

CO₂ valorization: A new alternative catalysis with Ag and Cu Metal Molecules

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Recently, sustainable technology strategies have been developed towards a moderate transition to low-carbon energy sources. This new industrial pathway involves using greenhouse gases emitted into the atmosphere, such as CO₂, as a reagent to form high value industrial products [1].

CO₂ utilization can include its use as a green solvent in its supercritical state, its mineralization with metal cations to produce carbonates, or its biological transformation into macromolecules such as lipids, proteins and pigments. [2]. However, one of the most ambitious applications is the catalytic transformation of CO₂ into high value-added fuel compounds such as methanol, synthetic natural gas, syngas and other compounds.

Reverse Water-Gas Shift (RWGS) is a CO₂ valorization reaction based on CO₂ hydrogenation to form syngas, that is composed mainly of H₂ and CO. For the manufacture of ammonia, methanol, or synthetic hydrocarbon fuels, syngas is a critical intermediate source. It is also utilized as an intermediary in the Fischer-Tropsch (FT) method to make synthetic raw oil, lubricants, and hydrocarbon fuels [3].

Reverse Water Gas Shift (RWGS) has been extensively studied using metal catalysts supported on metal oxides. Cu, Au, Rh, Ru, Ni and Fe are commonly deposited on TiO₂, Al₂O₃ or ZrO₂ supports [1] [4]. Nevertheless, literature has also described low selectivities and catalyst deactivation by carbon deposition or by structural change at high temperatures due to the presence of H₂O [1].

Recently, low atomicity Metal Molecules (M-M) were investigated obtaining excellent results in heterogeneous catalysis of CO₂ valorization reactions [5].

M-M are clusters of a few metal atoms, less than a nanometer in size, smaller than conventional metal nanoparticles. These novel compounds are characterized by an electronic structure composed of discrete energy levels and a band gap, the same as the HOMO-LUMO difference that occurs in molecules. This electronic structure causes physicochemical differences between M-M and other nanoparticles.

M-M shows high dispersion stability in aqueous solution [6], unlike traditional nanoparticles, which require a surfactant to maintain their dispersion stability. They are also very stable to oxidation, and stable in the full pH range, and when deposited on a metal oxide support, very stable to high temperatures, up to 900°C, even in oxidizing atmosphere or in the presence of H₂O.

Their unique structure is also responsible for their fluorescent, catalytic, photocatalytic, and biomedical properties [6] [7] [8], that differ greatly from large clusters, nanoparticles, or the same metal in bulk. They are suitable for catalyzing a broad range of chemical reactions including oxidation, reduction, and hydrogenation. Properties can be tuned through choice of metal, size of M-M, and choice support. Advantages in catalysis include lower activation energies, increased conversion and selectivity, lower temperature, and pressure operating conditions, and exceptionally high stability. Compared to conventional catalysts they are very resistant to typical poisons, such as sulfur and carbon monoxide.

As all the atoms of the metal molecules are surface atoms, all of them are available to react, so the loading needed for a given reaction is smaller than with traditional catalysts. Furthermore, M-M properties are primarily size dependent rather than element dependent. Low cost and abundant copper and silver M-M can be used as alternatives to PGM metals with similar results, offering a cost effective and environmentally sustainable alternative to conventional catalysts.

These new and unique compounds have been studied for many years in our company, NANOGAP. Their high stability, selectivity, and conversion in CO₂ valorization reactions such as RWGS has been demonstrated. The TOR that we have obtained at 400 °C is 0.245 mol/g_{Ag}*h that is 40 times higher than Ni based catalyst [9] and 7 times better than Au based catalyst at the same temperature [4]. Besides we have a 3 times lower activation energy than Au based catalyst [4]. In addition, selectivity for CO is 100%, with no production of methane or another undesirable side products, even at temperatures as high as 800 °C. This is remarkable, since the production of methane is favored at high temperatures, indicating the high specificity that MMs have for a given product.

Consequently, these results set a very important precedent in heterogeneous catalysis with M-M and demonstrate the great contribution that M-M can suppose to the sustainable energy transition that has been taking place in recent years.

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Figures

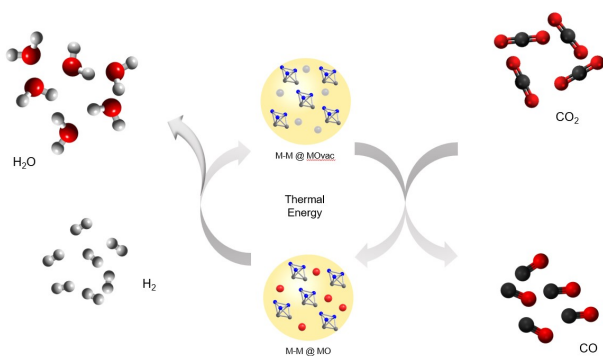


Figure 1. Scheme of RWGS catalyzed by M-M