UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY
DOCTORAL SCHOOL IN CHEMISTRY

PhD THESIS SUMMARY

Transition-metal-containing LDH-based catalysts for benzyl alcohol hydrodeoxygenation

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2025

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The primary aim of the present PhD thesis was the synthesis, characterization, and evaluation of new transition metal-based layered double hydroxide-derived catalytic materials in the hydrodeoxygenation (HDO) of benzyl alcohol as a model oxygenated compound present in biofuels.

The hydrodeoxygenation of bio-oil obtained from the pyrolysis of lignocellulosic biomass represents one of the most promising routes for producing advanced biofuels that are compatible with existing fuel infrastructure. Various catalysts have been tested for this process; however, commercial Co-MoS/Al_2O_3 (sulfided) catalysts suffer from the loss of their active phase (sulfide) and require the addition of sulfur to the feed. On the other hand, supported noble metal-based catalysts (e.g., Pt, Pd), while efficient and relatively stable, are extremely expensive and gradually lose their catalytic activity over time. In this context, transition metal-based catalysts derived from layered double hydroxide (LDH) precursors offer an attractive alternative, being low-cost, easy to synthesize, and possessing favorable acid-base and redox properties for HDO reactions.

This thesis is structured into four chapters:

Chapter 1. State of the Art: Provides an in-depth literature review on biofuels, with particular emphasis on advanced (second-generation) biofuels derived from lignocellulosic biomass. It discusses fast pyrolysis processes, the physicochemical limitations of the resulting bio-oils, and the key catalysts used in catalytic hydrodeoxygenation. The mechanisms involved in HDO for the most important classes of catalysts are presented, along with an overview of the role of catalyst supports, as well as catalyst deactivation and regeneration phenomena.

Chapter 2. Physicochemical Characterization Methods and Catalytic Tests: Describes the analytical techniques used for material characterization and the procedure used for catalytic testing.

Chapters 3 and 4 form the original core of the thesis. Chapter 3 focuses on the preparation, characterization, and catalytic testing of a series of MMgAlO catalysts derived from LDH precursors (where M = Mn, Fe, Co, Ni, Cu, and Zn), with an atomic Mg/Al ratio of 3 and 10 at. % transition metal content relative to the total number of cations. Since the CuMgAlO catalyst exhibited the best performance in the HDO of benzyl alcohol, a second series of Cu(x)MgAlO catalysts with different copper contents i.e., 5, 10, 15, and 20 at. % with respect to cations, and a fixed Mg/Al ratio of 3 was also synthesized and investigated. The best catalyst identified was Cu(15)MgAlO, which showed 97 % alcohol conversion and 96 % selectivity to toluene in optimized reaction conditions. It has been shown that surface reducible copper species are involved in catalysis.

Chapter 4 expands the study by analyzing the influence of the Mg/Al molar ratio on the HDO activity of Cu-MgAlO catalysts, including a detailed analysis of their structural properties and catalytic behavior. Thus, a series of CuMg(Al)O mixed oxides with 15 at. % Cu with respect to cations and different Mg/Al molar ratios, i.e., 0/1, 1/1, 3/1, 5/1 and 1/0, was synthesized by coprecipitation followed by thermal decomposition, characterized using a battery of techniques and, then, tested in benzyl alcohol HDO. It has been shown that the Mg/Al molar ratio strongly influences the physicochemical characteristics of the CuMg(Al)O mixed oxides and, hence, their catalytic performance. Specifically, the systems containing both Mg and Al were shown to be more active and selective than Mg-free and Al-free materials. Moreover, both CuMg(3)AlO and CuMg(5)AlO catalysts, which are obtained from well-crystallized LDH precursors, gave the best and practically the same HDO yield. Notably, benzyl alcohol conversion roughly followed the basicity of the catalysts in this series, while the HDO selectivity followed their acidity, confirming the key role played by the acid−base properties of the catalyst in this reaction. Nevertheless, morphological and structural changes of the mixed oxides accompanied by both copper leaching and a decrease in the Mg/Al ratio during the catalytic test resulted in lower performance after repeated catalytic runs.

The thesis ends with general conclusions that summarize the results obtained and suggest directions for future research, particularly focused on improving catalyst stability, selectivity, and hydrogen efficiency for industrial-scale bio-oil upgrading.