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Selective Methane Oxidation over Promoted Oxide Catalysts

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SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

SUMMARY OF PROGRESS

During this quarter, solid state ^{51}V NMR and double catalyst bed experiments were conducted to demonstrate the unfavorable effect of the presence of bulk crystalline V_2O_5 in V_2O_5-SiO_2 xerogel catalysts on selective oxidation of methane to methanol and formaldehyde.

Solid state ^{51}V NMR spectra obtained with 1.0 and 2.0 wt% V_2O_5-SiO_2 xerogel dehydrated samples showed a distinct peak with $\delta \approx -500$ ppm (designated as peak A). This peak was attributed to tetrahedral V surface species, proposed to be an active site for methane partial oxidation. When the vanadia content was 3.0 wt% or higher, two principal peaks (A and B) were obserbed in the NMR spectra. Peak B with $\delta \approx -280$ ppm increased in intensity as the vanadia content increased in the V_2O_5-SiO_2 xerogels. This peak was attributed to the octahedral V species of crystalline vanadia in the V_2O_5-SiO_2 xerogels. The NMR data coincide well with the catalytic testing results presented in quarter report DOE/MC/29228-11, which showed that the 2.0 wt% V_2O_5-SiO_2 xerogel catalyst gave the highest space time yields of and selectivities to methanol and formaldehyde, indicating that the presence of V_2O_5 in the catalysts diminished the space time yields of oxygenates for the partial oxidation of methane. This was observed although the V_2O_5-SiO_2 xerogel catalysts with higher vanadia content also contained a large amount of dispersed V species, e.g. 45.5% dispersed V species in the 20.0 wt% V_2O_5-SiO_2 xerogel.

Compared to dehydrated V_2O_5-SiO_2 xerogels, the NMR spectra of hydrated V_2O_5-SiO_2 xerogels showed that the peak intensity of the tetrahedral V species coincidentally decreased with an increase in the peak intensity of the octahedral species. This was caused by the tetrahedral surface V species coordinating with water molecules to form new distorted octahedral species. However, it is noticed that the NMR peak of the tetrahedral V species did not disappear, although the V_2O_5-SiO_2 xerogel samples were made wet with water, followed by drying at 120°C for 1 hr. This result suggests that some of the tetrahedral V species do not readily interact with water molecules in the V_2O_5-SiO_2 xerogels. Further studies are needed to establish the identity of this type of tetrahedral V species and to establish its relationship with the activity for partial methane oxidation.

Double catalyst bed experiments were carried out using two V_2O_5-SiO_2 catalysts having different vanadia content. Much higher space time yields of methanol and formaldehyde were observed over a double catalyst bed with 0.1 g 20.0 wt% V_2O_5-SiO_2 xerogel as the first bed and 0.1 g 3.0 wt% V_2O_5-SiO_2 xerogel as the second bed than when 0.1 g 3.0 wt% V_2O_5-SiO_2 xerogel was employed as the first bed and 0.1 g 20.0 wt% V_2O_5-SiO_2 xerogel as the second bed. This indicates that in the latter case the oxygenates produced over the first catalyst bed of the 3.0 wt% V_2O_5-SiO_2 were readily further oxidized as they passed the second catalyst bed of the 20.0 wt% V_2O_5-SiO_2, which contained a large quantity of crystalline vanadia. The data demonstrate a

deleterious effect of the crystalline vanadia in the V_2O_5-SiO_2 xerogel catalysts on the space time yields of oxygenates, especially methanol.

In an additional experiment, a Pd-modified V_2O_5-SiO_2 xerogel catalyst was prepared and catalytically tested. The results showed that addition of palladium into a 10 wt% V_2O_5-SiO_2 xerogel greatly enhanced the activity for methane oxidation but significantly diminished the selectivities to oxygenates.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

OBJECTIVES OF THE RESEARCH

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

$$2CH_4 + \tfrac{1}{2}O_2 \leftrightarrows C_2H_6 + H_2O \quad (1)$$

$$2CH_4 + O_2 \leftrightarrows C_2H_4 + 2H_2O \quad (2)$$

$$2CH_4 + 2CO_2 \leftrightarrows C_2H_4 + 2CO + 2H_2O \quad (3)$$

$$CH_4 + O_2 \leftrightarrows CH_2O + H_2O \quad (4)$$

$$CH_4 + \tfrac{1}{2}O_2 \leftrightarrows CH_3OH \quad (5)$$

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 that is active in the formation of methyl radicals that lead to C_2H_4 products can be doped with some Lewis acidic oxides or other groups to further increase its activity and selectivity to C_2H_4 products.

The research being carried out under this 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

Introduction

The V_2O_5-SiO_2 xerogel catalysts containing 1.0-25.0 wt% vanadia were previously catalytically tested for partial oxidation of methane to methanol and formaldehyde (Progess Report DOE/MC/29228-11). It was observed that the 2.0 wt% V_2O_5-SiO_2 xerogel catalyst gave the highest space time yields of and selectivities to methanol and formaldehyde in the temperature range of 575-650°C. The decrease in the space time yields of and selectivities to oxygenates with an increase in vanadia content was proposed to be caused by the existence of the bulk-like vanadia, which catalyzes the secondary oxidation of oxygenates to carbon oxides. During this quarter, double catalyst bed experiments and solid state ^{51}V NMR analyses were conducted to confirm this interpretation.

Solid state ^{51}V NMR is a powerful approach for studies of the local environments of ^{51}V nuclei in vanadia-supported catalysts due to the fact that the ^{51}V nucleus (I = 7/2) has a 99.76% natural abundance, a large magnetic moment, and short spin-lattice relaxation times. The direct proportionality of the NMR peak area to the number of nuclei makes this method an effective technique for quantitative studies. In recent years, solid state ^{51}V NMR has been widely used to characterize vanadia based solid catalysts, e.g. V_2O_5/Al_2O_3, V_2O_5/TiO_2, V_2O_5/ZrO_2, V_2O_5/SnO_2, V_2O_5/MgO, V_2O_5/TiO_2-ZrO_2, $Rh/V_2O_5/SiO_2$, $V_2O_5/AlPO_4$, and V_2O_5-$K_2S_2O_7$. The results of these studies have been previously discussed in a review paper (1). V_2O_5/SiO_2 catalysts prepared *via* impregnation were investigated by Lapina et al. (1) and Koranne et al. (3), and two NMR peaks at *ca.* - 300 and - 550 to -600 ppm were observed in the spectra of the V_2O_5/SiO_2 catalysts. Attempts have been made to assign the former peak to the octahedral V species of crystalline V_2O_5 and the latter to VO_4 tetrahedral surface species by comparing the peak positions with those of model compounds with established vanadium symmetries (1, 3).

Experimental

The V_2O_5-SiO_2 xerogel catalysts were prepared by sol-gel synthesis with vanadium triisopropoxide oxide ($VO(OC_3H_7)_3$) as precursor. A detailed description of the synthesis process was included in a previous quarter report (4).

A 10.0 wt% V_2O_5-0.05 wt% Pd/SiO_2 xerogel catalyst was synthesized by using the same method as that employed in the synthesis of V_2O_5-SiO_2 xerogel catalysts, but a mixture of $VO(OC_3H_7)_3$ and $Pd[(OCOCH_3)_2]_3$ in methanol was combined with a SiO_2 sol to form a V_2O_5-Pd-SiO_2 sol. The BET surface area and pore volume of the dried catalyst was 442 m^2/g and 0.31 cm^3/g, respectively.

The V_2O_5-SiO_2 and V_2O_5-Pd/SiO_2 xerogel catalysts were pretreated at 550°C for 0.5 hr in flowing air. Catalytic testing was carried out with a reactant stream of CH_4/air/steam = 150/100/56 ml/min at a pressure of 0.1 MPa. In double-bed experiments, 0.1 g of 3.0 wt% and 0.1 g of 20.0 wt% V_2O_5-SiO_2 catalysts were packed in a quartz reactor with quartz wool placed before and after the catalyst bed. In single-bed experiments, 0.1 g of 10.0 wt% V_2O_5-0.05 wt% Pd/SiO_2 was packed in the quartz reactor. The flow rates of methane and air were measured and controlled by mass-flow controllers (Brooks and Linde). The gases were preheated separately before entering the reactor. The exhaust gas lines from the reactor to the GC and from the GC to the ice trap used to collect condensable products were heated to 150°C to prevent condensation of the products in the exit line.

The exhaust gas was analyzed by a Varian 3700 gas chromatograph with helium as a carrier gas at a pressure of ca. 0.14 MPa with a flow rate of 30 ml/min using a Porapak Q column (2 m length x1/8-in. o.d.) and a 13X zeolite column (2 m length x 1/8-in. o. d.) in parallel and a thermal conductivity detector. The condensable products were trapped by using an ice bath at 0°C and were separately analyzed by a Hewlett Packard 5970 MSD GC/MS instrument.

Static solid state ^{51}V NMR spectra of 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, 15.0, and 20.0 wt% V_2O_5-SiO_2 xerogels were obtained at 78.93 MHz on a General Electric Model GN-300 spectrometer, which was equipped with a Nicolet 2090-IIIA high-speed digital oscilloscope and a 7-mm MAS-NMR Doty probe. The measurements were carried out with a simple one-pulse sequence (Bloch decay) with a pulse width of 1 μs, a preacquization delay of 10 s, a dwell time of 0.5 μs, a relaxation delay of 5-10 s, 4,000 data points and 3840 scans for each sample. Prior to Fourier transform, a line broadening factor of 600 Hz was applied. All chemical shifts are referenced against liquid $VOCl_3$. Prior to analysis, the V_2O_5-SiO_2 xerogel samples were dehydrated by calcination at 550°C for 4 hr, cooling in a desiccator containing dehydrated 4A zeolite, followed by transfer to an NMR sample holder in a glove box with a flow of dry nitrogen. Hydrated samples were obtained by exposing the dehydrated samples to the ambient atmosphere for a couple of days or wetting with water followed by drying at 120 °C for 1 hr.

Results and Discussion

Static Solid State ^{51}V NMR Studies

Figure 1 shows the static solid state ^{51}V NMR spectra of dehydrated V_2O_5-SiO_2 xerogel catalyst samples as a function of vanadia content. For 1.0 and 2.0 wt% V_2O_5-SiO_2 xerogels, only peak A with $\delta \approx -500$ ppm was observed. When the content of vanadia in the samples equaled or exceeded 3.0 wt%, a new peak (B) with $\delta \approx -280$ ppm appeared in the spectra. Peak B increased with an increase in vanadia content. Previous studies conducted by other researchers (1, 2) have indicated that peak A could be attributed to tetrahedral V surface species and peak B to octahedral V sites in crystalline V_2O_5. The use of a short pulse length (1 μs) and a long relaxation delay (5 to 10 s) allows us to determine signal fractions reliably. The signal fractions

and calculated compositions of two kinds of the V species are shown in Table 1, indicating that the dispersed V species increased with the increase of total vanadia content up to a critical dispersion capacity of ca. 9.5 wt% (10.5 g /g SiO_2).

Table 1. Relative ^{51}V NMR signal areas and compositions of two V species of V_2O_5-SiO_2 xerogel catalysts.

V_2O_5 (wt%)	Dehydrated Samples					Hydrated Samples	
	Signal Fraction (%)*		V Species**			Signal Fraction (%)*	
	Peak A	Peak B	Dispersed V_2O_5 (wt%)	Crystalline V_2O_5		Peak A	Peak B
				(wt%)	($g/gSiO_2$)		
1.0	100	0.0	1.0	0.0	0.000	67.3	32.7
2.0	100	0.0	2.0	0.0	0.000	--	--
3.0	81.7	18.3	2.5	0.5	0.005	45.9	54.1
4.0	78.6	21.4	3.1	0.9	0.009	--	--
5.0	76.7	23.3	3.8	1.2	0.012	48.0	52.0
10.0	78.6	21.4	7.9	2.1	0.021	40.7	59.3
15.0	63.6	36.4	9.5	5.5	0.058	--	--
20.0	45.7	54.3	9.1	10.9	0.122	37.7	62.3

* Estimated errors: ± 10%.

** Calculated from the relative ^{51}V NMR signal areas.

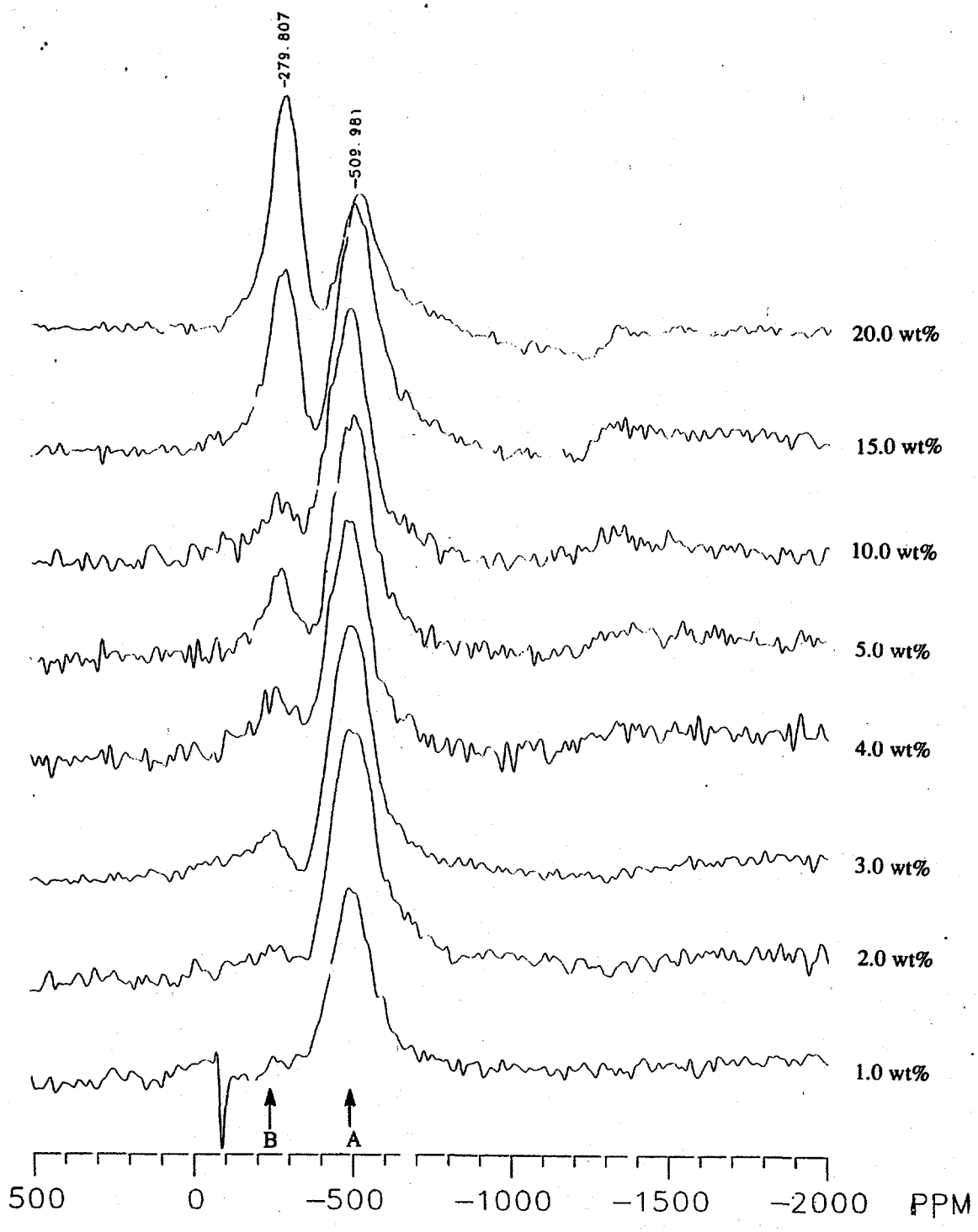

Figure 1. Static solid state ^{51} V NMR spectra of dehydrated V_2O_5-SiO_2 xerogel catalysts.

The above results coincide well with previously reported catalytic testing data for V_2O_5-SiO_2 xerogel catalysts, which showed that the 2.0 wt% $_2V_5O$ -Si_2O xerogel catalyst gave the highest space time yields of and selectivities to methanol and formaldehyde in the partial methane oxidation. The 2.0 wt% V_2O_5-SiO_2 catalyst possessed more tetrahedral V surface species acting as active sites for partial methane oxidation than the 1.0 wt% V_2O_5-SiO_2 catalyst. However, for the catalysts containing more than 3.0 wt% vanadia, the presence of crystalline V_2O_5 intensified the secondary oxidation of methanol and formaldehyde to carbon oxides although these catalysts contained more dispersed species than that in the 2.0 wt% xerogel catalyst. Therefore, an important issue for preparation of V_2O_5-SiO_2 catalysts is to design a suitable process not only to create a large amount of V surface species but also to avoid the formation of crystalline V_2O_5 in the final catalysts.

Water adsorption of V_2O_5-SiO_2 xerogels increased the signal intensity of peak B but decreased the intensity of peak A, as shown by comparing Figure 2 with Figure 1, suggesting that the tetrahedral surface V species interacted with water molecules to form distorted octahedral V sites, as reported previously by others for V_2O_5/SiO_2 catalysts studied by solid state NMR, EPR and IR (1, 3, 5). It was also found that peak A did not disappear even though the V_2O_5-SiO_2 samples remained in the air for a few days or were wetted with water (Figure 3). Even with exposure to excess water , the results indicate that some of the tetrahedral V species in V_2O_5-SiO_2 xerogel samples did not changed their coordination environment after water adsorption.

There is a possibility that a small fraction of the vanadium ions is immobilized in the silica matrix in the V^{4+} state, as previously known in V_2O_5-SiO_2 gels (6). The V^{4+} species has a tetrahedral coordination with oxygen atoms, which makes a contribution to peak A but does not interact with water molecules. However, Table 1 shows that the signal fraction of peak A in the hydrated samples was almost 50%, implying existence of another type of tetrahedral surface V species which is not readily coordinated by water molecules. This type of tetrahedral surface V species has been observed in V_2O_5/Al_2O_3 catalysts at low surface coverage by other researchers using EXAFS/XANES and NMR (3, 7). Further studies of the identity of the tetrahedral species in hydrated V_2O_5-SiO_2 xerogel catalysts are in progress. In addition, NMR will be employed to investigate the active site in V_2O_5-SiO_2 xerogel catalysts for partial methane oxidation by analyzing the catalyst samples treated in the reactant mixture.

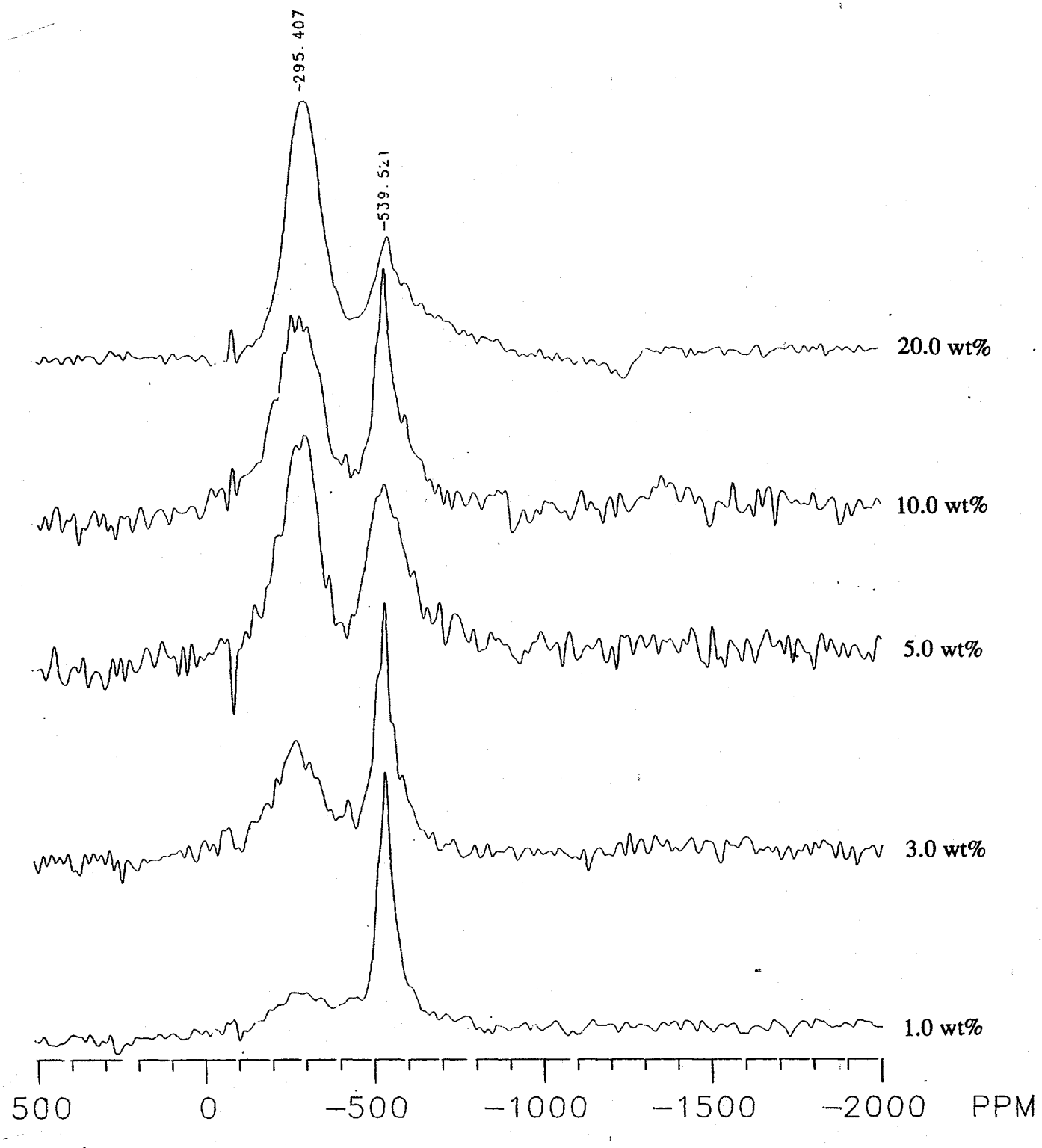

Figure 2. Static solid state ^{51} V NMR spectra of hydrated V_2O_5-SiO_2 xerogel catalysts.

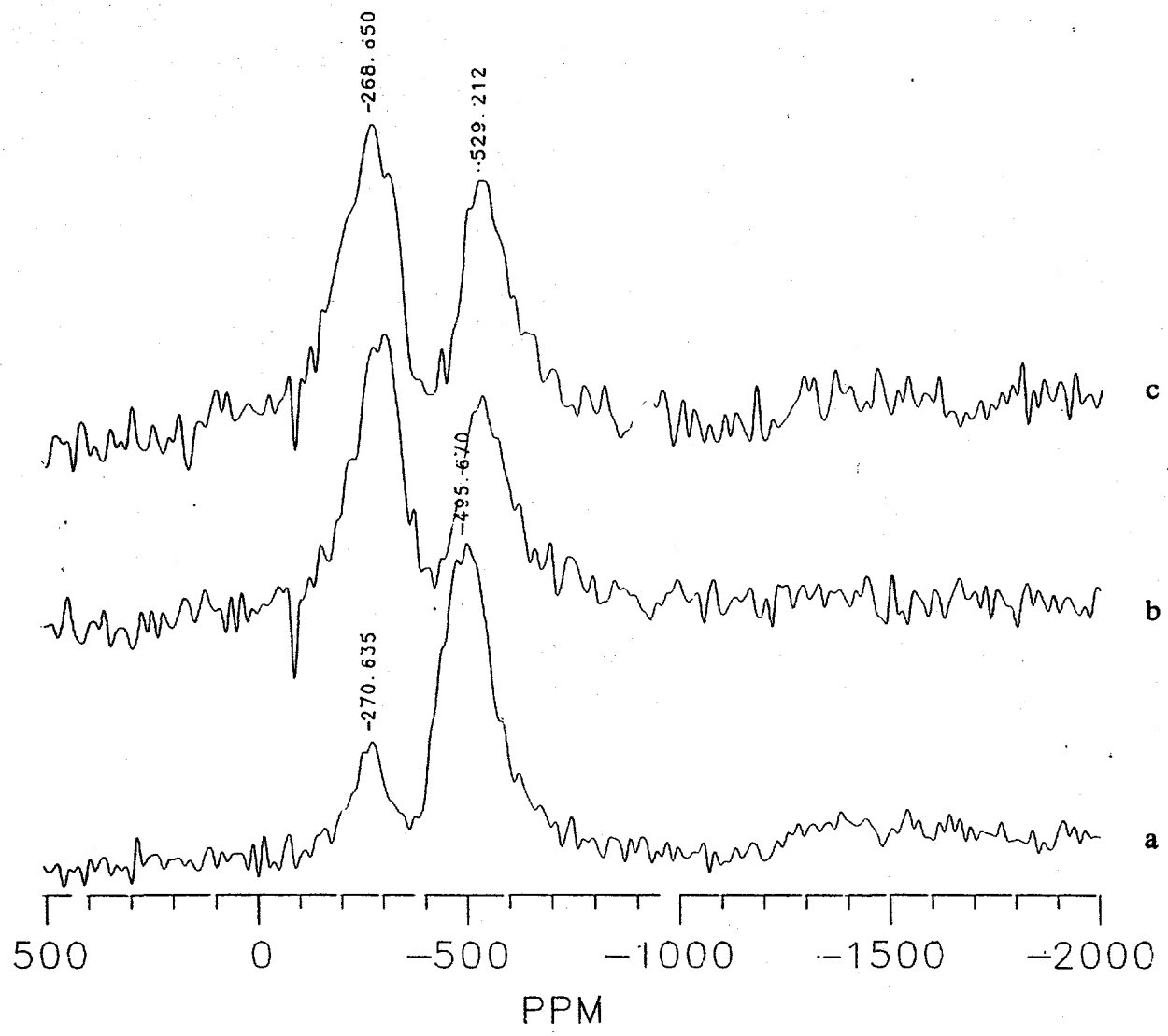

Figure 3. Static solid state ^{51} V NMR spectra of 5.0 wt% V_2O_5-SiO_2 xerogel catalysts. a. Dehydrated sample (its color was yellow); b. Hydrated (exposed to room air for 1 day, brown); c. Hydrated (water wetting followed by drying at 120°C for 1 hr, dark brown).

Catalytic Testing

V_2O_5-SiO_2 Catalysts. Table 2 presents the catalytic results of selective methane oxidation over a double-bed catalyst of 3.0 and 20.0 wt% V_2O_5-SiO_2 xerogels. When the 20.0 wt% V_2O_5-SiO_2 catalyst was used as the first bed and the 3.0 wt% V_2O_5-SiO_2 catalyst as the second bed, significantly higher space time yields of methanol and formaldehyde were observed in the temperature range of 575-625°C, compared to the case where the 3.0 wt% V_2O_5-SiO_2 catalyst was employed as the first bed and the 20.0 wt% catalyst as the second bed. The difference in the space time yield of methanol was remarkably large between the two double-bed configurations, while the difference in the space time yield of formaldehyde was also significant, especially at the

higher reaction temperatures.

Table 2. The conversion of methane and the space time yields and selectivities of products formed over a double catalyst bed of [A] 0.1 g 20 wt% V_2O_5-SiO_2 as the first bed and 0.1 g 3 wt% V_2O_5-SiO_2 as the second bed or [B] 0.1 g 3 wt% V_2O_5-SiO_2 as the first bed and 0.1 g 20 wt% V_2O_5-SiO_2 as the second bed. The reactant stream was CH_4/air/steam (by feeding deionized water) = 150/100/56 ml/min with total GHSV = 91,800 l/kg cat/hr (corresponding to 183,600 l/kg cat/hr for each individual catalyst bed). Catalyst testing was carried out at the temperatures indicated and at a pressure of 0.1 MPa.

Catalyst (Double-Bed)	T (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr Selectivities (C mol%)			
			CH_3OH	HCHO	CO	CO_2
[A]: 20 wt% V_2O_5-SiO_2‖3 wt% V_2O_5-SiO_2	550	0.03	3.1 (18.9)	12.5 (81.1)	0.0 (0.0)	0.0 (0.0)
	575	0.70	23.4 (5.7)	152.4 (39.9)	158.0 (44.4)	55.9 (10.0)
	600	1.25	28.8 (4.0)	266.2 (39.3)	312.2 (49.3)	74.2 (7.5)
	625	1.11	18.6 (2.9)	125.1 (20.9)	312.8 (55.9)	178.2 (20.3)
[B]: 3 wt% V_2O_5-SiO_2‖20 wt% V_2O_5-SiO_2	550	0.07	1.9 (4.7)	27.5 (73.7)	5.2 (14.8)	4.0 (7.2)
	575	0.49	5.1 (1.9)	94.8 (36.7)	139.7 (58.0)	13.1 (3.5)
	600	0.97	2.2 (0.40)	85.2 (16.6)	310.9 (64.8)	137.4 (18.2)
	625	1.57	1.9 (0.2)	72.7 (8.9)	535.1 (70.5)	250.3 (20.9)
	650	1.83	3.0 (0.3)	99.4 (10.4)	512.7 (57.3)	450.6 (32.1)

As previously shown, the 20.0 wt% V_2O_5-SiO_2 xerogel contained a large amount of detectable crystalline V_2O_5. The data presented here further suggest that the existence of

crystalline V_2O_5 in the catalysts remarkably diminished the space time yields of methanol and formaldehyde due to its strong ability for further oxidation of methanol and formaldehyde to carbon oxides at higher temperatures. In the case of 20.0 wt% V_2O_5-SiO_2 catalyst as the second bed, some of the methanol and formaldehyde formed in the first bed was further oxidized on the surface of crystalline V_2O_5 in the second catalyst bed. The results also showed that methanol was more easily oxidized than formaldehyde on the surfaces of V_2O_5 at 575-650°C.

Pd-Modified V_2O_5-SiO_2 Catalyst. The results given in Table 3 show that small amounts of methanol and formaldehyde could be produced from a reactant stream of CH_4/air/steam = 150/100/56 ml/min over a 10.0 wt%V_2O_5-0.05 wt% Pd-SiO_2 xerogel catalyst. The results showed that the Pd-modified V_2O_5-SiO_2 xerogel catalyst was more active than the V_2O_5-SiO_2 xerogel catalysts. For example, complete oxygen conversion could be achieved at 600°C and atmospheric pressure for the Pd-V_2O_5-SiO_2 catalyst, while this was not observed for the V_2O_5-SiO_2 catalysts. However, addition of Pd into the V_2O_5-SiO_2 xerogel catalyst did significantly lessen the selectivities to oxygenates.

TABLE 3. The conversion of methane and the space time yields and selectivities of products formed over 0.10 g 10.0 wt%V_2O_5-0.05 wt% Pd-SiO_2 xerogel catalyst. The reactant stream was CH_4/air/steam (by feeding deionized water) = 150/100/56 ml/min with GHSV = 183,600 l/kg catal/hr. Catalyst testing was carried out at the temperatures indicated and at a pressure of 0.1 MPa.

Temp. (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr (Selectivities, C mol%)			
		CH_3OH	HCHO	CO	CO_2
500	0.06	1.6 (2.5)	9.7 (16.0)	0.0 (0.0)	72.7 (81.6)
550	0.24	3.0 (1.1)	19.7 (7.8)	0.0 (0.0)	336.0 (91.1)
600	11.9	11.7 (0.1)	20.4 (0.2)	7821 (74.4)	4179 (25.3)

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