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Short communication

Mixed oxides based on SnO_2 impregnated with MoO_3: A robust system to apply in fructose conversion

Thatiane Veríssimo dos Santos, Débora Olimpio da Silva Avelino, Mario Roberto Meneghetti, Simoni Margareti Plentz Meneghetti*

Group of Catalysis and Chemical Reactivity, Institute Of Chemistry and Biotechnology, Federal University of Alagoas, Av. Lourival de Melo Mota, s/n°, Maceió, AL 57072-970, Brazil

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ABSTRACT

A series of nanostructured catalytic systems based on SnO_2 modified with MoO_3 (SnMoX, X = 5, 25, 50 and 75%) were evaluated in fructose conversion. SnMo25 catalyst at 150 °C led to significant conversion of fructose, with the lowest formation of insoluble materials and a high selectivity to the products obtained by the retro-aldol reaction. SnMo25 was used in six cycles, and no leaching or significant decrease in yield and selectivity was observed. These results indicate the high robustness of these catalytic systems and the potential of modulation of acid sites even in aqueous medium.

1. Introduction

Nowadays, the use of renewable and sustainable sources to produce energy and chemicals associated with the development of efficient catalysts is an important strategy. In this perspective, sugars derived from biomass, such as glucose and fructose, can be employed as raw materials to produce chemicals, which may complement or replace some petrochemical derivatives and exhibit great industrial potential [1–5].

Thus, the search for active and selective catalysts able to transform sugars into products of interest is increasing. In the literature, the use of inorganic acid catalysts [6], ionic liquids [7, 8], Sn(IV) complexes [9, 10], silica-included heteropolyacids [2], inorganic and organic potassium salts [11], among others, has been reported for research in biomass conversion. The use of heterogeneous catalysts has many advantages, mainly due to the possibility of recovery and reuse, reducing the costs of the final products [12].

A few examples are available in the literature concerning the use of mixed oxides and their application on biorefinery routes and the use of mixed oxides provides a great variety of Lewis and Bronsted acids present in the materials, which play an important role in the conversion and selectivity of the catalytic systems [13–16].

The present work aims to contribute to the field of sugar conversion and innovative catalyst design, by the systematic synthesis and investigation of robust catalytic systems based on tin and molybdenum mixed oxides (SnMo) at various proportions for application in the conversion of fructose. To the best of our knowledge, it is the first time that reusable mixed oxide systems, based on SnMo have been applied in fructose conversion in aqueous medium. The goal of this investigation is to obtain important structure-property relationships in order to open new perspectives for modulating the characteristics of mixed oxides systems for use in biorefinery processes.

2. Materials and methods

2.1. Synthesis and characterization of catalysts

SnO_2 was obtained commercially and used as received (Sigma-Aldrich, AR grade). MoO_3 was prepared by calcining ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$ - Sigma-Aldrich, grade AR) at 550 °C over 4 h. For the mixed oxide synthesis, an aqueous suspension of SnO_2 and MoO_3 in different proportions was stirred for 1 h, followed by heating to completely remove water. Next, the materials were softened and calcined at 550 °C for 4 h and stored under argon atmosphere. The SnO_2, MoO_3 and SnO_2/MoO_3 catalysts were designated Sn100, Mo100 and SnMoX (X = 5, 25, 50 and 75, according to the percentage of molybdenum present), respectively. The materials were careful characterized by several techniques (see supplementary information).

2.2. Conversion of fructose and analytical procedures

All experiments were performed in a 100 mL batch stainless-steel

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* Corresponding author.
E-mail address: simoni.plentz@iqb.ufal.br (S.M.P. Meneghetti).

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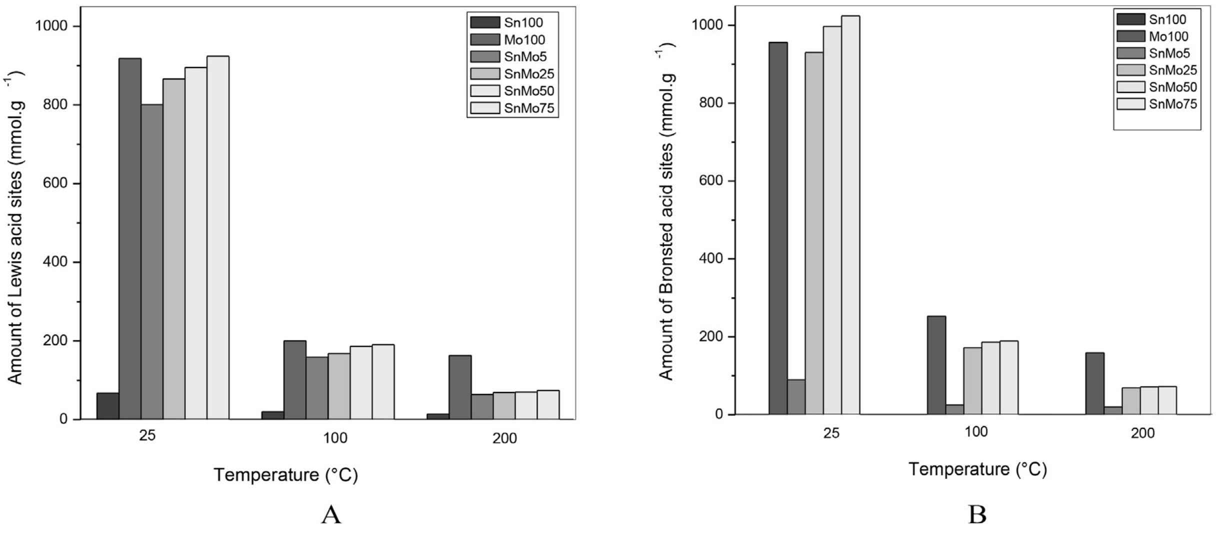

Fig. 1. Number of acid sites present in the catalytic systems at different temperatures: A = Lewis and B = Bronsted sites.

reactor coupled to a manometer, a temperature probe and a magnetic stirrer working at 1000 rpm. The fructose solution (0.48 g of fructose in 60 mL of deionized water) and, for some experiments, the catalyst (2.69×10^{-5} mol) were introduced in the reactor. Conversion, yield and selectivity were calculated from the results of quantification by HPLC (see supplementary information).

3. Results and discussion

Different nanostructured catalytic systems based on SnO_2 modified with several amounts of MoO_3 (SnMoX, X = 5, 25, 50 and 75%, according to the percentage of molybdenum impregnated) were synthesized, characterized, and evaluated in fructose conversion, in comparison to the pure oxides (Sn100 and Mo100).

From thermogravimetric curves (Fig. S1 - supplementary information) it is possible to establish that 6, 26, 50.1 and 74.1% of Mo is present in the different materials [17], in agreement to with the theoretical projections.

The FTIR and Raman spectra are presented, such as the discussion, at Fig. S2 and S3 (supplementary information). The observations are a strong indication that the oxides are in fact coordinated and that their structure has been modified. Additionally, the Raman spectrum was obtained for a physical mixture containing 95% Sn100 and 5% Mo100 to better understand the interactions in the mixed oxides (see Fig. S4, supplementary information). In this case, some absorptions detected for SnMo5 are not observed, especially the signal due to the vibrations E_g at 291 cm^{-1}, which are characteristics of the lattice defects due to structural modifications, by the replacement of Sn^{4+} by Mo^{6+} ions [18–26].

Fig. S5 (supplementary information) shows the X-ray patterns for the materials. Sn100 is in the rutile phase, which is confirmed by the crystalline planes assigned to the reflection lines (110), (201), (211), (220), (002), (310), (112), (301), (202), and (321) (JCPDS No. 41–1445). The α-MoO_3 phase formation is proven by the detection of the reflection lines at (110), (040), (021), (130), (111), (060), (200) and (002) (JCPDS No. 05–0508). The signals for the mixed oxide systems are intensified and shifted to higher angles. This intensification may be associated with the nanostructured nature of the impregnated systems, corroborating the results obtained by Raman spectroscopy. However, the shift to larger angles may be related to the difference in the ionic radii due to the substitution of Sn^{4+} (~ 0.71 Å) for Mo^{6+} (~0.62 Å).

From the XRD patterns (Fig. S5 – supplementary information), it was possible to calculate the crystallite size using the Scherrer equation and using the reflection line at (110). It is interesting to note that the size of the crystallite decreases substantially after impregnation with molybdenum ions.

These peculiar characteristics confirm the presence of defects caused by impregnation, which promotes distortion in the structure, which is then relaxed by the formation of vacancies.

To evaluate the type of acid sites present in the structure of these compounds, the materials were analyzed by infrared spectroscopy using pyridine as probe molecule (Fig. S6 – supplementary information). In the infrared spectra, when pyridine is employed, the absorption bands at approximately 1442, 1589 and 1607 cm^{-1} are related to the presence of Lewis acid sites, and those at 1537 and 1632 cm^{-1} are related to Bronsted acid sites [12, 13]. At 1486 cm^{-1}, the superposition of Lewis and Bronsted sites is observed [27, 28]. At 25 °C, Sn100 exhibits absorption bands of weak intensities regardless of the type of acid site. For the other systems, more intense signals were detected (See Fig. S6).

With the aim of determining the acid strength of different acid sites, the thermal stability of the pyridine-acid sites was evaluated by the acquisition of infrared spectra at 100, 200 and 300 °C. When pyridine is chemisorbed at the Lewis or Bronsted acid sites, this interaction can be classified as strong if it is broken at temperatures above 300 °C. Moderate interactions are broken at temperatures in the range of 200 to 300 °C and, in the case of the weak ones, at temperatures lower than 200 °C [27]. Additionally, using equation 2 (experimental section at supplementary information), it is possible to quantify the number of acid sites (Fig. 1A and B) at different temperatures. According to the obtained results, it is possible to affirm that all systems present weak to moderate acid sites since no signals were detected at 300 °C.

For Sn100, no Bronsted acid sites were identified, and only low concentrations of Lewis acid sites were detected, indicating that this material does not exhibit significant acidity. In contrast, Mo100 shows the highest number of acid sites (Lewis and Bronsted) at all temperatures examined, exhibiting weak to moderate strength. For all the mixed oxides, the results indicate that the number and strength of the acid sites increase proportionally with the amount of molybdenum present.

Finally, the surface areas were calculated by the BET method (Table T1), and the results indicate that all systems exhibited a low surface area. The surface area for impregnated systems gradually diminished with increasing concentration of Mo100, suggesting that the calcination and the addition of another oxide led to the contraction of the lattice.

In summary, based on the catalysts characterization results, it is possible to assume that the interaction perceived between the oxides increases the number of lattice defects due to oxygen vacancies, which play a strategic role in catalysis since they determines the highest

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