The Cu-ZnO synergy in methanol synthesis: Origin of active site explained by experimental studies and a sphere contact quantification model on Cu+ZnO mechanical mixtures

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Introduction

Methanol is widely used, as a common solvent, an alternative fuel and a starting material in chemical industry. In industrial process, methanol is produced from synthesis gas (CO/CO2/H2) under high temperature (220-300°C) and pressure (50-100 bar) using Cu/ZnO/Al2O3 catalyst. Nowadays, consequent efforts are made to replace CO by CO2 in the perspective of greenhouse gases valorization. This kind of catalysts has been used for decades, there is still intense debate concerning the nature of the active site. It is admitted that the so-called Cu-ZnO synergy is responsible for the observed activity, and 3 hypothesis are commonly used to this synergetic effect: i) a morphologic effect (surface) [1], ii) creation of active site through formation of Cu/Zn alloy, or a decoration of Cu with ZnO or oxygen vacancies [2,3], and iii) an atomic hydrogen reservoir located on ZnO particles [4]. The understanding of how the active site is created is the key of the comprehension of the effect of the Cu-ZnO synergy. The objective of this study is to understand the creation of the active sites and explain the Cu-ZnO synergy on the basis of structure – activity relationships. Here we show the impact of catalyst composition on its activity and explain the origin of active sites through a theoretical approach to explain the synergy between Cu and ZnO for methanol synthesis. Using mechanical mixtures of Cu and ZnO of different ratios, prepared with CuO and ZnO reference oxides. A new method has been developed to estimate the contacts between Cu and ZnO particles in the full range of composition based on the geometry of spherical particle agglomerates, which is applicable to mechanical mixtures. Experimental data are compared to theoretical calculations to validate the model.

Materials and Methods

Reference CuO and ZnO oxides were prepared by precipitation of nitrate metal ions with sodium carbonate. Physical mixtures were prepared by mixing different amounts of CuO and ZnO reference oxides. Several characterisation were performed: In situ X-ray diffraction (XRD) in the 20 range 20° to 80°, Transmission Electron Microscopy (TEM), Hydrogen and carbon dioxide. Methanol synthesis catalytic tests were performed at 30 bar and 250 °C in a continuous fixed-bed stainless-steel reactor using a feedstock composition of 3:1 (vol.) H2:CO. Before catalysis, the catalysts were reduced in situ at 350 °C for 60 min under a flow of H2 (30 mL min−1).

Results and Discussion

In this study, we prepared a batch of mechanical mixtures leading to Cu+ZnO catalysts with different composition, 100% selective to methanol. The catalysts activity for methanol production versus Zn content shows a volcano-like profile (fig1a), which is typical of the so-called Cu-ZnO synergy. Structural analysis (XRD) allowed to determine the migration of Zn according Kirkendall effect, his profile matched perfectly the activity for methanol production (fig1b). H2 chemisorption evidenced that this migration impacted also hydrogen activation, and followed the same volcano trend (fig1c). This knowledge of this experimental results allowed building a mathematical model based on the assumption that the creation of active sites, and therefore the synergy, is directly link to the contacts between Cu and ZnO during the reduction of the catalyst. The model for quantification of sphere contacts is based on geometrical properties of spheres and can be applied to mechanical mixtures. The variation of concentration of contacts versus Zn content matches the catalyst activity evolution (fig 1d), which shows that the migration can be controlled and improved by favouring contacts between the two metals during the synthesis. The developed model of contact quantification is a powerful predictive tool for the rational design of catalysts.

Significance

Knowledge of the migrated Zn amount is directly correlated to catalyst activity, giving a very easy pre-diagnosis tool for a methanol catalyst without running a catalytic test. This method greatly helps to understand the data presented resulting in a consistent picture for model catalysts/mechanical mixtures.

Figure 1: (a) methanol formation rate (b) amount of migrate Zn during the reduction process (c) chemisorbed hydrogen (d) concentration of number of contacts per gram of catalyst as function of Zn content in the catalyst

References