Tuning the properties of Pt/Ni supported catalysts for the reductive amination of furfural

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Significance and Relevance

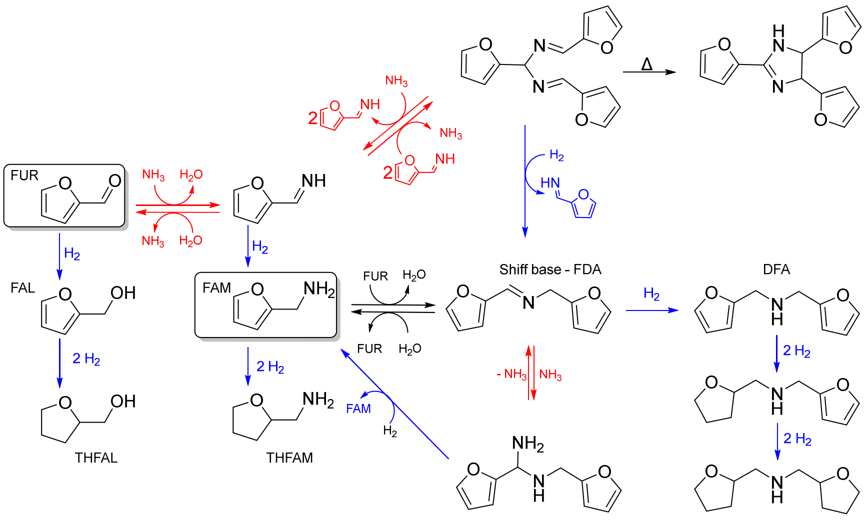
In the las years, the demand for nitrogenous compound has been increasing due to their key role in the synthesis of agrochemicals, pharmaceuticals, fine chemicals and polymers. Among the synthesis methods to produce nitrogen-containing molecules, the reductive amination reaction, using H_2 and NH_3, is the most common approach. Biomass-derived furfural (FAL) represents a promising renewable source for the preparation of amines through amination, however, obtaining satisfactory yields of amines in this reaction is challenging because side reactions like consecutive hydrogenation and self-condensation reaction cannot be ignored. Therefore, it is crucial to design and prepare catalysts with tuned hydrogenation active sites able to produce furfurylamine (FAM) in the presence of ammonia and hydrogen. Herein, this study exhibits the catalytic reductive amination of furfural to furfurylamine using well defined Pt/Ni supported catalysts synthetized from carbonyl clusters. The results highlighted the possibility of tuning the active phase to obtain very high yields of furfuryl amine in mild condition and low time of reaction.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion

Preferred presentation: Oral preferred

Introduction and Motivations

The synthesis of primary amines via reductive amination in the presence of NH_3 and H_2, as a green and sustainable process, has attracted increasing attention in the recent years. Thanks to its abundance and relatively low cost, ammonia is an interesting nitrogen source for the reductive amination of biomass-derived molecules, such as furfural, but controlling the production and selectivity of primary amine is a quite challenging aspect of this reaction [1]. Indeed, the reductive amination to primary amines has a complex mechanism, and many side reactions may occur during the process (Scheme 1). In this work, we prepared a series of Pt/Ni supported catalysts with the impregnation and decomposition of bimetallic carbonyl clusters over TiO_2, and their catalytic performances on the reductive amination of FAL to produce FAM were studied. The catalytic activity and the selectivity in the different products were correlated to the structure and surface properties of catalysts.



Scheme 1. Proposed reaction pathway for the reductive amination of furfural

Materials and Methods

A series of random alloy carbonyl clusters $[NBu_4]_2[Pt_{6-x}Ni_x(CO)_{12}]$ with different Pt:Ni molar ratios were synthesised [2] and supported on TiO_2 by wet impregnation, under nitrogen atmosphere. The final catalysts were obtained through a decomposition of the cluster under reductive atmosphere. Each catalyst was tested in the reductive amination of furfural, carrying out the reaction in a stainless-steel autoclave, in methanol, using a NH_3 solution in methanol as nitrogen source and under a pressure of H_2.

Results and Discussion

The use of bimetallic carbonyl clusters for catalysts synthesis allowed the preparation of final nanoparticle-based catalysts with precise metal composition. The synthesis of all the materials was monitored by means of FTIR spectroscopy, focusing on the νCO bands shift in the terminal and edge-bridging regions (2100 – 1700 cm^{-1}). TEM analysis on the final catalysts confirmed the formation of small nanoparticles with mean diameters around 1 nm.

The optimisation of various reaction parameters like time, temperature, H_2 pressure, and NH_3 concentration was studied with the catalyst Pt_3Ni_3/TiO_2. At the beginning of the reaction and a low temperature the main product formed were N-furfurylidenefurfurylamine (FDA), indicating that the FDA was the key intermediate of the reaction because of the high reactivity of FAM under given reaction conditions. Optimization of reaction conditions demonstrated the possibility to work in mild conditions, at 80°C and 1 h of reaction, using an excess of NH_3 respect to furfural (Figure 1A). Moreover, the study of catalyst with different Pt/Ni molar ratios (Figure 1B), showed that Ni insertion led to more selective catalysts. In particular, using Pt_2Ni_4/TiO_2 sample, complete furfural conversion and FAM selectivity higher than 90%, were obtained after one hour of reaction. In addition, the presence of nichel in Pt/TiO_2 systems was demonstrated to strongly enhance catalyst stability.

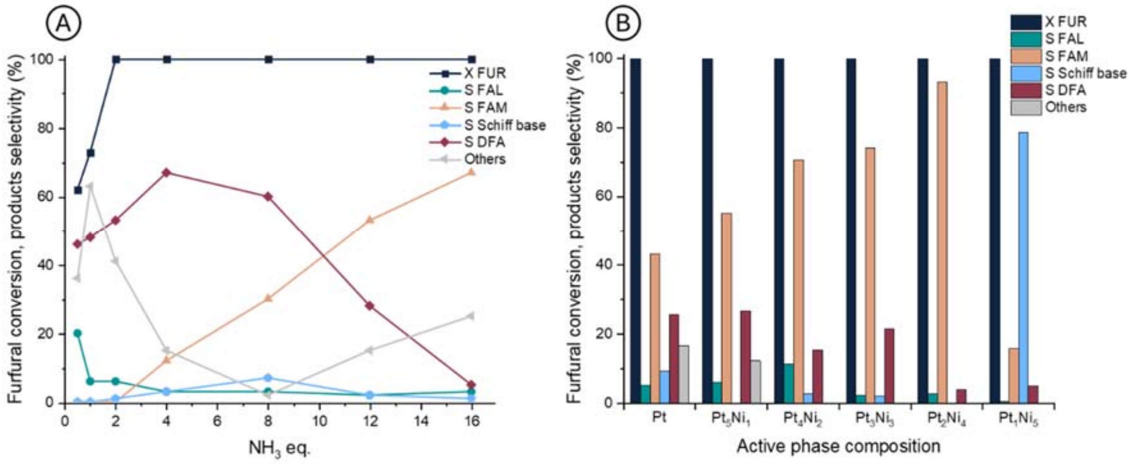


Figure 1. A) Furfural conversion and products selectivity as a function of NH_3/furfural molar ratio (reported on X axis as NH_3 equivalents) using Pt_3Ni_3/TiO_2 catalyst. B) Catalytic performances of Pt/Ni bimetallic catalysts with different Pt:Ni molar ratios. Reaction condition 80°C, 10 bar of H_2, 1 h, solvent methanol.

References

[1] N. S. Gould, H. Landfield, B.Dinkelacker, C. Brady, X. Yang, B. Xu, *ChemCatChem* **2020,** 12, 2106 – 2115.

[2] C. Cesari, B. Berti, M. Bortoluzzi, C. Femoni, M.C. Iapalucci, S. Zacchini, *Inorg. Chem.* **2021**, 60 (12), 8811–8825.