Hydroconversion of Methyl Esters over Ni-phosphide Catalyst on Composite Alumina-SAPO-11 Support

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Introduction Ni-phosphide catalyst on composite Al_2O_3-SAPO-11 support was studied in the hydrodeoxygenation-isomerization (hydroconversion – HC) of methyl esters with different amount of carbon atoms in the chain and different number of double bounds: C16:0 – methyl palmitate, C18:0 – methyl stearate, C18:1 – methyl oleate, C18:2 – methyl linoleate, and C18:3 – methyl linolenate. The catalyst was synthesized by impregnation of the support with aqueous solution of Ni hypophosphite with subsequent reduction in H_2 flow. The catalyst was characterized by ICP-AES analysis, N_2 physisorption, H_2-TPR, NH_3-TPD, XRD, and ^{27}Al MAS NMR. The hydroconversion experiments were carried out in a flow reactor at 310–340 °C, 2.0 MPa, 5.3 h^{-1}. 100% conversion of all esters was achieved. The number of carbon atoms was shown to influence the selectivity to iso-alkanes (at 340 °C for C16 ester it was ~22%, and for C18 esters it was ~30%), but the number of double bonds did not show any impact on the selectivity of iso-alkanes.

Support synthesis

AlOOH "Disperal 20" (70%) + SAPO-11 (30%) → peptization HNO_3 → extrusion → extrudates 1.1–1.2 mm → drying 110 °C, calcination 550 °C → Al_2O_3-SAPO-11

SAPO-11: $SiO_2/Al_2O_3/P_2O_5$ = 1.0/1.0/0.1

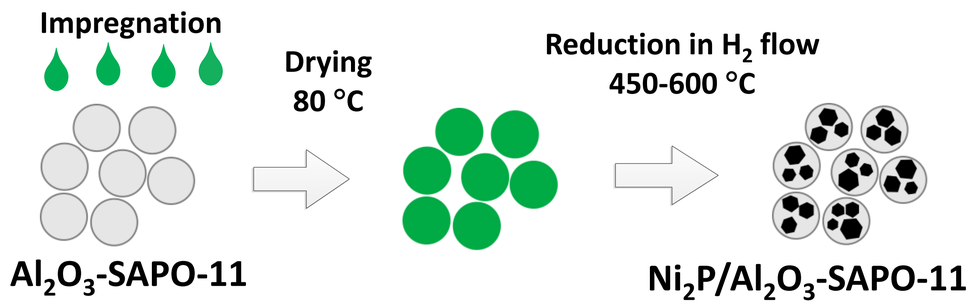
Catalyst synthesis

P precursor	Ni precursor	Ni:P init.
H_3PO_2	$Ni(OAc)_2$	1 : 2

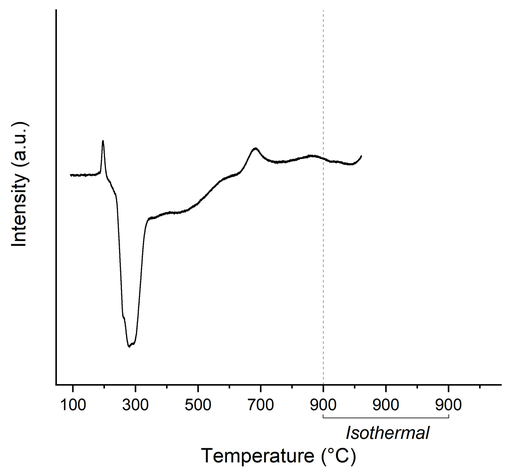
Al_2O_3-SAPO-11 was impregnated by aqueous solutions of phosphorus and nickel precursors (Ni - 2.1 mmol/g, ~7 wt.%) followed by drying and reduction in H_2 flow

Crushing and sieving to 0.25–0.5 mm

Impregnation → Drying 80 °C → Reduction in H_2 flow 450-600 °C



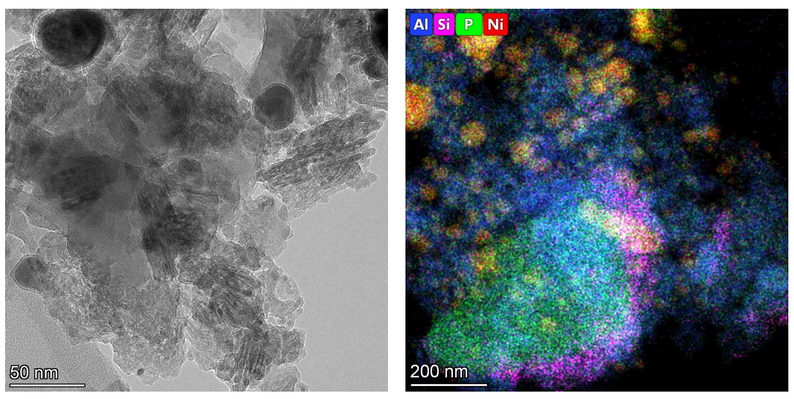
H_2 temperature-programmed reduction

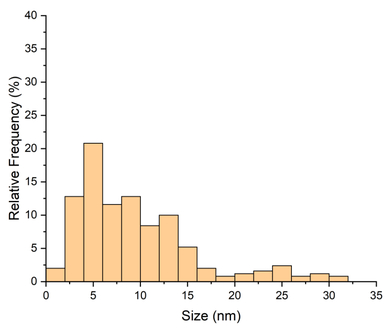


Physicochemical properties of reduced Ni_2P/Al_2O_3-SAPO-11

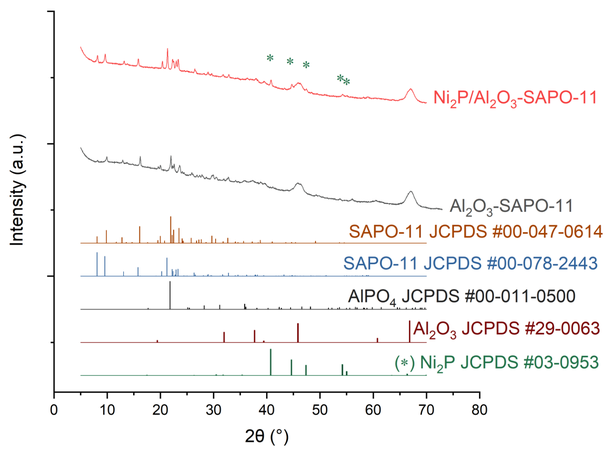
Sample	Ni, wt.%	P, wt.%	Ni/P	Al, wt.%	Si, wt.%	S_{BET}, m^2/g	V_p, cm^3/g	D_p, nm	NH_3-TPD, μmol-NH_3/g	D_{XRD}, nm	D_{TEM}, nm	Al in $AlPO_4$ form, at.%
Al_2O_3-SAPO-11	–	5.58	–	36.6	0.97	175	0.417	22.8	138	–	–	14
Ni_2P/Al_2O_3-SAPO-11	4.10	10.2	0.47	33.7	0.69	96	0.305	22.6	139	45	11.9	21

TEM images

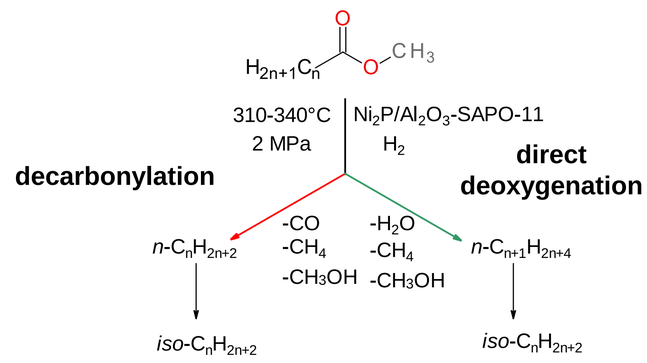


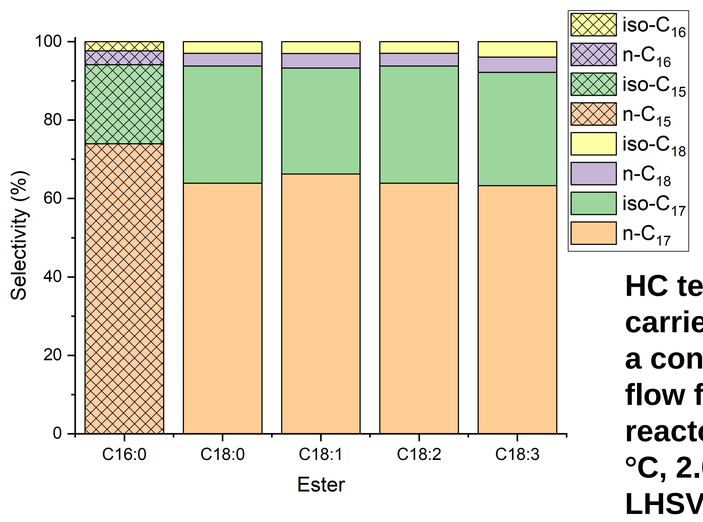


XRD patterns



Esters hydroconversion





HC tests were carried out in a continuous flow fixed-bed reactor at 340 °C, 2.0 MPa, LHSV=5.3 h^{-1}

Summary According to H_2-TPR the reduction and decomposition of precursor starts at ~190 °C. XRD and TEM confirmed formation of Ni_2P phase. ^{27}Al MAS NMR showed formation of small amounts of $AlPO_4$. Hydroconversion experiments of C16:0, C18:0, C18:1, C18:2, and C18:3 methyl esters were carried out in continuous-flow reactor at 310–340 °C. The esters and oxygen conversion were complete. The selectivity to iso-alkanes was shown to depend on the carbon chain length. At 340 °C C18 esters gave ~30% iso-alkanes, and C16 ester gave 22% iso-alkanes, which can be related to different stabilities of the carbocations. The number of double bonds in C18 esters did not influence the selectivity to iso-alkanes, probably, due to high rate of esters hydrogenation.

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