Rh–Ni Bimetallic Catalysts for Enhanced Production of Cyclohexylamine via Reductive Amination.

Doris Ruiz[1*], Karen Morales[1], Luciene S. Carvalho[2], André Rosa Martins[2], Adriana Ballarini[3], Andreia Peixoto[4], Ricardo Chimentão[1]

*[1]CATSVAL, Departamento de Físico Química, Facultad de Ciencias Químicas, Universidad de Concepción, Ed. Larenas 129, Casilla 160-C, Concepción, Chile. *doruiz@udec.cl*
[2]Instituto Federal da Bahia, Campus Camaçari, Av. Jorge Amado, s/nº, Jardim Limoeiro, 42.800-605, Camaçari-BA, Brasil.
[3]Instituto de Investigaciones en Catálisis y Petroquímica "Eng. José Miguel Parera" (CONICET-UNL), Colectora Ruta Nacional 168 Km 0, 3000, Santa Fe, Argentina
[4]REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal

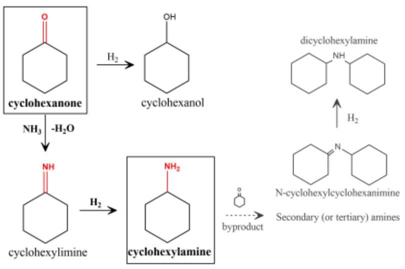
Abstract

The reductive amination of cyclohexanone with NH_3 and H_2 over Rh and Rh–Ni catalysts supported on SiO_2 was studied to produce cyclohexylamine, a key intermediate in fine chemicals. Catalysts with varying Ni loadings (1–10 wt.%) were prepared by wet impregnation and characterized by N_2 physisorption, TEM, XRD, XPS, H_2-TPR, and NH_3-TPD. Bimetallic Rh–Ni catalysts exhibited improved catalytic performance due to enhanced dispersion, reducibility, and acidity. The 2 wt.% NiRh/SiO_2 catalyst showed the best results, with 99.8% conversion, 96.4% yield, and 96.6% selectivity. Rh/SiO_2 reached 83.4% conversion and 99.1% selectivity. Reusability tests confirmed the stability of the bimetallic catalyst, which maintained 99.5% selectivity and 74.0% yield after four cycles.

Keywords: Rhodium-Nickel, Amination, Heterogeneous Catalysis, Bimetallic Catalysts

Introduction

Primary amines are key intermediates in pharmaceuticals, agrochemicals, polymers, and dyes, making their efficient synthesis a relevant challenge. Among several methods, reductive amination of carbonyl compounds stands out for its selectivity and green credentials (1). However, when using NH_3 and H_2, harsh conditions are often required, and overalkylation remains a challenge. Heterogeneous catalysts, especially noble metals like Rh and earth-abundant Ni, play a crucial role in improving selectivity under milder conditions (2,3). Rh is highly selective toward primary amines (4,5), while Ni offers a cost-effective alternative. In this context, cyclohexanone amination is industrially relevant for producing cyclohexylamine (Scheme 1).



Scheme 1. Reaction scheme for reductive amination of cyclohexanone.

This study investigates the catalytic behavior of Rh and Rh–Ni/SiO_2 catalysts under mild conditions (100 °C, 4 bar NH_3, 2 bar H_2), showing high selectivity to cyclohexylamine without forming secondary or tertiary amines, and highlighting the synergistic effect of Rh–Ni bimetallic systems.

Experimental

Rh/SiO_2 (1.7 wt.%) and Rh–Ni/SiO_2 (1–10 wt.% Ni) catalysts were prepared by wet and successive impregnation, calcined at 400 °C, and reduced under H_2. Textural properties were determined by N_2 physisorption (BET, BJH), while TEM, HRTEM–STEM–EDX, XRD, and XPS were used for structural and surface analysis. Reducibility and acidity were evaluated by H_2-TPR and NH_3-TPD. Catalytic tests were conducted in a glass-lined reactor at 100 °C, 4 bar NH_3, and 2 bar H_2, using 50 mL of cyclohexane and a 100:1 cyclohexanone/Rh molar ratio. Reusability was assessed by recovering, washing, and drying the catalyst after each run. Products were analyzed by GC-FID and confirmed by mass spectrometry.

Results and Discussion

The incorporation of Rh and Ni into SiO_2 significantly influenced the catalysts' textural and physicochemical properties. N_2 physisorption showed a decrease in surface area and pore volume after metal impregnation, except for the 2 wt.%NiRh/SiO_2 catalyst, which exhibited increased surface area, likely due to Rh redispersion. TEM and HRTEM (Figure 1) revealed small, well-dispersed nanoparticles (~2 nm), with a bimodal distribution in 10 wt.%NiRh/SiO_2 due to Ni agglomeration. XRD confirmed the presence of crystalline Ni and high Rh dispersion, while XPS indicated predominantly metallic Rh^0 and Ni^0 species. The 2 wt.%NiRh/SiO_2 catalyst showed the highest metal surface exposure.

H_2-TPR and NH_3-TPD analyses highlighted variations in reducibility and acidity. The 2 wt.%NiRh/SiO_2 catalyst exhibited favorable features: high dispersion, low acidity, and moderate H_2 uptake, correlating with improved selectivity in reductive amination. Overall, this catalyst achieved an optimal balance between metal accessibility and acid site density, favoring primary amine formation while minimizing side reactions.

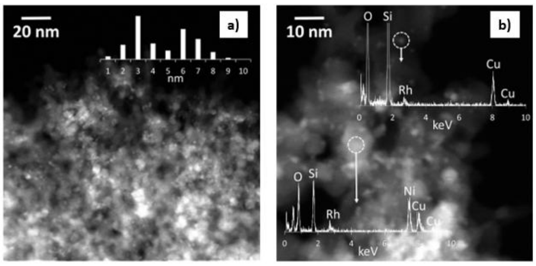
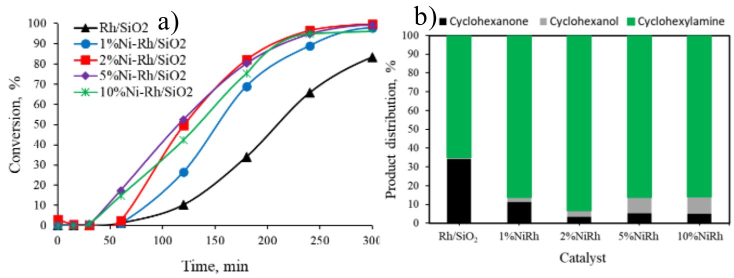


Figure 1. HRTEM Micrographs of 10wt.%NiRh/SiO_2 catalyst: a) HAADF-STEM, b) HAADF-STEM-EDX.

The reductive amination of cyclohexanone with NH_3 and H_2 was carried out using Rh/SiO_2 and NiRh/SiO_2 catalysts under mild conditions (100 °C, 4 bar NH_3, 2 bar H_2). The reduced Rh/SiO_2 catalyst reached 83.4% conversion and 99.1% selectivity to cyclohexylamine. Selectivity was strongly influenced by the NH_3/H_2 ratio, with ammonia promoting imine formation and hydrogen enabling its reduction.

The bimetallic 2 wt.%NiRh/SiO_2 catalyst exhibited superior performance, achieving 99.8% conversion and 96.6% selectivity at 300 min. Higher Ni loadings (>5 wt.%) led to reduced conversion and increased cyclohexanol formation, attributed to changes in metal dispersion and acidity.

Catalyst reuse confirmed the robustness of the 2 wt.%NiRh/SiO_2 system: after four cycles, it maintained 99% selectivity and 74% yield. These results demonstrate the advantages of bimetallic tuning in improving catalytic efficiency, selectivity, and recyclability for the selective synthesis of primary amines.



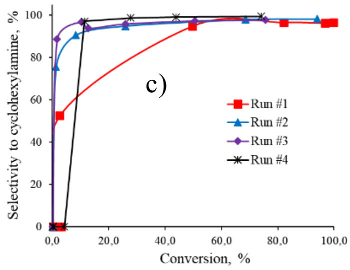


Figure 3. Cyclohexanone amination a) Conversion on time over NiRh/SiO_2, b) Product distribution over NiRh/SiO_2 at 240 min, c) Recycle of 2wt.%NiRh/SiO_2

Conclussion

The reductive amination of cyclohexanone over NiRh/SiO_2 catalysts demonstrated that bimetallic modification significantly enhances catalytic performance. While Rh/SiO_2 showed high selectivity (99.1%) and moderate conversion (83.4%), the incorporation of 2 wt.% Ni increased conversion to 99.8%, yield to 96.4%, and selectivity to 96.6%. This catalyst also maintained 99.5% selectivity and 74.0% yield after four reuse cycles, confirming its stability. The integration of Ni into Rh/SiO_2 provides a cost-effective, efficient, and recyclable system for the selective synthesis of primary amines.

Acknowledgments

To VRID-UdeC, FCQ-UdeC, FONDECYT 1220355, and Dr. Jordi Llorca (UPC, Spain) for HRTEM analysis.

References.

1. D. Ruiz; A. Aho; T. Saloranta; K. Eränen; J. Wärnå; R; Leino; D.Y. Murzin., *Chem. Eng. J.* **2017**, *307*, 739–749.
2. D. Ruiz; A. Aho; P. Mäki-Arvela; N. Kumar; H. Oliva; D.Y. Murzin, *Ind. Eng. Chem. Res.* **2017**, *56*, 12878–12887.
3. X. PJv; S. Sun; Q. Zhang; M. Du; L. Wang; B. Wang, *ACS Sustainable Chem. Eng.* **2020**, *8*, 1618–1626.
4. S. Kirschtowski; C. Kadar; A. Seidel-Morgenstern; C. Hamel, *Chem. Ing. Tech.* **2020**, *92*, 582–588.
5. J. Bianga; N. Kopplin; J. Hülsmann; D. Vogt; T. Seidensticker, *Adv. Synth. Catal.* **2020**, *362*, 4415–4424.