Alkali Metal Promotion in Higher Alcohols and Olefin formation from CO2 Hydrogenation: Shifting the Reaction Mechanism

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Introduction

In the global effort towards a sustainable society, the circular carbon economy is a tantalizing challenge.¹ Developing a new catalyst capable of converting carbon dioxide into specific products is the key to such a green future. Converting carbon dioxide by renewable hydrogen to higher alcohols (HAs) and olefins is particularly attractive, due to their versatile use in industry and as fuel blends. Achieving this has proven strenuous however. Catalysts for this type of reactions are often designed by combining traditional methanol synthesis metals (e.g. CuZn) and Fischer Tropsch type metals (e.g. FeZn) in the presence of alkali metals (AMs). The combination of Cu and Fe gives rise to a dual site catalyst for dissociative (Fe) and non-dissociative (Cu) CO₂ activation at the intersection of which HAs can be formed. The AMs tweak the electronics, structure and hydrogenation ability of the catalyst. Although AMs are widely used^{2,3} the difference in promotional effect of K, Rb and Cs on such catalysts is not well documented. Here we explore the superior promotion of Cs over K and Rb in increasing the selectivity to HAs and olefins by studying the role these AMS play in modifying the catalyst structure and opening up a unique CO insertion pathway, which gives rise to both alcohols and olefins.

To this end a series of X-Cu₄Zn₃Fe₃ (X=K, Rb, Cs) catalysts was tested with various AM concentrations. The effect of doping on the catalyst structure and the reaction mechanism are studied extensively using XRD, DRIFTS, H₂-TPR, TPD, TPSR, pulse experiments, XPS, XAS and insitu Mossbauer.

By comparing K, Rb and Cs we shine light on the widely reported, but only superficially understood promotional effect of AMs at the surface of CuZnFe type catalysts.

It was hypothesized that AMs promotion has 2 main effects:

- 1) Increased carburization leading to increased C-C coupling ability.⁴
- 2) Increased stabilization of CO species, which can insert into alkyl-chains to form HAs and olefins $^{\rm 5}$

Materials and Methods

AM (K, Rb, Cs) promoted Cu₄Zn₃Fe₃ catalysts were synthesized by coprecipitation using metal nitrates at a constant pH (~10) using Na₂CO₃ and NaOH followed by impregnation using K, Rb or Cs carbonate aqueous solutions. After calcination in air and reduction in 5%H₂ the CO₂ hydrogenation reaction was performed in a fixed-bed flow reactor at 45 bar at 270-330°C. Reaction products and conversion were quantified by GC by internal standard method. **Results and Discussion**

 $Doping \ K, \ Rb \ or \ Cs \ on \ our \ Cu_4 Zn_3 Fe_3 \ catalyst \ shows \ that \ Cs \ is \ superior \ to \ both \ Rb \ and \ K \ increasing \ the \ selectivity \ of \ CO_2 \ hydrogenation \ to \ HAs \ (13, \ 12 \ and \ 10\% \ respectively) \ while$

having a limited effect on conversion. Olefin selectivity is similar between K and Cs (36%) and is lower for Rb (30%). For undoped samples alcohols are 1.3 and olefins 0% showing the remarkable influence of AMs on the catalytic behavior.

Additionally the selectivity of hydrocarbons of carbon number higher than 4 increases for doped samples. However, at higher AMs concentrations, CO selectivity increases as well. Most strikingly, Cs is greatly superior in the suppression of CO formation favoring coupled products at all concentrations tested.

As expected, AM doping promoted carburization as indicated by XRD, XPS, XAS and Mossbauer. In effect, the AMs are able to induce a phase separation of the CuFeOx spinel phase during reaction, thereby ensuring the formation of metallic Cu and carburized Fe phases.

Interestingly, the catalytic behavior of these catalysts is also significantly affected before carburization as indicated by a stronger adsorption of CO as measurement by DRIFTS and TPSR. Surprisingly, the K doped catalyst stabilizes CO more than Rb and Cs, despite its (in principle) lower alkalinity. Additionally it shows an increase in particularly strongly rather than medium adsorbed CO. This may account for its overall higher CO selectivity during catalysis. We speculate that this difference between K, Rb and Cs is due to their different local environments.

In contrast to the general literature, we propose that the effect of AMs is not chiefly derived from the ability to suppress the hydrogenation ability, but rather is primarily based on facilitating CO insertion. Hereby both alcohols and olefins share an reaction pathway: CO is inserted into an alkyl chain and hydrogenated to HAs, which can either desorb to give HAs or dehydrate to form olefins. This is in line with our ethylene hydrogenation pulse experiments, which show no clear trend when comparing our different catalysts, while ethanol dehydration experiments and in-situ DRIFTS clearly show the viability of this reaction pathway over AM promoted catalysts.

Significance

The catalytic conversion of CO_2 to specific products is essential to establishing a circular carbon economy. To be able to establish such economy catalyst with a high degree of selectivity towards desired products are required. Considering the wide use of higher alcohols and olefins in industry it is imperative to have catalysts capable of synthesizing them from CO_2 and H_2 .

In order to move away from trail-and-error based research into rational design a detailed understanding of the interaction between catalysts and dopants is required. Alkali metal doping of CO₂ hydrogenation catalysts is widely employed, but the literature lacks a comprehensive understanding of their role on the reaction mechanism. Our research shines a light on the unique role of AMs on the reaction mechanism of CO₂ hydrogenation.

References

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