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Selective hydrogenation of methyl oleate on Ni catalysts supported on Nb-based mixed oxides

AUTHORS

Marcelo E. DOMINE / INSTITUTO DE TECNOLOGÍA QUÍMICA (ITQ, UPV - CSIC), AVDA LOS NARANJOS S/N, VALENCIA
Marisa B. NAVAS / INSTITUTO DE TECNOLOGÍA QUÍMICA (ITQ, UPV - CSIC), AVDA LOS NARANJOS S/N, VALENCIA
Zaher RAAD / INSTITUTO DE TECNOLOGÍA QUÍMICA (ITQ, UPV - CSIC), AVDA. LOS NARANJOS S/N, VALENCIA

PURPOSE OF THE ABSTRACT

In recent years, there has been a notable increase in interest in the production of fuels and different chemical products from alternative sources and, mainly, from renewable sources. Among them are triglycerides, obtained from vegetable oils, animal fats or frying oils [1]. Different routes have been developed to convert triglycerides into liquid fuels, for example, transesterification reactions to obtain biodiesel, or hydrodeoxygenation (HDO) to transform them into hydrocarbons that conform diesel fractions [2,3].
In this work, catalysts with Ni supported on metallic mixed oxides based on niobia were studied in the hydrogenation of methyl oleate. The supports were prepared by co-precipitation in alkaline medium and calcined at 600°C, whereas the Ni (12wt%) was incorporated via incipient wetness impregnation. All the materials were characterized by different techniques, such as N2 physisorption, XRD, ICP-AES and SEM. The main results are presented in Table 1. The highest values of surface area, pore volume and total acidity were achieved for the supports 0.4 ZrNb and 0.4 AlNb, without observing any defined crystalline phase in these cases, which indicated a homogenous mixed oxide formation. Formation of well-dispersed Ni nanoparticles was verified by SEM.

The catalysts were evaluated in the selective hydrogenation of methyl oleate as a model molecule. The reaction was carried out at 30 bar and 275 °C during 8 h in a 12 mL autoclave-type reactor. Liquid samples (?40 mg) were taken, then toluene and a standard solution of 1,2,4-butanetriol were added. The reaction products were derivatized by silylation with N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA). Samples were analyzed by GC-FID equipped with a Select Biodiesel for Glycerides Ultimetal capillary column.

The results of this first catalytic screening are presented in Table 2. As can be seen, in all cases a complete conversion of methyl oleate was achieved. The highest selectivity towards heptadecane (C17) and octadecane (C18), the hydrocarbons of interest, was found for Ni/0.4 AlNb catalyst. This may be due to an adequate combination of surface area, pore volume and acidity values, due to the presence of Al in the support composition.

The most active catalyst, Ni/0.4AlNb, was selected to evaluate the effect of the calcination temperature on the support (500°C and 600°C), and also the catalyst amount employed (50 mg and 100 mg). Then, 600°C was verified as the more suitable temperature. Besides, using 100 mg, higher selectivities to C17 and C18 were achieved (68% and 32% respectively).
Finally, in order to evaluate the Al content in the support, and decrease the final price of the catalyst, a new catalyst was prepared, containing 15% Ni and 10% Nb2O5 over Al2O3. A complete conversion of methyl oleate and selectivity only towards C17 was observed. This may be due to the high Lewis acidity of the support [4]. In

contrast, with the Ni/0.4 AlNb catalyst, both C17 and C18 were produced, due to the presence of a greater amount of niobium. This allows both decarbonylation and decarboxylation processes [5]. These active and selective systems based on niobia and alumina, and Ni particles, were suitable to obtain hydrocarbons from a model molecule, which can be largely found in vegetable oils, such as soybean oil.

FIGURES

Table 1. Main physicochemical and textural properties of the prepared supports

Support	Molar ratio X/Nb	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	d (nm)	Acidity (μmol/g)
0.4 ZrNb	0.33	108	0.18	-	157.9
0.4 TiNb	0.24	34	0.07	15	55.1
0.4 AlNb	0.42	70	0.10	-	95.9
0.4 WNb	n/d	15	0.05	16	47.0
0.4 SnNb	0.44	70	0.12	19	104.1
Nb_2O_5	-	8	0.03	34	-

Table 2. Catalytic results for the hydrogenation of methyl oleate over Ni supported on Nb-based mixed oxides.

Catalyst	Conversion (%Mol)	Selectivities (%Mol)						
		C17	**C18**	**Stearic alcohol**	**Methyl stearate**	**Stearic acid**	**Stearyl stearate**
11.8%Ni/0,4 ZrNb	100	1,3	1,8	0,5	71,9	14,6	9,9
12.3%Ni/0,4 TiNb	100	2,3	1,1	0,8	72,6	9,5	14,4
12.8%Ni/0,4 AlNb	100	**39,0**	**7,7**	2,9	23.0	8.0	19,3
12.5%Ni/0,4 WNb	100	1,8	1,9	1,1	79,8	10,2	5,3
11.6%Ni/0,4 SnNb	100	2,2	7.0	5,8	62,4	7,2	15,5

FIGURE 1
Table 1

Main physicochemical and textural properties of the prepared supports

FIGURE 2
Table 2

Catalytic results for the hydrogenation of methyl oleate over Ni supported on Nb-based mixed oxides

KEYWORDS
Vegetable oils | Methyl oleate | Ni catalysts | Nb mixed oxides

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