Selective Oxidation of Methane to Formaldehyde over doubly Copper–Iron Doped Zinc Oxide Catalysts *via* a Selectivity Shift Mechanism

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Formaldehyde formation from a CH_4–air mixture (1 : 1) is induced by a selectivity switch from C_2 hydrocarbon products over ZnO to the oxygenated product over doubly Cu–Fe doped ZnO to yield up to 76 g of CH_2O (kg cat.)$^{-1}$ h^{-1}.

There are two principal pathways for converting methane into more valuable products *via* partial oxidation. The most studied reaction consists of oxidative coupling of methane to form mainly C_2H_6 and C_2H_4.[1] A far more challenging process for heterogeneous catalysis is the pathway that leads from methane to the oxygenates CH_2O and CH_3OH.[2] The promotion of oxide catalysts such as MgO,[3] ZnO[4] and CaO[5] by doping with alkali metals (Li or Na) for the methane coupling reaction is now a well known process, and C_2 selectivities up to 72.5% (at a conversion level of 2.6%) have been reported.[3] For the partial oxidation of CH_4 to oxygenates, the most active catalysts are those initially reported[2,6] to contain MoO_3 or V_2O_5 supported on or in binary oxide compositions with ZnO, Fe_2O_3, VO_2 and UO_2 and more recently ternary Nb–Fe–B oxides.[7] The best results were obtained for $MoO_3{\cdot}Fe_2O_3$[8] and Nb–Fe–B–O[7] catalysts with 98 and 79.4% selectivity at 5 and 1.03% conversion, respectively, while pure Fe_2O_3 yielded complete oxidation of CH_4 to CO_2.[8] In this communication, an entirely new catalyst for the formation of CH_2O is shown to be obtained by doubly doping ZnO with small quantities of substitutional Fe and Cu ions in zinc sites.

The Cu–Fe–ZnO catalyst was prepared *via* a valence-pinning doping process by high-temperature firing of mixtures composed of ZnO (obtained by 350 °C calcination of synthetic hydrozincite), Cu_2O and $Fe_2O_3{\cdot}1.23H_2O$. An equimolar mixture of the Cu and Fe dopants was prepared by grinding

Table 1 Methane conversion, formaldehyde space time yields, and product selectivities over the ZnO and Cu–Fe promoted ZnO catalyst with CH_4–air (1 : 1) reactant at ambient pressure and gas hourly space velocity = 70 000 dm^3 (kg cat.)$^{-1}$ h^{-1}

	ZnO catalyst						Cu–Fe–ZnO catalyst					
			Selectivities[c]						Selectivities[c]			
T/°C	CH_4 Conv.[a]	CH_2O Yield[b]	CH_2O	C_2	CO_2	CO	CH_4 Conv.[a]	CH_2O Yield[b]	CH_2O	C_2	CO_2	CO
500	<0.02	0.53	7	—	93	—	<0.02	1.1	43	—	57	—
550	0.03	0.75	3	—	97	—	0.02	1.6	37	—	63	—
600	0.5	1.8	3	—	98	—	0.1	5.3	25	—	75	—
650	0.6	3.2	2	—	98	—	0.2	13.1	18	—	83	—
700	2.0	5.0	1	10	86	3	0.8	29.7	14	2	85	—
750	5.3	8.7	1	34	63	3	2.5	76.0	10	5	82	3
800	9.9	16.5	1	47	48	5	4.5	49.8	4	16	67	13
850	13.5	24.9	0	53	36	10	16.2	0.96	0	23	57	20

[a] Total methane conversion, Mol%. [b] Space time yield of formaldehyde, g (kg cat.)$^{-1}$ h^{-1}. [c] Selectivities are given in carbon atom%.

and then mixed with ZnO to achieve a 1% doping level of the Cu and Fe. The ZnO and Cu–Fe doped ZnO samples were subsequently thermally pretreated at 400 °C under N_2 and finally fired at 1000 °C in air for 22 h. The composition of the ternary catalyst corresponded to $Cu_{0.010}Fe_{0.011}Zn_{0.979}O$, as determined by atomic absorption spectroscopy.

All the final samples had low surface areas, *i.e.* 0.50 m^2 g^{-1} for ZnO and 0.25–0.35 m^2 g^{-1} for doubly doped Cu–Fe–ZnO. X-Ray diffraction patterns of the doped samples are in agreement with substitutional incorporation of the dopants into the ZnO matrix.[9,10] High resolution X-ray photoelectron analysis showed the dopants to be in the Cu^{I} and Fe^{III} valence states in tetrahedral coordination and both to be enriched on the catalyst surface to 3.5% surface concentration.[11] Thus, the Cu^{I} and Fe^{III} substituents for Zn^{II} make an ion pair that is subject to Coulombic attraction and travels in equimolar stoichiometric quantities from the bulk to the catalyst surface. Catalytic testing was carried out in the temperature range of 500–850 °C in a fixed-bed continuous-flow 6 mm OD quartz reactor that narrowed into a 2 mm ID capillary immediately below the 0.1144 g catalyst bed. A standard reactant mixture of CH_4–air (1 : 1) with a gas hourly space velocity of 70 000 dm^3 (kg cat.)$^{-1}$ h^{-1} at ambient pressure was used. The principal products observed by gas chromatographic on-line sampling were CH_2O, the C_2 coupling products ethane and ethene, CO + H_2, as well as CO_2 and water. Formaldehyde was also condensed and quantitatively determined by iodometric titration.

Detectable conversion of reactants over the catalysts was noted at 500 °C, and more than 90% of the oxygen was consumed at 800 °C over the Cu–Fe–ZnO catalyst. However, the oxygen conversion was still below 65% for undoped ZnO at the highest reaction temperature (850 °C) utilized. In Table 1, the effect of doping the ZnO on the formaldehyde yield is shown. It is evident that, while pure ZnO is a moderate catalyst for oxidative coupling of CH_4 to C_2 hydrocarbons, the Cu and Fe dopants significantly promoted the formation of CH_2O, and the highest yield of 76 g (kg cat.)$^{-1}$ h^{-1} was obtained at 750 °C over the Cu–Fe–ZnO catalyst. The undoped ZnO produced principally CO_2 until C_2 coupling products (ethane and ethene) began to be formed at the higher temperatures. Singly doped Cu–ZnO and Fe–ZnO catalysts were also tested and their activities were comparable with those of the Cu–Fe–ZnO catalyst. The singly doped Cu–ZnO catalyst promoted deep oxidation to CO_2 and H_2O and Fe–ZnO promoted selective oxidation to CH_2O. The inhibition of the C_2 products was most pronounced over the doubly doped Cu–Fe–ZnO catalyst. Thus, doping the ZnO with Cu and Fe resulted in a selectivity switch wherein the C_2 selectivity was suppressed while the selectivity toward CH_2O was enhanced.

The promotional effect of the Fe and Cu dopants of ZnO on formaldehyde formation is thought to be due to the fact that the dopants can execute a redox ($Cu^{I/II}$ or $Fe^{II/III}$) and a Lewis acid (Fe^{III}) function, trapping at surface sites the methyl radicals formed as intermediates in the methane activation step.[1] This can facilitate a further oxidation of the $^{\bullet}CH_3$ species to CH_2O by a redox process involving surface oxygen, formation of a surface methoxide and transfer of a hydride ion to the dopant redox couple.[11]

In conclusion, it has been demonstrated that, under the present reaction condition, doping of ZnO by small equimolar quantities of Cu^{I} and Fe^{III} promoted the formation of formaldehyde at the expense of CO_2 and C_2H_n products.

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