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Quantification of the available acid sites in the hydrocracking of nitrogen-containing feedstocks over USY shaped NiMo-catalysts

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Deduction of the expressions for activity and fraction of vacant sites in cyclohexane hydroconversion

The continuity equation for cyclohexane (CC₆) in a PFR is given by:

$$\frac{dF_{CC_6}}{dz} = -W_{cat}(-r_{CC_6})$$

Replacing the rate of consumption of cyclohexane by a first-order kinetics law on both the acid sites [1-4] and cyclohexane [1-6].

$$\frac{dF_{CC_6}}{dz} = -W_{cat}kn_{Al}^{vacant}P_{CC_6}$$

Assuming that the number of available acid sites remains constant along the reactor, the continuity equation, re-written in order to cyclohexane conversion, can be integrated over the whole reactor length.

$$\ln\left(\frac{1}{1-x}\right) = kP_{CC_6}^0 n_{Al}^{vacant} \frac{W_{cat}}{F_{CC_6}^0}$$

The catalytic activity, defined as the first-order apparent kinetic constant, is then given, in moles of reactant per catalyst weight per unit of time, by:

$$Activity = kP_{CC_6}^0 n_{Al}^{vacant} = \ln\left(\frac{1}{1-x}\right) \frac{F_{CC_6}^0}{W_{cat}MW_{CC_6}}$$

The activity with explicit dependencies can be written as follows:

$$Activity(catalyst, T, P_{CC_6}^0, P_{NH_3}^0) = k(T, catalyst)P_{CC_6}^0 n_{Al}^{vacant}(T, P_{CC_6}^0, P_{NH_3}^0)$$

The ratio of activities for the same catalyst at two different operating conditions a and b is given by:

$$\frac{Activity(catalyst, T, P_{CC_6,a}^0, P_{NH_3,a}^0)}{Activity(catalyst, T, P_{CC_6,b}^0, P_{NH_3,b}^0)} = \frac{k(T_a, catalyst)P_{CC_6,a}^0 n_{Al}^{vacant}(T_a, P_{CC_6,a}^0, P_{NH_3,a}^0)}{k(T_b, catalyst)P_{CC_6,b}^0 n_{Al}^{vacant}(T_b, P_{CC_6,b}^0, P_{NH_3,b}^0)}$$

For a well-balanced bifunctional catalyst, the turnover frequency is similar regardless of the metal to acid sites ratio [1,2], as discussed above. Considering the same reaction temperature as well, the kinetic constant is, hence, similar in this case and can be eliminated from the equation.

$$\frac{Activity(catalyst, T, P_{CC_6,a}^0, P_{NH_3,a}^0)}{Activity(catalyst, T, P_{CC_6,b}^0, P_{NH_3,b}^0)} = \frac{P_{CC_6,a}^0 n_{Al}^{vacant}(T, P_{CC_6,a}^0, P_{NH_3,a}^0)}{P_{CC_6,b}^0 n_{Al}^{vacant}(T, P_{CC_6,b}^0, P_{NH_3,b}^0)}$$

The coverage of Brønsted acid sites in the hydroconversion of alkanes has been demonstrated to be very low [7]. Therefore, in absence of ammoniac, the concentration of vacant Brønsted acid sites is approximately equal to the total concentration of Brønsted acid sites, which is temperature independent. In the same way, due to the very low coverage in hydrocarbon species, the concentration of vacant Brønsted acid sites in presence of ammoniac can be considered to be independent of the partial pressure of reactant.

When relating the activity of the same catalyst tested in a) presence and b) absence of ammoniac, the following expression can be used.

$$\frac{Activity(catalyst, T, P_{CC_6,a}^0, P_{NH_3,a}^0)}{Activity(catalyst, T, P_{CC_6,b}^0, 0)} = \frac{n_{Al}^{vacant}(T, P_{NH_3,a}^0) P_{CC_6,a}^0}{n_{Al}^{total} P_{CC_6,b}^0}$$

The fraction of activity sites can, thus, be estimated by the equation below. This corresponds to Eq. 3 of the manuscript.

$$\Psi_V(T_a, P_{NH_3,a}) = \frac{n_{Al}^{vacant}(T_a, P_{NH_3,a}^0)}{n_{Al}^{total}} = \frac{Activity(catalyst, T, P_{CC_6,a}^0, P_{NH_3,a}^0) P_{CC_6,b}^0}{Activity(catalyst, T, P_{CC_6,b}^0, 0) P_{CC_6,a}^0}$$

To reconcile activities at different temperatures, the Arrhenius law was employed in the following form:

$$\frac{k_1}{k_2} = \exp \left[-\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$

Transmission Electron Microscopy

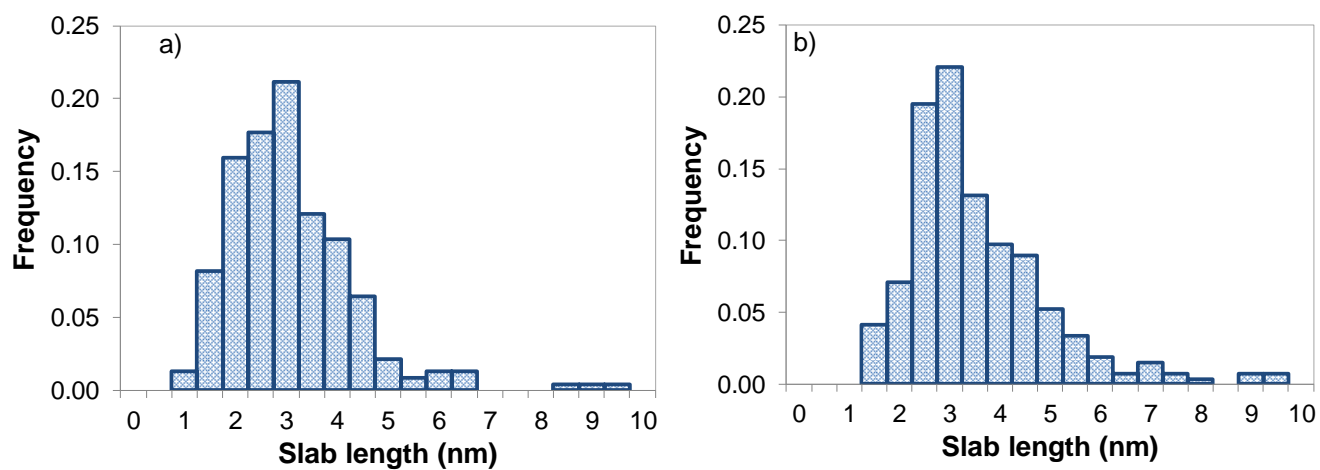


Figure S1: Histogram of NiMoS slabs length for a) 12%NiMoS/(HUSY+Al₂O₃) and b) 16%NiMoS/(HUSY+Al₂O₃) samples according to TEM measurements.

X-Ray Photoelectron Spectroscopy

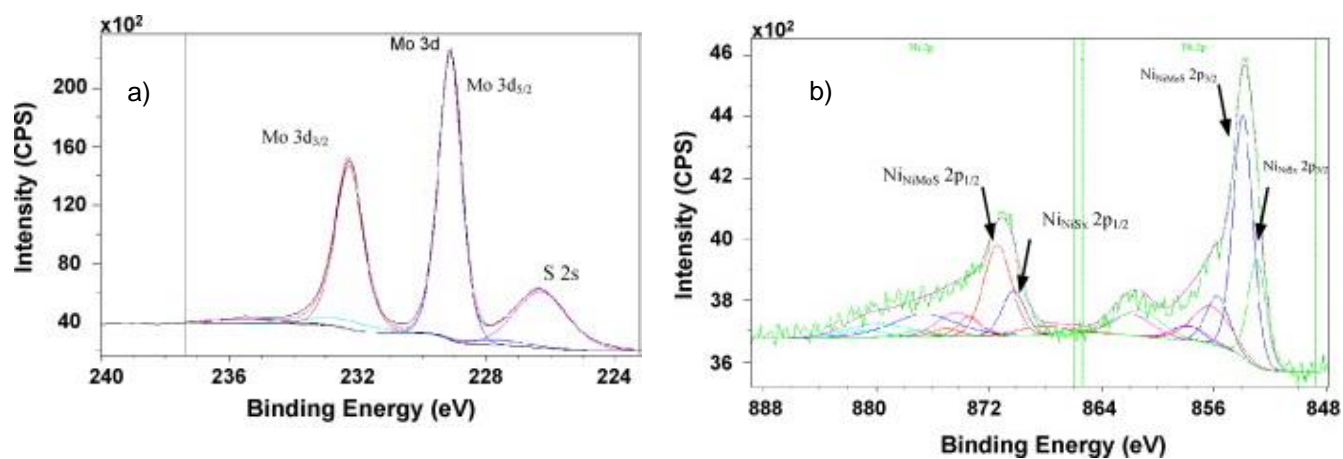


Figure S2: XPS spectra of unsupported molybdenum sulphides-based a) MoS₂ and b) NiMoS [24].

Table S1: Distribution of chemical species within each element for NiMo-containing samples.

Mo content (wt.%)	Molybdenum			Nickel			Sulphur		
	Mo-O (wt.%)	Mo ⁺⁵ (wt.%)	Mo-S (wt.%)	Ni-O (wt.%)	Ni-S (wt.%)	NiMoS (wt.%)	Sulphur (wt.%)	Oxysulphur (wt.%)	Sulphate (wt.%)
12	18	13	69	17	28	55	79	15	6
16	9	18	73	2	47	51	91	9	0

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