DOE/MC/29228-- 5457
Distribution Category UC-132

Selective Methane Oxidation over Promoted Oxide Catalysts

Quarterly Report

June 1 - August 31, 1996

By
Kamil Klier
Richard G. Herman
Chuan-Bao Wang

Work Performed Under Contract No.: DE-FG21-92MC29228

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Zettlemoyer Center for Surface Studies
Department of Chemistry
Lehigh University
7 Asa Drive, Sinclair Lab
Bethlehem, Pennsylvania 18015

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

SUMMARY OF PROGRESS

Further data analyses for the conversion of methane to oxygenates over high surface area V_2O_5/SiO_2 xerogel catalysts that were synthesized by a sol-gel process have been carried out. As previously described, the vanadia loading of the catalysts was varied between 0-25 wt% [1]. Turnover numbers (T.O.N.) have been calculated for methane conversion to products and for the synthesis of methanol and formaldehyde, where T.O.N. is defined as molecules converted or formed per dispersed tetrahedrally coordinated vanadium atom as determined by ^{51}V NMR analyses. It is found that highly dispersed tetrahedrally coordinated V^{5+} is the active site for the selective conversion of methane to methanol and formaldehyde. Based on the catalyst characterization and this further data analysis that was carried out, a manuscript to be submitted for publication has been drafted and is being revised.

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.

$2CH_4$	+	$½O_2$	=	C_2H_6	+	H_2O			(1)
$2CH_4$	+	O_2	=	C_2H_4	+	$2H_2O$			(2)
$2CH_4$	+	$2CO_2$	=	C_2H_4	+	$2CO$	+	$2H_2O$	(3)
CH_4	+	O_2	=	CH_2O	+	H_2O			(4)
CH_4	+	$½O_2$	=	CH_3OH					(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

High surface area V_2O_5/SiO_2 xerogel catalysts were previously synthesized by a sol-gel process and tested for selective oxidation of methane to oxygenates, as described in a previous quarterly progress report [1]. The catalysts contained vanadia nominally in the range of 1.0 to 25.0 wt% V_2O_5. It was shown that no crystalline V_2O_5 was detected in the V_2O_5/SiO_2 xerogel catalysts (dehydrated at 550°C) by X-ray powder diffraction (XRD) when the catalysts contained <5 wt% V_2O_5 [1]. These V_2O_5/SiO_2 catalysts were also analyzed using ^{51}V NMR after dehydration at 550°C [2], and all of the samples contained a peak, located at $\delta \approx -500$ ppm, attributed to tetrahedral vanadium. A second peak, at $\delta \approx -280$ ppm, was observed with samples containing 3 wt% V_2O_5 or higher, and this peak was assigned to vanadium in an octahedral environment, i.e. in crystalline V_2O_5 [2]. Therefore, the portions of V^{5+} present in a highly dispersed state and as microcrystalline vanadia could be calculated from the NMR data. These analyses indicated that the vanadia was very highly dispersed and that most or all of the V was present as a submonolayer dispersion, which depends on the quantity of vanadium added to the silica-based xerogel catalysts.

Using only the portion of vanadium present as tetrahedral (surface dispersed) species [2], the turnover numbers (T.O.N.) for methane conversion to products and of the formation of methanol and formaldehyde over these catalysts have been calculated, and they are given in Table 1 on the next page. Also given in this table are the methane conversions, space time

TABLE 1. Methane conversions, turnover numbers (T.O.N.), space time yields, and product selectivities observed over 0.10 g V_2O_5/SiO_2 xerogel catalysts containing 1.0-25.0 wt% vanadia. The reaction mixture consisted of CH_4/air/steam = 1.5/1.0/0.56 with GHSV = 183,600 ℓ/kg catal/hr. Catalyst testing was carried out at the temperatures indicated and at a pressure of 0.45 MPa.

V_2O_5 (wt%)	T (°C)	CH_4 Conv. (mol%)	T.O.N. (10^{-2} s^{-1})			Space Time Yield (g/kg cat/hr)		Selectivities (C mol%)					
			CH_4	CH_3OH	HCHO	CH_3OH	HCHO	CH_3OH	HCHO	C_2H_6	C_2H_4	CO	CO_2
Wool	625	0.05	—	—	—	3.2	40.1	5.9	79 4	0 0	0.0	0.0	14.6
Blank	625	0.20	—	—	—	20.0	184	8.8	36.0	0.0	0.0	0.0	5 2
1.0	550	0 42	4.27	0.08	1.58	9.1	168.9	1.9	37 0	0 0	0.0	0.0	61.1
	575	0.77	7 80	0 64	2.86	61.9	262.0	8.1	36.6	0.0	0.0	3.0	52.3
	600	4.25	43.2	0 95	5.01	92.7	455.5	2.2	11.6	4 7	15.4	30.9	35 2
	625	10.70	109.6	0.76	5.32	77.6	503.9	0 7	4.9	6.0	15.1	56.5	16 8
2.0	550	0.31	1.58	0.31	0.88	66.0	175.8	19.7	56.0	0.0	0 0	0 0	24.3
	575	1.10	5.61	0.70	0.56	144.8	108.7	12.4	10.0	0.0	25.8	0 0	51.8
	600	2.00	10.2	0 73	1.29	154.5	252.9	7 2	12.6	0 0	20 6	36 0	23.6
	625	3.06	15.6	1.05	2.01	213.0	308.7	6.7	12.9	4.7	11.2	45.8	18.7
	650	4.87	24.8	1.06	1.76	213.2	328.2	4.3	7 1	2.1	9.5	63.0	14.1
3.0	550	0.28	1.14	0 24	0.67	66.5	176.0	20.8	58.8	0 0	0.0	0.0	20.3
	575	0.75	3.06	0.38	1.66	108.4	448.2	12.3	54.4	0.0	0.0	0.0	33.3
	600	1.15	4 69	0.35	2.03	99.9	542.1	7.5	43.3	0.0	0.0	36.4	12.8
	625	1.57	6.41	0.54	2.10	155.0	560.1	8.5	32.8	0 0	0.0	42.1	16.6
	650	1.91	7.79	0.64	2.01	181.4	533.0	8.2	25.8	0 0	0.0	50.1	15.9
5.0	550	0.10	0.27	0.05	0.10	21.3	41.0	18.1	37.2	0.0	0.0	0.0	44.7
	575	1.25	3.36	0.13	0.38	19.9	150.2	1.4	11.4	0 0	0 0	0 0	87.2
	600	1.67	4.48	0.13	0.80	50.9	301.3	2.8	17.9	0.0	0.0	0.0	79.3
	625	2.07	5.56	0.13	0.90	51.0	357.2	2.3	17.0	5.7	17.6	7.4	49 9
10.0	575	1 05	1.36	0.06	0.20	52.4	153.9	4.7	14.7	0.0	0.0	13.1	67 5
	600	1.24	1.60	0.06	0.45	51.4	349.0	3.9	28.2	0.0	0 0	4.1	63 8
	625	1.50	1.94	0.09	0.62	76 6	495.2	4.7	32.2	0 0	12.3	3.3	47.6
	650	1.19	1.56	0.12	0.24	102.6	182.7	8.1	15.4	0.0	16.1	8.4	52.1
20.0	550	0.04	0.05	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100
	575	0.09	0.10	0.00	0.01	0.0	10.5	0.0	10.7	0.0	0.0	0.0	89 3
	600	0.35	0.39	0.00	0.01	0.0	12.0	0.0	3.3	0.0	0.0	0.0	96.7
	625	3.2	3.59	0.00	0.02	0.0	16.7	0.0	0.6	0.0	0.0	0.0	99 4
	650	4.26	4.78	0.00	0.02	2.8	15.2	0.1	0.4	0.0	0.0	0.0	99.6
25.0	550	0.11	—	—	—	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100
	600	2.28	—	—	—	2.9	161.3	0.1	6.6	0.0	0.0	0.0	93.3
	625	2.60	—	—	—	3.1	224.8	0.1	8.5	0 0	0.0	1.5	89.2
	650	3.43	—	—	—	11.7	144.5	0.3	4.2	0.0	0.0	29.1	66.4

yields of methanol and formaldehyde, and the product selectivities that were given in a previous quarterly report [1].

The turnover numbers for the 1.0-5.0 wt% V_2O_5/SiO_2 xerogel catalysts at approximately 1 mol% methane conversion are tabulated in Table 2. This level of conversion was principally observed at a reaction temperature of 575°C. The turnover numbers are expressed as molecules of methane converted per dispersed V atom, where the number of vanadium atoms was determined from NMR analyses as previously noted. While there is scatter in this data, the turnover numbers suggest that methane activation and conversion needs only one type of active site. At higher vanadia contents (>5 wt% V_2O_5), the observed turnover numbers were appreciably lower at reaction temperatures such as 575-600°C, indicating that the active tetrahedral vanadium species in these samples were less available for activation of methane. This lower activity of dispersed V sites as the concentration of this tetrahedrally coordinated type of species increases might be due to polymerization of the active surface-held V to form less active dimers, trimers, etc.

The turnover numbers reported in Table 2 are in the same range as those reported for methane conversion to products from a <u>water-free</u> CH_4/air = 1.5/1.0 reactant mixture over 0.25-5.0 wt% V_2O_5/SiO_2 catalysts prepared by incipient-wetness impregnation of Cab-O-Sil under a N_2 atmosphere using a methanol solution of vanadium(V) triisopropoxide ($VO[i\text{-}OC_3H_7]_3$) [3]. This indicates that the two series of V_2O_5/SiO_2 catalysts that were prepared by significantly different preparation procedures contain vanadium active sites that function in the same way in activating methane. However, the selectivities were significantly different because of the presence of water in the reactant mixture over the xerogel catalysts,

TABLE 2. Turnover numbers for methane conversion to products over V_2O_5/SiO_2 xerogel catalysts from a CH_4 /air/steam = 1.5/1.0/0.56 vol ratio reactant mixture with GHSV = 183,600 ℓ/kg catal/hr at 0.45 MPa.

V_2O_5 Content (wt%)	% Dispersed V [a]	Dispersed V (wt% V_2O_5)	Temp. (°C)	CH_4 Conv.[b] (mol%)	T.O.N. (10^{-2} sec^{-1})
1.0	100	1.0	575	0.77	7.80
2.0	100	2.0	575	1.10	5.61
3.0	81.7	2.5	575	0.75	3.06
3.0	81.7	2.5	600	1.10	4.69
5.0	76.7	3.8	575	1.25	3.36

[a]Expressed as equivalent $\%V_2O_5$, calculated from the intensities of the ^{51}V NMR signal assignable to a T_d environment relative to the total intensities of the ^{51}V peaks, from Reference 2.
[b]From Reference 1.

resulting in a significant productivity of and selectivity toward methanol. In contrast, with the impregnated V_2O_5/SiO_2 catalysts and using water-free CH_4/air = 1.5/1.0 reactant mixture, formaldehyde and CO were formed, but no methanol was produced and the product mixture contained only small quantities of CO_2 (<10% selectivity toward CO_2) [3,4].

Some of the catalytic data are represented in Figure 1 for the production of methanol, formaldehyde, carbon monoxide, and carbon dioxide. It is evident that methanol and formaldehyde were preferentially formed at low reaction temperature over V_2O_5/SiO_2 xerogel catalysts containing 2 or 3 wt% vanadia. On the other hand, carbon monoxide was formed at high reaction temperatures over these same catalysts. Carbon dioxide was preferentially formed when the vanadia content of the catalysts was high, e.g. when

crystalline V_2O_5 was present in the catalysts.

In contrast to the high selectivities of methanol and formaldehyde that were obtained at low reaction temperatures, high productivities of these oxygenate products were obtained at high reaction temperatures, as shown in Figure 2. These results from the higher conversions of methane were achieved at the higher reaction temperatures. Again, catalysts containing lower quantities of V_2O_5 exhibited a preference toward methanol and formaldehyde, while the catalysts containing high vanadia contents formed proportionately larger quantities of carbon dioxide. The same trends for the formation of formaldehyde and methanol are reflected in the calculated turnover numbers, as shown in Figure 3.

The data in Figure 1 show that CO_2 formation is favored by high vanadia content in the catalysts, i.e. when microcrystalline V_2O_5 is present. Formation of CO is favored by higher reaction temperatures and vanadia contents of 2-3 wt% V_2O_5. The selective formation of formaldehyde and methanol is favored by a vanadia content in the range of 2-5 wt% and the lower range of reaction temperatures that were utilized (Figure 1). However, in terms of productivity of formaldehyde and methanol, Figure 2 shows that the middle range of reaction temperatures is beneficial. In terms of turnover numbers for formaldehyde and methanol synthesis, low vanadia contents are desired, as shown in Figure 3, and only catalysts having the lower levels of V^{5+} that is highly dispersed on the surface of the silica support exhibit high activity for the synthesis of these oxygenates.

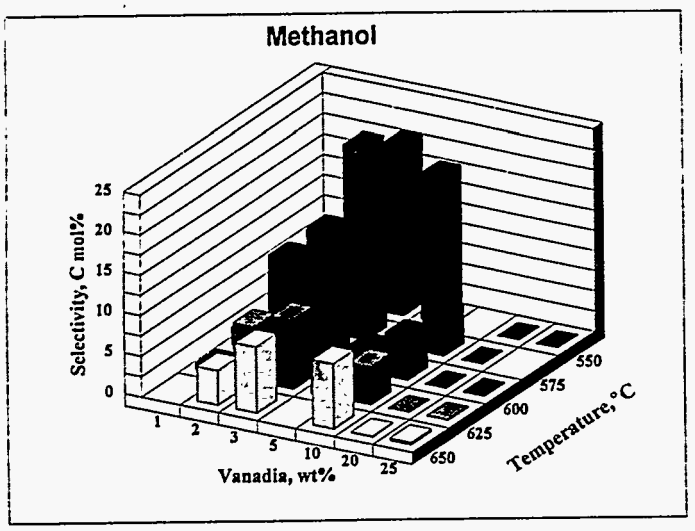
REFERENCES:

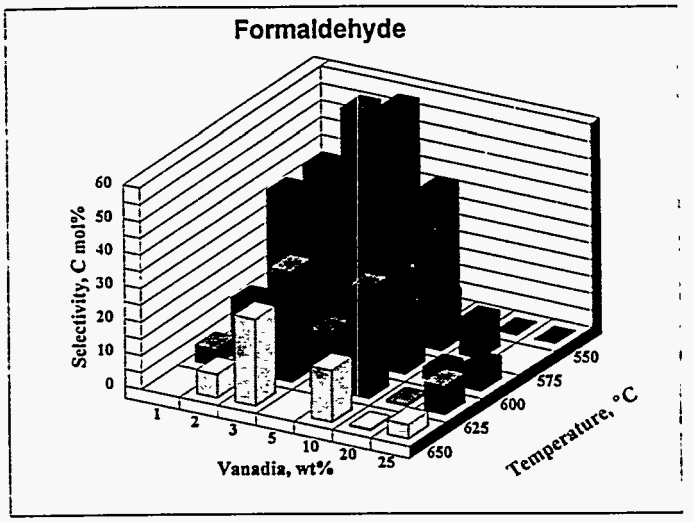
1. Klier, K., Herman, R. G., Wang, C.-B., Shi, C., and Sun, Q., Quarterly Technical Progress Report DOE/MC/29228-11 (August 1995).

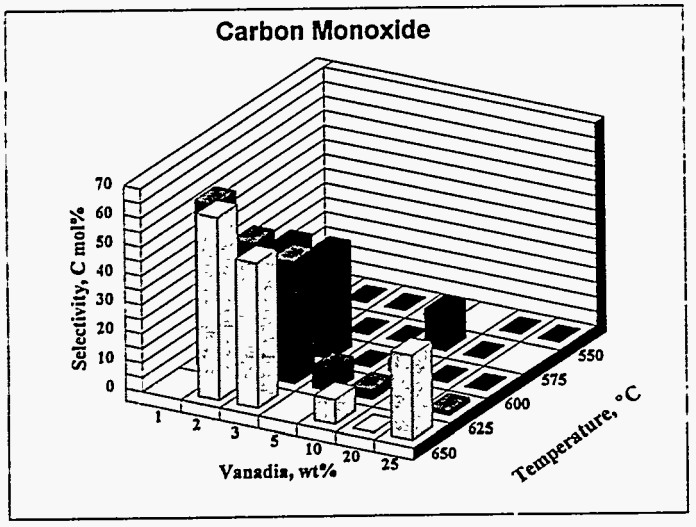
2. Klier, K., Herman, R. G., Wang, and C.-B., Shi, C., Quarterly Technical Progress Report DOE/MC/29228-13 (February 1996).

3. Klier, K., Herman, R. G., Sárkány, J., and Sun, Q., Quarterly Technical Progress Report DOE/MC/29228-5 (January 1994).

4. Sun, Q., Jehng, J.-M., Hu, H., Herman, R. G., Wachs, I. E., and Klier, K., "*In situ* Raman Spectroscopy During the Partial Oxidation of Methane to Formaldehyde over Supported Vanadium Oxide Catalysts," J. Catal. (1996); in press.







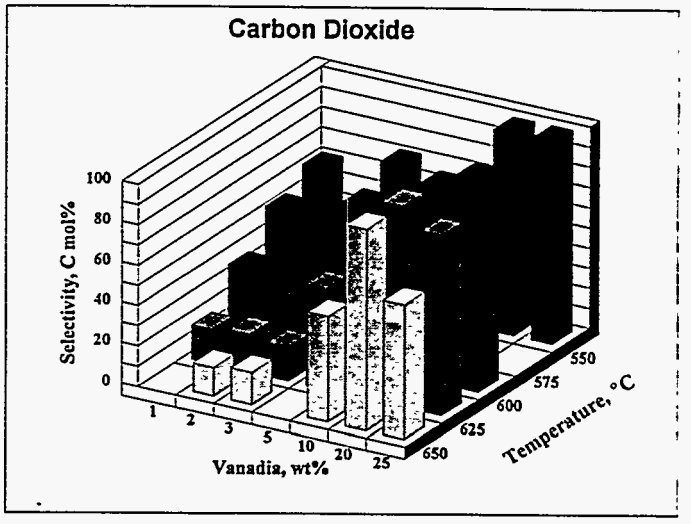
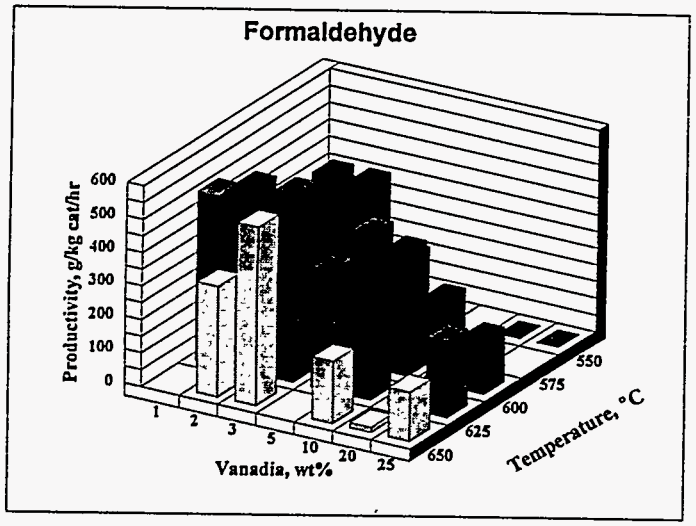


FIGURE 1. Selectivities of products as functions of the reaction temperature and vanadia content of the V_2O_5/SiO_2 xerogel catalysts. Reaction conditions are given in Table 1.



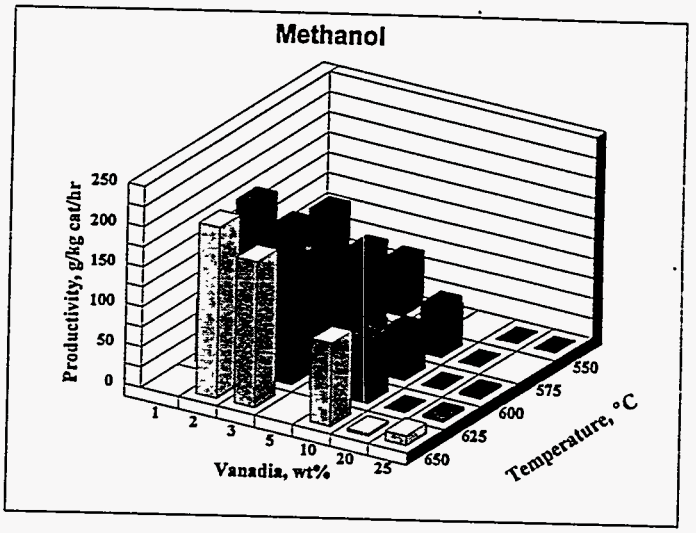


FIGURE 2. Space time yields of formaldehyde and methanol as functions of the reaction temperature and vanadia content of the V_2O_5/SiO_2 xerogel catalysts. Reaction conditions are given in Table 1.

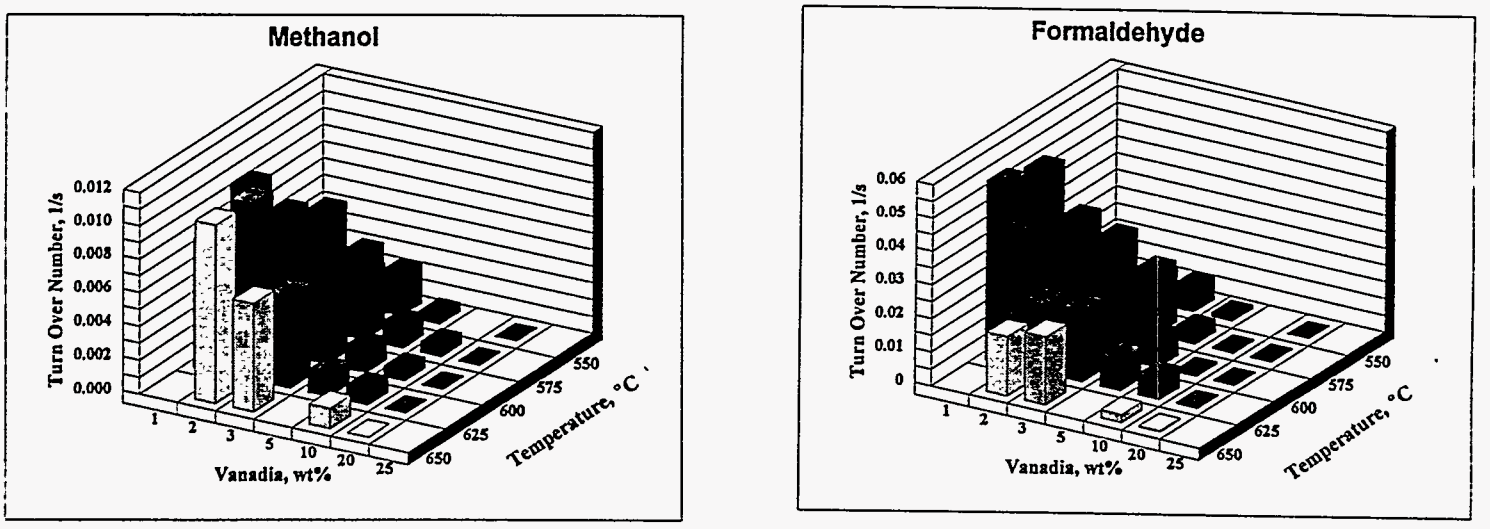


FIGURE 3. Turnover numbers of formaldehyde and methanol as functions of the reaction temperature and vanadia content of the V_2O_5/SiO_2 xerogel catalysts. Reaction conditions are given in Table 1.