METHANE OXIDATION OVER DUAL REDOX CATALYSTS

Quartely Technical Report Progress Report
April-June, 1989

Kamil Klier, Richard G. Herman, and Zbigniew Sojka

Zettlemoyer Center for Surface Studies
and
Department of Chemistry
Lehigh University
Bethlehem, PA 18015

June 1989

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Prepared for

U. S. DEPARTMENT OF ENERGY
Morgentown Energy Technology Center
Under Contract No. DE-FG21-89MC26039

7/28/92
Wan
MASTER
do

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

METHANE OXIDATION OVER DUAL REDOX CATALYSTS

DE-FG21-89MC26039

INTRODUCTION

The objective of this research is to develop the scientific background for direct catalytic oxidation of methane over oxides that are doubly doped with transition metal ions. The desired process aims at employing of a double redox mechanism, where one redox couple is utilized for activation of oxygen and another for the conversion of $\text{CH}_3^\cdot$ radicals to carbocations via electron transfer reaction. The latter species can react with surface OH^- groups to form methanol or formaldehyde.

To establish the foundations for such a process, two groups of the catalysts, one containing dispersed redox centers ($\text{Cu}^{\text{I}}/\text{Fe}^{\text{III}}/\text{ZnO}$ and $\text{Cu}^{\text{I}}/\text{Sn}^{\text{IV}}/\text{ZnO}$) and a second of delafossite-type oxides containing concentrated redox centers (CuFeO_2 , CuCoO_2) were synthesized and chemically analyzed for composition. For the sake of comparison, undoped ZnO treated in the same way as doped zinc oxide catalysts was also prepared. The samples were characterized by X-ray diffraction, BET surface area measurements and preliminarily by scanning electron microscopy.

A catalytic testing unit and reactor to study the title reaction were designed and constructed.

TECHNICAL PROGRESS

1. Catalyst preparation.

1.1. $\text{Cu}^{\text{I}}/\text{Fe}^{\text{III}}/\text{ZnO}$.

$\text{Cu}^{\text{I}}/\text{Fe}^{\text{III}}/\text{ZnO}$ catalysts were prepared by firing at 1000°C a mixture composed of Cu_2O , hydrous Fe_2O_3 and of ZnO . The samples were previously treated at 400°C for 2 h in dry and oxygen free nitrogen. The general three-step preparation procedure is depicted in Fig. 1a. It involves preparation of starting oxides by precipitation from nitrate solutions and thermal decomposition, two-step mixing of the oxides by grinding in alumina mortar, and finally thermal treating the samples according the program shown in Fig. 1b to form solid solutions.

Hydrous iron oxide was obtained by adding 5% NH_4OH (5 ml/min) to a 75.96 g of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ dissolved in 1000 ml of distilled water at 50°C to reach the final pH of 4.13. After washing until no presence of nitrate was detected in the effluent, the reddish brown residue was filtered and dried for 3 weeks. The actual content of Fe (61.42 %) was determined by titration with 0.01 N KMnO_4 according to the Zimmermann-Reinhard method [1]. This corresponds to the stoichiometric formula $\text{Fe}_2\text{O}_3 \cdot 1.23\text{H}_2\text{O}$. The phase composition determined by X-ray diffraction shows the presence of hematite (three most intense lines at 2.70, 2.52, 1.67 Å; ASTM card 24-72) and goethite (peaks at 4.18, 2.69, 2.45 Å; ASTM card 17-536) in proportion of 40 and 60 %. Zinc oxide was obtained by thermal decomposition at 350°C for 50 h of hydrozincite prepared as described in [2]. Cuprous oxide was obtained by thermal decomposition of copper hydroxycarbonate at 1050°C and cooling to room temperature in a stream of nitrogen. All oxides were preliminarily ground for 1 h. In order to assure a good dispersion and stoichiometry of the doped zinc oxide catalysts, an equimolar mixture of Cu_2O and $\text{Fe}_2\text{O}_3 \cdot 1.23\text{H}_2\text{O}$ was prepared by grinding 4.2924 g of cuprous oxide with 4.7907 g of hydrous iron oxide for 1 h. Then 1.1576 g of this mixture was intimately mixed for 2 h with 56.8176 g of ZnO until a uniform pale pink powder was obtained. The actual chemical composition of the starting oxide mixture corresponded to $\text{Cu}_{1.02}\text{Fe}_{1.07}\text{Zn}_{97.91}\text{O}$ as determined by atomic absorption spectroscopy. The samples were thermally pretreated in a stream of deoxygenated and water free nitrogen at 400°C for 2 h in specially constructed Pyrex glass apparatus, which enabled a direct transfer of the samples to attached quartz vessels for further evacuation (2 h) and high temperature treatment. Typically the samples were fired in closed evacuated silica vessels for 18 h at 1000°C and for 22 h at 1000°C in evacuated or open to air quartz ampoules. For the sake of simplicity, these samples will be labelled as Cu/Fe/ZnO-18v , Cu/Fe/ZnO-22v and Cu/Fe/ZnO-22a , respectively. After the different thermal treatments a change of color was observed, the samples heated at 400°C became pale blue, while those fired at 1000°C in evacuated vessels were black, and those fired in air at 1000°C were gray.

1.2 Cu^I/Sn^{IV}/ZnO.

Cu^I/Sn^{IV}/ZnO catalysts were prepared according to the same procedure as described above. Hydrous tin oxide was obtained according to Ref. [3] by rapid mixing of 100 ml of 2M solution of SnCl₄ with an equivalent amount of NH₄OH. Purification of the white precipitate was achieved by successive washing with distilled water for 30 days until no positive reaction for Cl⁻ ions was obtained. The formed gel was dried at room temperature for two weeks and then chemically analyzed by atomic absorption. It contained 69.4% of tin, which corresponds to the empirical formula SnO₂·x1.13H₂O. After 2 h of grinding of 1.0995 g of the equimolar mixture of Cu₂O + SnO₂·x1.13H₂O with 56.1178 g of ZnO, a starting pale pink mixed oxide was obtained. Its composition was determined by atomic absorption to be Cu_{0.01}Sn_{0.0046}Zn_{0.9854}O. After firing at 1000°C the Cu/Sn/ZnO-18v and -22v samples became beige and Cu/Sn/ZnO-22a became green.

Additionally three undoped ZnO samples ZnO-18v, ZnO-22v and ZnO-22a were obtained exactly in the same way. They exhibited a yellow color after the final thermal treatment.

1.3. CuFeO₂.

CuFeO₂ was obtained from Cu₂O (certified Fisher) and Fe₂O₃ (C.P. Baker) according to the reaction Cu₂O + Fe₂O₃ → 2 CuFeO₂ [4]. A stoichiometric mixture of both oxides was homogenized by grinding in an alumina mortar for 2 h, pelleted under the pressure of 3 tons/cm², crushed, put into a quartz vessel, and then evacuated to 10⁻⁴-10⁻⁵ Torr for 2 h. The sample was fired at 1050 °C for 4 days until almost only single phase delafossite was detected by X-ray diffraction (ASTM card 12-752). An impurity phase exhibiting d spacings 2.344, 2.03, and 1.31 Å was completely removed after leaching with 1 N HNO₃ [4].

1.4. CuCoO₂.

A CuCoO₂ catalyst was prepared by the exchange reaction CuCl + LiCoO₂ → CuCoO₂ + LiCl as described by Shannon et al. [5]. Starting reagents CuCl (Aldrich) and LiCoO₂ (Johnson-Matthey) were mixed in a nitrogen-filled glove box, pressed (3 tons/cm²) and heated in an evacuated silica tube for 4 days at 600 °C. The reaction product was recovered as a black powder by washing with water to remove LiCl byproduct and subsequently with 1 N HNO₃.

2. Characterization of the catalysts.

2.1 Surface area and particle size.

The ZnO and doped ZnO catalysts were routinely examined for the surface area by the BET method using argon adsorption at liquid nitrogen

temperature. Typically about 2 g of the sample were evacuated at 150°C at 10^{-3} Torr for at least 6 h prior to the surface area determination. Helium was used to calibrate the dead volume.

The average particle size diameter t_d was estimated from the broadening of the XRD diffraction peaks by use of the Scherrer formula [6]:

$$t_d = 0.9\lambda / (B_d^2 - B_s^2)^{1/2},$$

where λ is the X-ray wavelength, B_d is the broadening of the diffraction line at half its maximum intensity and B_s is the diffractometer constant determined from X-ray patterns of Si and NaCl standards.

The results of the BET surface and particle size determination are presented in the form of a histogram in Fig. 2.

The values of surfaces area 0.6-0.45 m²/g for pure ZnO and 0.5-0.25m²/g for the doped zinc oxide conform well with the literature [7,8]. For all samples, the surface areas decreased with increasing time of firing and exhibited lower values when sintered in air for the same time as in evacuated vessels, which was previously observed by Gray for pure ZnO [9]. The undoped zinc oxide samples exhibited higher surface areas compared to doped catalysts, indicating that doping of ZnO with the Cu, Fe or Sn ions facilitates the sintering process. The promotion effect of doping by transition metal ions on sintering of oxides was attributed by Morgan et al. to an increase of lattice diffusion induced by the additives [10].

The particle sizes determined from XRD varied from 400- 520 Å for Cu/Sn/ZnO catalysts to 900-1100 Å for ZnO and Cu/Fe/ZnO samples. The latter values, despite the considerable error caused by the small broadening of X-ray lines by particles larger than 1000 Å, remains in good agreement with the data obtained from electron microscopy. Analysis of electron micrographs of the Cu/Fe/ZnO-22v and Cu/Fe/ZnO-22a catalysts prove that most (about 60%) particles were of 1000-1500 Å of diameter. An example of an electron micrograph of the Cu/Fe/ZnO-22a sample is presented in Fig. 3.

There is no apparent relationship between the surface area and crystallite size. Pure ZnO catalysts having the greatest values of surface area had also the largest particle dimensions and vice versa, the Cu/Sn/ZnO-22v and Cu/Sn/ZnO-22a samples exhibited the lowest surface areas together with the smallest crystallite sizes (Fig. 2). These results indicate that the samples either have different microporosity (caused by different rates of crystallite and particle growth [11] of pure and doped ZnO), or that additional X-ray line broadening takes place due to extra lattice imperfections caused by doping. This latter effect is especially pronounced in the case of tin doped catalysts.

2.2. Phase and lattice parameter determination.

2.2.1. Phase analysis.

The X-ray diffraction patterns were recorded in the 30-150°(2 θ) range with a Philips Diffractometer using CuK α radiation. The samples were exposed to air during measurements or recorded in nitrogen atmosphere in an air-tight sample holder equipped with 3.6 μ thick mylar film window for X-ray penetration. The six highest angle α_2 reflections of zinc oxide indexed as 302, 006, 205, 106, 214, 220, which gave well resolved α_1 - α_2 doublets, were

utilized for lattice parameter determination by least squares procedure of Appleman and Evans [12].

The typical X-ray diffraction pattern of undoped zinc oxide treated at 1000°C is presented in Fig. 4. It shows distinct lines as listed in the ASTM card No 5-0664. However, five weak peaks listed in Table 1, do not conform with a hexagonal lattice with typical zinc oxide parameters. Their appearance may be explained by a disorder of the lattice caused by the layer stacking sequence fault. In the perfect hexagonal lattice, the atoms in the second layer are above hollows in the first layer and the atoms of the third layer reproduce the positions the atoms in the first layer. This results in the stacking sequence of the type ABABAB etc. However, if in some places of ZnO crystallite the atoms of the third layer were displaced to the hollows of the second layer so that it does not reproduce the first layer, the stacking sequence becomes partially irregular ABABCABABABADCABAB etc. This results in the change of the lattice type from hexagonal to face centred cubic in the regions of ABC type stacking and will produce extra lines in XRD pattern. The diffraction peaks positions calculated on the base of this model (Table 1) agree very well with the experimentally observed positions of extra lines. However, the value of lattice parameter $a = 4.06 \text{ \AA}$ of this cubic unit cell is smaller then that observed for the cubic form of zinc oxide, $a = 4.28 \text{ \AA}$ [13].

Table 1

Comparison of the experimental and calculated positions (d spacings) of extra lines observed in zinc oxide with layer stacking fault, assuming the cubic lattice parameter $a = 4.06 \text{ \AA}$.

$d_{\text{obs.}}$	I/I'_0	$d_{\text{calc.}}$	hkl
2.34	0.2-0.4	2.34	111
2.03	3.-1.4	2.03	200
1.43	0.25	1.436	220
1.22	3.4-2.5	1.22	311
1.12	2.-1.6	1.17	222

I'_0 is the intensity of the strongest line in the whole pattern.

The XRD patterns of all Cu/Fe/ZnO catalysts after sintering at 1000°C showed the absence of any other diffraction peaks than that already stated for pure ZnO (Fig. 5), indicating formation of solid solutions. In the case of Cu/Sn/ZnO samples (Fig. 6) five new weak peaks (listed in Table 2) were also detected and described to Zn_2SnO_4 , in addition to the lines characteristic for ZnO phase.

Table 2

Comparison of the XRD peak positions, d-spacings, and relative intensities attributable to Zn_2SnO_4 .

$d_{\text{obs.}}$	I/I'_0	d_{ASTM}	I/I_0	hkl
2.16	0.4	2.165	25	400
1.76	0.34	1.768	7	422
1.66	0.8	1.665	30	511
1.53	1.52	1.53	35	440
0.995	1.5	0.9905	8	751

I'_0 is the intensity of the strongest line in the whole pattern.

All other lines of relative intensity greater than 8 (hkl indices 311, 533, 622, 731, 844, 951) are coincident with the positions of ZnO peaks.

This result indicates that in the case of Cu/Sn/ZnO catalysts a partial segregation takes place, probably caused by the volatility of tin dioxide [14].

2.2.2. Variation of lattice parameter.

The incorporation of the Cu, Fe and Sn ions into the zinc oxide matrix is directly proven by the variation of the lattice parameters a , axial ratio $C = c/a$ and unit cell volume V (Figs. 7,8). The experimental results show that while a and V increase, the axial ratio C decreases upon doping of ZnO. Assuming that all dopant cations will occupy substitution positions for zinc, and taking into account the values of ionic radii of Cu^+ , Fe^{3+} , Sn^{4+} and Zn^{2+} equal to 0.96, 0.65, 0.69 and 0.75 Å respectively., it would be expected that replacement of two Zn^{2+} ions by the $\text{Cu}^{1+}\text{-Fe}^{3+}$ couple and three Zn^{2+} ions by $2\text{Cu}^{1+}\text{-Sn}^{4+}$ ensembles would expand the lattice as observed. A simultaneous decrease of the axial ratio C indicates that this deformation is anisotropic. Similar deformation of the lattice, i.e. increase of lattice parameter a accompanied by decrease of axial ratio C upon doping of zinc oxide with tri- (In, Ga) and divalent (Cu, Co) ions was observed by Cimino [14] and Schiavello et al. [8,15].

The lattice parameter determined for undoped ZnO $a = 3.2498$ Å remains in good agreement with the values obtained by Cimino for ZnO fired at 1000°C ($a = 3.2498$ Å), but is slightly greater than that obtained for spectroscopically standardized ZnO ($a = 3.2495$ Å) [16]. The value of parameter a is affected by the presence of interstitial zinc, and the $\Delta a/a$ ratio is of the same order of magnitude as Zn_i/ZnO [16]. This allows an estimate of the concentration of interstitial zinc in the samples fired at 1000°C to be of an order of 60 ppm.

3. High temperature reaction system.

A new reactor and associated heating unit operating up to 1200K has been designed and constructed. The split cylindrical furnace consists of

three heating zones, each controlled independently in PID (Proportional-Integral-Derivative) regime, so that very good temperature control can be maintained. The tubular quartz reactors of 6, 9, 12 mm of OD are connected to capillary quartz tubing of 2mm ID to rapidly remove products from the heated zone. In the reactor of 12mm OD the thermocouple is axially centered in the reactor (Fig. 9b), and for the reactors with 6 and 9 mm OD, it is placed parallel in outside quartz capillary attached directly to the reactor wall. In both cases the tip of the thermocouple can be displaced to measure the temperature gradient in the reactor, or be located close to catalyst bed. A schematic of the reaction system that will be used for testing the synthesized double redox catalysts for methane oxidation at temperatures up to 1200K is shown in Fig. 9a, b.

REFERENCES

1. A.I. Vogel, "Quantitative Inorganic Analysis", J.Wiley Pub., 1961, p.287
2. K. Klier, R.G. Herman, Z. Sojka, "Report DOE/MG/26039-1", 1989
3. E.W. Giesekke, H.S. Gutowsky, P. Kirkov, H.A. Laitinen, Inorg. Chem., 1967,6, 1294
4. J.P. Doumerc, A. Wichainchai, A. Ammar, M. Pouchard, P. Hagemuller, Mater. Res. Bull., 1986,21,745
5. R.D. Shannon, D.B. Rogers, C.T. Prewitt, Inorg. Chem., 1971, 10, 713
6. B.D. Cullity, "Elements of X-ray Diffraction", Addison-Wesley Pub., 1978, 284
7. P. Schindler, H. Althaus, W. Feitknecht, Helv. Chim. Acta, 1964, 47,982 and 1965,48,1204
8. M. Schiavello, F. Pepe, S.De Rossi, Z. Physik. Chem. Neue Folge, 1974, 92,109
9. T.J. Gray, J. Am. Ceram. Soc., 1954,37,534
10. P.E.D. Morgan, A.J.E. Welch, "Reactivity of Solids", Proc. of 4-th Intern. Symp. 1960, J.H. de Boer Edit., Elsevier, 1961, p.105
11. D. Louer, R. Vargas, J-P. Auffredic, J. Am. Ceram. Soc., 1984,67,136
12. D.E. Appleman, H.T. Evans Jr., U.S. National Technical Information Service, PB2-16188, 1973
13. C.H. Bates, W.B. White, R. Roy, Science, 1962,137,993
14. A. Cimino, G. Mazzone, P. Porta, Z. Physik. CXhem. Neue Folge, 1965,45,153
15. F. Pepe, M. Schiavello, G. Ferraris, J. Solid State Chem., 1975,12,63
16. A. Cimino, G. Mazzone, P. Porta, Z. Physik. Chem. Neue Folge, 1964, 41,154
17. C.W. Tucker, J.B. Sampson, Acta Metallurgica, 1954,2,433

Figure Captions

- Fig. 1a Preparation scheme for Cu and Fe doped zinc oxide catalyst.
1b Temperature program for thermal treatment of doped ZnO catalyst.
- Fig. 2 BET surface area and XRD crystallite sizes for ZnO, Cu/Fe/ZnO and Cu/Sn/ZnO samples. ZO1 stands for ZnO-18v, CSZO1 for Cu/Sn/ZnO-18v, CFZO1 for Cu/Fe/ZnO-18v, ZO2 for ZnO-22v, CSZO2 for Cu/Sn/ZnO-22v, CFZO2 for Cu/Fe/ZnO-22v, ZO3 for ZnO-22a, CSZO3 for Cu/Sn/ZnO-22a and CFZO3 for Cu/Fe/ZnO-22a.
- Fig. 3 Electron micrographs of Cu/Fe/ZnO-22a catalysts.
a. 14,000 magnification, b. 64,000 magnification.
- Fig. 4 XRD pattern of undoped zinc oxide fired at 1000°C (ZnO-22a). The positions of extra lines due to layer stacking faults are marked by arrows.
- Fig. 5 XRD pattern of the Cu/Fe/ZnO-22a sample fired at 1000°C.
- Fig. 6 XRD pattern of the Cu/Sn/ZnO-18v catalyst fired at 1000°C. Arrows indicate diffraction peaks assigned to Zn_2SnO_4 .
- Fig. 7 Variation of lattice parameter a and axial ratio $C = c/a$ with doping and thermal treatment.
- Fig. 8 Variation of unit cell volume V with doping and thermal treatment.
- Fig. 9 Schematic of methane oxidation catalytic test system.
a. catalytic test unit, b. reactor.

FIG. 1

BET surface area and XRD particle size

FIG.2

a

b

FIG 3

RELATIVE INTENSITY

FIG. 4

FIG.5

RELATIVE INTENSITY

FIG. 6

DEGREES, (2θ)

Variation of the lattice parameter a and the axial ratio $C = c/a$

FIG. 7

Variation of the unit cell volume V

FIG. 8

FIG. 9

**DATE
FILMED**
8/27/92