Supporting Information

Co_3Mo_3N as an alternative for noble-metal catalyst in hydrodeoxygenation of methyl palmitate to diesel range hydrocarbons

Jiequan Wang, Xiao Chen*, Xiaozhen Chen, Chenxi Zhao, Yu Ling, Changhai Liang*

State Key Laboratory of Fine Chemicals & Laboratory of Advanced Materials and Catalytic Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

* To whom correspondence should be addressed: E-mail: xiaochen@dlut.edu.cn (X. Chen); changhai@dlut.edu.cn (C. Liang)

Keywords: Co_3Mo_3N, Hydrodeoxygenation, Fatty ester, Diesel range hydrocarbons, Reaction kinetics

Total number of pages : 8 (S1-S11)

Total number of figures :6 (Figure S1-S6)

Total number of tables : 1 (Table S1)

Contents

1. Calculation of mass transfer limitation over Co_3Mo_3N catalyst

It has to determine whether it's limited by internal and external diffusion when the rate constant k is calculated.

Weisz-Prater Criterion for Internal Diffusion:

If $C_{WP} = \frac{r_{(obs)}\rho_c {R_p}^2}{D_{eff}C_{As}} < 1$, then internal mass transfer effects can be neglected.

Mears Criterion for External Diffusion:

If $C_M = \frac{r_{(obs)}\rho_b R_p n}{k_c C_{Ab}} < 0.15$, then external mass transfer effects can be neglected.

Where:

$\mathbf{r_{obs}}$ is the observed reaction rate in mol/kg_{cat}·s ;

$\boldsymbol{\rho_b}$ and $\boldsymbol{\rho_c}$ are bulk density of catalyst bed in kg/m^3;

$\mathbf{R_p}$ is catalyst particle radius in meter;

n is the reaction order;

$\mathbf{k_c}$ is external mass transfer coefficient in m/s;

$\mathbf{C_{Ab}}$ is bulk gas concentration of A in mol/m^3;

$\mathbf{C_{As}}$ is gas concentration of A at the external surface of the catalyst in mol/m^3;

D_{eff} is effective diffusivity in m^2/s;

In the present work, the HDO of MPA was carried out in a fixed-bed reactor with high pressure mass flow meters and a HPLC pump. The hydrogen pressures are 4.0 MPa at T = 543 K, a catalyst particle size of 0.007 mm was employed for the kinetic study.

$r_{obs} = 3.1\times10^{-5}$ mol/kg_{cat}·s

n= 1

$R_p = 7.33\times10^{-6}$m

$\rho_c = \rho_b = 3.42\times10^3$ kg/m^3

$D_{eff} = 1.38\times10^{-5.4}$ m²/s

$C_{As} \approx C_{bs} \approx 2.21\times10^{-3}$ mol/m³

$k_c \approx 1.35$ m/s

$C_{WP} = [(3.1\times10^{-5}\ \mathrm{mol/kg_{cat}\cdot s}) \times (3.42\times10^{3}\ \mathrm{kg/m^3}) \times (7.33\times10^{-6}\mathrm{m})^2] / [(1.38\times10^{-5.4}\ \mathrm{m^2/s}) \times (2.21\times10^{-3}\ \mathrm{mol/m^3})] = 1.87 \times 10^{-3.6} < 1$

$C_M = [(3.1\times10^{-5}\ \mathrm{mol/kg_{cat}\cdot s}) \times (3.42\times10^{3}\ \mathrm{kg/m^3}) \times (7.33\times10^{-6}\ \mathrm{m}) \times 1] / [(2.21\times10^{-3}\ \mathrm{mol/m^3}) \times 1.35] = 2.61\times10^{-4} < 0.15$

The absence of both external and internal mass transfer limitations is found for these catalytic systems used in the work.

2 Supplementary Figures

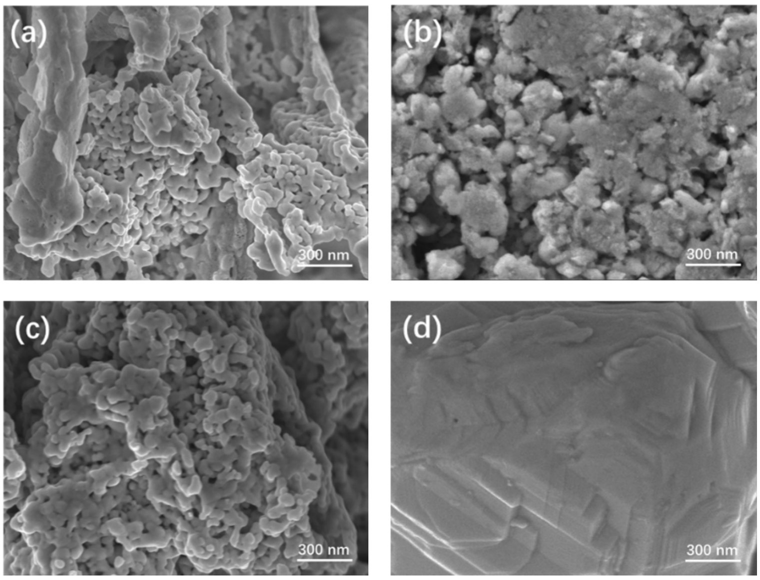

Figure S1. SEM images of (a) Mo_2N (b) $CoMo_2N$ (c) $CoMo_{1.2}N$, and (d) Co_3Mo_3N samples.

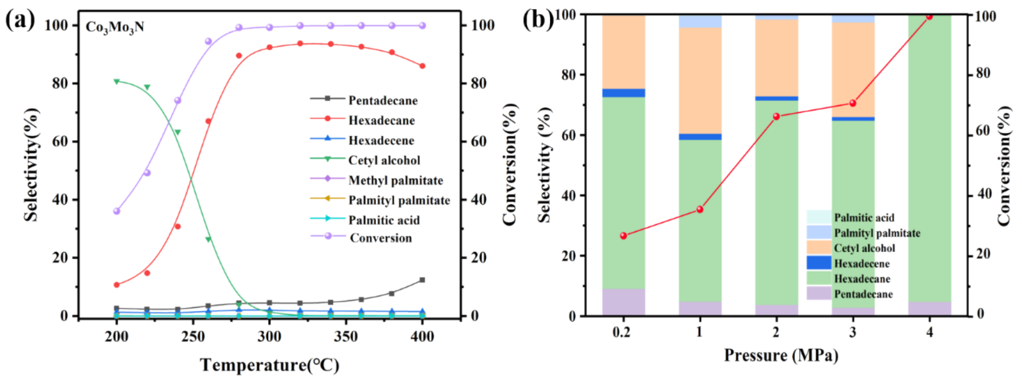

Figure S2. (a) The temperature and (b) H_2 pressure effect on the conversion of MPA and selectivity to products over Co_3Mo_3N catalyst.

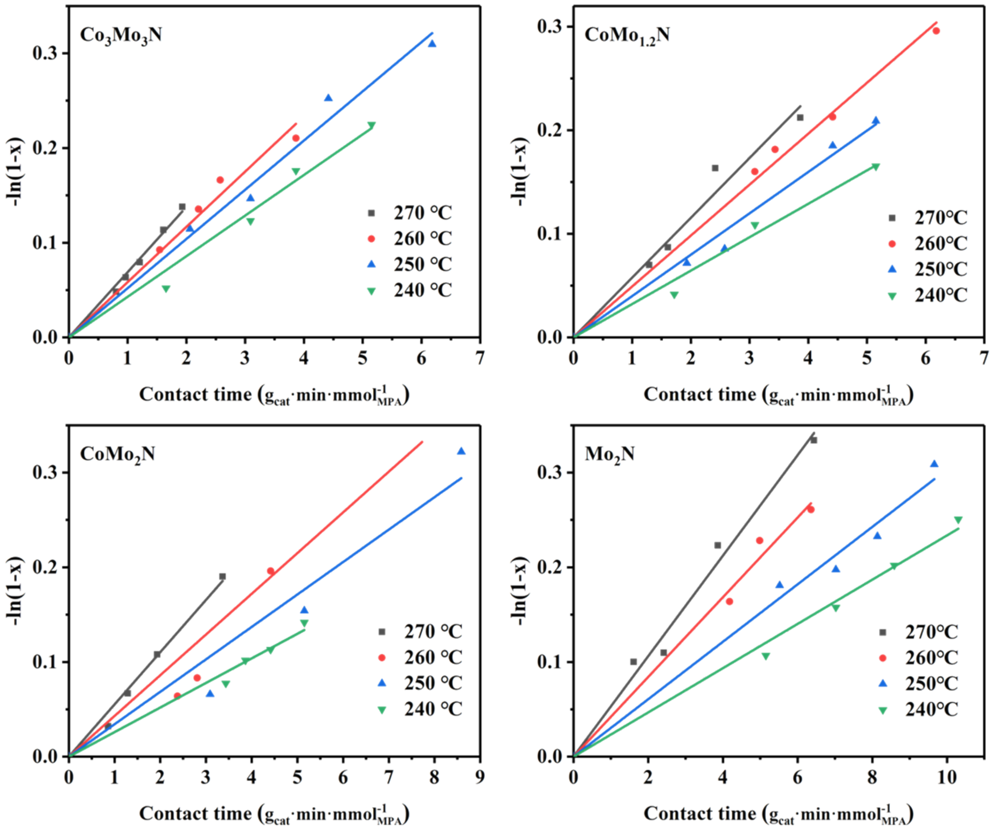

Figure S3. The reaction kinetic of the hydrogenation of MPA over Co_xMo_yN bimetallic nitrides catalysts at 240 - 270 °C.

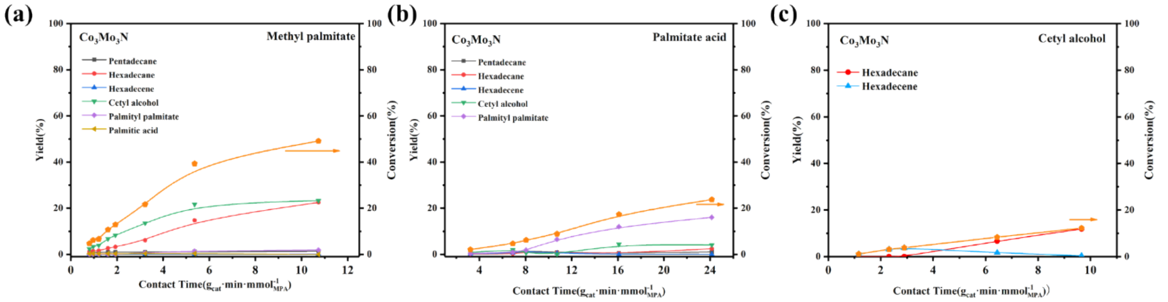

Figure S4. Products yield and conversion for the HDO of (a) MPA, (b) palmitate acid, and (c) cetyl alcohol over Co_3Mo_3N catalyst at varying contact times, respectively. Reaction conditions: 270 ^oC, 4 MPa H_2, and 0.05 g catalyst with H_2/oil = 400.

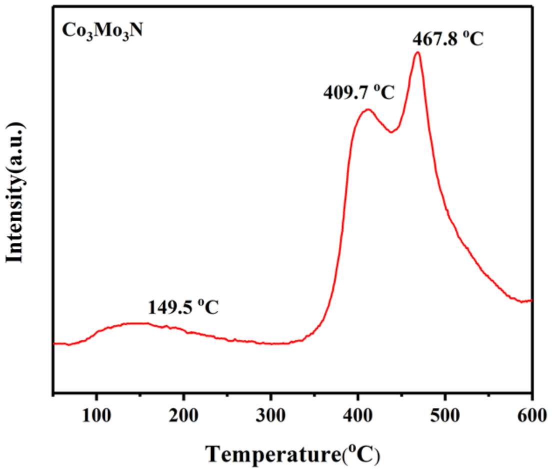

Figure S5. The NH_3-TPD profile of Co_3Mo_3N catalyst.

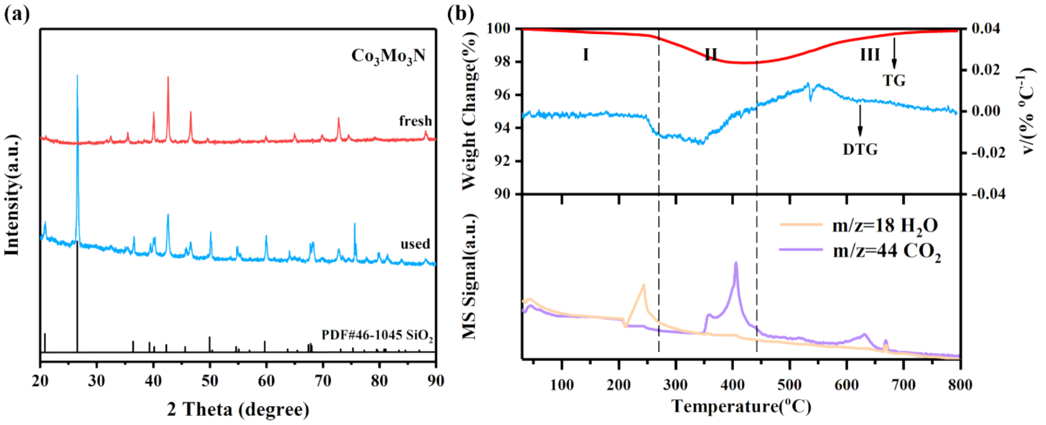

Figure S6. (a) XRD patterns of the fresh and used Co_3Mo_3N catalyst, (b) TG-MS profile of used Co_3Mo_3N catalyst.

3 Supplementary Table

Table S1. Reaction Rate Constants for the HDO of MPA over Co_xMo_yN Bimetallic Nitrides Catalysts in Different Temperatures

Temperature (°C)	Rate constant k (min^{-1})			
	Co_3Mo_3N	$CoMo_{1.2}N$	$CoMo_2N$	Mo_2N
270	1.87	1.57	1.50	1.44
260	1.58	1.33	1.17	1.14
250	1.41	1.08	0.93	0.82
240	1.16	0.87	0.70	0.63