METHANE OXIDATION OVER DUAL REDOX CATALYSTS

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INTRODUCTION

The objective of this research is to develop approaches to direct catalytic oxidation of methane over oxides that are doubly doped with transition metal ions. The desired process aims at employing a double redox mechanism, where one redox couple is utilized for activation of oxygen and another for the trapping of $\text{CH}_3^\cdot$ radicals. The methyl radicals can either recombine, giving C_2 hydrocarbons, or be converted, via electron transfer reaction, to carbocations. The latter species can react with surface OH^- groups to form methanol or formaldehyde.

To choose from several possible catalytic systems, this research initially involved the characterization of the micromorphology and crystalline dimensions of zinc oxide catalysts doped with Cu, Fe, and ^(TIN)Sn by scanning electron microscopy. In addition, the determination of surface composition and oxidation states by X-ray photoelectron spectroscopy was carried out with these catalysts.

A newly constructed high temperature catalytic testing system has been calibrated (flow meters and temperature controllers), tested for possible gas leaks and integrated with a gas chromatographic analytical unit. A preliminary catalytic test study over a Cu/Fe/ZnO sample was performed. The following products of the methane coupling reaction were found: C_2H_6 , C_2H_4 , and H_2O together with CO_2 . The maximum space time yield of 14 mmol C_2 hydrocarbons/g cat/h was obtained at 848°C .

TECHNICAL PROGRESS

1. Characterization of the Catalysts

1.1 Catalyst Microstructure

The influence of thermal treatment and doping on the micromorphology and the particle sizes of the synthesized catalysts was studied by scanning electron microscopy using a Cambridge Stereoscan 150 Instrument. The samples were dispersed on a double-stick tape placed on an aluminum holder and coated with a thin carbon film by vacuum evaporation.

The scanning electron micrographs of the three different catalysts revealed the presence of randomly aggregated crystallites with rather uniform dimensions and blunt confined shapes (Fig. 1, 2), indicating that sintering of the zinc oxide catalysts results in the coarsening of particles without significant densification. The distinct differences observed in the micromorphologies and particle shapes were dependent on doping and also principally on sintering conditions. Generally, the catalysts prepared by firing in evacuated ampoules showed larger crystallite dimensions, with more uniform size and shape, than those treated in air. The $\text{Cu}^{\text{I}}/\text{Fe}^{\text{III}}/\text{ZnO}$ catalysts tended to form a looser structure with more interparticle voids in comparison to the $\text{Cu}^{\text{I}}/\text{Sn}^{\text{IV}}/\text{ZnO}$ samples which formed more compact aggregates. The strongest influence of sintering on the microstructure of catalysts was found for the Cu/Sn doped ZnO. The samples sintered in evacuated ampoules exhibited large, very uniform, round crystallites typical of the final state of coalescence (Fig. 1c). Those treated in air for the same period of time showed a broader distribution of grain sizes (Fig. 2c). In the later case, the particles were interconnected by relatively thin necks forming oblong structures, which is characteristic of the intermediate state of the grain ripening process. A similar effect was also observed for the Cu/Fe/ZnO and

ZnO (Fig. 1a,b, 2a,b) catalysts. However, in those samples the neck growth in the contact area between particles was more developed, resulting in the final stages of the grain boundaries migration away from the contact plane (Fig. 2b). Similar sintering behavior, i.e. coarsening of particles without appreciable structure densification, was observed for ZnO [1] and a number of other oxides [2-4] by Readey and coworkers.

The obtained results strongly suggest that the Greskovich-Lay mechanism [5] of sintering may operate during high temperature treatment of catalysts. The mechanism involves the growth of a neck between two particles and subsequent migration of the boundary followed by spheridization of the remaining single particle. The neck growth is principally due to vapor or surface diffusion [5]. The large difference in the crystallite shapes and sizes for the same samples treated in air or in evacuated ampules points to a significant mass transport that can occur via the vapor phase dissociation reaction $\text{ZnO}_{(s)} \rightarrow \text{Zn}_{(g)} + 1/2\text{O}_{2(g)}$. The equilibrium pressure of $\text{Zn}_{(g)}$ and the rate at vapor transport is thus controlled by the partial pressure of oxygen [1]. In the later stages of coarsening when the necks disappeared, the grain boundaries became curved due to the difference in size of the two original particles and migrated toward the center of curvature. This process therefore involved a larger grain engulfing neighboring smaller ones, forming, in intermediate stages, clusters of particles whose size and shape depend on the initial particle size and number of mutual contacts. In Fig. 1 and Fig. 2 all these stages, i.e. formation of necks (Fig. 2a,b,c), their growth (Fig. 1a,b), cluster building (1b, 2b) and particle spheridization can be distinguished.

The average particle sizes varied from 1-1.5 μm for pure ZnO fired in air to 2-3 μm for $\text{Cu}^{\text{I}}/\text{Fe}^{\text{III}}/\text{ZnO}$ and 2-4 μm for $\text{Cu}^{\text{I}}/\text{Sn}^{\text{IV}}/\text{ZnO}$ samples fired in

evacuated vessels. This effect was less pronounced for doped samples treated in air, where particles with diameters of about 2 μm for $\text{Cu}^{\text{I}}/\text{Fe}^{\text{III}}/\text{ZnO}$ and about 1.5 μm for $\text{Cu}^{\text{I}}/\text{Sn}^{\text{IV}}/\text{ZnO}$ dominated. BET surface areas of 0.45-0.50 m^2/g for pure ZnO, 0.30-0.35 m^2/g for iron-doped, and 0.25-0.30 for tin-doped samples fired for 22 h were obtained. These surface areas correspond to mean values of spherical particles having diameters of 2-4 μm , in agreement with the SEM micrographs.

1.2 Surface Analysis of the Catalysts

The surface analysis of $\text{Cu}^{\text{I}}/\text{Fe}^{\text{III}}/\text{ZnO}$ and $\text{Cu}^{\text{I}}/\text{Sn}^{\text{IV}}/\text{ZnO}$ samples was carried out using the Physical Electronics X-Ray Photoelectron Spectrometer Model 548 equipped with a $\text{Mg}(\text{K}_{\alpha})$ line) X-ray source. Multiple scans were signal averaged by a Nicolet Model 1972 Multichannel Analyzer. The survey scans were recorded in the binding energy range of 60-1060 eV. For quantitative analysis, 20 or 50 eV scans were used. The estimated size of the sample circular analysis area ranged from 1-3 mm in diameter depending on the pass energy used. The peak positions were reformed with respect to the carbon 1s line (BE = 284.6 eV). The intensities were integrated after previous smoothing of the spectra by a Fourier-transform procedure and base line correction.

1.2.1 Surface Composition

The determination of surface concentration of copper, iron, and tin in doped zinc oxide catalysts was based on a model of bulk sample with even distribution of dopants and neglecting a possible attenuation term arising from a contamination layer. The integrated intensities were corrected by atomic sensitivity factors reported by Briggs et al. [6]. The results of the analysis are summarized in Table 1.

TABLE 1

Determination of the Surface Concentrations of Cu, Fe, and Sn Dopants in Zinc Oxide Catalysts

Catalyst	Dopant Surface Concentration (atom fraction)		
	Cu	Fe	Sn
Cu/Fe/ZnO - 18v	0.11	0.04	-
Cu/Fe/ZnO - 22v	0.084	0.027	-
Cu/Fe/ZnO - 22a	0.039	0.041	-
Cu/Sn/ZnO - 18v	0.038	-	0.022
Cu/Sn/ZnO - 22v	0.044	-	0.026
Cu/Sn/ZnO - 22a	0.04	-	0.03

The samples fired in sealed evacuated ampoules for 18 or 22 hours are labeled with the suffix -18v or 22v while those fired in air are given the suffix -22a.

Analyses of the surface concentrations of dopants by XPS demonstrated in all cases that the surface of the catalysts was dopant enriched. However, the extent of surface enrichment depended on the particular dopant and the kind of sample treatment. A non-uniform enrichment was observed for Cu/Fe/ZnO catalysts treated in 1000°C in evacuated ampoules. For those samples, the surface copper concentration reached 8-11% while the iron concentration was 3-4%, which indicated approximately a three-fold increase in the surface Cu/Fe ratio compared to the bulk value. In contrast, the samples fired in air showed nearly equal enrichment (4%) at the surface by both dopants, preserving the bulk stoichiometric ratio.

The effect of pretreatment conditions on surface concentration of

dopants was less apparent for the Cu/Sn/ZnO samples. The surfaces of all tin-containing catalysts were enriched with both dopants at the level of 2-3%. However, in contrast to the iron-containing catalysts, the surface stoichiometry of the tin-based samples treated in evacuated vessels (Cu:Sn = 1.7:1) was closer to the bulk value (2:1) than for those treated in air (1.3:1).

1.2.2 Chemical State Identification

For determination of the oxidation states of the dopants, the XPS spectra were analyzed using the $2p_{1/2}$ - $2p_{3/2}$ lines for Cu and Fe and the $3d_{3/2-5/2}$ lines for Sn. Due to the insufficient resolution of the recorded XPS spectra, only the major oxidation states of some dopants could be determined. A typical survey spectrum of Cu/Fe/ZnO - 22a catalysts with an expanded Cu 2p doublet in the inset is presented in Fig. 3. The spectrum is dominated by the ZnO pattern, and only the most intense 2p peaks of copper and iron can be distinguished. The Cu core level $2p_{3/2}$ line was observed at 932.5-933.1 eV, depending on the kind of catalyst. The Sn $3d_{5/2}$ line appeared at 486.3-486.5 eV, while the Fe $2p_{3/2}$ line was observed at 711.1-711.3 eV. The binding energies of Cu $2p_{3/2}$, Fe $2p_{3/2}$, and Sn $3d_{5/2}$ lines are summarized in Table 2 for different oxidation states.

TABLE 2

The Binding Energies of the $2p_{3/2}$ Levels of Cu and Fe and $3d_{5/2}$ Level of Sn for Various Oxidation States

	BE [eV]	Reference
	Cu $2p_{3/2}$	
Cu	932.4-932.5	6,7,8
Cu ₂ O	932.5-933.1	6,7,8
CuO	933.8-933.5	6,7,8
CuFe ₂ O ₄	933.7	9
Cu/Fe, Sn/ZnO	932.5-933.1	this work
	Fe $2p_{3/2}$	
Fe	708.6-706.9	6,10
FeO	709.5	6,10
Fe ₂ O ₃	710.3-711.0	6,10
CuFe ₂ O ₄	710.8	10
Cu/Fe/ZnO	711.1-711.3	this work
	Sn $3d_{5/2}$	
Sn	484.8-485	6
SnO	486.7-486.8	6
SnO ₂	486.6	6
Cu/Sn/ZnO	486.3-486.5	this work

The binding energies of the iron $2p_{3/2}$ level increase in the order $BE(Fe) < BE(Fe^{2+}) < BE(Fe^{3+})$, and Fe^{2+} can be distinguished from Fe^{3+} based solely on the $2p_{3/2}$ level position. The position of this line in the Cu/Fe/ZnO catalyst agrees with those reported for trivalent iron [7,11]. The copper $2p_{3/2}$ line for Cu^{2+} in CuO is shifted ca 1.3 eV above that of

metallic Cu. Usually a well defined satellite structure is associated with this line with main peak positions at 3.0, 7.7 and 9.8 eV after the $2p_{3/2}$ peak, assigned to ligand to metal $O_{2p} \rightarrow Cu_{3d}$ charge transfer shake-up transitions [11]. For monovalent copper in Cu_2O , practically no chemical shift ($\Delta < 0.1$ eV) can be detected with respect to the Cu^0 $2p_{3/2}$ binding energies. Moreover, Cu^I and Cu^0 having a completely filled d shell do not exhibit an associated satellite structure as do the paramagnetic Cu^{2+} ions [9]. The observed features of the Cu 2p spectra ($2p_{3/2}$ line at 932.5-933.1eV) together with the lack of prominent satellite structure on the high binding energy side indicate that this line is due to Cu^+ or Cu^0 .

The oxidation states of Cu^+ and Cu^0 , as well as Sn^{2+} and Sn^{4+} , cannot be distinguished from one another due to very small chemical shifts between their core line positions. However, the different colors of the Sn-containing samples treated in evacuated ampoules (beige) and in air (green) indicate differences in the electronic state of Sn in both ampoules. Diffuse reflectance spectroscopy and the high resolution SCIENIA ESCA-300 instrument, having an extraordinary sensitivity and resolution that will allow the application of Wagner's two dimensional XPS-AES approach [12], will be used for more precise determination of valence states.

2. Methane Oxidation Over the Cu/Fe/ZnO - 18v Catalysts

2.1 Calibration of the Catalytic Test Unit

A schematic of the complete catalytic test unit that is being used in this research was presented in a previous quarterly report [13]. The unit was assembled, leak tested and integrated via an in-line heated, two six-port valve-sampling system with gas chromatograph. Electronic mass flow meters were calibrated for methane, oxygen and helium. The optimum

parameters for temperature control in the PID (Proportional-Integral-Derivative) regime for the Omega CN 9111 controllers were determined for each heated zone. The actual temperature profiles along the furnace were determined for optimum positioning of the catalyst [Fig. 4].

2.2 CH₄ Oxidation Over Cu/Fe/ZnO - 18v Catalyst

The catalyst that was used in preliminary catalytic studies was the Cu/Fe/ZnO-18v oxide prepared by firing at 1000°C for 18 h in evacuated ampoules. A 0.553 or 0.144 g portion of the catalyst was loaded into the reactor, 9 mm OD, which was connected at the exit to a 2 mm ID capillary to allow rapid product removal, and was placed in the furnace as shown in Fig. 4. Quartz wool plugs, 3 cm in height, were used to fix the catalyst in the reactor. Product analyses were achieved by sequential on-line injection into parallel columns consisting of a 3.2 mm x 2 m Porapak Q packed fused silica GC column and a 3.2 mm x 2 m packed 13X zeolite column in a Hewlett-Packard 5730A gas chromatograph interfaced with a 5880A integrator.

The preliminary examination testing program consisted of the following three steady state runs where the composition of reactants, the reaction temperature, and the gas hourly space velocity (GHSV) were varied under ambient pressure:

1. CH₄/O₂ = 98:2, GHSV = 7000 l/kg cat/hr
2. CH₄/O₂/He = 4.54:1:6.26, GHSV = 16000 l/kg cat/hr
3. CH₄/O₂/He = 12.8:1:33.6, GHSV = 57000 l/kg cat/hr.

Appreciable conversion of reactants was noted at 490°C, and all oxygen was consumed at reaction temperatures of 692°C, 744°C, and 848°C for runs 1, 2, and 3, respectively. In Fig. 5a, an example of the dependence of O₂ and CH₄ conversion with temperature (catalytic run 3) is shown. In all 3 cases, the products detected were CO₂, C₂H₆, and H₂O at 795°C, and above that

temperature C_2H_4 was also observed (run 3). The CO_2 , C_2H_6 , and C_2H_4 contents in the exit gas during run 3 are shown in Fig. 5b. It is apparent that the main reaction taking place was the total oxidation of methane. The selectivity to CO_2 increased with increased temperature, partial pressure of oxygen, and methane conversion. The yield of CH_4 coupling products increased with temperature, giving at $848^\circ C$ a maximum space time yield of 14 mmol/g cat/h of C_2 hydrocarbons, a value similar to that obtained by Matsura for Li_2O doped ZnO at $720^\circ C$ using five times greater space velocity [14]. Systematic catalytic test studies over all synthesized catalysts together with empty reactor blank experiments are now in progress in order to differentiate between the catalytic and gas phase reactions.

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a

b

c

Figure 1

a

b

c

Figure 2

Figure 3

Figure 4

CH₄ oxidation over CuFeZnO-18v catalyst O₂ and CH₄ conversion

a

CH₄ oxidation over CuFeZnO-18v catalyst CO₂, C₂H₆ and C₂H₄ formation

b

Figure 5

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