	0.6	28.2	11.9	4.0	1.6	76.0	18.4

The data in Table 1 show that the V_2O_5/SiO_2 catalyst performed the best with respect to oxygenate yields. The Fe_2O_3/SiO_2, Cu_2O/SiO_2, MoO_3/SiO_2 and Re_2O_7/SiO_2 catalysts also gave appreciable space time yields of formaldehyde and methanol, although they were much less active than the V_2O_5/SiO_2 catalyst. The MoO_3/SiO_2 catalyst produced little CO_2 and exhibited notable selectivity to formaldehyde and methanol, but the activity of this catalyst was very low. Under the reaction conditions utilized, the Cr_2O_5/SiO_2 was the most active catalyst, but CO_2 was the dominant product, accompanied by CO. The data in Table 1 also indicate that gas phase free radical reactions were negligible since C_2 hydrocarbons were not formed. Since the Cab-O-Sil exhibited almost no catalytic activity, the data emphasize the important role played by the catalyst surface in oxygenate production.

Additional experiments were carried out wherein steam was added to the reactant mixture passing over the catalysts. Steam was utilized in the reagent mixture because of its capability of enhancing the productivities of oxygenates over the V_2O_5/SiO_2 catalyst [5-7]. The catalysts studied were the Cab-O-Sil supported V_2O_5, MoO_3, and Re_2O_7 catalysts, and the reaction mixture consisted of CH_4/air/steam = 1.5/1.0/0.2. Moderate temperatures were used to obtain low conversion methane levels under differential reactor conditions, and the activation energies were calculated using the data shown in Figure 1. As indicated in the figure, the 1 wt% V_2O_5/SiO_2 catalyst exhibited the highest activation energy for methane conversion to products.

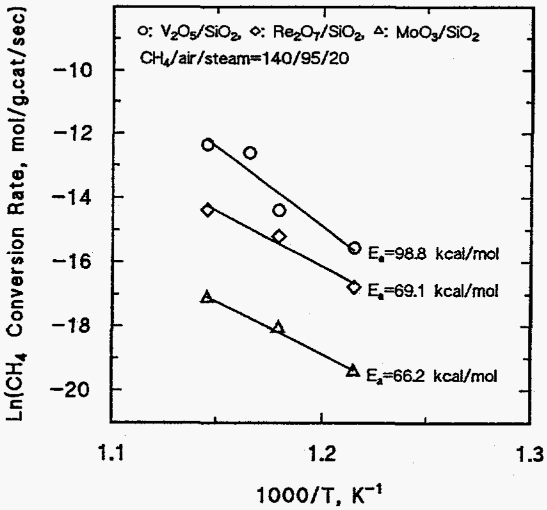

FIGURE 1. The relationship of methane conversion to products over 1 wt% V_2O_5/SiO_2, MoO_3/SiO_2, and Re_2O_7/SiO_2 catalysts (0.1 g) as a function of the reaction temperature in the range of 500-600°C with a methane/air/steam = 1.5/1.0/0.2 reaction mixture at 0.1 MPa and GHSV = 153,000 ℓ/kg catal/hr.

Using the 1 wt% V_2O_5/SiO_2 catalyst, the effect of contact time on the activity and methanol productivity was examined. The contact time was varied by altering the flow rate of CH_4/air/steam = 4/1/1 reactants over the catalyst or by changing the mass of the catalyst in the reactor. The results are shown in Figure 2, where it is seen that increasing the contact time increased the methane conversion level. However, it is also seen that the higher space time yields of methanol were achieved at the shorter contact times, which is a reflection of the higher selectivities at the short contact times. Indeed, the selectivity toward methanol increased from 0.6 mol% to 2.1 mol% as the contact time decreased.

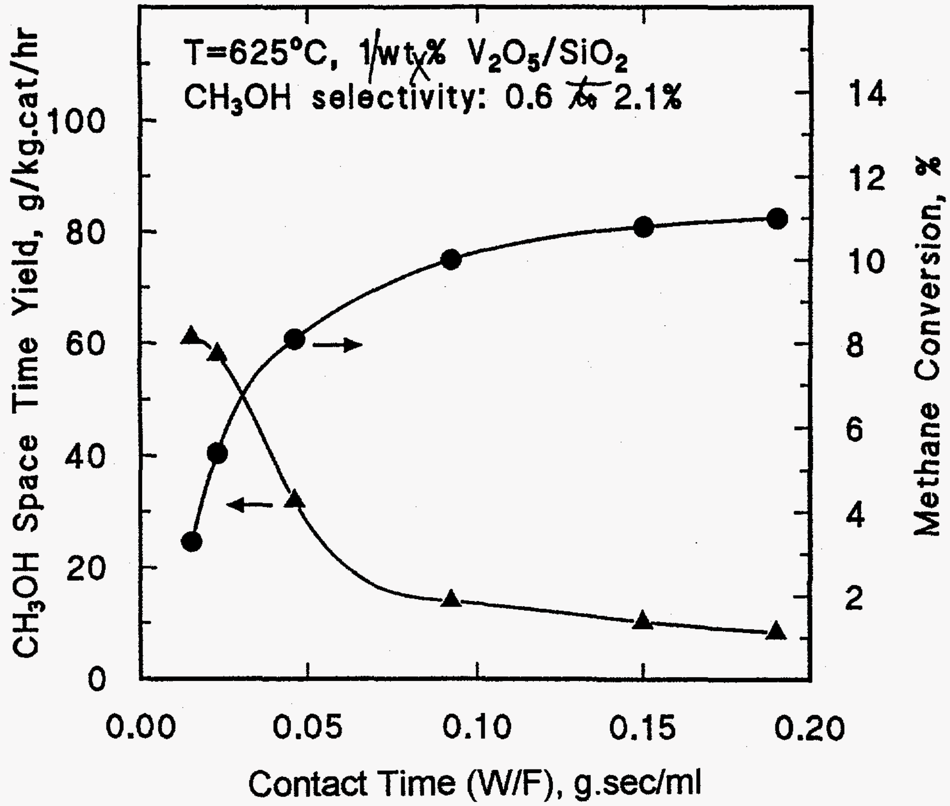

FIGURE 2. Trends in methane conversion and methanol space time yields as the contact time of a CH_4/air/steam = 4/1/1 reactant mixture was varied over a 1 wt% V_2O_3/SiO_2 catalyst at 625°C and ambient pressure.

Since the V_2O_3/SiO_2 catalyst exhibited the highest CH_2O and CH_3OH productivities among the silica-supported transition metal oxide catalysts from steam-free reactants (see Table 1), the influence of vanadia content on the methane conversion and oxygenate productivity was determined using a CH_4/air/steam = 4/1/1 reactant mixture. These experiments were carried out in part to complete the study of the influence of vanadia content on the activity and selectivity that initially was only probed the range of 0.5 to 2.0 wt% V_2O_5 [5]. The results are shown in Figure 3 for catalysts containing 0.25 to 7.0 wt% vanadia. It is seen that the trends in methane conversion, formaldehyde productivity, and methanol productivity are parallel to one another. The maximum in methane conversion was observed at ≈1.5 wt% V_2O_5, while the productivities of the oxygenates exhibited maxima at ≈2.0 wt% V_2O_5. High productivities of the oxygenates were achieved under these reaction conditions, i.e. slightly more than 1000 g CH_2O/kg catal/hr and ≈180 g CH_3OH/kg catal/hr were produced at 600°C.

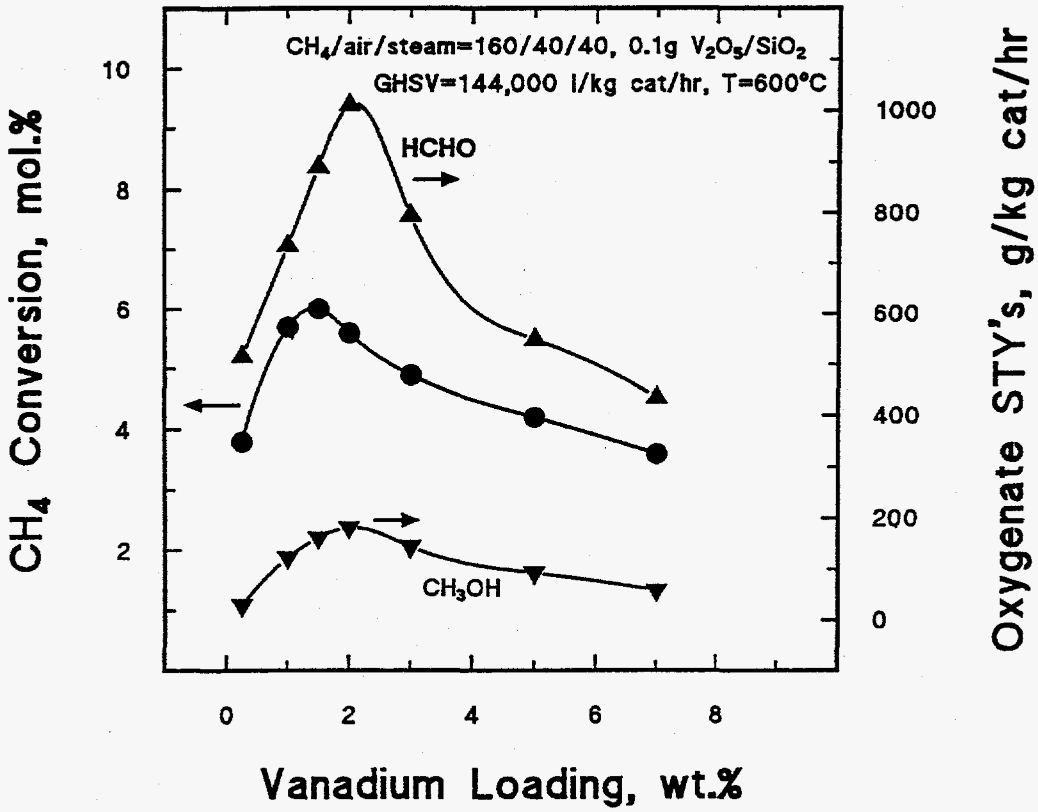

FIGURE 3. Methane conversion and space time yields of formaldehyde and methanol at 600°C from CH_4/air/steam = 4/1/1 with GHSV = 144,000 ℓ/kg catal/hr as functions of the vanadia content of V_2O_5/SiO_2 catalysts.

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