HYDROGEN PRODUCTION VIA BIO-ETHANOL STEAM REFORMING ON CeO_2-BASED CATALYSTS

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One of the most perspective ways of drastic automotive pollution reduction is the transition from internal combustion engines to electric ones powered by hydrogen fuel cells. Besides application in transportation hydrogen fuel cells are prospective replacements for convenient batteries in home electronics. However there are a lot of limitations for pure hydrogen storage, transportation and filling connected with its extremely low density and heavy explosion ability. Thus the most promising technology is on-board catalytic conversion of suitable organic compounds to the mixture of hydrogen and CO_2. Currently methanol-water mixture reforming is the most common technology for hydrogen production on-board. However methanol as a fuel has some important disadvantages connected with its high toxicity, low availability on ordinary basis and coal-natural gas based production technology, which will lead to additional CO_2 emissions.

Another approach is the use of biomass derived ethanol reforming for on-board hydrogen production preventing additional CO_2 emissions. Ethanol-water mixture is a non-toxic liquid easily accessible in our daily life. There are two types of reactions which allow converting ethanol-water mixtures to hydrogen: ethanol steam reforming (1) and ethanol auto-thermal reforming with an addition of oxygen (2):

$CH_3CH_2OH + 3\ H_2O \rightarrow 2\ CO_2 + 6\ H_2$ (1)

$CH_3CH_2OH + 3\text{-}n\ H_2O + n/2\ O_2 \rightarrow 2\ CO_2 + (6\text{-}n)\ H_2$ (2)

The main difference between these two processes is the temperature of reaction, because in the case of the reaction (2) the part of necessary energy comes from oxidation reaction. The side products of this reaction are carbon monoxide, acetone, acetaldehyde, methane and some other low weight hydrocarbons depending on the nature of the catalyst. The catalyst for these reactions should have

high oxidation activity coupled with ability of hydrocarbons activation. For these reason we have used metal-supported ceria catalysts known to possess high activity in CO or CH_4 oxidation.

CeO_2-supported catalysts activity crucially depends on surface area and particle structure. We have developed a new method of nanocrystalline ceria powder preparation using CeO_2 precipitation in alcohol-water mixtures. Average particles diameter of obtained ceria samples is between 4-6 nm, particle size distribution obtained by XRD and TEM shows that they sizes are uniform and they possess rather good temperature stability – no changes in TEM micrographs after 24 h exposure to 500 ^{O}C in air. Another valuable property of the ceria support was its hydrophilic nature which allows us to use incipient wetness method for metal deposition from water nitrate solutions. Using this method 5% Ni, Co, Fe and also a set of 0.5%, 1%, 3%, 5%, 10%, 20%, 30% Cu/CeO_2 catalysts were prepared. The size of metal oxide particles after calcination of obtained samples at 400 ^{O}C was below 10 nm and for most samples TEM micrographs shows no particles larger than CeO_2 size.

The conversion of ethanol-water mixtures (molar ratio 1:3) was studied at the range of temperatures 350-600 ^{O}C in a continuous flow fixed-bed reactor with total WHSV = 3000 h^{-1}. Pure CeO_2 itself is active as a catalyst in ethanol steam reforming reaction at 550 ^{O}C, however, conversion of ethanol is low (<50%) with average hydrogen yield 1 mol of H_2 per mole of ethanol and high level of methane and ethylene production. Cu, Ce, Fe and Co oxides deposited on CeO_2 increase ethanol conversion up to 90-95% at 550 ^{O}C, with an average concentration of hydrogen at the outlet of reactor up to 65%. The concentration of side products depends on metal nature, in the case of $5\%Ni/CeO_2$ catalyst CO and CH_4 concentrations are around 7% and the concentration of acetone and ethylene is low – 1-2%. $5\%Cu/CeO_2$ catalyst generates low amount of CO (1-2%) giving preference to acetone and other oxygenates (up to 17%). A careful study of metal loading in Cu/CeO_2 catalyst reveals that the optimal Cu loading is 3-10%, lower and higher copper content decrease ethanol conversion.

Obtained results shows that nanocrystalline CeO_2 based systems are promising catalysts for steam ethanol reforming – the process for hydrogen generation from biomass derived renewable feedstock.