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Promotion of Methanol Synthesis over Cu/ZnO Catalysts by Doping with Caesium

John Nunan, Kamil Klier,* Chyi-Woei Young, Paul B. Himelfarb, and Richard G. Herman Seeley G. Mudd Building 6, Department of Chemistry, Lehigh University, Bethlehem, PA 18015, U.S.A.

The rate of methanol formation from H_2/CO synthesis gas over the binary Cu/ZnO catalyst can be greatly increased on doping with caesium without increasing the formation of higher oxygenate products above 1.1 mol%.

Alkali metal promotion is a well established phenomenon in heterogeneous catalysis and was first described by Dobereiner¹ when he observed that contacting platinum with NaOH or KOH greatly increased its oxidation power toward alcohols. The effect of alkali metal on a given catalyst can manifest itself in a number of ways, e.g. (i) increase in selectivity, (ii) increase in activity, and (iii) increase of catalyst lifetime. The reaction types promoted by alkali metals range from ammonia synthesis,² Fischer-Tropsch synthesis,³ and ethylene oxidation⁴ to higher alcohol synthesis.⁵⁻⁷ Promotion of higher alcohol synthesis over methanol synthesis catalysts by doping with alkali metal ions such as K, Rb, and Cs has been shown to occur both over the older higher pressure (20.3-25.3 MPa) (1 atm = 0.1013 MPa) and higher temperature (673–723 K) zinc chromite catalysts⁵ and the new copper based catalysts.^{6,7} However, the effect of alkali metal doping on the synthesis of methanol has so far been reported to include mainly the retardation of the reaction and lowering of the selectivity to methanol. Over transition metal catalysts such as palladium supported on silica,⁸ alkali metal doping inhibits methanol formation, whereas over copper based methanol synthesis catalysts the patent literature⁹ specifies the absence of alkali metal from the catalyst for the selective synthesis of methanol. In this communication, doping with Cs is shown to give rise to over a two-fold increase in methanol yield with the Cu/ZnO catalyst, with higher oxygenate formation remaining very low so that better than 98.9 mol% selectivity for methanol is achieved for all caesium concentrations used.

Catalyst preparation involved the initial precipitation of a hydroxycarbonate precursor that was shown to be aurichalcite¹⁰ [Cu_{1.5}Zn_{3.5}(CO₃)₂(OH)₆], followed by stepwise calcina-





Figure 1. Yield of methanol as a function of Cs loading over the calcined-doped (\blacksquare) and reduced-doped (\bigcirc) binary Cu/ZnO catalysts. For conditions see footnote a, Table 1.



Figure 2. Yield of methyl formate (\blacktriangle) and ethanol (\bigcirc) as a function of Cs loading over the calcined-doped Cu/ZnO catalysts. For conditions see footnote a, Table 1.

tion to 623 K to give the corresponding oxide CuO/ZnO. Cs-doping with CsO₂CH in aqueous solution was carried out either after calcination, termed 'calcined–doped' catalysts, or after reduction of the catalysts with 2% H_2/N_2 at 523 K, termed 'reduced–doped' catalysts. In the latter case, the catalysts were prepared by removing the reduced catalyst (Cu/ZnO) from the reactor under a N_2 atmosphere and adding 2.5 g to 25 ml of N_2 -purged CsO₂CH solution at 323 K. The

Table 1. Comparison of the apparent activation energies for methyl formate, methanol, and ethanol formation over the 0.34 mol% Cs calcined–doped Cu/ZnO catalyst.^a

Product	$E_{\mathbf{A}^{\mathbf{app.}}}/\mathrm{kJmol^{-1}}$	Temperature range/K
Methyl formate	65.5	488-523
Methanol	76.6	483523
Ethanol	148.5	531562

^a $H_2/CO = 2.333$; P = 7.6 MPa; GHSV = 6120 l (at STP) (kg catalyst)⁻¹ h⁻¹; T = 523 K.



Figure 3. Plot of selectivity for higher oxygenate formation (defined as mol% of methyl formate + ethanol in the product mixture) as a function of Cs loading over the calcined-doped Cu/ZnO catalysts. For conditions see footnote a, Table 1.

solution was then evaporated to dryness under flowing N₂ and the resulting doped catalyst transported under N₂ to the reactor for activity determination. Catalyst testing was carried out in a fixed bed continuous flow reactor operating at a total pressure of 7.6 MPa. Details of reactor construction and mode of operation have been described in detail previously.^{10,11} Catalyst activities were determined at 523 K with a synthesis gas ratio of $H_2/CO = 2.333$ and a gas hourly space velocity $(GHSV) = 6120 l (at STP) (kg catalyst)^{-1} h^{-1}$. Steady state activities, which were achieved after 24 h of catalyst testing, are reported here. Reaction products consisted of methanol with accompanying low yields of methyl formate and ethanol. X-Ray photoelectron spectroscopic analyses of the used catalysts showed that within experimental error the Cs was highly dispersed in submonolayer form on the catalyst surface with no clustering occurring. These analyses and data treatments are reported elsewhere.12

In Figure 1 the effect of Cs loading on the rate of methanol formation both for the calcined-doped and reduced-doped Cu/ZnO catalysts is shown. It is evident that the different preparations produced identically active catalysts. Up to 0.4 mol% loading of Cs, the activity for methanol formation increased rapidly from 260 to 550 g (kg catalyst)⁻¹ h⁻¹, beyond which the rate goes through a broad maximum at 0.8 mol% Cs followed by a rapid decrease in activity. The effects of Cs loading on the calcined-doped Cu/ZnO catalysts for methyl formate and ethanol formation are shown in Figure 2.

The surface Cs dopant promotes the formation of both products but even at the highest Cs loading of 2.13 mol% they account for less than 1.1% of the product composition. This is clearly demonstrated in Figure 3 where the selectivity for methyl formate and ethanol is plotted as a function of Cs loading.

Linear Arrhenius plots were obtained from data for the 0.34 mol% Cs calcined-doped catalyst for methanol, methyl formate, and ethanol formation, and the resultant apparent activation energies are presented in Table 1. It is noted that the activation energy for ethanol formation is *ca*. twice that for methanol or methyl formate formation, thus indicating that low reaction temperatures further favour methanol selectivity. The activation energy for methyl formate formation compares well with that found for the homogeneous carbonylation of methanol, catalysed by sodium metal (67.7 kJ mol⁻¹),¹³ where it was proposed that reaction occurs through the direct coupling of the methoxy anion and CO, *i.e.* MeO-Na⁺ + CO \rightarrow [MeOCO]⁻ Na⁺. Over the Cs doped Cu/ZnO catalyst a similar reaction may be occurring where the metallocarboxylic ester is converted into methyl formate by surface protons.

The promotional effect of Cs on methanol synthesis is reminiscent of previous results on the effects of CO₂ and H₂O on the rate,^{11,14} where it was observed that small levels of both gases promoted methanol synthesis, followed by severe retardation at higher concentrations. As in the case of water promotion,11 the existence of a maximum in methanol synthesis activity as a function of Cs loading can be explained by the bifunctional nature of methanol synthesis. The effects of Cs doping are thought to be to increase the concentration and reactivity of surface hydroxy groups and to promote the formation of intermediate formate and acetate species on the catalyst surface that ultimately lead to methanol and ethanol after hydrogenation by hydrogen activated on the ZnO surface. Excessive doping with Cs poisons the hydrogenation function of the catalyst, and this has a greater retarding effect on methanol than on higher oxygenate synthesis.

In conclusion, it has been demonstrated that under the present reaction conditions Cs doping promotes the formation of methanol over the binary Cu/ZnO catalyst and that the promotion of methanol by alkali metal ion doping (in this case Cs) can be accomplished with minor changes in selectivity toward higher oxygenate formation.

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