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Ecosustainable quinoxaline synthesis promoted by silica-supported MoO3 nanoparticles

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Resumo/Abstract

RESUMO – Neste trabalho, nós estudamos o desempenho de uma série de catalisadores de óxido de molibdênio (MoOx) suportados em sílica (teores de Mo iguais a 0,5, 1,0 e 3,0% em peso, rotulados como SiMo0,5, SiMo1 e SiMo3, respectivamente) na síntese ecosustentável de 2-fenilquinoxalina a partir de *o-*fenilenodiamina e α-hidroxiacetofenona. A área específica dos catalisadores diminui com o teor de Mo: 331, 262 e 238 m2/g para os catalisadores SiMo0,5, SiMo1 e SiMo3, respectivamente. Os padrões de DRX revelam picos de difração associados à fase cristalina hexagonal MoO3 (tamanho de cristalito ~26 nm) apenas para SiMo3, indicando que os MoOx estão completamente dispersos ou como fases amorfas em cargas de Mo inferiores a 3% em peso. Todos os catalisadores exibem duas bandas LMCT em 240 e 320 nm no espectro UV-vis que correspondem a espécies poliméricas de molibdato octaédricas. O SiMo3 também exibe uma banda LMCT em 260 nm relacionada aos cristalitos de MoO3. Todos os catalisadores apresentam alta atividade na síntese seletiva de 2-fenilquinoxalina, com o SiMo3 apresentando a maior conversão (95% após 180 min de reação a 80 ºC), mesmo quando diferentes *o-*fenilenodiaminas substituídas foram empregadas. Além disso, o SiMo3 manteve alta atividade após três corridas consecutivas.

*Palavras-chave: oxido de molibdênio, nanopartículas, quinoxalinas.*

ABSTRACT – This work investigates the performance of a series of silica-supported MoOx catalysts (Mo loadings of 0.5, 1.0, and 3.0 wt.%, labeled as SiMo0.5, SiMo1, and SiMo3, respectively) in the ecosustainable synthesis of 2-phenylquinoxaline from *o-*phenylenediamine and α-hydroxyacetophenone. The specific surface area of the catalysts decreased with Mo loading: 331, 262, and 238 m2/g for SiMo0.5, SiMo1, and SiMo3, respectively. The XRD patterns reveal diffraction peaks associated with the hexagonal crystalline MoO3 phase (crystallite size of ~26 nm) only for SiMo3, indicating that MoOx are either completely dispersed or amorphous at Mo loadings lower than 3 wt.%. All catalysts display two LMCT bands at 240 and 320 nm in the UV-vis spectra that correspond to octahedral polymeric molybdate species. SiMo3 also exhibits a LMCT band at 260 nm related to the MoO3 crystallites. All catalysts show high activity in the selective synthesis of 2-phenylquinoxaline, with SiMo3 displaying the highest conversion (95% after 180 min of reaction at 80 ºC), even when different substituted *o-*phenylenediamines were employed. Furthermore, SiMo3 maintained its high activity after three consecutive runs.

*Keywords: molybdenum oxide, nanoparticles, quinoxaline.*

## Introduction

Silica-supported molybdenum oxide catalysts have been extensively used for important reactions, such as olefin metathesis and selective oxidation of alcohols, alkanes, and alkenes [1]. However, as far as we know, the use of these catalysts is not widespread for the synthesis of heterocyclic compounds with biological activity.

Among the diverse heterocyclic compounds, quinoxalines hold particular importance, as they are commonly found in a wide range of natural products, agrochemicals, and synthetic drugs with biomedical applications. Recent advancements in catalysis have highlighted the potential of porous carbons, including acidic biomass-derived porous carbons and transition metal-doped carbon aerogels, for sustainable quinoxaline synthesis [2].

In this study, we investigate the activity of a series of easily prepared silica-supported MoOx catalysts with Mo loadings of 0.5, 1.0, and 3.0 wt.% (labeled as SiMo0.5, SiMo1, and SiMo3, respectively) for the efficient and ecosustainable synthesis of 2-phenylquinoxaline at high conversions and short reaction times.

Experimental

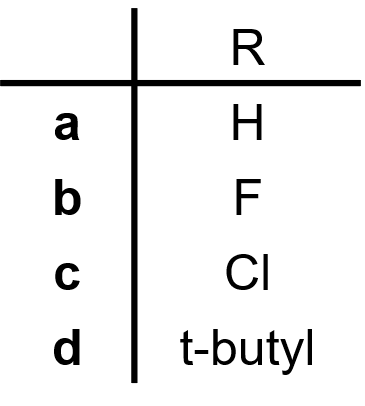
*2.1 Catalyst Synthesis.*

The silica-supported MoOx catalysts were synthesized by the incipient-wetness impregnation (IWI) method. For this, an adequate amount of ammonium heptamolybdate (AHM; (NH4)6H2Mo7O21∙4H2O, Sigma-Aldrich, >99.99%) was dissolved in deionized water and added to the silica support (Davisil, 401 m2/g). The samples were dried at 110 ºC overnight and calcined at 500 ºC (5 ºC/min) for 5 h.

*2.2 Catalyst Characterization.*

The specific surface area was calculated *via* N2 physisorption experiments using an ASAP 2020 (Micromeritics). X-ray powder diffraction (XRD) measurements were performed on a PANalytical X’Pert Pro diffractometer using: CuKα radiation (λ = 1.540 Å), Bragg angle (2θ) range of 5-90°, step size of 0.02°, and counting time of 50 s. Crystalline phases were identified using the JCPDS database. The crystallite size was calculated using the Scherrer equation. The UV−vis spectra were taken using a Cary 5000 UV−vis−NIR spectrophotometer: 200− 800 nm range at 25 °C, scan rate of 15 nm/min, and a signal averaging time 0.6 s. The FTIR spectra were acquired using a Varian 660 spectrophotometer in the absorbance mode: 4000-400 cm-1 and resolution of 2 cm-1.

*2.3 Catalytic activity*

Typically, 100 mg of each catalyst was added to a mixture of *o-*phenylendiamine **1** (0.5 mmol) and α-hydroxyacetophenone **2** (0.5 mmol) in of toluene (5mL) at 80 ºC. The samples were periodically taken at 15, 30, 60, 120, 180, and 240 min. The catalyst was removed by centrifugation and decantation, and the solvent was evaporated in *vacuo*. The reaction products were characterized by 1H RMN spectroscopy.

Results and Discussion



**a)**

**b)**

**c)**

**d)**



*3.1 Catalysts Characterization.*

Fig. 1. Catalysts characterization: a) N2 adsorption-desorption isotherms, b) XDR patterns, c) UV-vis DRS spectra, and d) FT-IR spectra.

The specific surface area of the catalysts decreased with Mo loading, which can be attributed to the partial plugging of the silica pores by the supported Mo oxides, limiting the accessibility of N2 molecules (Fig. 1a). The XRD patterns reveal diffraction peaks associated with the crystalline MoO3 phase (crystallite size of ~26 nm) only for SiMo3, indicating that Mo oxides are completely dispersed or as amorphous phases at Mo loadings lower than 3 wt.% (Fig. 1b). SiMo0.5 and SiMo1 display two LMCT bands at 240 and 320 nm related to octahedral polymeric molybdate species (Fig 1c). SiMo3 also exhibits a LMCT band at 260 nm related to the MoO3 crystallites. The FTIR spectra exhibit characteristic Si-O-Si bands with decreased intensity as function of Mo loading (Fig. 1d).

*3.2 Catalitic activity.*

All the catalysts were efficient in the synthesis of quinoxalines (Scheme 1, Fig. 2).

Diagrama

Descripción generada automáticamente

**Scheme 1.** Synthesis of quinoxaline **3-4** from *o-*phenylendiamine **1** and α-hydroxyacetophenone **2** in toluene, at 80 °C, catalyzed by MoOx/SiO2 samples.

Gráfico

Descripción generada automáticamente

**Fig. 2.** Synthesis of 2-phenylquinoxalines **3-4**: a) catalyzed by MoOx/SiO2 catalysts, b) catalyzed by SiMo3 catalyst.

The SiMo3 catalyst was the most efficient selectively leading to 2-phenylquinoxaline with 95% of conversion, after 180 min of reaction time at 80 °C, possibly due to the Mo phase and crystal size observed (Fig. 2a). Highly dispersed catalysts, SiMo1 and SiMo0.5, presented similar conversions although notably lower regarding the SiMo3 sample but high selectivity.

Conclusion

The SiMo3, with MoO3 supported nanoparticles, shows the highest conversion (95% after 180 min of reaction at 80 ºC), and remains active after three consecutive runs.

Bibliography

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