RSC advances

ARTICLE

Supporting information

Effect of precursor on the catalytic properties of Ni_2P/SiO_2 in methyl palmitate hydrodeoxygenation

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1. FID relative sensitivities

Relative sensitivities of methyl palmitate and HDO products are listed in Table S1.

Table S1 Relative sensitivities for hydrogen flame detector according to W. A. Dietz.[1]

Compound	Composition	Relative Sensitivity
methyl palmitate	$C_{15}H_{31}COOCH_3$	0.78
palmitic acid	$C_{15}H_{31}COOH$	0.65
palmityl palmitate	$C_{15}H_{31}COOC_{16}H_{33}$	0.30
Hexadecanal	$C_{15}H_{31}CHO$	0.78
hexadecan-1-ol	$C_{16}H_{33}OH$-1	0.85
hexadecan-2-ol	$C_{16}H_{33}OH$-2	0.85
pentadecene	$C_{15}H_{30}$	1.03
hexadecene	$C_{16}H_{32}$	1.02
n-pentadecane	$C_{15}H_{32}$	0.97
n-hexadecane	$C_{16}H_{34}$	0.98
methane	CH_4	0.97
methanol	CH_3OH	0.23

2. Weisz-Prater calculations

Table S2 Physical properties of reagents for Weisz-Prater calculations

Designation	Description	Value	Reference
T	System temperature	563 K	
p_{H_2}	Hydrogen pressure	3.0 MPa	
$R_{particles}$	Catalyst particles radius	0.5 mm	
r_{pore}	Catalyst pore radius	12.7 nm	
$C_{S\,H_2}$	Surface concentration of hydrogen	$2.24 \cdot 10^{-4}$ mol/cm^3	[2]
$C_{S\,MP}$	Surface concentration of methyl palmitate	$2.77 \cdot 10^{-4}$ mol/cm^3	
A_{MP}	Observed HDO rate	$2.74 \cdot 10^{-6}$ mol/(s·cm^3)	
r_{H_2}	Radius of hydrogen molecule	0.120 nm	
r_{MP}	Radius of methyl palmitate molecule	0.395 nm	
λ_{MP}	r_{MP}/r_{pore}	0.0311	
λ_{H_2}	r_{H_2}/r_{pore}	0.0095	
P	Fitting parameter for silica	16.3	
X	*n*-Dodecane association parameter	1	
$M_{Dodecane}$	Molecular weight of n-dodecane	170.34 g/mol	
$\eta_{Dodecane}$	Viscosity of *n*-dodecane	0.25 mPa·s	
V_{H_2}	Molar volume of hydrogen at normal boiling point	0.0286 m^3/kmol	
V_{MP}	Molar volume of methyl palmitate at normal boiling point	0.4357 m^3/kmol	calculated according to the method, described in [3]
$V_{Dodecane}$	Molar volume of *n*-dodecane at normal boiling point	0.2872 m^3/kmol	calculated according to the method, described in [3]
L_{MP}^{vap}	Enthalpy of vaporization of methyl palmitate at normal boiling point	96.8 kJ/mole	[4]
$L_{Dodecane}^{vap}$	Enthalpy of vaporization of *n*-dodecane at normal boiling point	61.51 kJ/mol	[5]
$D_{H_2\|Dodecane}$	Diffusion coefficient of hydrogen in *n*-dodecane	$2.91 \cdot 10^{-4}$ cm^2/s	
$D_{MP\|Dodecane}$	Diffusion coefficient of methyl palmitate in *n*-dodecane	$7.37 \cdot 10^{-5}$ cm^2/s	
$D_{eff\,H_2\|Dodecane}$	Effective diffusion coefficient of hydrogen	$2.47 \cdot 10^{-4}$ cm^2/s	
$D_{eff\,MP\|Dodecane}$	Effective diffusion coefficient of methyl palmitate	$4.59 \cdot 10^{-5}$ cm^2/s	
$N_{W\text{-}P\,H_2}$	Weisz-Prater number for hydrogen	0.017	
$N_{W\text{-}P\,MP}$	Weisz-Prater number for methyl palmitate	0.076	

References

1 W. A. Dietz, *J. Gas Chromatogr.*, 1967, **5**, 68–71.

2 W. Gao, R. L. Robinson and K. A. M. Gasem, *J. Chem. Eng. Data*, 1999, **44**, 130–132.

3 W. Schotte, *Chem. Eng. J.*, 1992, **48**, 167–172.

4 J. S. Chickos, H. Zhao and G. Nichols, *Thermochim. Acta*, 2004, **424**, 111–121.

5 J. S. Chickos and J. A. Wilson, *J. Chem. Eng. Data*, 1997, **42**, 190–197.

3. H_2-TPR of passivated NiP_Ah sample

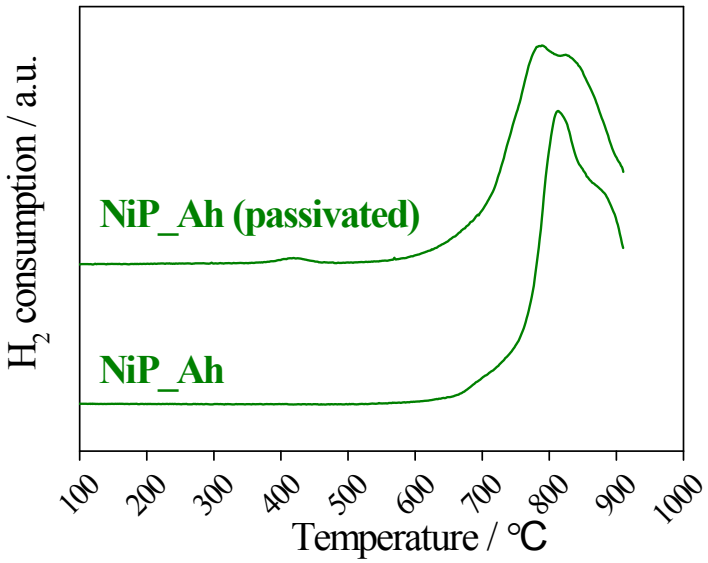

Fig. S1 H_2-TPR curves of calcined NiP_Ah precursor and NiP_Ah sample after reduction at 600 °C and subsequent passivation

4. C_{16}/C_{15} molar ratio

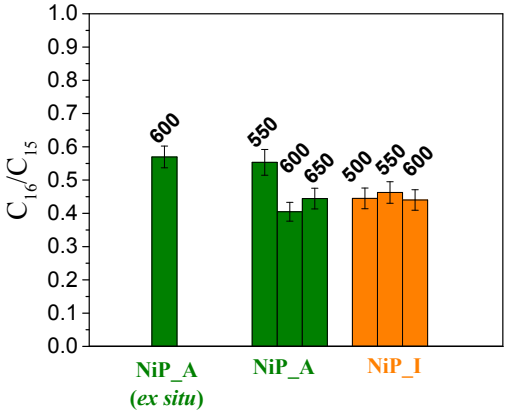

Fig. S2 C_{16}/C_{15} ratio of NiP_A samples reduced *ex situ* at 600 °C, *in situ* at 500, 550 or 600 °C and NiP_I samples reduced *in situ* at 500, 550 and 600 °C. WHSV = 48 h^{-1}, reaction temperature = 290 °C, reaction pressure = 3.0 MPa

5. Methyl palmitate and oxygen-containing compounds conversions over NiP_A catalyst

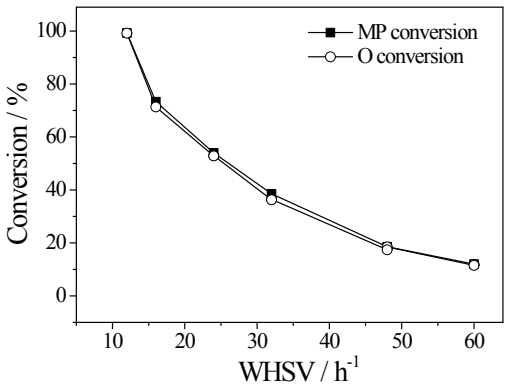

Fig. S3 Methyl palmitate and oxygen-containing compounds conversions during methyl palmitate HDO over NiP_A catalyst at a temperature of 270 °C and pressure 3.0 MPa