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Experimental search for new active methanol catalysts using ternary transition-metal alloys

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Introduction
The methanol economy is a possible solution for making our current energy consumption more sustainable while keeping the same infrastructure[1]. To that end it is desired to synthesize the methanol de-localized alongside electrolysis. As such the synthesis should run in small-scale and preferably from recycled carbon dioxide. Thus, an effective and easy applicable methanol economy calls for new catalysts that runs effectively at milder conditions (temperature and pressure) while suppressing the reverse water gas shift reaction.

We report the synthesis and characterization of methanol catalysts based on first-row transition metals in ternary alloys. These ternary alloys open the possibilities of advanced multi-structures, depending on the different heats of formation, the concentration of each component and the synthesis. The resulting alloy can both be an intermetallic or a solid solution of the species in question. The starting point has been gallium containing alloys with inspiration from several papers showing that gallium enhance the methanol selectivity and activity of the catalysts[2]–[4]. Especially the so-called Heusler alloys[5] are known stable intermetallics containing the desired atomic species. Additionally this line of intermetallics have given improvements to the catalysts of some other reactions[6], [7].

Experimental work
Our initial approach has been to survey different elemental compositions using incipient wetness impregnation of nitrate salts into fumed silica. The activity and selectivity towards methanol synthesized from a stoichiometric mixture of carbon dioxide and hydrogen-gas have been tested at 1 atm tested in a plug-flow reactor using Gas Chromatography. The subsequent characterization of these catalysts have included in situ transmission electron microscopy under reducing conditions and in situ X-ray diffraction under both reducing and reaction conditions.
Results and discussion

These gallium-containing alloys have shown activity and selectivity comparable to that of Cu/ZnO, and by optimizing the conditions of which the catalysts are formed under, activity at least as high as Cu/ZnO has been achieved with an optimum working temperature as low as 190°C. These catalysts struggle from coking, but this deactivation is reversible by hydrogen reduction, and the lower operation temperature prolong the active state of these catalysts. In situ characterization shows structural differences linking to the activity, though on-going work is focused on explaining the active sites, especially the presence and state of the gallium.

References


