REVIEW

from Prof. Dr. Anton Naydenov

on dissertation on the topic:

"Development of new metal oxide catalysts with application in alternative energy sources and ecology"

for awarding the educational and scientific degree "Doctor"

Doctoral student: **Alexandra Atanasova Mileva**

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Alexandra Atanasova Mileva graduated from the University of Chemical Technology and Metallurgy, Faculty of Chemical Technology in 2015, and in 2016 she was enrolled as a full-time doctoral student at the Institute of Organic Chemistry with a center in phytochemistry, BAS. The dissertation is written on 288 pages, citing 742 literature sources.

The topic of the dissertation is extremely relevant in view of the increased consumption of fuels for industry, transport and household, as well as the emerging depletion of conventional traditional energy sources and the increasing requirements for environmental protection. Interest in hydrogen is growing as it is considered a pure energy carrier, but its widespread use is limited by the necessary safety measures for its storage. Alternatively, the use of methanol as one of the most preferred compounds for the production of hydrogen, incl. and from renewable sources. The decomposition of methanol is an efficient method due to the lack of need for additional reactants and provides an additional opportunity to obtain energy by combustion the by-product carbon monoxide. For practical application of this process it is necessary to develop efficient and inexpensive catalysts that provide high catalytic activity, stability and selectivity in the decomposition of methanol to hydrogen and, if possible, to operate at relatively low temperatures. Within the framework of the literature review of the world literature the achievements in terms of the possibilities for the use of hydrogen as a pure and efficient energy carrier have been studied. The options for using activated carbon based on waste raw materials for use as a catalyst carrier are considered. At the same time, multicomponent metal oxide systems, composites based on TiO_2 with CeO_2 and ZrO_2, as well as three-component CuO-CeO_2-TiO_2 and CuO-ZrO_2-TiO_2, as well as ferrites - both their structure and their application as catalysts were studied. It has been shown that the properties of Ce-Ti binary oxides can be regulated by varying the Ce / Ti ratio and the temperature of the hydrothermal treatment, with the lower relative Ce / Ti ratio favoring the stabilization of highly dispersed CeO_2 particles on oxygen vacations in TiO_2. This ensures a high specific surface area and pore volume and oxygen mobility. An increase in catalytic activity and selectivity in the reaction of methanol decomposition to gas synthesis has been reported. The relatively high Ce / Ti ratio in the bicomponent materials facilitates the production of larger Ti^{4+} CeO_2-donated crystallites, which in turn leads to a deterioration of the texture parameters and reduces the number of redox pairs Ti^{3+} -Ti^{4+} and Ce^{3+} -Ce^{4+}. A decrease in catalytic activity with a simultaneous increase in selectivity to methane was measured. At higher temperatures of hydrothermal synthesis, larger particles of individual oxides are formed, leading to a weakening of their close contact. In the case of bicomponent materials obtained by precipitation with urea, more high dispersion and improved textural characteristics compared to monocomponent oxides, showing the presence of close contact between different metal oxide particles in bicomponent materials. As a consequence, an improvement in dispersion and their reducibility was observed.

The behavior of bicomponent oxides in the catalytic decomposition of methanol is characterized by some peculiarities compared to monocomponent oxides, which is related to the improved textural characteristics of mixed oxides and the interaction between individual oxides, controlled by the Ce / Ti ratio. It is concluded that homogeneous precipitation with urea and the hydrothermal method using the template are suitable techniques for the synthesis of nanosized cerium-titanium materials with a high specific surface area and pore volume. As a result of the strong bond between CeO_2 and TiO_2, as well as the increased dispersion of CeO_2 - TiO_2, mixed oxides improve their redox activity. On the other hand, in contrast to the homogeneous precipitation with urea, the hydrothermal method produces materials with higher homogeneity, improved dispersion and developed mesoporosity, and their higher degree of defect changes their acid-base properties, which causes more low catalytic activity and selectivity in the methanol decomposition reaction. It has been found that mesoporous copper-cerium-titanium oxide composites have high catalytic activity in the reaction of complete catalytic oxidation of ethyl acetate and high activity in the decomposition of methanol to synthesis gas at relatively low temperatures. It is assumed that the catalytic properties of these materials are determined by the activity of CuO crystallites and facilitated electronic transition in "conjugated" Ti-Ce-Cu redox centers in the interface layer, as the mechanism of growth of CuO crystallites is controlled by the method used. As a result of the insertion of isolated copper ions into the carrier lattice when applying the impregnation method, the formation of a relatively small number of accessible, easily reducible and highly active catalytic centers was registered, and it is assumed that the behavior of these composites is determined mainly by "conjugated" Ti-Ce-Cu redox centers in the interface layer. It is concluded that the catalytic activity in ternary composites is controlled by a complex mechanism of the Ce / Ti ratio of the carrier by generating surface functionality and oxygen vacations, structural and textural changes of the carrier and changes in the electronegativity of ions near copper.

In studies on the application of the hydrothermal method using template and homogeneous precipitation with urea, it has been shown that it is possible to obtain nanostructured mesoporous ZrO_2-TiO_2 bicomponent materials with different Zr / Ti ratio. It has been found that the incorporation of Zr^{4+} into the TiO_2 lattice facilitates the crystallization of large anatase particles in samples with a small Zr / Ti ratio, stabilization of the finely dispersed tetragonal ZrO_2 phase in samples with high zirconium content and dominance of amorphous $Zr_xTi_{1-x}O_2$ solution. On the other hand, it has been shown that the hydrothermal method does not exclude solid-phase interaction between individual TiO_2 and ZrO_2 oxides, resulting in materials with higher crystallinity and well-defined mesoporous texture, again controlled by Zr / Ti ratio and hydrothermal synthesis temperature. It has been demonstrated for the first time that the increase in the catalytic activity of bicomponent materials is extremely related to the improvement of the textural characteristics in them. It has been shown that all studied triple composites show high specific surface area and pore volume as well as high reducing ability due to facilitated electronic transfer in the Cu-Zr-Ti interface layer. The role of this interesting layer in the catalysis is controlled by the composition of the samples and the modification method used. The ternary composites obtained by the wetting impregnation technique demonstrate extremely high catalytic activity, which is associated both with the improved texture characteristics and with the specific interaction of the copper oxide particles with the carrier. The higher dispersion of the modifications obtained by the chemisorption-hydrolysis technique promotes the catalytic activity at a lower temperature, but the rapid reduction changes with the copper oxide particles under the influence of the reaction medium lead to rapid changes in the catalytic behavior of the composites. It has been shown that activated carbons obtained from Bulgarian peach pits can be a suitable carrier for the preparation of efficient catalysts for the decomposition of methanol with potential use in the production of hydrogen, and the state of the metal oxide particles deposited on the carrier can be easily regulated by the procedure for obtaining activated carbon and post-synthesis treatment, but this effect strongly depends on the nature of the applied metal oxides. In comparison, in iron modifications, the increase in the relative portion of the mesopores at a higher activation temperature promotes the formation of finer-dispersed magnetic particles.

The dispersion and availability of zinc oxide particles in zinc modifications is facilitated by the formation of additional surface acid groups during the pretreatment of carbon materials with nitric acid. In the case of binary modifications, due to the limited deposition of metal oxide particles in the micropores of the carrier, the combination of lower activation temperature of the carbon carrier and pretreatment with nitric acid contributes to the formation of highly active ferrite nanoparticles. Activated carbons with higher mesoporosity and surface functionality, derived from polyolefin wax, favor the aggregation of metal oxide particles, which leads to a decrease in their dispersion and the degree of zinc substitution in the ferrite phase, causing lower catalytic activity. Activated carbon obtained from agricultural residues (peach pits) may be a suitable matrix for stabilizing finely divided ferrite nanoparticles. Their formation strongly depends on the texture characteristics and reduction properties of the carbon carrier. In the case of activated carbon, polyolefin wax can be used as a carrier for stabilizing nanosized mono- and bicomponent iron and zinc oxide particles. They, in turn, are characterized by higher mesoporosity and surface functionality than those derived from peach pits. For the first time, high-quality activated carbons based on spent motor oils have been obtained and their potential as carriers of methanol decomposition catalysts has been studied. Compared to peach pitted activated carbon, motor oil-based activated carbon is characterized by a higher mesoporosity, which provides a higher availability of reactants to the metal oxide particles deposited on them and, as a result, improved catalytic activity. The possibilities for utilization of waste materials (peach pits, polyolefin wax and used motor oils) for the production of activated carbon and their potential application as carriers of effective catalysts for the decomposition of methanol are generally mentioned. It has been found that the state of the deposited metal oxide particles can be easily regulated by changes in the precursor and the procedure for the production of activated carbon, which reveals great opportunities for the synthesis of catalysts with adjustable properties with pronounced economic and environmental effect.

Conclussion

The dissertation presented by doctoral student Alexandra Atanasova Mileva on "Development of new metal oxide catalysts with application in alternative energy sources and ecology" fully meets the requirements for awarding educational and scientific degree "Doctor". The dissertation contains results that represent an original contribution to science. Doctoral student Alexandra Atanasova Mileva has in-depth theoretical and practical knowledge and skills in the field of Chemical Sciences. Therefore, I confidently give my positive assessment of the research presented in the above-reviewed dissertation, abstract and I suggest to the esteemed scientific jury to award Alexandra Atanasova Mileva the educational and scientific degree ‘Doctor’.

Sofia,29.12.2020.

Reviewer:

Prof. Dr. Anton Naydenov