Electronic supplementary material:

Unveiling the Ir single atoms as selective active species for the partial hydrogenation of butadiene by *operando* XAS

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Table SI1. Ir content in Ir-SAC and Ir-NC, determined by ICP-OES, and N, C and H concentration in AC, and Ir-SAC, determined by CHNS.

Figure SI1. HAADF-STEM images of Ir-SAC and TEM images of Ir-NC with an average size of 1.3 nm.

Figure SI2. XANES spectra of Ir bulk (black), Ir-NC (red), Ir-SAC (blue) and IrO_2 (green) showing the difference in peak heights for these samples, and the parameters *a* and *b* used for the assessment of the oxidation state.

Figure SI3. EXAFS fitting of Ir-SAC before pre-treatment under He flow at 25°C (a, b) and after reaction under He flow at 25°C (c, d).

Figure SI4. XANES spectra (A), EXAFS signals (B) and related modulus of the Fourier Transform of the k^2-weighed EXAFS signals (C) of the Ir-NC recorded at room temperature for the following states: initial (under air), initial under flow of H_2/He, after pre-treatment under H_2/He at 250 °C and after reaction at 200 °C. Examples of EXAFS fittings (D and E).

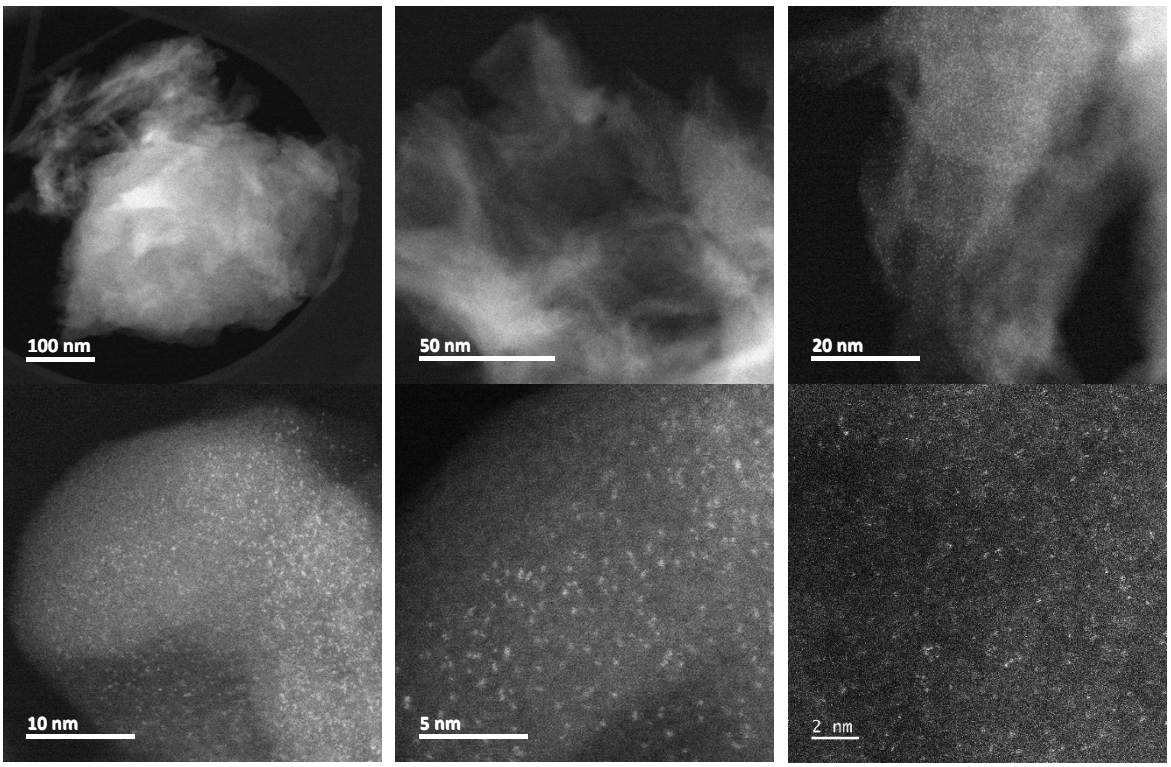
Figure SI5. Mass spectrometry monitoring of hydrocarbon reactant and products during the hydrogenation of butadiene on Ir-SAC and Ir-NC.

Figure SI6. Ex situ STEM-HAADF images of Ir-SAC as-prepared (A), after treatment under H2/Ar flow at 250 °C (B) and 400 °C (C).

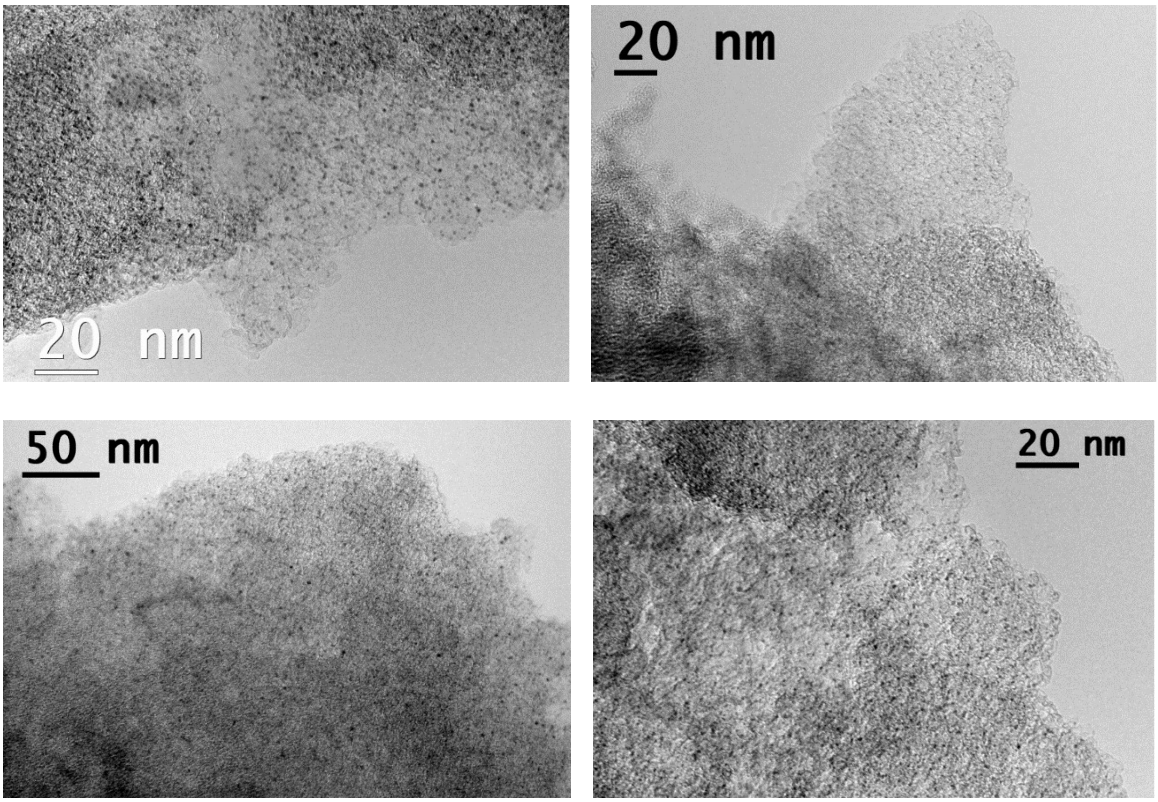
Table SI1. Ir content inf Ir-SAC and Ir-NC, determined by ICP-OES, and N, C and H concentration in AC, and Ir-SAC, determined by CHNS.

Sample	ICP-OES	CHNS		
	Metal content (wt. %)	N (wt. %)	C (wt. %)	H (wt. %)
AC	-	0.47 (±0.08)	78.39 (±0.81)	0.22 (±0.04)
Ir-SAC	0.99 (±0.01)	14.07 (±0.15)	68.97 (±0.11)	0.43 (±0.03)
Ir-NC	3.70 (±0.02)	-	-	-

Figure SI1. HAADF-STEM images of Ir-SAC and TEM images of Ir-NC with an average size of 1.3 nm.



Six HAADF-STEM images of Ir-SAC. No nanoparticles could be noticed in the low magnification images.



Four TEM image of Ir-NC. Well dispersed Ir nanoparticles are visible in these TEM images.

Figure SI2. XANES spectra of Ir bulk (black), Ir-NC (red), Ir-SAC (blue) and IrO_2 (green) showing the difference in peak heights for these samples, and the parameters *a* and *b* used for the assessment of the oxidation state.

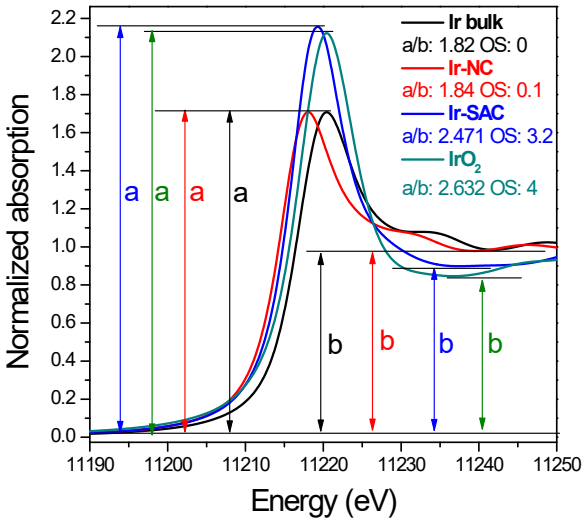


Figure SI3. EXAFS fitting of Ir-SAC before pre-treatment under He flow at 25°C (a, b) and after reaction under He flow at 25°C (c, d).

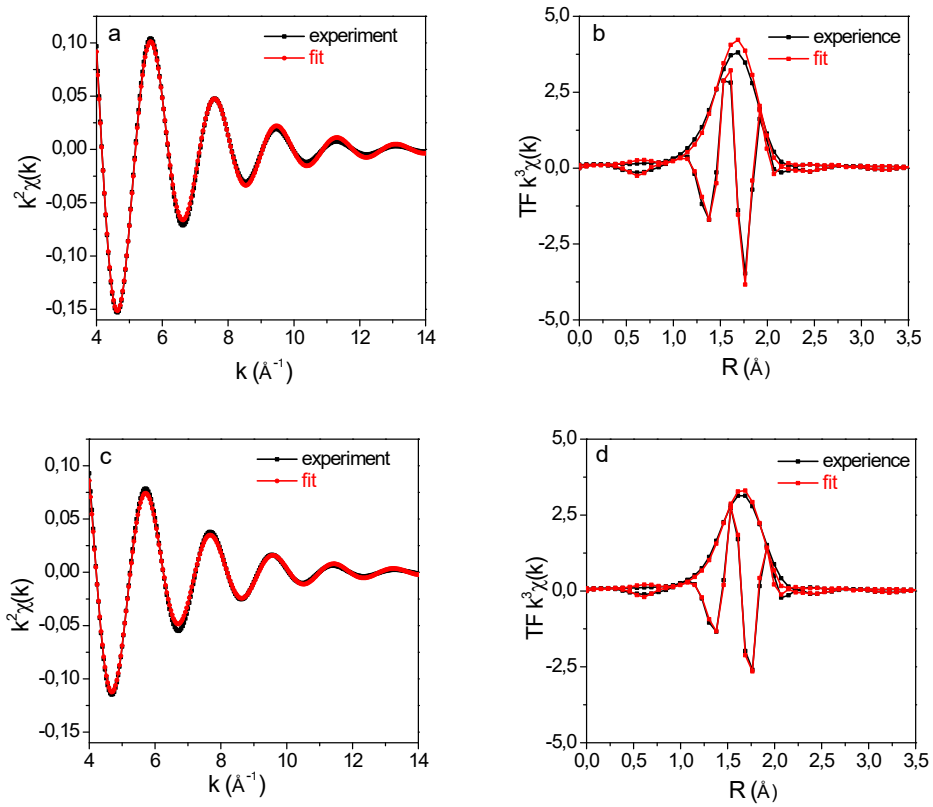
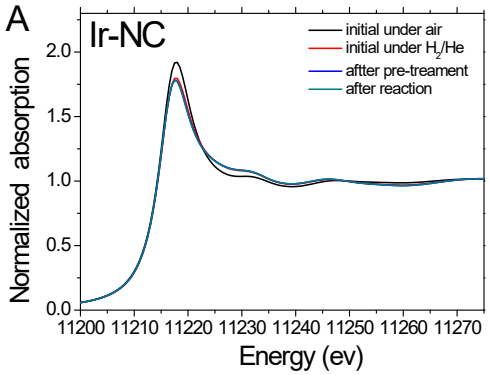
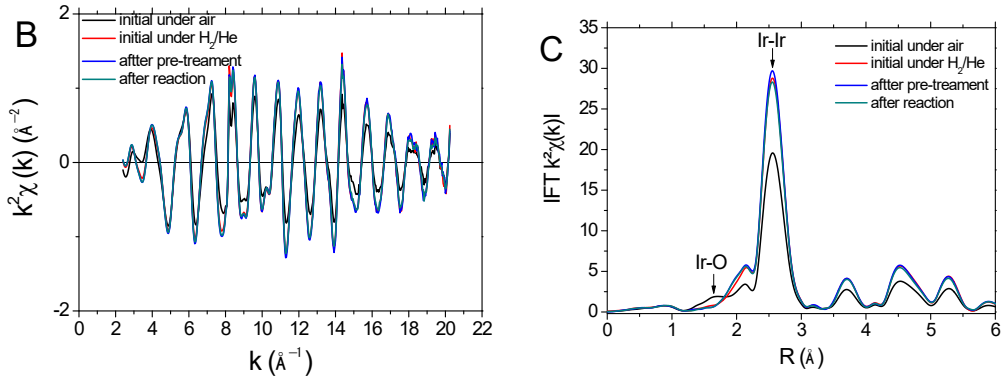


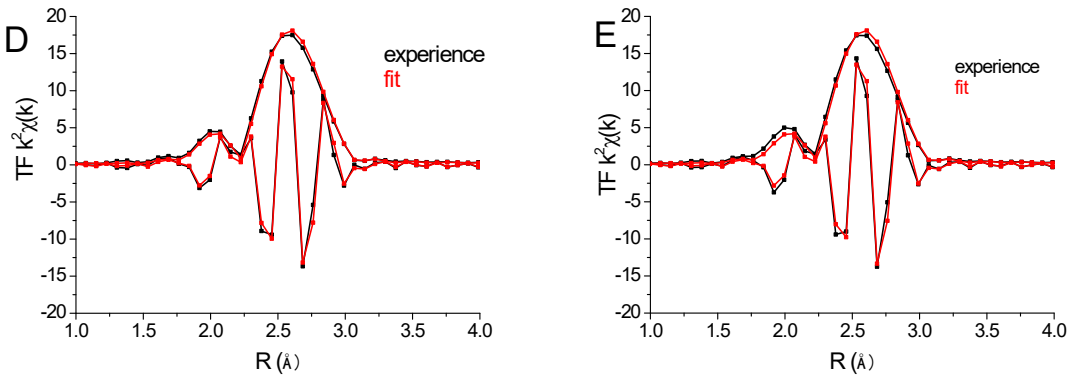
Figure SI4. XANES spectra (A), EXAFS signals (B) and related modulus of the Fourier Transform of the k^2-weighed EXAFS signals (C) of the Ir-NC recorded at room temperature for the following states: initial (under air), initial under flow of H_2/He, after pre-treatment under H_2/He at 250 °C and after reaction at 200 °C. Examples of EXAFS fittings (D and E).



XANES spectra of the Ir-NC recorded at room temperature for the following states: initial (under air), initial under flow of H_2/He, after pre-treatment under H_2/He at 250 °C and after reaction at 200 °C.

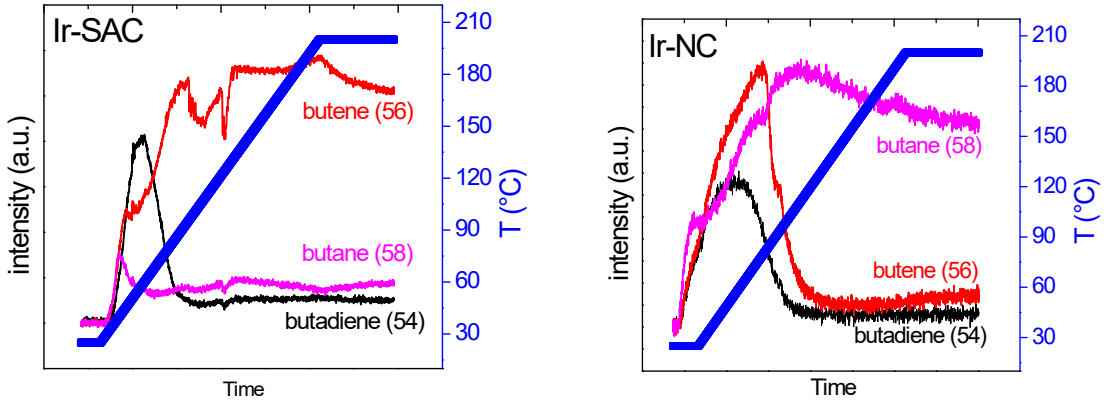


EXAFS spectra and related modulus of the Fourier Transform of the k^2-weighed EXAFS signals recorded at room temperature for the Ir-NC for the following states: initial (under air), initial under flow of H_2/He, after pre-treatment under H_2/He at 250 °C and after reaction at 200 °C.



Examples of EXAFS fitting for Ir-NC initial under flow of H_2/He at room temperature (D) and after reaction at room temperature (E).

Figure SI5. Mass spectrometry monitoring of hydrocarbon reactant and products during the hydrogenation of butadiene on Ir-SAC and Ir-NC.



The gaseous product distributions during reaction of both Ir-SAC and Ir-NC were detected by mass spectroscopy during XAS experiments. The peaks of the fragments from butadiene, butene and butane in MS spectrum range from m/z=15 to m/z=59 and their product pools are very similar. After a careful selection, the pristine m/z=54, m/z=56 and m/z=58 signals were chosen to represent butadiene, butenes and butane during reaction, respectively, although they are not the principal peaks in the mass spectroscopy standard data (https://webbook.nist.gov).

Ir-SAC was highly active and selective to butenes while butane was the principal product for Ir-NC. The result is consistent with laboratory catalytic tests, confirming that *operando* XAS experiments were conducted in the same conditions.

Figure SI6. Ex situ STEM-HAADF images of Ir-SAC as-prepared (A), after treatment under H_2/Ar flow at 250 °C (B) and 400 °C (C).