Nobel metal-based bifunctional catalysts for bioethanol conversion into ethyl acetate

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Bioethanol is a lignocellulosic biomass-derived chemical that can be directly used as a fuel or converted into chemicals. Since 1975, bioethanol is used as fuel in Brazil and in recent years there has been a growing interest in converting ethanol into important chemicals, such as ethylene, butadiene and ethyl acetate. Ethyl acetate, for example, is widely used as a replacement for aromatic solvents in paints, inks and dyes; moreover, it can be used in the pharmaceutical, cosmetic, and food industry. While this solvent is commercially produced from non-renewable sources, in countries with high bioethanol production, such as the USA and Brazil, there is an increasing commercial and environmental interest in its synthesis from bioethanol.

The most studied reaction route for bioethanol conversion into ethyl acetate is in inert atmosphere using copper based catalysts (for example, $CuCr_2O_4$ and Cu/ZrO_2 catalysts) and involves the dehydrogenation of ethanol into acetaldehyde (catalyzed on the copper surface) followed by a coupling reaction between the acetaldehyde and an ethanol molecule (catalyzed by both copper and support). The main advantages of this process are the use of inexpensive metal catalysts, and the coproduction of hydrogen, a valuable chemical for industry. Contrarily, there are several drawbacks: the reaction is endothermic, it requires high temperatures and high metal loadings, catalysts deactivate relatively fast, and it is observed the formation of byproducts that form azeotrope with the ethyl acetate. It is also important to mention that copper catalysts are not active in a more straightforward (and exothermic) one-pot route for ethyl acetate synthesis, i.e., the oxidation of bioethanol to acetic acid followed by the esterification with ethanol. The reaction schemes for both routes of ethanol conversion into ethyl acetate are shown below:

Dehydrogenation/Coupling (inert atmosphere)
Step 1: $CH_3CH_2OH \rightleftharpoons CH_3CHO + H_2$
Step 2: $CH_3CHO + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2$
Overall reaction: $2\ CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + 2\ H_2$

Oxidation/esterification
Step 1: $CH_3CH_2OH + ½\ O_2 \rightleftharpoons CH_3CHO + H_2O$
Step 2: $CH_3CHO + ½\ O_2 \rightleftharpoons CH_3CO_2H$
Step 3: $CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$
Overall reaction: $2\ CH_3CH_2OH + O_2 \rightleftharpoons CH_3CO_2CH_2CH_3 + 2H_2O$

Herein, gold and silver-based bifunctional catalysts were studied for bioethanol conversion into ethyl acetate in both inert (dehydrogenation/coupling) and oxidant (oxidation/esterification) atmosphere. Catalysts preparation involved the modification of supports such as metal oxides, silica and aluminosilicates with gold or silver.

From the catalysts tested, the best results were obtained using gold supported on m-ZrO_2 (monoclinic phase). In inert atmosphere at 523 K, the selectivities for ethyl acetate and acetaldehyde were, respectively, 63 and 28 % (at 71 % ethanol conversion). The main byproducts formed were crotonaldehyde (4 %), acetone, diethyl ether and methyl ethyl ketone (< 2 % each). Compared to classical copper catalysts (for example, Cu/ZrO_2), the Au/ZrO_2 catalyst led to similar ethyl acetate yield, but lower formation of byproducts (mainly methyl ethyl ketone, which forms an azeotrope with both ethyl acetate and ethanol). In the copper system, several condensation reactions are observed yielding heavy compounds, however it is not fully understood if they happen in the Cu or zirconia surface. In the gold catalysts, these side condensation reactions are minimized and depending on the conditions, ethyl acetate and acetaldehyde accounts to 91-98 % of the products. Replacing monoclinic zirconia by other supports such as silica, alumina, silicalumina, or tetragonal zirconia, led to a significant decrease in the ethyl acetate selectivities. The support nature affects significantly the catalyst performance because the reaction takes place in the interface between metal and support. While the dehydrogenation of ethanol to acetaldehyde happens in the gold surface, the aldehyde has to be coordinated in a metal site close to the interface with the support in order to undergo coupling reaction to form ethyl acetate.

Au/ZrO_2 was also tested in the one-pot conversion of ethanol on ethyl acetate in oxidant atmosphere. In this mechanism, gold catalyze the oxidation of ethanol to acetic acid, while the support is responsible for the esterification of acetic acid with ethanol to yield ethyl acetate. This reaction can be carried out in temperatures as low as 448 K and selectivities for acetaldehyde and ethyl acetate of 49 and 44 % were, respectively, obtained (70 % conversion of ethanol). The main byproducts observed were diethyl ether (5 %) and crotonaldehyde (1 %). The results indicate that zirconia was effective catalyzing the esterification reaction; however, in the conditions used, a significant part of the ethanol is oxidized to acetaldehyde instead of acetic acid.

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