JOURNAL OF SOLID STATE CHEMISTRY **60**, 101–106 (1985)

Preparation of Ferric Tungstate and Its Catalytic Behavior toward Methanol

W. T. A. HARRISON, U. CHOWDHRY, C. J. MACHIELS,
AND A. W. SLEIGHT

Central Research and Development Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

AND A. K. CHEETHAM

University of Oxford, Chemical Crystallography Laboratory, 9 Parks Road,
Oxford, OX1 3PD, England

Received November 14, 1984; in revised form April 1, 1985

Pure ferric tungstate, $Fe_2(WO_4)_3$, has been prepared and characterized for the first time. Ferric tungstate has a structure very similar to that of ferric molybdate with a unit cell volume about 1.5% larger. Decomposition to Fe_2WO_6 and WO_3 occurs at about 600°C. Ferric tungstate was tested as a catalyst for the selective oxidation of methanol and shown to have very different properties from ferric molybdate for this reaction. Whereas over the molybdate the predominant reaction is oxidation of methanol to formaldehyde, over the tungstate it is dehydration to dimethyl ether. © 1985 Academic Press, Inc.

Introduction

The iron/molybdenum/oxygen catalyst system for selective oxidation is of great importance in the chemical industry. Reactions catalyzed include oxidation of propene to acrolein, ammoxidation of propene to acrylonitrile, and most importantly, the selective oxidation of methanol to formaldehyde (*1*). The method was developed as early as 1931 by Adkins and Peterson (*2*), and developed industrially after 1950 (*3–5*). This industrial importance has helped to provide the impetus for detailed studies of the preparation and properties of transition metal molybdates and related systems over the last 15–20 years.

Much less is known about the tungstates of iron than about its molybdates. The only well-characterized tungstate is Fe_2WO_6, first prepared by Kozmanov (*6*), then by Trunov (*7*) by solid-state reaction of Fe_2O_3 and WO_3 at 1000°C. The crystal structure of Fe_2WO_6 has been determined by various workers. Below ca. 800°C Fe_2WO_6 adopts the columbite structure (*8*), and above this temperature the tri-α-PbO_2 structure (*9, 10*). Both are superlattice variants of the basic α-PbO_2 structure. The magnetic (*11, 12*) and photoelectric (*13*) properties of Fe_2WO_6 have recently been investigated.

Ferric tungstate, $Fe_2(WO_4)_3$, was reported by Nassau (*14*) as a compound melting at 1065°C without further details. Pernicone and Fagherazzi (*15*) claimed to have prepared a compound $Fe_2W_3O_{12}$ following

0022-4596/85 $3.00

Kerr's method (*16*), and a high-temperature (700°C) anneal to produce a mixture of $Fe_2W_3O_{12}$ and WO_3; they suggested a tetragonal unit cell for the new tungstate. Very recent work by Tennakone and Dharmaratna suggests that a low-temperature preparation of $Fe_2(WO_4)_3$ undergoes a nonmetal to metal transition at 182°C (*17*). We believe that in fact none of these previous workers prepared crystalline $Fe_2W_3O_{12}$.

Although in many patents on catalysts for methanol oxidation to formaldehyde, tungsten is an additive to the Fe/Mo/O catalyst system, there have been very few reports on the catalytic properties for methanol oxidation of tungstates or tungsten trioxide. Popov *et al.* (*18*) describe experiments with tungsten trioxide and tungstates of Fe(II), Mn, Co, Ni, Cu, and Zn and find all to be selective catalysts for methanol to formaldehyde. Fe(II) tungstate was the most active. Popov (*19*) also studied the Fe–W–O system with atomic ratios of W/Fe varying from 0.5 to 6. He postulated a ferric tungstate phase in his preparations, but there was no positive identification. He found his catalysts to be not very active and they produced mostly formaldehyde. There was no mention of any other products formed.

Mann *et al.* (*20*) studied the properties of mixtures of molybdenum and tungsten oxides. They found maximum activity for methanol oxidation and the lowest selectivity to formaldehyde for pure tungsten trioxide and the reverse for pure molybdenum trioxide. Presumably the only other products are carbon oxides. Klafkowski *et al.* (*21*) studied the systems Fe(III)–O–X, where X = Mo, V, and W, and found the tungstate to be the least active catalyst for methanol oxidation. Again there is no mention of products other than formaldehyde and there is no evidence that ferric tungstate was indeed the phase studied.

In this study, we have for the first time prepared ferric tungstate, $Fe_2(WO_4)_3$, using a precipitation method followed by low-temperature annealing. Previous workers failed to produce crystalline $Fe_2W_3O_{12}$ mainly due to the conditions of calcination. Some (*14, 15*) were too high in temperature, and they actually obtained a mixture of Fe_2WO_6 and WO_3. Others (*17*) were too low in temperature to produce a crystalline product. No previous authors reported an X-ray diffraction pattern similar to the one we observed.

Catalyst Preparation and Properties

Ferric tungstate, $Fe_2(WO_4)_3$, was prepared by a modified version of Kerr's ferric molybdate preparation (*16*), as follows:

(i) Sodium tungstate hydrate, $Na_2WO_4 \cdot 2H_2O$, 20 g (6.06×10^{-2} mole), was dissolved in 200 ml of distilled water at room temperature, resulting in a clear solution.

(ii) Ferric nitrate hydrate, $Fe(NO_3)_3 \cdot 9H_2O$, 16.32 g (4.04×10^{-2} mole), was dissolved in 200 ml of pure water at room temperature, resulting in a yellow solution.

(iii) The nitrate solution was slowly (5 min) added to the tungstate solution while stirring the mixture. A creamy yellow precipitate was formed immediately. The slurry was left stirring for 30 min.

(iv) The mixture was heated to dryness on a steambath overnight, the result being yellowish lumps.

(v) These lumps were ground up and washed with distilled water in a Buchner funnel and dried in a vacuum oven at 100°C for 30 min. This step was repeated twice.

(vi) The resulting yellow powder, completely amorphous to X rays, was fired at 475°C in air for 6 hr to obtain the product, a light yellow powder.

The critical step is the washing of the precipitate. If any traces of sodium nitrate are left at the annealing stage, then Na_2WO_4 is reformed and this phase dominates the resulting powder pattern, along with a minor phase of $NaFe(WO_4)_2$. The tungstate de-

TABLE I

INDEXED POWDER DIFFRACTION PATTERN FOR $Fe_2(WO_4)_3$

h	k	l	d_{cal}	d_{obs}	I_{obs}
2	0	0	6.436	6.434	W
0	1	2	5.803	5.801	W
1	2	0	4.366	4.369	M
2	1	4	4.108	4.104	M+
$\bar{2}$	2	2	3.946	3.943	W
0	2	2	3.937		
$\bar{3}$	1	4	3.922	3.916	M
$\bar{1}$	1	4	3.905		
$\bar{4}$	0	2	3.898	3.888	S
2	0	2	3.873		
2	2	0	3.764	3.765	M
$\bar{4}$	1	2	3.594	3.588	W
2	1	2	3.574		
$\bar{3}$	2	2	3.488	3.478	M
$\bar{3}$	2	2	3.476		
$\bar{2}$	2	4	3.260	3.258	M
4	0	0	3.218	3.220	W
$\bar{4}$	2	2	2.985	2.976	M
$\bar{4}$	0	6	2.977		
2	2	2	2.974		
$\bar{2}$	0	6	2.966		
$\bar{4}$	2	4	2.915	2.909	W
0	2	4	2.901		
0	3	2	2.857	2.856	W

composes to Fe_2WO_6 and WO_3 at elevated temperature, decomposition occurring below 600°C. Thus the earlier high temperature (700°C) solid-state methods of Nassau (*14*) and Pernicone (*15*) could not have produced $Fe_2(WO_4)_3$. The X-ray powder diffraction pattern of $Fe_2(WO_4)_3$ was found to be very similar to that of $Fe_2(MoO_4)_3$, both with regard to line positions and intensities. Thus, the $Fe_2(WO_4)_3$ pattern was indexed by analogy to $Fe_2(MoO_4)_3$. The indexed powder pattern is given in Table I, and a comparison of the tungstate and molybdate unit cell dimensions is given in Table II. It seems highly likely that ferric tungstate has substantially the same structure as the molybdate. Further confirmation of the identity of the new iron phase comes from X-ray microanalysis. Using Fe_2WO_6 as standard (prepared following Trunov's method (*7*)), a Cliff–Lorimer (*23*) analysis gives an iron : tungsten ratio close to that predicted for $Fe_2(WO_4)_3$. The surface area of the ferric tungstate sample was 7.7 m^2/g, determined by the standard N_2 BET method.

Ferric Tungstate for Methanol Oxidation

Three grams of the ferric tungstate sample (10- to 20 mesh particles) was tested for the catalytic oxidation of methanol in a continuous flow reactor with external recycle (*22*). Similar studies with ferric molybdate and other molybdates (*22*) had shown that the product distribution consisted of mainly formaldehyde with small amounts of dimethyl ether, carbon monoxide, and methyl formate. At low methanol conversion and low temperature, there also was a relatively large amount of dimethoxymethane produced as a result of reaction between formaldehyde and methanol. The reaction of methanol over molydates was shown to be nearly zero order in oxygen, between one-half and first order in methanol, and minus one-half order in water. Apparent activation energies were around 20 kcal/mole.

In the reactor study on ferric tungstate, the temperature was varied between 200 and 350°C with most of the experiments in the range 250–325°C. The catalyst showed no loss of activity after 1 week on stream, nor did it appear to have changed; the X-ray powder pattern was identical to that of

TABLE II

UNIT CELL DIMENSIONS

	$Fe_2(MoO_4)_3$	$Fe_2(WO_4)_3$
a (Å)	15.69	15.86
b (Å)	9.23	9.28
c (Å)	18.21	18.32
β (°)	125.25	125.76
Volume (Å³)	2154	2189

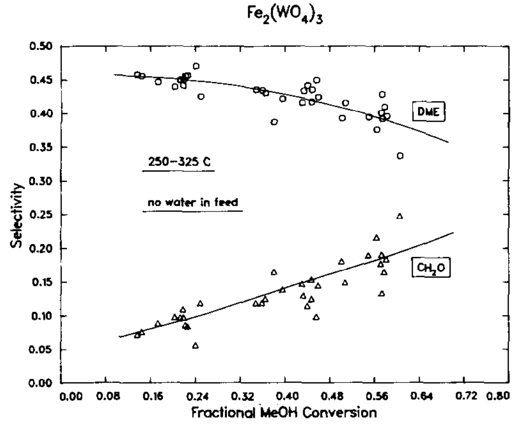

FIG. 1. Product distribution as a function of fractional MeOH conversion.

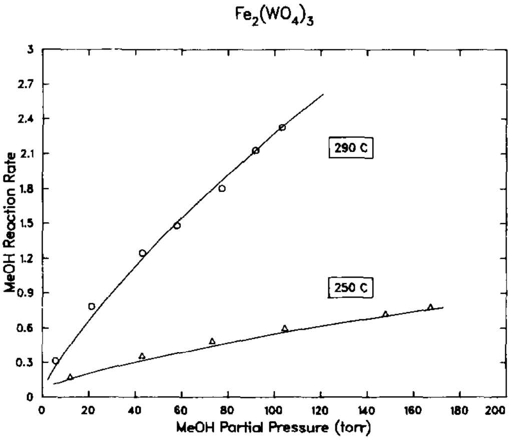

FIG. 3. Reaction rate of methanol versus MeOH partial pressure.

the fresh sample. During the experiments, the concentrations of oxygen and methanol in the feed were varied and in some cases water was also added; nitrogen was used as an inert carrier. The ratio of oxygen to methanol in the reactor and in the effluent varied from 0.2 to 35, that of water to methanol from 0.2 to 2. Methanol conversion varied from 10 to 60%.

Figure 1 shows the product distribution as a function of methanol conversion. Selectivity to a product is defined as the moles of product formed per mole of methanol reacted. No dimethoxymethane, carbon monoxide, or methyl formate was observed. Clearly this catalyst shows a product distribution very different from that of the corresponding molybdate. Dimethyl ether, the dehydration product, is the main product and reaction to formaldehyde is much slower. Addition of water to the feed increases selectivity to formaldehyde and decreases dimethyl ether selectivity similar to the molybdates (*22*).

The kinetics were found to be very similar to the molybdate case: Figures 2, 3, and

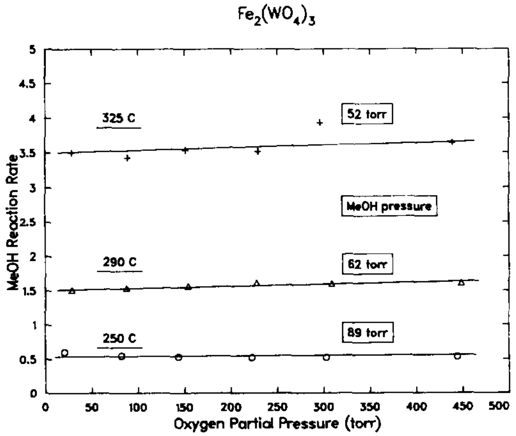

FIG. 2. Reaction rate of methanol versus oxygen partial pressure.

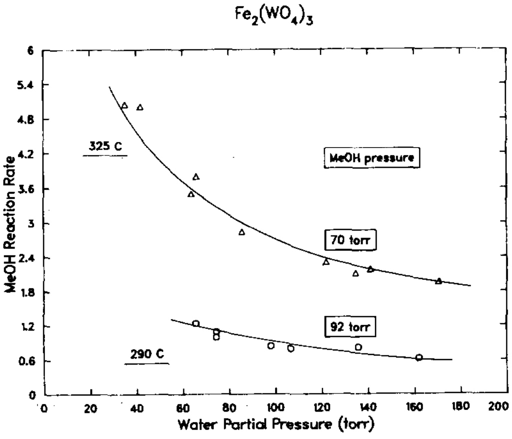

FIG. 4. Reaction rate of methanol versus water partial pressure.

TABLE III

Parameter Values in a Power-Law Rate Expression: Methanol Oxidation over $Fe_2(WO_4)_3$

$$\text{Rate} = k_1 \exp(-E_a/RT)\, P_{O_2}^{k_2} P_{MeOH}^{k_3} P_{H_2O}^{k_4}$$

250–325°C

$k_1 = 0.17 \times 10^9$ (mmol/g · sec · Torr$^{0.29}$)

$E_a = 22.6$ kcal/mole

$k_2 = 0.05$

$k_3 = 0.79$

$k_4 = -0.55$

---

4 show the rate of reaction of methanol as a function of partial pressures of oxygen, methanol, and water, respectively, keeping all other partial pressures constant. All the experimental data were also fitted to a rate expression of the power-law type which yielded an excellent fit with parameters listed in Table III. These parameter values are very similar to those for the molybdate, but the activity of the tungstate per unit surface area is approximately 7 times lower. Closer examination shows that ferric tungstate and ferric molybdate have nearly identical reaction rates of methanol to dimethylether, but the reaction rate to formaldehyde is about 20 times smaller for the tungstate and this leads to the very different production distribution.

The reason for the difference in the catalytic properties of $Fe_2(MoO_4)_3$ and $Fe_2(WO_4)_3$ is most likely related to the ease of reduction of molybdates vs tungstates. The rate of methanol oxidation is a function of the number of surface methoxys and their rate of oxidation. If we assume similar surface coverages under similar conditions for both $Fe_2(MoO_4)_3$ and $Fe_2(WO_4)_3$, the rate of methoxy oxidation depends on the relative rates of reduction of the two compounds. (The rate of reoxidation of these compounds is not rate limiting as evidenced by the near zero-order dependence on oxygen partial pressure.) Since Mo^{6+} is a stronger oxidizing agent than W^{6+}, methanol oxidation will occur at a faster rate on a molybdate than on an isostructural tungstate. The relative rates of dimethyl ether formation over $Fe_2(MoO_4)_3$ and $Fe_2(WO_4)_3$ are essentially the same because this reaction does not involve redox chemistry.

Acknowledgement

We are grateful for assistance from C. Foris in the indexing of the $Fe_2(WO_4)_3$ powder pattern.

References

1. J. F. Walker, "Formaldehyde," Reinhold, New York (1964).
2. H. Adkins and W. R. Peterson, *J. Amer. Chem. Soc.* **53,** 1512 (1931).
3. P. Jiru, B. Wichterlova, and J. Ticky, "Proc. 3rd International Congress on Catalysis, Amsterdam 1964," p. 199.
4. M. Dente, R. Poppi, and I. Pasquon, *Chim. Ind. (Milan)* **46,** 1326 (1964).
5. M. Dente and I. Pasquon, *Chim. Ind. (Milan)* **47,** 359 (1965).
6. Yu. D. Kozmanov, *Zh. Fiz. Khim.* **31,** 1861 (1957).
7. V. K. Trunov and L. M. Kovba, *Izv. Akad. Nauk SSSR Neorg. Mater.* **2,** 151 (1966); *Inorg. Mater. (Engl. Transl.)* **2,** 127 (1966).
8. C. Parant, J. C. Bernier, and A. Michel, *C. R. Acad. Sci. Paris Ser. C* **276,** 495 (1973).
9. J. Galy and J. Senegas, *C. R. Acad. Sci. Paris Ser. C* **275,** 665 (1972).
10. J. Galy and J. Senegas, *J. Solid State Chem.* **10,** 5 (1974).
11. H. Weitzel, *Acta Crystallogr. A* **32,** 592 (1976).
12. H. Pinto, M. Melamund, and H. Shaked, *Acta Crystallogr. A* **33,** 663 (1977).
13. H. Levia, K. Dwight, and A. Wold, *J. Solid State Chem.* **42,** 41 (1982).
14. K. Nassau, H. J. Levenstein, and G. M. Loiacono, *J. Phys. Chem. Sol.* **26,** 1805 (1965).
15. N. Pernicone and G. Fagherazzi, *J. Inorg. Nucl. Chem.* **31,** 3323 (1969).
16. P. F. Kerr, A. W. Thomas, and A. M. Langer, *Amer. Miner.* **48,** 14 (1963).
17. K. Tennakone and W. L. D. Dharmavanta, *J. Chem. Soc. Faraday Trans. 1* **78,** 1699 (1982).
18. G. Bliznakov, T. Popov, and D. Klissurski,

Izv. Inst. Obshta Neorg. Khim. Bulg. Akad. Nauk, **4,** 83 (1966).

19. T. Popov, "Proceedings, 4th International Symposium on Heterogeneous Catalysis, Sofia, Bulgaria," p. 291 (1979).

20. R. S. Mann, S. K. Jain, and M. K. Dosi, *J. Appl. Chem. Biotechnol.* **27,** 198 (1977).

21. A. Swinarski and W. Klafkowski, *Rev. Roum. Chim.* **23,** 171 (1978).

22. C. J. Machiels and A. W. Sleight, "4th International Conference, Chemistry and Uses of Molybdenum, Golden, Colorado, 1982" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 411.

23. G. Cliff and G. W. Lorimer, *J. Microsc. (Oxford)* **103,** 203 (1975).