Mesoporous Aluminosilicates as Catalyst Supports for Conjugated Linoleic Acid Formation by Hydrogenation/Isomerisation of Safflower Oil

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Introduction

During catalytic hydrogenation of vegetable oils, some of the naturally occurring *cis* double bonds are isomerized to *trans* fatty acids (TFA). High levels of *trans* fats in the diet are linked to higher occurrence of coronary health diseases [1]. However, all *trans* fatty acids are not harmful, some conjugated linoleic acid (CLA) isomers are reported to have anti-carcinogenic, -atherogenic, -diabetic and lean body mass-enhancing properties [2].

Noble metals are known as very active hydrogenation catalysts but their performance for conjugative isomerization has been scarcely reported. Even though there is evidence for the occurrence of CLA in partially hydrogenated oils, thorough investigation to optimize the production of CLA isomers has not been attempted using heterogeneous catalysts.

The present work aims at studying the hydrogenation/isomerization of safflower oil over novel bifunctional Rh catalysts supported on mesoporous aluminosilicates. This approach is investigated as a new chemocatalytic technique to produce health-beneficial conjugated CLA.

Materials and Methods

1) Catalysts. The new Rh/mesoporous aluminosilicate was prepared by impregnating nanostructured acidic silica support (Al_SBA-15, molar Si/Al ratio of 100) with an aqueous solution of rhodium acetyl acetonate. The mixture was dried at room temperature for 24 h. The solid was calcined at 540 °C for 5h and reduced under hydrogen flow at 400 °C for 3h [3]. **2) Catalyst characterizations**. Nitrogen adsorption/desorption isotherms of supports and catalysts were obtained using a volumetric adsorption analyzer (Model Autosorb-1, Quantachrome Instruments, Boyton Beach, FL). Powder X-ray diffraction (XRD) patterns were obtained using an Ultima III Rigaku Monochromatic Diffractometer using CuKα radiation (λ=1.5406 Å). Solid state ^{27}Al NMR experiments were performed on a BRUKER MSL 500NMR spectrometer. **3) Material**. Refined safflower oil was used as model-oil because of its high linoleic acid content (71 to 79%). **4) Hydrogenation/Isomerization Reaction tests**. Reactions were carried out in a 600-mL Parr Reactor Model 4560 (Parr Instrument Co., Moline, IL, USA).All other details were reported in our previous works [4].

Results and Discussion

The BET surface area of SBA-15 is 931 $m^2.g^{-1}$ with a total pore volume of 1.2 $cm^3.g^{-1}$ and 6.17 nm pore size. By addition of aluminum *via* direct synthesis, the BET surface area increased to 1006 $m^2.g^{-1}$ for Al_SBA15 (100). This aluminosilicate material shows binodal pore size distributions at 4.7 and 6.8 nm. This may be due to the presence of aluminum in the silica walls [5] Therefore, incorporation of aluminum has a consequential impact on the BET specific surface area, total pore volume and pore size of the materials. The ^{27}Al NMR spectra of Al_SBA(100) sample is shown in Figure 1. As seen, only one strong resonance signal at 49.87 ppm is shown and is assigned to the presence of aluminum in tetrahedral coordination only indicating that under our synthesis conditions all aluminum atoms are incorporated into the framework of SBA-15 material.

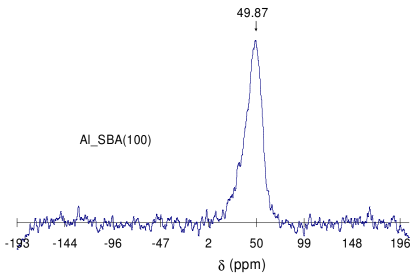

Figure 1. ^{27}Al-MAS NMR spectra of Al_SBA(100).

The preliminary results obtained from partial hydrogenation and isomerization of safflower oil in the presence of a typical formulated catalyst show that, 22.4 % of initial linoleic acid were converted to produce about 1.0 % of *cis*-C18:1, 2.6 % of *trans*-C18:1, 6.7 % of *trans*-C18:2, and only 0.3 % of saturated fatty acid C18:0. These products were ascribed to two distinct catalyst activities, hydrogenation and *cis/trans* isomerization representing 8 % and 55 %, respectively, of all the catalyst's activities. Moreover, a net production of 7 % (70 mg/g lipids) CLA isomers was obtained which was ascribed to the conjugation isomerization representing 37 % of the catalyst's reaction activities. Mainly (9*cis*, 11*trans*), (10*cis*, 12*trans*), (10*trans*, 12*cis*) and (*cis, cis*) CLA isomers were produced and they accounted for 67 % of total CLAs. While (*trans*, *trans*) CLA isomers represented 33 % of total CLAs.

Significance

This research is quite innovative because, until now no catalyst has been developed for efficient and selective isomerization/hydrogenation of vegetable oils, with the focus on the production of health-beneficial CLA, without any additives such as organic solvents or sulfur in oil.

References

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