

Supporting information

Balance between (de)hydrogenation and acid sites:
comparison between sulfide-based and Pt-based
bifunctional hydrocracking catalysts

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Effect of NH₃ on isomer yield

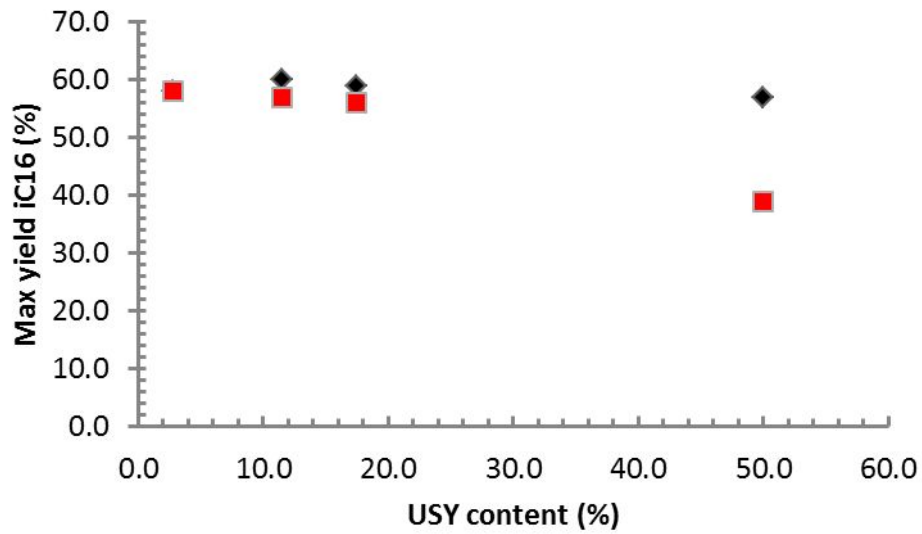


Figure S1. Maximum yield of i-C₁₆ for Pt-USY-Al₂O₃ catalysts with different USY content, in the presence of NH₃ (black diamond symbols) and in the absence of NH₃ (red squares).

Rate in the presence and absence of NH₃

According to the model of Degnan and Kennedy, the reaction rate can be written as

$$r = \frac{n_{acid}(1-\theta_{acid})k_{isom}}{p_{H2}} \cdot \frac{p_{nC16}}{1 + \frac{n_{acid}(1-\theta_{acid})k_{isom}}{n_{metal}(1-\theta_H)^2 k_{deh}}}$$

In the absence of NH₃, the coverage of acid sites is low and the expression can be simplified as

$$\begin{aligned} r &= \frac{n_{acid}k_{isom}}{p_{H2}} \cdot \frac{p_{nC16}}{1 + \frac{n_{acid} \cdot K_{H2} \cdot p_{H2}}{n_{metal}} \frac{k_{isom}}{k_{deh}}} \\ &= \frac{n_{acid}k_{0,isom}p_{nC16}}{p_{H2}} e^{-E_{isom}/RT} \cdot \frac{1}{1 + \sigma \cdot K'_{0,H2} \frac{k_{0,isom}}{k_{0,deh}} \cdot e^{-(E_{isom} - E_{deh} + \Delta H_{H2})/RT}} \end{aligned}$$

In the presence of NH₃, the coverage of acid sites is governed by the adsorption of NH₃

$$\begin{aligned} r_{NH3} &= \frac{n_{acid}k_{isom}}{p_{H2}} \frac{1}{K_{NH3}p_{NH3}} \cdot \frac{p_{nC16}}{1 + \frac{n_{acid}}{n_{metal}} \frac{K_{H2}p_{H2}}{K_{NH3}p_{NH3}} \frac{k_{isom}}{k_{deh}}} \\ &= \frac{n_{acid}k_{0,isom}p_{nC16}}{p_{H2}} \frac{1}{K_{0,NH3}p_{NH3}} e^{-(E_{isom} - \Delta H_{NH3})/RT} \cdot \frac{1}{1 + \sigma \cdot \frac{k_{0,isom}}{k_{0,deh}} \frac{K'_{0,H2}}{K_{0,NH3}p_{NH3}} \cdot e^{-(E_{isom} - \Delta H_{NH3} - E_{deh} + \Delta H_{H2})/RT}} \end{aligned}$$

If we admit that $E_{deh} - \Delta H_{H2}$ is smaller than E_{isom} and that the denominator is not dominating, then $r \approx r_{NH3}$ if

$$\frac{1}{K_{0,NH3} p_{NH3}} e^{-\frac{(E_{isom} - \Delta H_{NH3})}{RT_2}} = e^{-\frac{E_{isom}}{RT_1}}$$

$$-\ln(K_{0,NH3} p_{NH3}) - \frac{E_{isom} - \Delta H_{NH3}}{RT_2} = -\frac{E_{isom}}{RT_1}$$

This fixes the relationship between the temperature T_2 in the presence of NH_3 , which leads to the same activity as T_1 in the absence of NH_3 .

We can now compare the terms $\varepsilon^* \sigma$ for the two situations. In the absence of NH_3 at T_1 , $\varepsilon^* \sigma$ is

$$(\varepsilon \cdot \sigma)_1 = \frac{k_{c,0}}{k_{deh,0}} \cdot \frac{n_{acid}}{n_{metal}} \cdot K_{0,H2} \cdot e^{-\frac{(E_{crack} - E_{deh} + \Delta H_{H2})}{RT_1}}$$

In the presence of NH_3 , at T_2 we obtain

$$(\varepsilon \cdot \sigma)_2 = \frac{k_{c,0}}{k_{deh,0}} \cdot \frac{n_{acid}}{n_{metal}} \cdot \frac{K_{0,H2}}{K_{0,NH3} p_{NH3}} e^{-\frac{(E_{crack} - E_{deh} - \Delta H_{NH3} + \Delta H_{H2})}{RT_2}}$$

In order to improve the metal-acid balance by adding NH_3 (the inhibition being compensated by an increase of temperature from T_1 to T_2) and hence the selectivity, $(\varepsilon^* \sigma)_1$ must be bigger than $(\varepsilon^* \sigma)_2$.

$$\ln(\varepsilon \cdot \sigma)_1 > \ln(\varepsilon \cdot \sigma)_2$$

$$-\frac{E_c - E_{deh} + \Delta H_{H2}}{RT_1} > -\ln(K_{0,NH3} p_{NH3}) - \frac{E_c - E_{deh} - \Delta H_{NH3} + \Delta H_{H2}}{RT_2}$$

In order to introduce the relationship between T_1 and T_2 , we define $\Delta E = E_c - E_{isom}$

$$\frac{\Delta E - E_{deh} + \Delta H_{H2}}{RT_1} < \frac{\Delta E - E_{deh} + \Delta H_{H2}}{RT_2}$$

Since $T_2 > T_1$, this relationship is true if $\Delta E - E_{deh} + \Delta H_{H2} < 0$. ΔE is close to zero (Thybaut 2005), E_{deh} has a positive value and ΔH_{H2} a negative value. We can, thus, be sure that the condition is fulfilled.