Mo/zeolite catalysts for the hydrodeoxygenation of biomass-derived compounds

Gabriel B. Báfero1, Mateus M.M.R. Duenha1, Daniela Zanchet1,\*

1 Institute of Chemistry, University of Campinas, UNICAMP, Campinas, SP, 13083-970, Brazil

\* Corresponding Author: zanchet@unicamp.br

Resumo/Abstract

RESUMO - A crescente demanda por produtos químicos e combustíveis renováveis tem estimulado a busca por matérias-primas alternativas. Nesse caminho, a biomassa tem despertado interesse da academia e da indústria, sendo a sua valorização a compostos de maior valor agregado ainda um grande desafio. A utilização de catalisadores bifuncionais, como os sistemas metal/zeólita, parece o melhor caminho para a conversão de derivados da biomassa *via* hidrodesoxigenação (HDO). Tais catalisadores são capazes de mediar muitas das rotas reacionais envolvidas na reação de HDO. Alguns conceitos-chave sobre esses sistemas devem ser levados em consideração, como o balanço e a proximidade entre os sítios ácidos zeolíticos e os sítios metálicos. Alguns óxidos metálicos reduzíveis, como MoO3, em condições reacionais, podem apresentar sítios hidrogenantes, sendo boas alternativas aos metais convencionalmente empregados. Nesse caminho, o presente trabalho visa avaliar esses conceitos-chave utilizando catalisadores Mo/zeólita frente a reação de HDO de acetona, uma molécula modelo representativa de derivados da biomassa muito útil na sondagem de diferentes funcionalidades catalíticas.

*Palavras-chave: catálise, hidrodesoxigenação, zeólita, molibdênio, catalisadores bifuncionais*

ABSTRACT - The growing demand for renewable chemicals and fuels has stimulated the search for alternative raw materials. In this way, biomass has gained space in research and industry, however the biomass valorization to compounds with higher added value is still a great challenge. The use of bifunctional catalysts, such as metal/zeolite systems, seems to be the best way to convert biomass derivatives *via* hydrodeoxygenation (HDO). Such bifunctional systems can mediate many of the reaction pathways involved in the HDO reaction. Some key concepts about these catalysts must be considered, such as the balance and the proximity between the zeolitic acid sites and the metallic sites. Some reducible metal oxides, such as MoO3, under reaction conditions, can present hydrogenating sites, being good alternatives to the metals conventionally used in these systems. In this way, the present work aims to evaluate these key concepts using MoO3/zeolite catalysts in the acetone HDO reaction. Acetone is a representative model molecule of biomass derivatives, very useful in probing different catalytic functionalities.

*Keywords: catalysis, hydrodeoxygenation, zeolite, molybdenum, bifunctional catalysts*

## **Introduction**

In fossil fuel refineries, the basic chemical building blocks that currently serve as platform molecules are normally apolar/low reactivity hydrocarbons, and upgrading these compounds requires the activation of the C–C and C–H bonds. On the other hand, biomass-derived compounds are usually polar, highly reactive, and extensively functionalized oxygenates. Further upgrading involves activation and cleavage of C–O bonds leading to deoxygenated products.

The hydrodeoxygenation reaction (HDO) is one of the main biomass-derived upgrading processes, in which a H2-rich atmosphere combined with a solid catalyst is used to reduce the high oxygen content by the selective cleavage of C-O bonds, besides saturating aromatics and alkenes (1). The set of reactions usually found in the HDO of biomass-derived compounds may include hydrogenations, hydrogenolyses, direct deoxygenations, dehydrations, isomerizations, decarbonylations, decarboxylations, and carbonyl condensations (2). In this sense, using catalysts that combine different functionalities in a single material seems economically and energetically advantageous.

For reactions requiring acidity and hydrogenation activity, such as HDO, zeolites can be particularly useful for constructing bifunctional materials, once presenting chemical and hydrothermal stability, high surface area, porosity, and intrinsic acidity. Metallic sites can be included through a variety of simple and effective procedures: impregnation, ion exchange, deposition-precipitation, or encapsulation (during synthesis) (3). The optimization of the site-ratio of different catalytic functions is vital to achieve specific products distributions. Synergistic effects are expected if acid sites and hydrogenation functions are put close to each other (4,5). This type of site engineering in metal/zeolite systems is currently being extensively explored.

Therefore, the main objective of this work is to evaluate the bifunctional properties of MoO3/zeolite catalysts through the HDO reaction of different model molecules, starting with acetone. Acetone is the simpler ketone representative, but still, the acetone HDO reaction network is extensive, leading to different products, according to the nature of the catalytic sites (6). Besides being considered a reducible metal oxide with moderate oxophilicity (7), which facilitates oxygen vacancies generation, MoO3 can present other functionalities under HDO stream. Previous results showed the formation of oxycarbide phases (MoOxCy), capable of stabilizing Mo5+ species, which were assigned to efficient hydrogenation activity (8). This way, impregnated zeolite samples with different Mo/acid site ratios will be prepared, seeking to modulate their catalytic contributions.



## **Experimental**

*Materials and Methods*

The catalysts were prepared following a conventional wet impregnation procedure. Ammonium heptamolybdate tetrahydrate ((NH4)6Mo7O24.4H2O, Merck) was used as the Mo source, while commercial ZSM-5 zeolite (Si/Al = 140, Zeolyst) and fumed silica (Aerosil 380, Evonik) were employed as the supports. 10 % w/w catalysts were initially prepared and called MoO3@ZSM-5 and MoO3@SiO2. The silica impregnated catalyst as well as a commercial MoO3 sample (nanopowder, Sigma-Aldrich) were used for comparison purposes.

The crystalline structure of the catalysts and the MoO3 phase dispersion were initially evaluated by powder X-ray diffraction (XRD), collected in a Bruker D8 Advance Eco diffractometer.

*Catalytic Evaluation*

Gas-phase acetone HDO reaction was conducted in a plug-flow tubular reactor equipped with a quartz tube (inner diameter of 8.1 mm), with a catalytic bed composed of 50 mg of supported catalysts (or 5 mg of MoO3) and 150 mg of diluent (Al2O3; <100 mesh). Acetone (HPLC Plus Grade, ≥ 99.9%) was introduced into the reactor by using a saturation flask (2.4 mL min-1 of acetone) and He as the carrier gas. H2 was also fed to the reactor (51 mL min-1; 21 mol H2:mol acetone), using He for balance achieving a total feed flow of 100 mL min-1. The reactions were conducted isothermally at 400 °C for 3 h. Finally, the reaction products were analyzed by an online gas chromatograph (GC; Agilent Technologies, model 7890A) equipped with an HP-1 column (50 m x 0.32 mm i.d., 0.17 μm). The catalytic activity was evaluated through acetone conversion and products distribution. The main products detected in acetone HDO were propane (C3A), propene (C3E), isobutene/isobutane (C4) and 4-methylpent-3-an-2-one/4-methylpentan-2-one (C6O).

## **Results and Discussion**

Figure 1 presents the XRD patterns of the commercial MoO3 sample, as well as the 10% w/w impregnated catalysts. The MoO3 initial phase matched the orthorhombic crystal structure (ICSD CollCode 166363), essentially composed of Mo6+ species, forming double lamellae of MoO6 octahedrons. The MoO3@SiO2 catalyst presented a flat diffractogram with a discreet halo between 20 and 30 °2θ, compatible with the silica amorphous nature. In turn, the MoO3@ZSM-5 catalyst showed a XRD pattern that agrees with ZSM-5 literature standards (9). It is important to highlight that no distinguishable peaks referring to MoO3 were observed for the impregnated catalysts. This is a first indication that the MoO3 phase must be well dispersed, without extensive formation of large crystalline aggregates, which would show long-range organization.

**Figure 1.** XRD patterns of the MoO3 sample and the 10% w/w impregnated catalysts, MoO3@SiO2 and MoO3@ZSM-5.

When subjected to acetone HDO reaction for 3 h at 400 °C, the catalysts showed similar conversions (around 15-20%), but different product distributions, as shown in Figure 2 and Table 1. The MoO3 sample presented higher selectivity to C6O, mediated by acid sites. To a lesser extent, it also converted acetone to C3E and C3A, products of deoxygenation and subsequent hydrogenation, respectively. Acetone deoxygenation to C3E can follow a direct pathway through oxygen vacancies or a two-step pathway, in which it is first hydrogenated to isopropanol that is then dehydrated to C3E. The distinction between these two mechanisms is difficult to follow experimentally, since MoO3 presents active sites for both situations under HDO atmosphere (9). The prevalence of C6O may be related to the small mass of catalyst used for this test, since it was intended to match the amount of MoO3 in the catalyst bed to the impregnated samples (10% m/m). In this way, the diluent excess would be also contributing to the conversion and products distribution. In preliminary tests using only Al2O3 (not shown), it was seen that, under the same reaction conditions, this amount of diluent presents about 18% conversion to C6O alone.

**Figure 2.** Acetone conversion (black squares) and products distribution (colored bars) of acetone HDO reaction at 400 °C for the MoO3 and the 10% w/w impregnated catalysts, MoO3@SiO2 and MoO3@ZSM-5. TOS = 3 h.

**Table 1.** Catalytic data of acetone HDO reaction at 400 °C for the MoO3 and the 10% w/w impregnated catalysts, MoO3@SiO2 and MoO3@ZSM-5.

|  |  |  |
| --- | --- | --- |
|  | **Products distribution (%)a** |  |
| **Catalyst** | **C3A** | **C3E** | **C4** | **C6O** | **DOD (%)b** |
| **MoO3** | 2 | 7 | - | 91 | 9 |
| **MoO3@SiO2** | - | 48 | 11 | 41 | 59 |
| **MoO3@ZSM-5** | - | 21 | 79 | - | 100 |

a after 3h on stream, b deoxygenation degree

The MoO3@SiO2 catalyst showed better results than MoO3 in terms of products distribution, since it showed a higher deoxygenation degree, 59 against 9%. Chemically, the silica matrix does not present any properties to which these differences could be attributed, however its specific surface area is significantly larger than MoO3, ~380 versus ~7 m2 g-1. The dispersion of the MoO3 phase certainly enhanced the amount of available active sites, reflected in the larger selectivity to deoxygenated products, especially C3E.

Finally, the MoO3@ZSM-5 catalyst showed the ability to deoxygenate all the converted acetone (DOD = 100%), with the predominance of C4, a different result from that presented by the other MoO3 catalysts studied, supported or bulk. These C4 products, isobutene/isobutane, are obtained by the direct action of acidic sites through the condensation of acetone to C6O, followed by the β-scission of C6O to isobutene in the presence of water (10). Isobutene can be further hydrogenated to isobutane. Zeolites are recognized by the abundance of acid sites, especially strong Brønsted acid sites, which are distributed along an extensive microporous framework of channels and cavities, presenting high specific surface area (~400 m2 g-1 for ZSM-5). In the MoO3@ZSM-5 system, while the MoO3 phase probably yielded C3E, the condensation of acetone to C6O via acid sites, whether from MoO3, Al2O3 or the zeolite itself, was suppressed by the conversion of C6O to C4. As the preference for this reaction pathway was not visualized for the other catalysts, it is plausibly associated with the zeolite matrix and its acid sites.

## **Conclusions**

The ZSM-5 Si/Al ratio equal to 140 and the 10% m/m loading of MoO3 converge to a Mo/acid site ratio around 7. Little can be said about the proximity and synergy between these functionalities so far, however, the preliminary results obtained showed that the zeolite acid sites were able to deoxygenate acetone condensation products to C4, while MoO3 led to the deoxygenation of acetone itself to C3E. Combined, they presented the best performance among the studied catalysts. Future investigations varying Mo/acid sites ratio and conducting extensive surface characterization look promising.

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