Catalysis Letters 2 (1989) 403–412

PARTIAL OXIDATION OF METHANE OVER $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$

Inhee LEE and K.Y.S. NG *

Department of Chemical Engineering, Wayne State University, Detroit, Michigan 48202, U.S.A.

Received 10 February 1989; accepted 22 May 1989

Methane partial oxidation, high temperature superconductor as catalyst

In this communication we report our study on using high-temperature superconductors as partial oxidation catalysts. We have also investigated fluorinated superconducting materials, since the presence of a strong oxidizing agent should favor partial oxidation selectivities.

1. Introduction

The high-temperature superconductor $Y_1Ba_2Cu_3O_{6+X}$ has stimulated extensive research on this class of material. Most studies have focused on electrical properties and microstructures [1–6]. However, little is known of this material's catalytic behavior or chemical reactivity. Recently, two studies were published on the catalytic behavior of superconductor materials [7,8]. Hansen et al. [7] reported that $Y_1Ba_2Cu_3O_{6+X}$ can be used as a catalyst that facilitates both mild and deep oxidation of toluene in the presence of molecular oxygen and ammonia. It was found that it gives better selectivity and activity toward benzaldehyde and benzonitrile in oxidation and ammoxidation of toluene than other oxides such as V_2O_5. Mizuno et al. [8] investigated the reaction of NO with CO over $Y_1Ba_2Cu_3O_{6+X}$, and observed the uptake of large quantities of NO and CO during the reaction. It was believed that NO and CO were absorbed by interaction or reaction in the bulk catalyst, since surface adsorption alone cannot explain the large quantity involved. Eventually, CO_2 and N_2 were produced as major products.

In the past few years, our laboratory has been involved in identifying and fabricating new catalyst materials for partial oxidation of methane. There is still no commercial oxidation process utilizing the direct oxidation mechanism. Direct catalytic partial oxidation of methane to methanol or formaldehyde is more attractive than the energy-intensive two-step process of producing liquid fuels and chemical feed stocks. Liu et al. [9] reported that high selectivity of methanol

---

* To whom correspondence should be addressed.

and formaldehyde could be achieved at very low conversion by the use of molybdenum supported on silica and using N_2O as an oxidant. Similar findings were reported by Khan and Somorjai [10]. Rare earth metal oxides were also studies as potential oxidation catalysts [11]. Otsuka et al. [11] investigated a range of rare earth metal oxides, and found that Sm_2O_3 and Dy_2O_3 are selective catalysts in the oxidative coupling of methane. The C_2-compound's selectivities observed for Sm_2O_3 and Dy_2O_3 using N_2O as the oxidant were as high as 90% at 823 K. However, in case of Y_2O_3, La_2O_3, Pr_2O_3, and Nd_2O_3, the selectivities are 15%, 51%, 45%, and 25%, respectively. With both the Mo-based catalysts and rare-earth metal oxides, high selectivity can be obtained only at low conversions.

In this communication we report our study on using high-temperature superconductors as partial oxidation catalysts. We have also investigated fluorinated superconducting materials, since the presence of a strong oxidizing agent should favor partial oxidation selectivities.

2. Experimental

MATERIALS

The superconducting material $Y_1Ba_2Cu_3O_{6+X}$, was prepared by grinding together a stoichiometric mole ratio of Y_2O_3 (Rare Earth Products, 99.9%), $BaCO_3$ (Aesar, 99.9%) and CuO (JMC, Grade 1). For the fluorinated sample, $Y_1Ba_2Cu_3O_{2+X}F_4$, the desired amounts of Y_2O_3, BaF_2 (JMC, Grade 1), and CuO were mixed and ground. The resulting mixture was heated in air for 10 hr at 950 ° C, cooled slowly for 1 day, reground, and heated at 950 ° C for an additional 10 hr. $Y_1Ba_2Cu_3O_{4+X}F_2$ was prepared by a 1:1 mole ratio mixture of $Y_1Ba_2Cu_3O_{6+X}$ and $Y_1Ba_2Cu_3O_{2+X}F_4$. The mixture was reground and followed by the same treatment procedure outlined above. Cab-O-Sil M-5 (Kodak, Scintillation grade) was used as a support after drying at 120 ° C for 2 hr, followed by calcination at 500 ° C for 4 hr. A 2.0% Mo/SiO_2 was also prepared by the dry impregnation method. It was prepared by dissolving the desired amount of ammonium heptamolybdate in double-distilled water; the solution was impregnated on the support. The resulting mixture was stirred thoroughly and dried at 120 ° C for 2 hr, followed by calcination at 500 ° C for 4 hr. The surface area, as determined by BET measurement, was found to be 175 ± 0.3 m^2g^{-1} for Mo/SiO_2(2%) and to be on the order of 1.0 m^2g^{-1} for $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ catalysts.

REACTOR SYSTEM

A 6 mm I.D. quartz U-tube reactor, with a reduction of I.D. to 2 mm immediately following the catalyst bed, was used. The reactor design, which

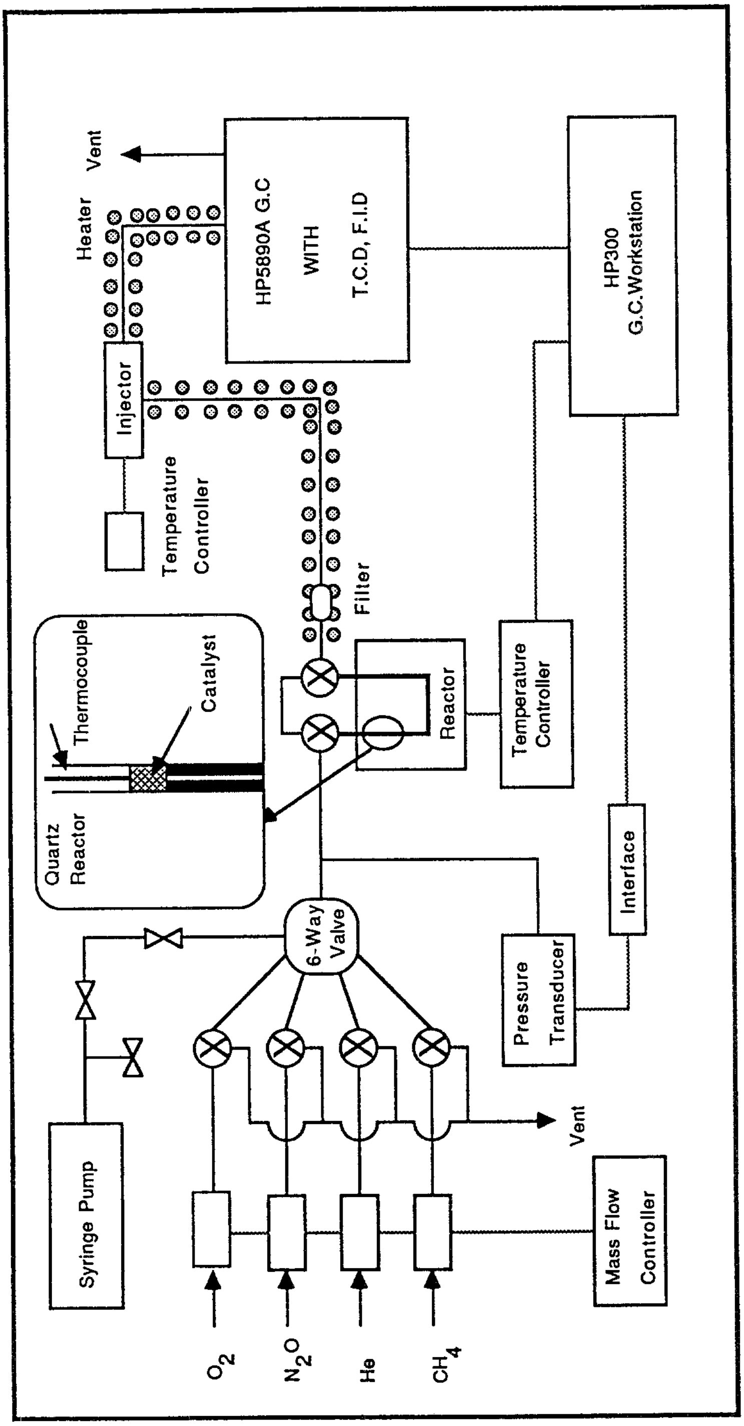

Fig. 1. A schematic of the reactor-gas chromatography system.

allows fast removal of products from the furnace, is intended to minimize the gas phase oxidation reactions. A K-type thermocouple with an Omega temperature controller was used to control the reactor temperature to $\pm 1.0\,^{\circ}$C. The thermocouple was located just above the catalyst bed with the probe touching the catalyst. All the catalyst used in this experiment was in powder form, with a typical weight of 0.375 g. No further pretreatment was performed on the catalysts. Total gas flow rate is 30 c.c./minute with a composition of $CH_4:N_2O:H_2O = 1:4:2$. The compressed gases used–methane (99.99%), nitrous oxide (99.0%), oxygen (99.99%), helium (99.995%), hydrogen (99.9%), nitrogen (99.9985%), and air (zero grade)–were from Air Products and were used as received. The mass flow rates of reactants were controlled by Tylan mass flow controllers to $\pm 0.1\%$. The pressure was measured by an Omega PX304 pressure transducer and the pressure drop across the catalyst bed was found to be less than 2 psia. The whole system is heat-traced with heating wire, and insulated to prevent possible condensation of products and reactants. The products were analyzed using an HP-5890A gas chromatograph equiped with TCD and FID detectors. A 20 ft. Haysep A column and a 10 ft. Porapak QS column were used. A schematic of the reactor-gas chromatography system is shown in fig. 1.

3. Results and discussion

Figure 2 shows the conversion-selectivity relationships for the catalysts that were studied. Most of data were taken four times under identical conditions. The selectivity reported is for formaldehyde. In our studies, only a trace of methanol and C_2-compound were observed. The Mo/SiO_2(2%) catalysts were used to compare the catalytic behavior on the partial oxidation of methane with the $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ ($Z = 0, 2, 4$) catalysts under identical reaction conditions. The conversion-selectivity of the Mo/SiO_2(2%) catalyst is found to be similar to previously-reported values (15% combined selectivity towards methanol and formaldehyde at 14% conversion by Liu et al. [9], and 56% selectivity at 2.6% conversion by Khan and Somorjai [10]). On the other hand, the selectivity as a function of conversion of superconductor compounds is markedly different: instead of a monotonic decrease in selectivity as conversion increases (Mo/SiO_2), the superconducting compounds possess a maximum in selectivity at around 5% conversion. It should be noted that the rate of decrease in selectivity as a function of conversion is much higher in the Mo/SiO_2(2%) system. When conversion of methane is below 5%, the selectivity of Mo/SiO_2(2%) catalyst is found to be higher than $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ ($Z = 0, 2, 4$) catalysts. However, the fluorinated samples, $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ ($Z = 2, 4$), give a higher selectivity than the Mo/SiO_2(2%) catalyst for conversions higher than 5%. In general, it was observed that the higher the fluorinated content, the higher the selectivity. For example, the selectivities observed for the $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ catalysts ($Z =$

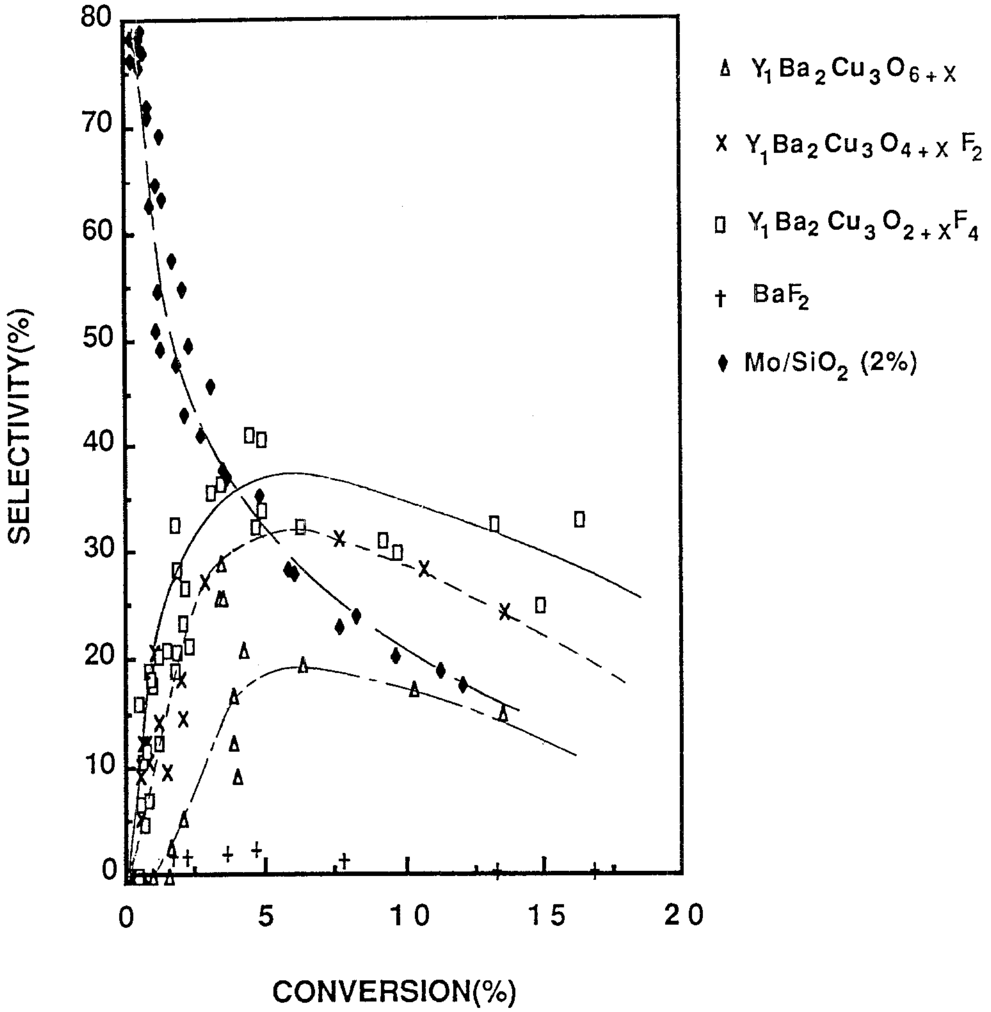

Fig. 2. The conversion-selectivity relationship of Mo/SiO_2(2%), BaF_2, and $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ catalysts. The superconductor samples all have a maximum in the conversion-selectivity curve, which is in contrast to the Mo/SiO_2 catalysts.

4, 2, 0) at 15% conversion are: 30%, 21%, and 12% respectively. It is apparent from this result that on $Y_1Ba_2Cu_3O_{2+X}F_4$ the fluoride has an enhanced effect on selectivity. The incorporation of fluorine in $Y_1Ba_2Cu_3O_{6+X}$ should play an important role in this enhancement, as we can see that BaF_2 itself is not a selectivity catalyst (only a trace amount of formaldehyde was detected at 15% conversion). At present, the structure and the surface active sites of $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ ($Z = 0, 2, 4$) catalysts are not known. According to Ovshinsky et al. [12], multiphases, such as $Y_1Ba_2Cu_3O_{7-\Delta}$, $Y_1Ba_2Cu_3O_X : F$, $Y_2Ba_1Cu_1O_X : F$, $Y_1Cu_2O_X : F$, BaF_2, CuO are present in the bulk $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ ($Z = 0$, 1, 2, 3, and 4) depending on Z. However, some

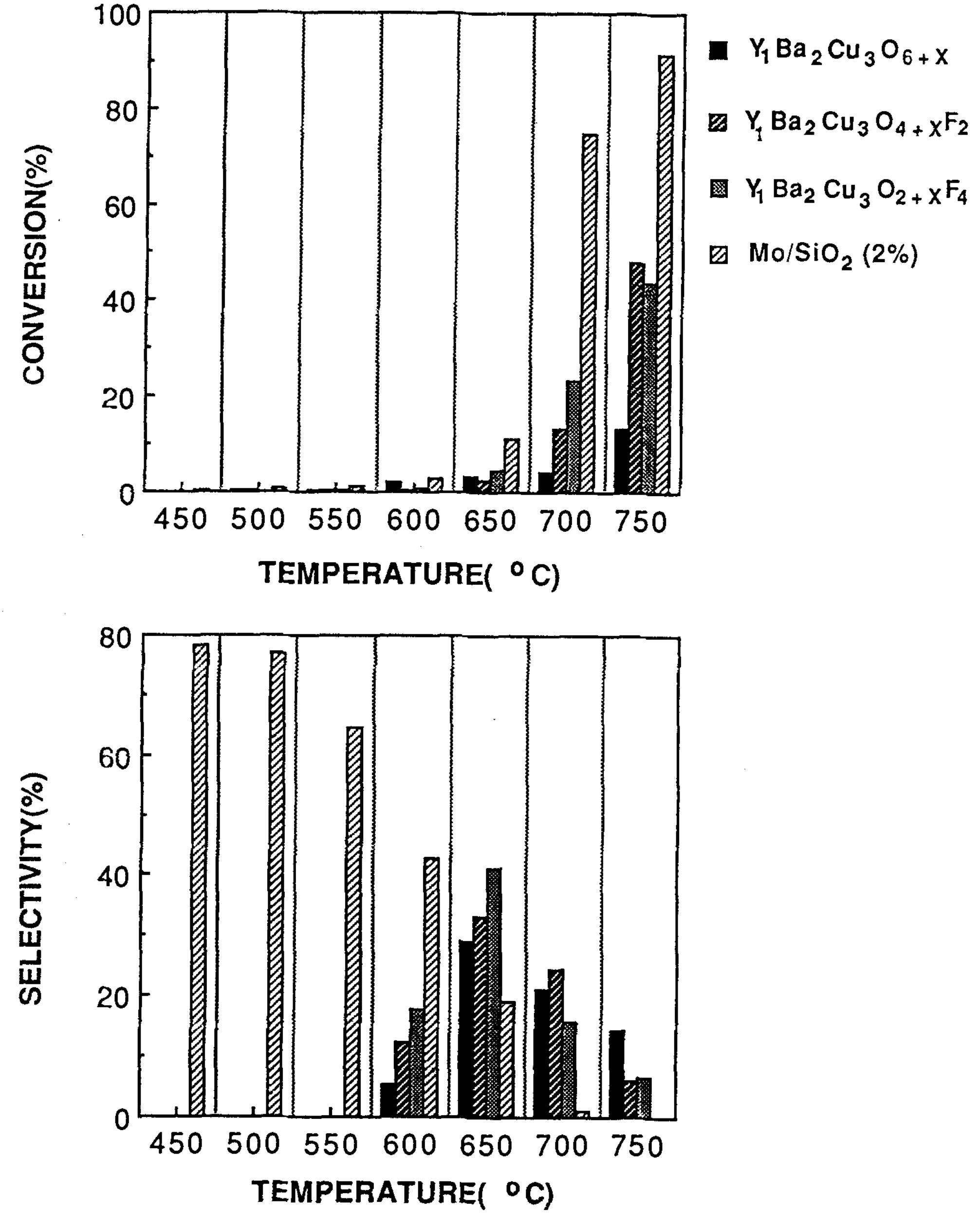

Fig. 3. Effect of temperature on conversion and selectivity of catalysts. Note that superconductor samples have some selectivity even at high temperatures (700, 750 ° C).

XRD studies suggest that no fluorinated $Y_1Ba_2Cu_3O_{7-\Delta}$ species is present through solid state reaction [13,14]. Further experiments are underway to elucidate the effect of fluorine modification on the catalyst structure and on activity and selectivity.

Table 1
Effect of temperature on selectivity and conversion.

Temperature	Catalysts			
	Mo/SiO_2(2%)	$Y_1Ba_2Cu_3O_{6+X}$	$Y_1Ba_2Cu_3O_{4+X}F_2$	$Y_1Ba_2Cu_3O_{2+X}F_4$
	Selectivity (Conversion)	Selectivity (Conversion)	Selectivity (Conversion)	Selectivity (Conversion)
450	78.5 (0.2)	0.0 (0.1)	0.0 (0.1)	0.0 (0.1)
500	77.1 (0.6)	0.0 (0.2)	0.0 (0.2)	0.0 (0.1)
550	64.5 (1.1)	0.0 (0.6)	0.0 (0.4)	0.0 (0.29)
600	42.9 (3.0)	5.2 (2.0)	12.4 (0.6)	17.85 (0.95)
650	19.2 (11.2)	29.3 (3.4)	33.2 (2.6)	40.4 (4.4)
700	1.0 (75.1)	21.3 (4.2)	22.3 (13.5)	13.9 (23.4)
750	0.1 (91.8)	14.3 (13.5)	5.3 (48.1)	6.4 (44.0)

Figure 3 shows the effect of temperature on conversion and selectivity. For Mo/SiO_2(2%), the conversions are 0.2%, 0.6%, 1.1%, 3.0%, 11.2%, and 76% at 450 °C, 500 °C, 550 °C, 600 °C, 650 °C, and 700 °C respectively. It should be noted that the high conversion (76%) data is not reliable because of the significant heat and mass transfer effects; however, the data is included for qualitative comparison purposes. The corresponding selectivities are 78.5%, 77%, 65%, 42.9%, 19.2%, and 1%. This trend toward temperature dependence on conversion-selectivity is typical of Mo/SiO_2 catalysts, as previously reported [9,10]. The relationship suggests that molybdena is a good catalyst for oxydizing formaldehyde to carbon oxides. Therefore, as temperature increases, the selectivities drop significantly. Thus, the total yield of desired products is limited. As for $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ catalysts (fig. 3 and table 1), the conversion of methane increases as a function of temperature. However, the selectivity did not show the same temperature-dependent behavior as the Mo/SiO_2(2%) catalyst. The selectivity curves of the three $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ catalysts have maxima at about 650 °C. These catalysts are not active at 450 °C, 500 °C, and 550 °C. At 600 °C, detectable selectivities were obtained, and the selectivities increase to a maximum as the temperature increases to 650 °C. This is in sharp contrast to the Mo-based system, where an increase in conversion is accompanied by a decrease in selectivity. As temperature increases further, the conversion increases and selectivities decrease. It should be noted that at 700 °C and 750 °C the molybdenum-based catalysts have very poor selectivity, while the superconductor samples can still maintain some selectivity. This suggests that superconductor samples are relatively poor total oxidation catalysts as compared to molybdenum. High conversion coupled with good selectivity should allow a higher total yield of desired products. During our experiments, a reddish film formed on the reactor wall, indicating some possible loss of Cu from the catalyst. It has been reported that water vapor, which is one of the products formed in oxidation, can cause the

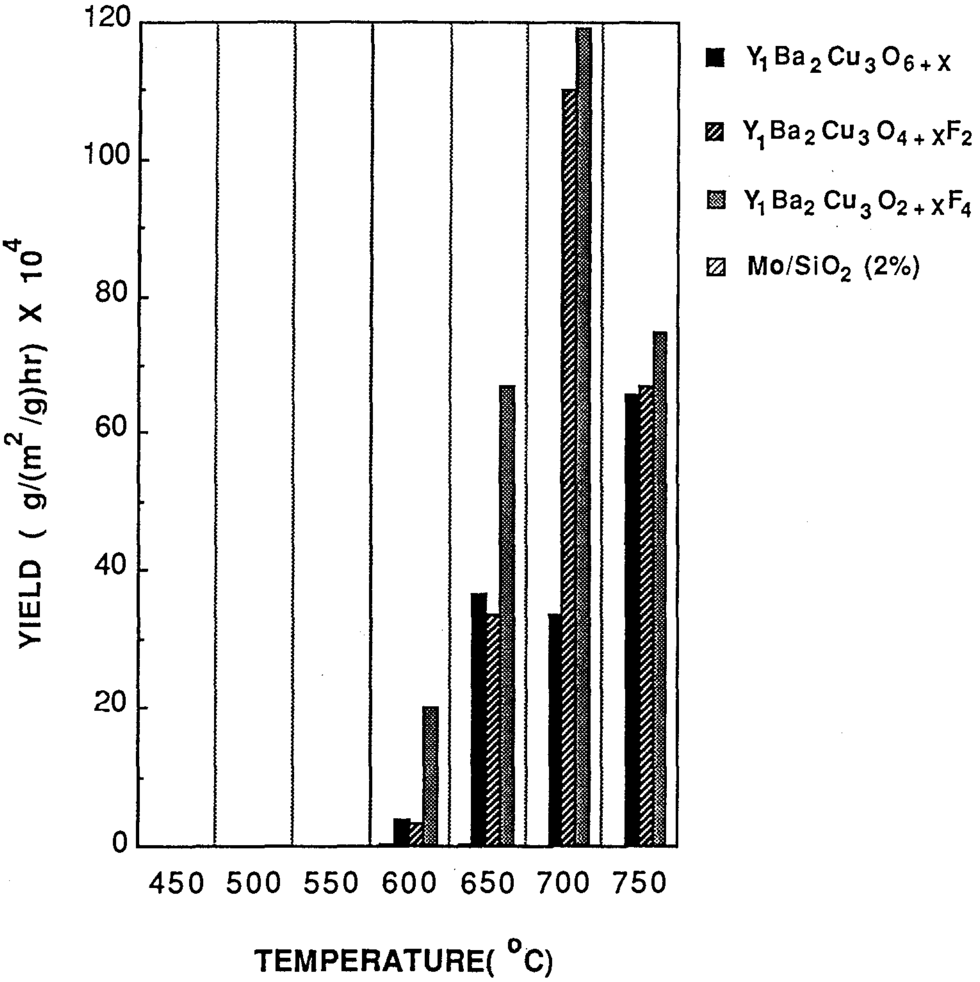

Fig. 4. Effect of temperature on yield based on BET surface area. The yield of Mo/SiO_2, which is 1–2 orders of magnitude lower than the superconductor samples, is too small to be seen on these bar charts.

decomposition of $Y_1Ba_2Cu_3O_{6+X}$ [15,16]. This decomposition is probably due to the presence of nonequilibrium Cu^{3+} ions in this compound. In particular, the $Y_1Ba_2Cu_3O_7$ phase can decompose in the presence of water to CuO, $Ba(OH)_2$, and Y_2BaCuO_5, and oxygen is evolved. Nevertheless, we did not observe significant deactivation during a 24-hour run on the superconductor samples.

Figure 4 shows the effect of temperature on yield. The yield was calculated based on the BET surface area of the catalyst. The surface area, as determined by BET measurement, was found to be on the order of 1.0 m^2g^{-1} for all the $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ catalysts, and 175.2 m^2g^{-1} for the Mo/SiO_2(2%) catalyst. No attempt was made to determine the number of active sites by chemisorption measurements. The temperature-yield relationship observed on the Mo/SiO_2(2%)

catalyst, based on weight of catalyst, is similar to previously-reported results [9,10]. On the other hand, the yield based on BET surface area showed a dramatic difference between the Mo/SiO_2(2%) catalyst and the $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ ($Z = 0, 2, 4$) catalysts. The calculated maximum yield of the Mo/SiO_2(2%) catalyst was 4.5×10^{-5} $g/(m^2g^{-1}hr)$ at 650 °C, but the $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ ($Z = 0, 2, 4$) catalysts gave at least an order of magnitude higher yield. The maximum yield was found to be 6.5×10^{-3}, 1.1×10^{-2}, 1.2×10^{-2} $g/(m^2g^{-1}hr)$ for $Z = 0, 2, 4$ respectively, which indicates that high fluorine content facilitates the production of formaldehyde. As shown in fig. 4, for the temperature range studied the $Y_1Ba_2Cu_3O_{2+X}F_4$ catalyst gave higher yield than the $Y_1Ba_2Cu_3O_{4+X}F_2$ and $Y_1Ba_2Cu_3O_{6+X}$ catalysts. The yield enhancement may be attributed to fluorine being incorporated in the $Y_1Ba_2Cu_3O_{6+X}$, since BaF_2 alone shows much lower activity and selectivity.

4. Conclusion

The partial oxidation of methane over a series of fluorinated superconductor samples was studied. The superconductor samples demonstrated activity and selectivity behavior markedly different from that of the most-studied Mo/SiO_2 catalyst. The selectivity curves of the superconductor samples all show characteristic maxima which are very different from the monotonic decrease behavior observed in the Mo-based catalysts. Moreover, these catalysts also demonstrated relatively poor total oxidation capability, which offers the possibility of obtaining high conversion with reasonable selectivity. In terms of total yield of formaldehyde (based on BET surface area), the superconductors were found to be 1–2 orders of magnitude higher than the Mo/SiO_2 catalyst.

We have demonstrated the potential of using $Y_1Ba_2Cu_3O_{6+X-Z}F_Z$ as a partial oxidation catalyst. These catalysts contain unique active sites that warrant further investigation. Moreover, the promotion effect of fluorine may offer a potential route to further enhancing the total yield. Work is in progress to study the reaction kinetics, the behavior of oxygen as oxidant, the effect of fluorine, and the dispersion of these materials on a support. Characterization of catalyst structure using Auger, FTIR, and Raman spectroscopy is underway.

Acknowledgement

Financial support of this research by American Natural Resources and by Wayne State University's Institute for Manufacturing Research is gratefully acknowledged. The authors would like to thank to Mr. Sendjaja Kao for preparing the superconductor samples, and Mr. Yulin Gu for measuring the BET surface area.

References

[1] I.W. Chen, S.J. Keating, C.Y. Keating, X. Wu, J. Xu, P.E. Reyes-Morel and T.Y. Tein, Solid State Commun. 63(11) (1987) 997.

[2] A. Barkatt, H. Hojaji and K. Michael, Mat. Res. Bull. 23 (1988) 735.

[3] H.W. Zandbergen, R. Gronsky, K. Wang and G. Thomas, Nature 331 (1988) 596.

[4] A. Oumazd, J.A. Rentschler, J.C.H. Spence, M. O'Keeffe, R.J. Graham, D.W. Johnson Jr and W.W. Rhodes, Nature 327 (1987) 308.

[5] D. Kirillov, J.P. Collman, J.T. McDevitt, G.T. Yee, M.J. Holcomb and I. Bozovic, Phys. Rev. B, 37(7) (1988) 3660.

[6] R.M. Macfarlane, H. Rosen and H. Seki, Solid State Commun. 63(9) (1987) 831.

[7] S. Hansen, J. Otamiri, J.O. Bovin and A. Andersson, Nature 334 (1988) 143.

[8] N. Mizuno, M. Yamato and M. Misono, J. Chem. Soc., Chem. Commun. (1988) 887.

[9] H.F. Liu, R.S. Liu, K.Y. Liew, R.E. Johnson and J.H. Lunsford, J. Am. Chem. Soc. 106 (1984) 4117.

[10] M.M. Khan and G.A. Somorjai, J. Cat. 91 (1985) 263.

[11] K. Otsuka and T. Nakajima, Inc. Chim. Acta. 120 (1986) L27.

[12] S.R. Ovshinsky, R.T. Young, D.D. Allred, G. DeMaggio and G.A. Van der Leeden, Phys. Rev. Lett. 58 (1987) 2579.

[13] A.K. Tyagi, S.J. Patwe, U.R.K. Rao and R.M. Iyer, Solid State Commun. 65(10) (1988) 1149.

[14] H.W. Hau, J.M. William, A.M. Kini, H.C.I. Kao, E.H. Appelman, M.Y. Chen, J.A. Schlueter, B.D. Gates and S.L. Hallenbeck, Inorganic Chemistry 27(1) (1988) 5.

[15] M.F. Yan, R.L. Barns, H.M. O'Bryan, Jr., P.K. Gallagher, R.C. Sherwood and S. Jin, Appl. Phys. Lett. 51 (1987) 532.

[16] R.L. Barns and R.A. Laudise, Appl. Phys. Lett. 51 (1987) 1373.