



Mo/ γ -Al₂O₃ catalysts for the Biginelli reaction. Effect of Mo loading



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ABSTRACT

Alumina supported Mo catalysts with varying metal loading (2–12 wt%) were tested in the Biginelli reaction under solvent free conditions for synthesis of 3,4-dihydropyrimidin-2-(1H)-one (DHPM). The DHPM yield increased with Mo loading, going through a maximum for 7 wt% Mo. Alumina supported Mo catalysts appeared to be highly stable and reusable materials for this reaction.

A suite of characterization techniques that included X-ray diffraction, Fast Fourier Transform analysis and FTIR of adsorbed pyridine revealed that the DHPM formation is related to the existence of Brønsted acid sites that would be linked to the presence of Al₂(MoO₄)₃ phase.

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1. Introduction

The development of new reactions, capable of forming multiple connections, in a single step, with good overall yields, while respecting the environment, has become an important challenge for academic and industrial laboratories. The multicomponent reactions (MCRs) are fully in line with this context since they lead to atom and step economies. They are defined as the assembly process in a single step of at least three or more reactants that will participate in the structure of the final product [1–3]. One such MCRs is the Biginelli reaction, one of the most important reaction for generating the dihydropyrimidinones (DHPMs) with diverse medicinal applications [4]. DHPMs and their derivatives have in fact exhibited remarkable therapeutic and pharmacological activities as calcium channel blockers [5], antiviral, antibacterial, antitumor, antioxidant and anti-inflammatory [6–9].

The classical Biginelli procedure for the preparation of dihydropyrimidinones is through a one-pot cyclocondensation of aldehyde, β -ketoester, urea/thiourea under strong acidic conditions [10]. However, this protocol suffers from drawbacks such as long reaction times, high reaction temperatures, environmental pollution by using organic solvents and frequently low yields, especially in the case of some substituted heteroaromatic aldehydes [11]. In order to enhance the efficiency of Biginelli reaction, various Lewis and/or Brønsted acid catalysts have been studied

such as PPh₃ [12], ZrOCl₂·8H₂O [13], trifluoromethanesulfonic acid [14], Cu(NH₂SO₃)₂ [15] and TaBr₅ [16]. Furthermore, the use of heterogeneous catalysts has received a lot of attention for this transformation since it offers easy recovery and recycling of the catalytic material. For example, Fe₃O₄/PAA-SO₃H [17], Sr(OTf)₂ [18], ZnO [19], TiO₂/CNT [20], H₃PW₁₂O₄₀/SiO₂ [21] and sulphated tin oxide (TSO) [22] revealed high selectivity toward DHPMs with a short reaction time and reusability of catalysts for several times.

The goal of the present work was to evaluate the influence of molybdenum loading on the catalytic properties of Al₂O₃-supported Mo for the Biginelli reaction under solvent free conditions (Scheme 1). The catalysts were characterized by electron microscopy, Fast Fourier Transform analysis, X-ray diffraction and FTIR of adsorbed pyridine. These characterization results were further combined with catalytic data obtained for the Biginelli reaction, to derive conclusions regarding the structure-reactivity correlations for the Mo/ γ -Al₂O₃ system.

2. Experimental

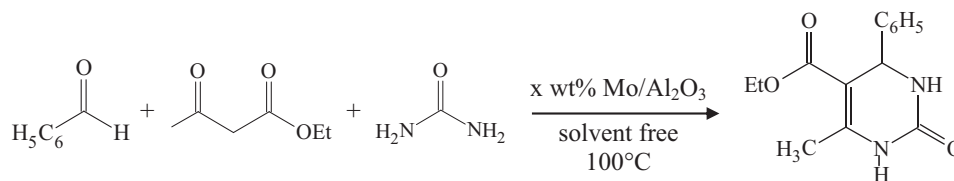
2.1. Catalyst preparation

The support was a γ -alumina with a specific surface area of 213 m² g⁻¹. The support was calcined in flowing air at 500 °C for 5 h.

Mo based catalysts with different metal loadings were prepared by wet impregnation of the γ -alumina support at room temperature using an aqueous solution of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O). After impregnation, the catalysts were

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Scheme 1.

dried at 120 °C for 48 h and then calcined at 500 °C (heating rate = 2 °C min⁻¹) in air for 5 h. The resulting catalysts are denoted in this manuscript as xMoAl, where x indicates the weight percentage of Mo.

2.2. Catalyst characterization

All the characterizations were performed on previously calcined samples.

The molybdenum content of the different catalysts was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, model optima 2000 DV) after digestion in an acid solution.

The BET specific surface areas were measured by nitrogen adsorption–desorption at –196 °C using a Micromeritics Tristar apparatus. The BJH method was used to determine the mean pore size. Prior to these physisorption measurements, the samples were degassed at 250 °C for 5 h.

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Panalytical Empyrean instrument, using Cu K α radiation (λ K α = 0.1504 nm) and scanning 2θ from 10° to 80° with a step of 0.05° and a time per step of 240 s. Crystalline phases were identified by comparison with the Powder Diffraction Files (PDF) standards from the Inorganic Crystal Structure Database (ICSD).

The morphology of the catalysts was studied by high resolution transmission electron microscopy (HRTEM) to determine the particle size over the alumina support. HRTEM measurements were carried out on a Jeol JEM 2100 UHR equipped with a LaB₆ filament. The apparatus has a linear resolution of 0.14 nm and is equipped with a Gatan Ultrascan CCD camera with a resolution of $2k \times 2k$. The phase composition and structure were obtained in the same electron microscope by microanalysis EDS and Fast Fourier Transform (FFT), respectively. Interreticular distances d_{hkl} as well as lattice parameters were calculated from the distances between the spots and the angles formed by the lines passing through these spots. A program [23,24] allows one to check the calculated values by drawing the theoretical pattern along the same zone axis and by comparing it to the experimental pattern. Before analysis in the electron microscope, powder sample was dispersed in ethanol, and the solution dropped on a nickel grid previously covered with a holey carbon film.

The surface acidity of the solids was investigated through Fourier Transform Infrared (FTIR) spectroscopy of pyridine adsorption with an intention of obtaining a comparative evaluation of Lewis (L) and Brønsted (B) acid sites in the catalysts. Pyridine FTIR spectra were recorded on a Thermo Nicolet Nexus FTIR spectrometer. Samples were compacted into thin pellets and activated at 450 °C under a secondary vacuum (10^{-6} mbar) overnight. After cooling until room temperature, pyridine adsorption was performed for 5 min after pressure stabilization. The cell was then kept under a secondary vacuum for 1 h. The thermo desorption of pyridine was carried out at 150 °C for 30 min. The IR spectra were recorded at room temperature in a spectrometer equipped with a DTGS detector (Deuterium TriGlyceride Sulfur) and KBr beam splitter, with a resolution of 2 cm⁻¹ and 64 scans.

Table 1

Characteristics of xMoAl catalysts calcined at 500 °C.

Catalysts	2MoAl	5MoAl	7MoAl	9MoAl	12MoAl
Mo theor. (wt%)	2.0	4.6	6.6	8.6	12.0
Mo exp. (wt%)	2.2	4.5	6.4	8.5	11.9
S_{BET} (m ² g ⁻¹)	139	127	117	97	70
V_{Pore} (cm ³ g ⁻¹)	0.20	0.18	0.17	0.14	0.11

2.3. Catalytic test

The Biginelli reaction was chosen as a model reaction to test the catalytic activity of the xMoAl materials. The reaction was performed under solvent free conditions.

In a 25 mL single-neck round bottom flask with an air cooler, a mixture of benzaldehyde (2 mmol), ethyl acetoacetate (2 mmol), urea (3 mmol) and xMoAl catalyst (0.2 g) was stirred at 100 °C for 1 h. The reaction was monitored by thin layer chromatography (hexane/ethyl acetate: 6/4). After one-hour reaction time, the resulting solidified mixture containing the catalyst was cooled down to room temperature. Since DHPM is soluble in hot ethanol, the mixture was washed with boiling ethanol and then filtered to remove the catalyst. The filtrate was poured into crushed ice involving recrystallisation of a residue suspended in solution. The residue (containing DHPM) was then subsequently collected by filtration and once again recrystallized from hot ethanol to afford pure product. The isolated catalyst was dried at 100 °C overnight and was reused in the next runs without further purification.

DHPM was identified by comparing its melting point and analytical spectroscopic data (IR, ¹H, ¹³C NMR) with those reported in literature [25–27]. Melting points were determined using an Electrothermal SMP 11. IR spectra were recorded on a Shimadzu FTIR-8400 spectrometer. NMR experiments were recorded with a Bruker Avance 400 spectrometer at 400 MHz for ¹H nuclei and at 100 MHz for ¹³C nuclei. The chemical shifts are expressed in part per million (ppm) relative to TMS (δ = 0 ppm) and the coupling constant J in Hertz (Hz). NMR multiplicities are reported using the following abbreviations: br = broad, s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet.

3. Results and discussion

3.1. Catalyst characterizations

3.1.1. Physical properties

The chemical analysis and textural properties of xMoAl catalysts after calcination are summarized in Table 1. The weight loading of Mo was varied between 2 and 12 wt%. The experimental Mo weight loading corresponds well to nominal loading. The specific surface area (S_{BET}) values decrease progressively, as the molybdenum loading increases, from 213 m² g⁻¹ for the bare support to 70 m² g⁻¹ for 12MoAl. This behaviour agrees with literature [28–30]. A likely cause for this loss could be a partial blocking of the micropores of the γ -Al₂O₃ support by the crystallites of dispersed metal oxides, since the pore volume (V_{Pore}) decreases with increasing Mo loading (Table 1). Solid state reactions leading to new phases may also be responsible for the diminishing surfaces areas.

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