Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


# Supporting Information

# Synergistic Effect of Mo-W Carbides on Selective Hydrodeoxygenation of Guaiacol to Oxygen-Free Aromatic Hydrocarbons

Chi-Cong Tran[a], Yinglei Han[b], Manuel Garcia-Perez[b], and Serge Kaliaguine*[a]

[a.] *Prof. Serge Kaliaguine, PhD. Chi Cong Tran. Department of Chemical Engineering Laval University. Quebec G1V 0A6 (Canada). E-mail: Serge.Kaliaguine@gch.ulaval.ca*

[b.] *A.Prof. Manuel Garcia-Perez. Department of Biological System Engineering. Washington State University. Pullman, WA 99614-6120 (United States)*

**External and internal mass transfer evaluation via Mears' criteria and Thiele module.**

The Mears' criterion, $C_m$, is the ratio of the rate of reaction to the external diffusion rate [1]. The effect of external mass transfers can be neglected if the Mears' criterion calculated to be below than 0.15:

$$C_m = \frac{-r_{A(obs)} \times \rho_b \times R \times n}{k_c \times C_{Ab}} < 0.15$$

where $r_{A(obs)}$ is the observed reaction rate per unit mass of catalyst (kmol kg$^{-1}$ s$^{-1}$); $p_b$ is catalyst bed density (kg m$^{-3}$) calculated as $p_b = (1-\varepsilon)\, p_c$ ($\varepsilon$ is catalyst bed porosity, $p_c$ catalyst density); $R$ is catalyst particle radius (m); n is the reaction order; $k_C$ is mass transfer coefficient for reactant (m s$^{-1}$); $C_{Ab}$ is the concentration of reactant (kmol m$^{-3}$).

The $\varepsilon$ porosity of catalyst bed is estimated as 0.3 and $p_c$ catalyst density is reported to be 760 kg m$^{-3}$. In order to calculate the Mears' criterion, determination of $k_c$ is required. Mass transfer coefficient ($k_c$) is estimated via the equation of Sherwood number (Sh): Sh = ($k_c$ × 2R)/$D_e$ (where $D_e$ is the estimated diffusivity of reactant and is calculated as 7.6 × 10$^{-6}$ cm$^2$ s$^{-1}$ by using Wilke-Lee equation [2]). The influence of external mass transfer can be neglected due to the calculated Mears' criterion lower than 0.15 (Table S1)

**Table S1**. Parameters and data for calculating the Mears' criterion to estimate the external mass transfer limitation in guaiacol HDO reaction.

| Parameters | |
|---|---|
| $r_{A(obs)}$ (kmol kg$^{-1}$ s$^{-1}$) | 2.06 × 10$^{-6}$ |
| $p_b$ (kg m$^{-3}$) | 532 |
| $R$ (m) | 1.0 × 10$^{-4}$ |
| $n$ | 0.99 |
| $k_c$ (m s$^{-1}$) | 0.076 |
| $C_{Ab}$ (kmol m$^{-3}$) | 0.45 |
| Estimated Mears' criterion | 3.17 × 10$^{-6}$ |

Thiele module, $\phi$, is the ratio of reaction rate to diffusion rate inside the catalyst and is calculated below:

$$\Phi = \frac{-r_{A(obs)} \times \rho_c \times R^2}{D_e \times C_{As}} = \eta\phi^2$$

where $r_{A(obs)}$ is the observed reaction rate per unit mass of catalyst (kmol kg$^{-1}$ s$^{-1}$); $p_c$ is the catalyst density (kg m$^{-3}$); $R$ is catalyst particle radius (m); $D_e$ is the estimated diffusivity of reactant at 623K (m$^2$ s$^{-1}$); $C_{As}$ is the reactant concentration at the catalyst surface (kmol m$^{-3}$); $\eta$ is the internal effectiveness factor and $\phi$ is the Thiele module. If $\eta \rightarrow 1$, the internal mass transfer inside the catalyst pellet has no resistance and in contrast, if $\eta \rightarrow 0$, the internal mass diffusion is the rate limiting step. Due to the negligible external mass transfer, $C_{Ab}$ supposes to be equal to $C_{As}$. Based on the date in Table S1 and the calculated $D_e$ earlier, Thiele module $\phi$ is calculated to be 0.0021. Small value of the Thiele module indicates the rate of the internal mass transfer is faster than the reaction rate, thus the effect of internal mass diffusion can be neglected.

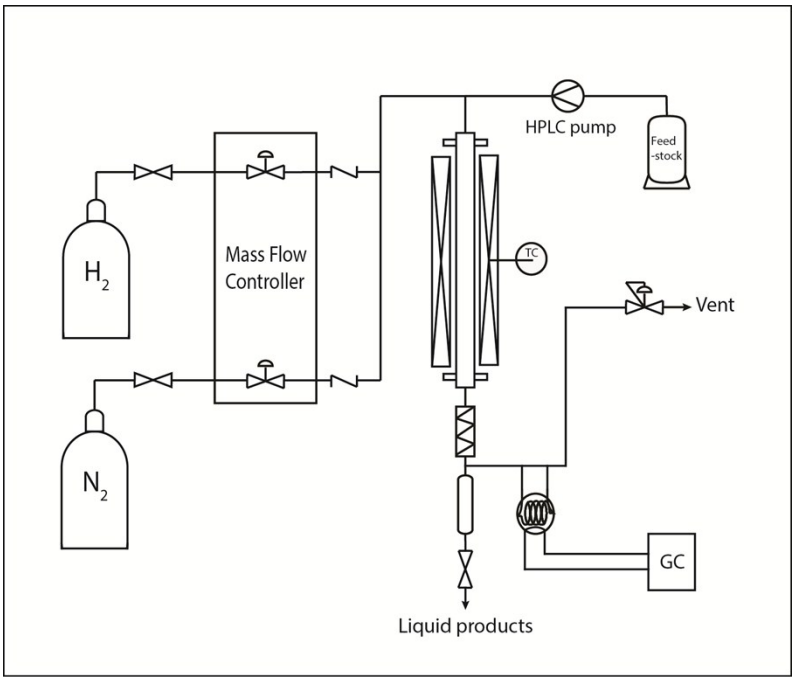


**Figure S1**. Continuous flow process diagram of HDO system

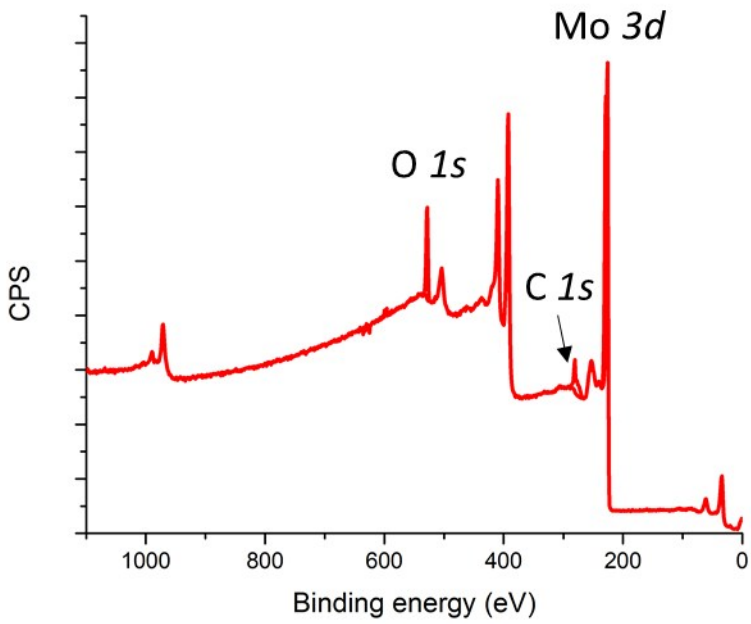


**Figure S2**. XPS survey spectrum of $Mo_2C$.

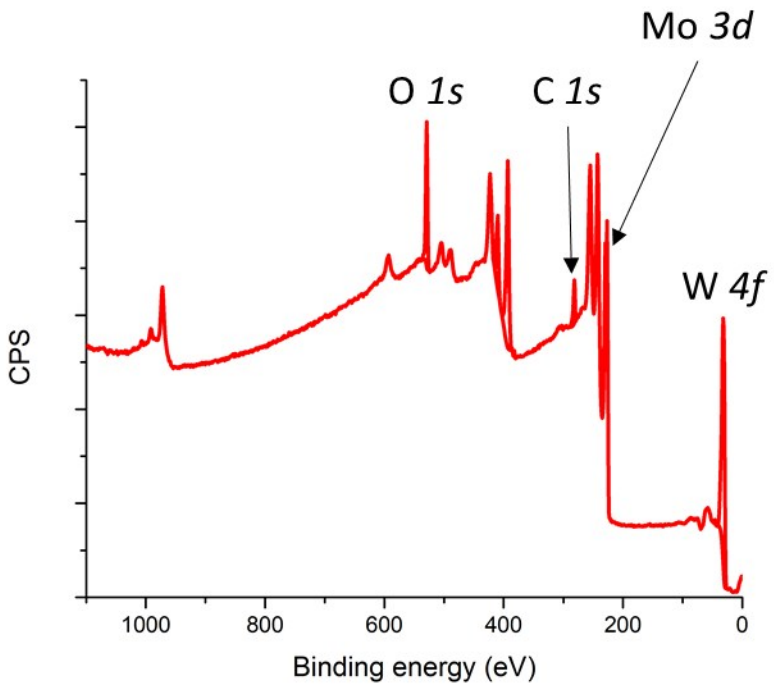


**Figure S3**. XPS survey spectrum of MoWC

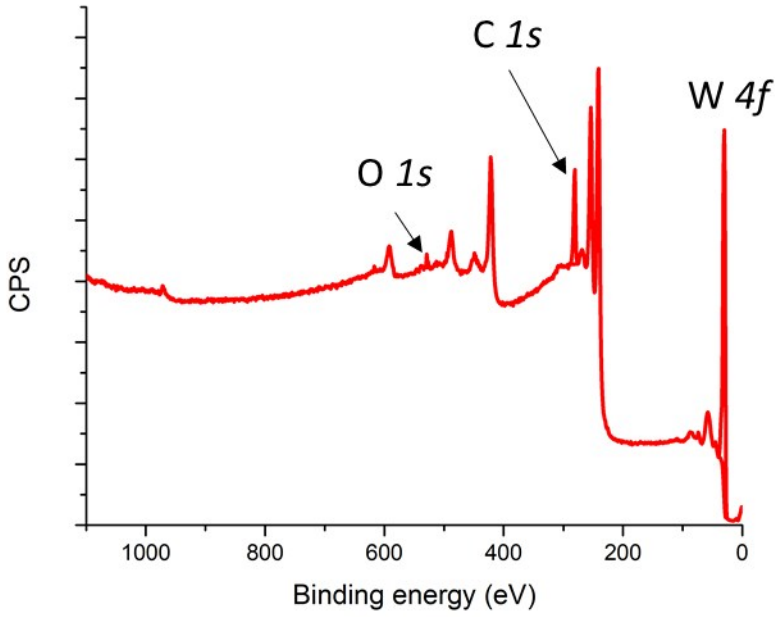


**Figure S4**. XPS survey spectrum of WC-700

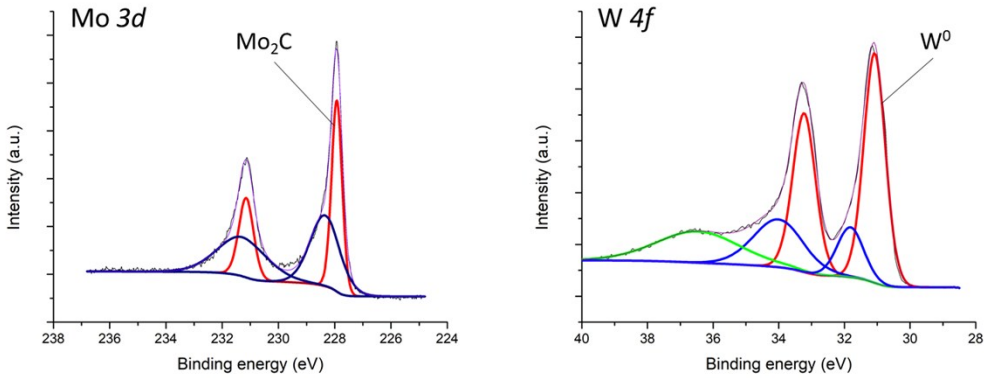


**Figure S5**. Mo *3d* and W *4f* XPS spectra of mechanically mixed $Mo_2C$+WC sample.

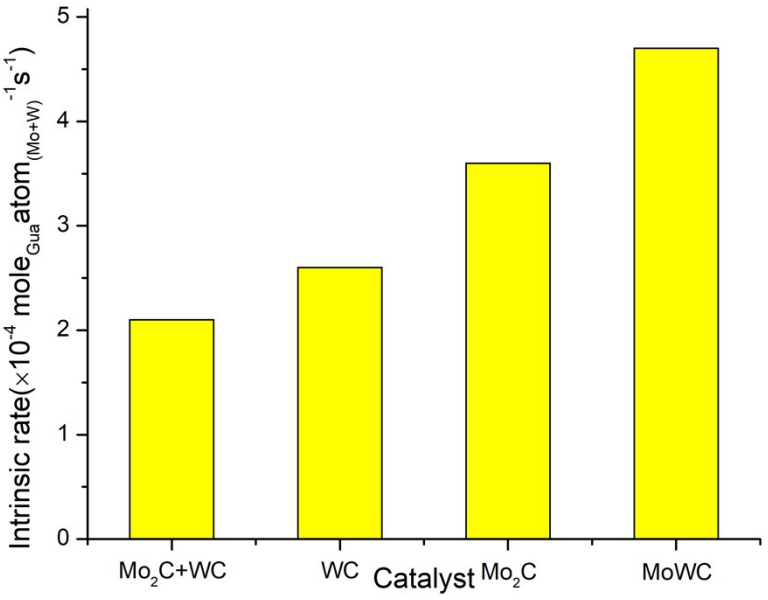


**Figure S6**. Intrinsic rates of guaiacol conversion over metal carbides at 350°C and 400 psig.

**Table S2**. Comparison of deoxygenation activity of guaiacol over various catalysts

| Catalyst | Reactor | Temperature (°C) | P (psig) | Major product | Conversion (%) | Deoxygenation (%)[a] | Ref |
|---|---|---|---|---|---|---|---|
| Ru/C | Fixed-bed | 350 | 580 | benzene | 34.2 | 39.6 | 3 |
| Pd/C | Fixed-bed | 350 | 580 | methoxy-cyclohexane | 15 | 23.3 | 3 |
| Pt/MgO | Fixed-bed | 300 | 20 | phenol | 9 | □0.3 | 9 |
| $Pt/AL_2O_3$ | Fixed-bed | 300 | 20 | Catechol | 6 | □0.1 | 9 |
| $PtRh/ZrO_2$ | Batch reactor | 300-400 | 725 | methoxy-cyclohexanol | 100 | 40 | 7 |
| $Pt/Mo_2C$ | Fixed-bed | 350 | 70 | benzene | 98 | 99 | 8 |
| $Pd/Mo_2C$ | Fixed-bed | 350 | 70 | benzene | 99 | 81 | 8 |
| $\alpha$-$MoC_{1-x}$/AC[b] | Batch reactor | 340 | ambient | phenol | 87 | - | 4 |
| $Mo_2C$/CNF[d] | Batch reactor | 350 | 725 | phenol | 99 | 3 | 5 |
| $Mo_2C$/CNT[c] | Batch reactor | 350 | 580 | catechol | 91 | - | 6 |
| $Mo_2C$/CNF | Batch reactor | 300 | 290 | phenol | 67 | | 10 |
| CoMo | Batch reactor | 400 | 725 | phenol | < 15 | - | 7 |
| NiMo | Batch reactor | 400 | 725 | cyclohexane | < 15 | - | 7 |
| $W_2C$/CNF | Batch reactor | 350 | 725 | phenol | 66 | 4 | 5 |
| NiMoW sulfide | Fixed-bed | 350 | 400 | phenol | 99 | 28 | 11 |
| MoWC | Fixed-bed | 350 | 400 | benzene | 93 | 92 | This report |

[a] Total selectivity of non-oxygen containing compounds (i.e. benzene, toluene, hexane, hexene)
[b] Activated carbon; [c] Carbon nanotube; [d] Carbon nanofiber

**Table S3.** Conversion of guaiacol at various temperatures over metal carbides and the intrinsic reaction rate at 350°C and 400 psig, 1 hour on stream

| Catalyst | Conversion (%) | | | Intrinsic rate* ($10^{-4}$ $mole_{Guai}$ $atom_{(Mo+W)}^{-1}$ $s^{-1}$) |
|---|---|---|---|---|
| | 250°C | 300°C | 350°C | |
| $Mo_2C$ | 35.1 | 72.4 | 78.1 | 3.6 |
| WC | 12.1 | 14.8 | 27.2 | 2.6 |
| MoWC | 52.9 | 77.6 | 93.3 | 4.7 |
| $Mo_2C$+WC | 25.5 | 27.6 | 38.9 | 2.1 |

* Average rate over the first 60 mins

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