Probing molybdenum oxycarbide catalytic sites through acetone hydrodeoxygenation reaction

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Resumo/Abstract

RESUMO - As propriedades de superfície de MoO3 foram estudadas através da reação de hidrodesoxigenação de acetona (HDO) em fase gasosa, permitindo ampla discussão acerca da correlação entre as diferentes etapas reacionais e os sítios ativos. Sob condições de redução/carburação, como é o caso de HDO, outros óxidos (MoOx) e oxicarbetos (MoOxCy) de molibdênio foram formados, apresentando estados de oxidação variáveis. Medidas de XPS mostraram a estabilização de espécies Mo5+ na fase MoOxCy, que exibiram comportamento hidrogenante. Além disso, a acidez total aumentou com a transição de MoO3 para as fases MoOx/MoOxCy, participando das etapas de condensação e desidratação. MoOxCy ainda promoveu sítios de ácido de Brønsted mais fortes, conforme mostraram os espectros de 31P RMN no estado sólido das amostras com TMPO adsorvido. A atuação das vacâncias de oxigênio na desoxigenação direta através do mecanismo de Mars-van-Krevelen reverso foi mais difícil de acompanhar, no entanto, a formação contínua de sítios de Lewis Moδ+ é um bom indício de que esses sítios também estão ativos.

*Palavras-chave: catálise, hidrodesoxigenação, óxido de molibdênio, oxicarbeto de molibdênio, sítios ativos*

ABSTRACT – The surface properties of MoO3 catalysts were addressed through the gas-phase acetone hydrodeoxygenation (HDO) reaction, allowing extensive discussion over the correlation between the different reaction pathways and the active sites. Under HDO reduction/carburization conditions, other molybdenum oxides (MoOx) and oxycarbides (MoOxCy) were generated, presenting variable oxidation states. XPS measurements showed the stabilization of Mo5+ species over MoOxCy, which exhibited hydrogenating behavior. Furthermore, the overall acidity was increased with the MoO3 transition to MoOx/MoOxCy phases, catalyzing condensation and dehydration steps. Particularly, strong Brønsted acid sites were promoted on stream, as revealed by 31P MAS-NMR spectra of TMPO loaded samples. Oxygen vacancies function through the direct deoxygenation *via* the reverse Mars-van-Krevelen mechanism was more difficult to follow up, but the continuous formation of Lewis-type Moδ+ sites was a good indication that these sites were also active.

*Keywords: catalysis, hydrodeoxygenation, molybdenum oxide, molybdenum oxycarbide, active sites*

## **Introduction**

The hydrodeoxygenation (HDO) of biomass-derived compounds has gained increasing attention considering the economic and environmental issues related to fossil fuels. However, the complexity and high oxygen content of biomass and its derivatives are still a challenge (1). The main product obtained via the fast pyrolysis of crude biomass is the bio-oil, which is composed of carbonyl-compounds (ketones, aldehydes, and furanes), carboxylic acids, sugars, and aromatics (2).

Acetone HDO reaction network is extensive, leading to different products, according to the nature of the catalytic sites. Therefore, in addition to its direct interest in terms of biomass upgrading, the study of acetone HDO represents an attractive approach to evaluate the presence of different catalytic sites and their role in the C-O, C-C, and C-H bonds activation and cleavage (3).

Reducible metal oxides can promote the selective cleavage of C–O bonds through the reverse Mars–van Krevelen mechanism on oxygen vacancies, therefore calling attention for biomass upgrading (4). Among these metal oxides, MoO3 is considered a reducible metal oxide with moderate oxophilicity (4). Under usual HDO conditions, its Mo-O bonds seem weak enough to allow oxygen vacancies to form easily, but strong enough not to be rapidly and extensively reduced. The HDO reducing/carburizing stream leads to MoO3 transition to MoO2 and MoOxCy phases, which present variable oxidation states, allowing a fine-tuning of several catalytic processes (5). However, MoO2 has been reported as a poorer catalyst (6,7).

MoO2 and MoOxCy phases have shown the ability to catalyze different reaction pathways that require acid (Bronsted or Lewis), metallic, or the combination of more than one site, in bifunctional mechanisms (8). In HDO, while dehydration and condensation steps are typically catalyzed by Bronsted/Lewis acid sites alone, oxygen vacancies participate in direct deoxygenation routes. In turn, hydrogenation/hydrogenolysis sites are commonly mediated by metallic sites, and in the case of oxides and/or oxycarbide phases they are not straightforwardly defined.

Several catalytic reports involving bulk and supported MoO3 in HDO reactions have proposed the main reaction pathways and the catalytic sites involved in each of these steps (9-13). However, the influence of the formation of new phases under reaction conditions associated with surface modifications are much less understood.

Therefore, this work aims to shed light on the properties of MoO3, focusing on the phase which was formed during acetone HDO stream. Textural, structural, and electronic characterization, according to the reaction conditions, allowed us to elucidate the nature of the active sites in the Mo-based catalysts. The MoOxCy phase presented sites responsible for hydrogenation/hydrogenolysis steps, in addition to enhanced acidity. Stronger Brønsted acid sites were particularly promoted, favoring the two-step acetone deoxygenation pathway, which yields propene through isopropanol dehydration.

## **Experimental**

*Materials and Characterization*

Commercial molybdenum oxide (MoO3, nanopowder) supplied by Sigma-Aldrich, was used in all catalytic tests. Other reagents eventually employed were purchased in high purity grade from Sigma-Aldrich, Merck, Synth, Alfa Aesar, and ECIBRA.

The crystalline structure of the samples was verified by powder X-ray diffraction (XRD) collected in a Bruker D8 Advance Eco diffractometer. The surface electronic characterization was performed through X-ray photoelectron spectroscopy (XPS) measurements using a monochromatic Al Kα source on a K-alpha spectrometer (Thermo Fisher Scientific) equipped with a 180° double focusing hemispherical analyzer with a 128-channel detector. The acid sites in the samples were probed by 31P MAS-NMR analysis of adsorbed trimethylphoshine oxide (TMPO) in a 400 MHz (9.4 T) Bruker Avance-II+ equipped with a 4 mm MAS 4BL CP BB probe. To perform the acid sites quantification, the TMPO-loaded samples were subjected to phosphorus (P) elemental analysis by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), carried out in an ICP-OES Analytik Jena apparatus, Model Quanta Elite, 1200 W. Thermogravimetric analyzes (TGA) were performed in a TA equipment, model SDT Q600, to monitor the fraction of water and phase transitions during heating.

*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 catalyst and 150 mg of diluent (quartz powder; <100 mesh). Acetone 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 catalyst was heated under H2 to the target temperature and then the substrate was introduced. 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, products distribution and yield. The main products detected in acetone HDO were methane (C1), ethene/ethane (C2), propane (C3A), propene (C3E), isobutene/isobutane (C4), 2-methyl-pentene/2-methyl-pentane and structural isomers (C6), isopropanol (IPA), and 4-methylpent-3-an-2-one/4-methylpentan-2-one (C6O). Carbon balances were commonly close to ideal, slightly dropping with the advancement of TOS and/or depending on the temperature (still > 85 %).

## **Results and Discussion**

Acetone HDO reaction was carried out over MoO3\_comm as a function of time at two temperatures: 350 °C (350C), in which acetone conversion were reported to be promoted by the presence of MoOxCy, and at 400 °C (400C), in which high deactivations were observed in the absence of MoOxCy (6). Figure 1 presents the results as a function of TOS during 6 h. At 350 °C (Figure 1A), it is possible to visualize a change in the conversion and products distribution after about 2-3 h on stream. Acetone conversion started around 6% and ended around 12%. This increase can be possible attributed to the MoO3 transition to MoO2 and MoOxCy phases, as shown by the post-reaction XRD patterns in Figure 2A (350C1h and 350C6h). The initial products were C3E (55%), IPA (30%), and C6O (15%). As the conversion began to change, C3A and Cn (C1, C2, C4, and C6) products appeared, while IPA decreased significantly. After 6 h on stream C3E (34%), C3A (36%), and C6O (18%) were the major products observed. IPA and C3A were both products from hydrogenation sites, which makes their opposite behaviors strange. Therefore, the IPA decrease should be associated with its consumption through dehydration to propene, catalyzed by acid sites. Nevertheless, as C6O production did not present significant changes, different acid sites should mediate dehydration and condensation steps. Finally, the formation of C3A and Cn products in the presence of MoO2 and MoOxCy indicate the promotion of hydrogenating/hydrogenolysis sites.

**Figure 1.** Products distribution (colored bars) and conversion (triangles) of acetone HDO reactions for MoO3\_comm: 350C, isothermal at 350 °C (A), and 400C, isothermal at 400 °C (B). TOS: 6 h. WHSV = 7.14 gacetone gcatalyst-1 h-1.

****Under isothermal conditions at 400 °C (Figure 1B), acetone conversion reached almost 50% but gradually dropped to about 20%. It is interesting to note that since the beginning of TOS, MoO3 transitioned to MoO2 solely, as shown by Figure 2A (400C1h and 400C6h). The same products observed at 350 °C were formed, but their distribution was distinct. Propene was the major product throughout the reaction and, as well as C3A and Cn, seemed to slightly decrease following the conversion. C6O went on the opposite way, increasing from 3 to 14 %. The greatest difference observed when ordered MoOxCy appeared was the hydrogenation degree. 350C6h present C3A/C3E ratio around 2.0, while a value of 0.5 was found for 400C6h.

**Figure 2.** (A) XRD patterns and (B) XPS spectra of Mo 3d region: MoO3\_comm (as received) and 350C1h, 350C6h, 400C1h, and 400C6h catalysts after acetone HDO reaction. The spin-orbit splitting of 3.1 eV was considered for each Mo species.

Electronic characterization of the catalysts surface was conducted using XPS, as shown in Figure 2B. The spectra of the Mo 3d region demonstrated that several Mo species were formed depending on the reaction temperature and TOS, in agreement with XRD data (Figure 2A). MoO3\_comm 3d5/2 peaks at 233.5 eV and 232.3 eV were attributed to Mo6+ (75.6%) and Mo5+ (24.4%) species. The formation of Mo5+ species is related to the MoO3 surface reduction induced by the X-ray probe (14). The spectrum of the 350C1h catalyst presented a similar profile to that observed for MoO3\_comm. On the other hand, the 350C6h catalyst presented a mix of Mo species, composed of Mo6+ (21.8%), Mo5+ (22.6%), and Mo4+ (55.6%). 400C1h and 400C6h catalysts also presented a mix of Mo species. No significant changes were observed between them and Mo4+ was the predominant species (around 80%). According to the literature, the presence of Mo6+ species can be attributed to a surface layer of MoO3, while Mo5+ species can be majorly related to MoOxCy phase and Mo4+ to MoO2 and/or MoOxCy phases (14,15).

Even not being straightforwardly defined, Mo5+ species was assigned in many reports as possessing an important role in HDO reaction, preventing overreduction and as an active site itself (6,9,10). It is interesting to note that this species was more significantly observed in the 350C6h catalyst surface, which, as mentioned, showed the greatest hydrogenation rate. Thus, it is possible that Mo5+ could perform a catalytic role that approaches the hydrogenation behavior of metallic sites.

In an insightful work, Kurlov *et al.* (16) submitted a carbon-supported MoO3 sample to *in situ* carburization followed by XRD and XANES analyzes. As shown by the XRD patterns, MoO3 transitioned to MoO2 around 400 °C and then fully converted into Mo2C at 750 °C; no other crystalline phases were observed during heating. On the other hand, XANES data presented a C component that pointed to a different contribution that lies between MoO2 and Mo2C. Thus, it was proposed that this new contribution is associated with an oxycarbide phase that may be formed due to carbon incorporation during annealing, but retaining the bulk MoO2 structure. These findings agree with previous studies (17,18) and suggest the existence of a disordered oxycarbide phase at 400 °C. The electronic properties of 400C1h, together with increased acid sites (especially stronger Brønsted ones) and specific surface area, add up to strong evidence for a different contribution than MoO2.

Our spent catalysts presented distinct thermogravimetric profiles under N2 and O2 atmospheres (Figure 4). Under oxidizing conditions, the 350C1h catalyst did not present any major weight loss or gain events, in line with the more oxidized MoO3 structure. Above 400 °C, a minor 0.5% weight loss was observed and related to the oxidation of the partially reduced surface or coke oxidation (6). Below 330 °C, the 350C6h, 400C1h, and 400C6h catalysts showed weight losses that varied between 2.7 and 3.3%, attributed to H2O evolution (19). Above this, two distinguishable weight gain events were observed. The first one, between 330 and 400 °C, varied from 1.0 to 1.3%, and could be associated with the oxidation of MoOxCy into MoO3; the second one, between 400 and 500 °C, varied from 7.0 to 7.5%, and could be associated with the oxidation of MoO2 into MoO3 (19). The fact that all these samples present similar profiles is further evidence for the coexistence of an oxycarbide phase and MoO2 at 400 °C, even when only the latter was retained as a bulk structure (400C1h and 400C6h). Considering the weight gains under O2 and the losses under N2 from 330 to 500 °C, an average 10.4% weight gain was found for these catalysts, in agreement with the 12.4% theoretical weight gain associated with the full oxidation of MoO2 into MoO3. In this case, MoOxCy contribution is difficult to address, since this phase can present different compositions depending on the H2/carbon stream, temperature, and TOS.

**Figure 4.** dTG curves obtained from the thermogravimetric analysis of 350C1h, 350C6h, 400C1h, and 400C6h catalysts after acetone HDO reaction under (A) N2 and (B) air atmosphere.

Since the acid sites play an important role in the acetone HDO reaction pathways, MoO3\_comm, 350C6h, and 400C1h samples had their acid properties probed by TMPO adsorption monitored by 31P MAS-NMR spectroscopy (20). Figure 3 shows the spectra for the three selected samples, where a broad multi-contribution signal in the region of ~30 to ~90 ppm could be detected. Signal deconvolution allowed addressing and quantifying each of the 5 distinguished contributions (21). The signal around 40 ppm (Phys), present to a greater extent in the MoO3\_comm and 400C1h catalyst, can be associated with physisorbed TMPO. In turn, the signal centered in 60 ppm is often attributed to Lewis acid sites, presenting this sole contribution on metal oxides (22). Finally, Brønsted acid sites can be found from close to 50 ppm to over 80 ppm, encompassing 4 possible contributions, B1 to B4, increasing in acid strength (21). The analyzed samples showed all these contributions, however, the 350C6h catalyst clearly presented a larger percentage of stronger Brønsted acid sites (B2-B4), followed by 400C1h.

The total amount of acid sites followed the order MoO3\_comm < 400C1h < 350C6h, as shown in Table 1. Between MoO3\_comm and 400C1h catalyst, the acid sites increased by almost 3-fold, from 19 to 56 µmol g-1. The Brønsted/Lewis ratios for these same samples were very similar and approached 1.0, showing that they present similar concentrations of both sites. In turn, 350C6h catalyst features 70 µmol g-1, which is about the concentration of the other two catalysts combined. The most interesting feature of this sample, as already mentioned, is that the catalyst showed a significant increase in stronger Brønsted acid sites after exposure to acetone HDO atmosphere. The ratio between stronger and weaker sites showed that 400C1h has about three times stronger acid sites than MoO3\_comm, while 350C6h has ten times as many (Table 1). Thus, it is plausible to infer that the stronger Brønsted acid sites are related to the formation of the oxycarbide phases.

The reduction/carburization over MoO3 continually alters the surface properties. In this case, the poorly ordered MoOxCy structure, or even a more amorphous phase, combined with the less polarized C-Mo bonds should increase the concentration and acidity of Brønsted acid sites, as seen for the 350C6h and 400C1h catalysts.

**Figure 3.** 31P NMR spectra of adsorbed TMPO on: (bottom) MoO3\_comm (as received), and (middle) 350C6h, and (top) 400C6h catalysts after acetone HDO reaction.

**Table 1.** Acid data of MoO3\_comm (as received), and 350C6h and 400C1h catalysts after acetone HDO reaction.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **ASa,b** | **BASa,b** | **LASa,b** | **SB/WBb** |
| **MoO3\_comm** | 19 | 10 | 9 | 1.9 |
| **350C6h** | 70 | 48 | 22 | 19.5 |
| **400C6h** | 56 | 30 | 26 | 5.5a in µmol g-1b obtained by 31P NMR of adsorbed TMPO\* AS = acid sites, BAS = Brønsted AS, LAS = Lewis AS, SB = Strong BAS, WB = Weak BAS |
|  |  |  |

In summary, MoO3 showed increasing oxygen vacancies with the progress of surface reduction, active sites for acetone hydrogenation, and the lowest acid sites concentration. On the other hand, the ordered MoOxCy phase, observed in the 350C6h catalyst, presented the highest acid sites concentration, with the predominance of stronger Brønsted ones. Besides that, this phase was significantly active for both hydrogenation and hydrogenolysis, a behavior attributed to its singular electronic characteristics, which comprise Moδ+ species halfway between more oxidized and more reduced oxidation states, close to +5. Finally, the disordered MoOxCy phase, proposed to be present in the 400C1h catalyst, was the trickiest to unravel due to its amorphous nature. This phase showed reasonable hydrogenation/hydrogenolysis sites activity. There were also few acid sites, but still more and stronger when compared to MoO3.

## **Conclusions**

With this work, we hope to have contributed to the understanding of the properties of the oxycarbide phases, invariably recurrent in Mo-based catalysts under reducing/carburizing conditions, as is the case of HDO reactions employing different substrates. We were able to address electronic and acid characteristics that were still underexplored for MoOxCy: the hydrogenating behavior of Mo5+ species and the stronger Brønsted acidity, unusual for metal oxides. Furthermore, the acetone HDO reaction proved to be a useful tool in probing different functionalities, given its extensive ramifications.

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