Supplementary Materials

Catalytic Conversion of *n*-C7 asphaltenes and resins II into Hydrogen Using CeO2-based Nanocatalysts

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S.1- Solid-Liquid Equilibrium model

Solid-Liquid Equilibrium model bases on adsorption and association theory of molecules in microporous surfaces, described by the following equations.

$$C = \frac{\psi H}{1 + K\psi} e^{\left(\frac{\psi}{q_m A}\right)}$$

(S1)

$$\psi = \frac{-1 + \sqrt{1 + 4K\xi}}{2K}$$

(S2)

$$\xi = \frac{q_m q}{(q_m - q)} A$$

(S3)

where C (mmol·mol⁻¹) represents the asphaltenes and/or resins concentration, A (m²·g⁻¹) is the surface area of nanoparticles, H (mmol·mol⁻¹) refers to the affinity between nanoparticles and resins and/or asphaltenes. Similarly, K (mmol·mol⁻¹) indicates the self-association degree of *n*-C7 asphaltenes and/or resins II molecules on the surface of the nanoparticles, and q_m (mol·mol⁻¹) is the maximum adsorption capacity [1].

S.2- Activation energy estimation

Instantaneous reactivity is represented by Equation S4.

$$\frac{d\alpha}{dt} = K_a \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{S4}$$

where, K_a is the Arrhenius pre-exponential factor, R is the ideal gas constant and E_a the effective activation energy. In addition, $d\alpha/dt$ refers to the change in conversion (α) of asphaltenes and/or resins II concerning time. Integration of Equation (S4) bearing in mind isothermal conditions, lead Equation S5:

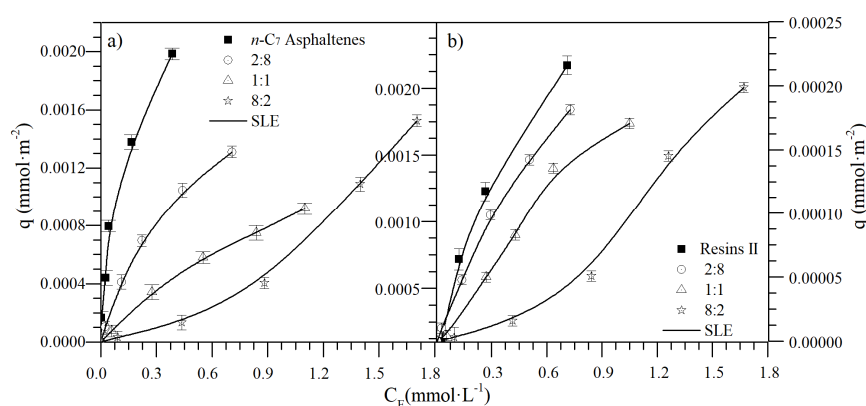$$g(\alpha) = K_a \exp\left(-\frac{E_a}{RT}\right) t \tag{S7}$$

Applying natural logarithm on both sides of Equation S5, the expression can be written in linear terms as Equation S6

$$ln\left(t_{a,i}\right) = ln\left(\frac{g(\alpha)}{K_a}\right) + \frac{E_a}{RTi} \tag{S6}$$

By graphing $ln(t_{a,i})$ against $1/T_i$, effective activation energy values can be obtained by the slope.
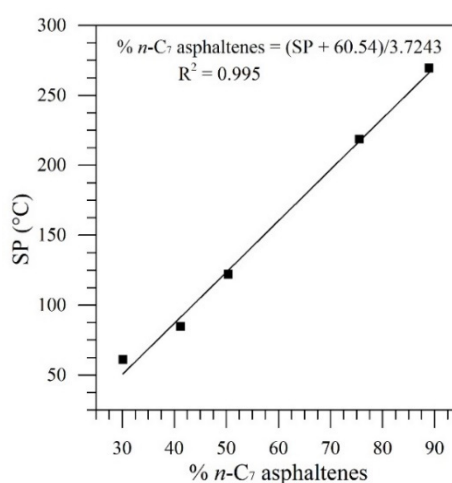
Figure S1. Softening point calibration curve.

Figure S2. Adsorption isotherms constructed for (a) *n*-C$_7$ asphaltenes and (b) resins II on CeNi1Pd1 nanoparticles for different R:A ratios. The dotted lines are from the SLE model and the symbols are experimental data.

Table S1. Estimated SLE model parameters for adsorption isotherms of *n*-C$_7$ asphaltenes and/or resins II on different nanocatalysts and different Resins-Asphaltene (R:A ratios). *H* represents the Henry's law constant, *K* gives an idea about the self-association degree of asphaltenes over nano-particle surface, and q$_m$ is the maximum amount adsorbed.

Sample		*n*-C$_7$ asphaltenes				Resins II			
	R:A	*H* (mmol·g^{-1}) x10^{-3}	*K* (mmol·g^{-1}) x10^{-3}	q$_m$ (mmol·m^{-2}) x10^{-3}	% RSM	*H* (mmol·g^{-1}) x10^{-2}	*K* (mmol·g^{-1}) x10^{-2}	q$_m$ (mmol·m^{-2})	% RSM
CeNi1Pd1	Individual	6.97	4.36	0.21	0.01	7.60	0.61	0.19	0.01
CeFe1Pd1	Individual	7.25	4.39	0.19	0.01	8.05	0.21	0.18	0.05
CeCo1Pd1	Individual	6.99	6.36	0.21	0.01	9.17	1.66	22.51	0.02
CeO$_2$	Individual	11.15	22.81	0.13	0.01	11.50	7.96	19.40	0.01
CeNi1Pd1	2:8	8.38	5.75	0.20	0.01	171.68	9.06	23.47	0.02
	1:1	13.90	6.24	0.15	0.01	0.18	8.53	31.57	0.01
	8:2	117.05	6.91	28.18	0.01	4.42	3.35	0.25	0.02

Table S2. Estimated slope and intercept of the linear plots of q$_{predicted}$ as a function of q$_{experimental}$ for the adsorption and desorption of *n*-C$_7$ asphaltenes in absence and presence of resins II in the systems at different R:A ratios.

R:A Ratio	*m*	*b* (x10^{-3})	R^2
n-C$_7$ Asphaltenes	1.0	0.0	1.0
2:8	1.03	-1.11	0.99
1:1	1.05	-2.80	0.98
8:2	1.04	-3.21	0.99

References

1. Montoya, T.; Coral, D.; Franco, C.A.; Nassar, N.N.; Cortés, F.B. A novel solid–liquid equilibrium model for describing the adsorption of associating asphaltene molecules onto solid surfaces based on the "chemical theory". *Energy & Fuels* **2014**, *28*, 4963-4975.