

Electronic Supplementary Information (ESI)

A selective and stable Fe/TiO₂ catalyst for selective hydrogenation of butadiene in alkene-rich stream

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Chemicals and Methods

1. Catalysts preparation

The Fe/TiO₂ catalyst was prepared using the method of deposition-precipitation with urea (DPU) to reach an iron loading of 2.5wt%. Briefly, after filling a double wall reactor with 300 ml of distilled water degassed with bubbling N₂, an appropriate amount of FeCl₂·4H₂O was added into the reactor to achieve the desired nominal iron loading (2.5 wt% Fe loading). The solution was continuously bubbled with N₂ to prevent the Fe²⁺ oxidation. The reactor was heated to 80 °C by a water heating system and then 3 g of support (TiO₂ P25 Evonik, 80% anatase and 20% rutile, 50 m² g⁻¹) were added. Meanwhile, urea was added to achieve a urea to iron molar ratio of 100. The mixture was kept at 80 °C in the closed reactor for 20 h under continuous stirring. The solid was finally separated from the liquid by centrifugation and subsequently washed with distilled water and centrifuged (three times) and then further dried under vacuum at room temperature (RT) for 24 h (as-prepared sample).

Before characterization or catalytic reaction, the as-prepared sample was calcined under air at 400 °C for 2 h with a heating rate of 5 °C min⁻¹, then reduced under pure H₂ at 400 or 500 °C for 2 h with a heating rate of 3 °C min⁻¹.

2. Instrumentation and measurements

The metal loading was estimated by X-ray fluorescence (XRF) with a spectrometer XEPOS HE (AMETEK). The method used for the XRF analyses is based on calibration curves obtained from standards for each element.

The reduction of the samples was followed by temperature programmed reduction (TPR), which was performed on a Micromeritics Autochem II Automated Catalyst Characterization System under 5% H₂/Ar gas mixture (25 mL min⁻¹). 75 mg of catalyst was

filled into the reactor and the hydrogen consumption was recorded during temperature increase from RT to 900 °C with a heating rate of 10 °C min⁻¹.

XRD analysis was performed under air with a diffractometer (D8 Bruker Company) using the Cu K α radiation (1.5418 Å; 40 kV and 30 mA) with/and a Ni filter. The crystallite sizes were calculated using Scherrer equation ¹, and correction for instrumental broadening was applied. In the diffractograms, the (200) peak of anatase TiO₂ at 2 θ = 48.1° was used as a reference to determine the position of the diffraction peaks of iron-containing compounds as it does not interfere with any of them.

The Scherrer's equation is :

$$\bar{d} = \frac{K \lambda}{\beta \cos\theta}$$

Where d is the average particle size (diameter in nm), λ is the wavelength of the X-ray (0.15406 nm); ; K is a dimensionless shape factor with a value close to 0.89, θ is the Bragg angle in ° and, finally, β is the full width at half the maximum intensity (FWHM) with rad unit (1° = $\pi/180$ rad). Both Bragg angle and FWHM are obtained through XRD patterns using EVA software.

The samples were observed by Transmission Electron Microscopy (TEM) on a JEOL 2100Plus, operating at 200 kV and equipped with a LaB6 gun. To better distinguish metal particles from the support, scanning transmission electron microscopy in high-angle annular dark-field mode (STEM-HAADF) were also performed to study small particles. The image was obtained by a CCD Orius camera Gatan. Energy-dispersive X-ray spectroscopy (EDX) characterization was carried out using Oxford, SDD 80 mm² Xmax with Aztec as software.

XPS analyses were performed using an Omicron Argus X-ray photoelectron spectrometer, equipped with a monochromated AlK α radiation source ($h\nu$ = 1486.6 eV) running with a 280 W electron beam power. The emission of photoelectrons from the sample

was analyzed at a takeoff angle of 45° under ultra-high vacuum conditions ($\leq 10^{-9}$ mBar). Binding energies were calibrated against the Ti2p_{3/2} binding energy at 458.6 eV and element peak intensities were corrected by Scofield factors. The peak areas were determined after subtraction of a Shirley background. The spectra were fitted using Casa XPS v.2.3.15 software (Casa Software Ltd, U.K.) and applying a Gaussian-Lorentzian (70%/30%) functions.

3. Butadiene selective hydrogenation reaction

The reaction of butadiene hydrogenation in an excess of propene was carried out on 250 mg of a mixture containing 50 mg of catalyst (2.5 wt% Fe/TiO₂) and 200 mg of SiC (sieve fraction, 125-200 μm) in a plug flow microreactor (4 mm of internal diameter). The *ex situ* calcined catalysts were reduced *in situ*, under pure H₂ (100 mL min⁻¹) from RT to 400 or 500 °C (3 °C min⁻¹) then held for 2 h at the final temperature. After cooling down to reaction temperature under H₂, the reaction mixture consisting of 0.3% butadiene, 30% propene and 20% hydrogen in He was introduced with a total flow rate of 50 mL min⁻¹, which corresponded to a space velocity of 12 L g⁻¹ h⁻¹ (GHSV = 17,000 h⁻¹). The analysis of the reaction products was performed by gas chromatography (GC Perichrom PR 2100, FID detector), with a GC analysis performed every 15 min. The C₄ carbon balance was above 98% for all the experiments. In addition to the various butenes, butane and propane, traces of methane and ethane among the reaction products were also detected at high conversion level, but not quantified.

The detailed calculations of the conversions and selectivities for the various reactants and products are reported below :

$$\text{Conversion}_{\text{Butadiene}} = \frac{\text{Butadiene}_{in} - \text{Butadiene}_{out}}{\text{Butadiene}_{in}}$$

$$Selectivity_{alkenes} = \frac{\sum Alkenes_{out}}{\sum Alkenes_{out} + \sum Alkanes_{out}}$$

with $\sum Alkenes_{out} = 1 - butene_{out} + cis - 2 - butene_{out} + trans - 2 - butene_{out} + propene_{out}$

and $\sum Alkanes_{out} = butane_{out} + propane_{out}$

$$Selectivity_{C_4} = \frac{C_{4,out}}{Butadiene_{in} - Butadiene_{out}}$$

with $C_{4,out} = 1 - butene_{out}$ or $trans - 2 - butene_{out}$ or $cis - 2 - butene_{out}$ or $butane_{out}$

Figures

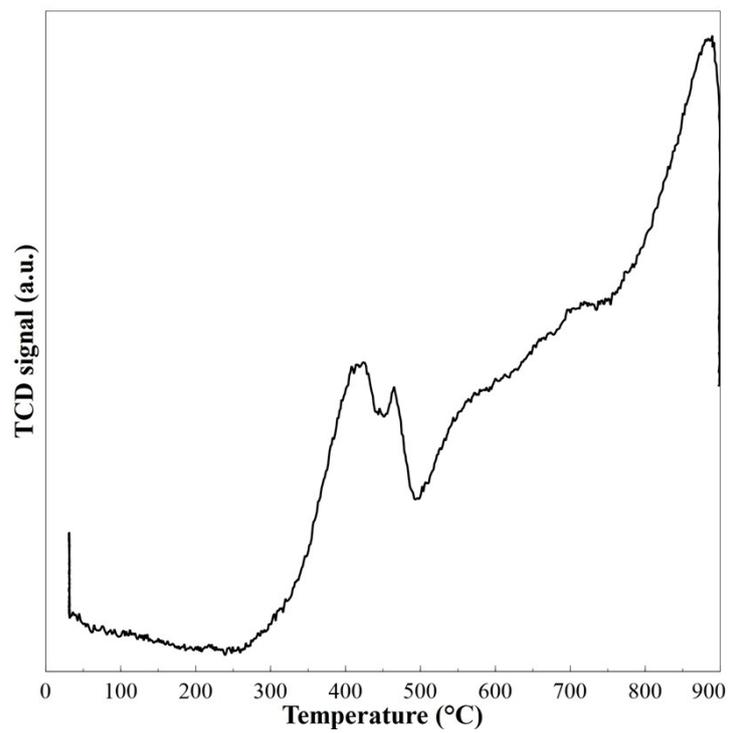


Fig. S1 TPR of the Fe (2.5 wt%)/TiO₂ catalyst pre-calcined at 400°C (heating rate = 10 °C min⁻¹)

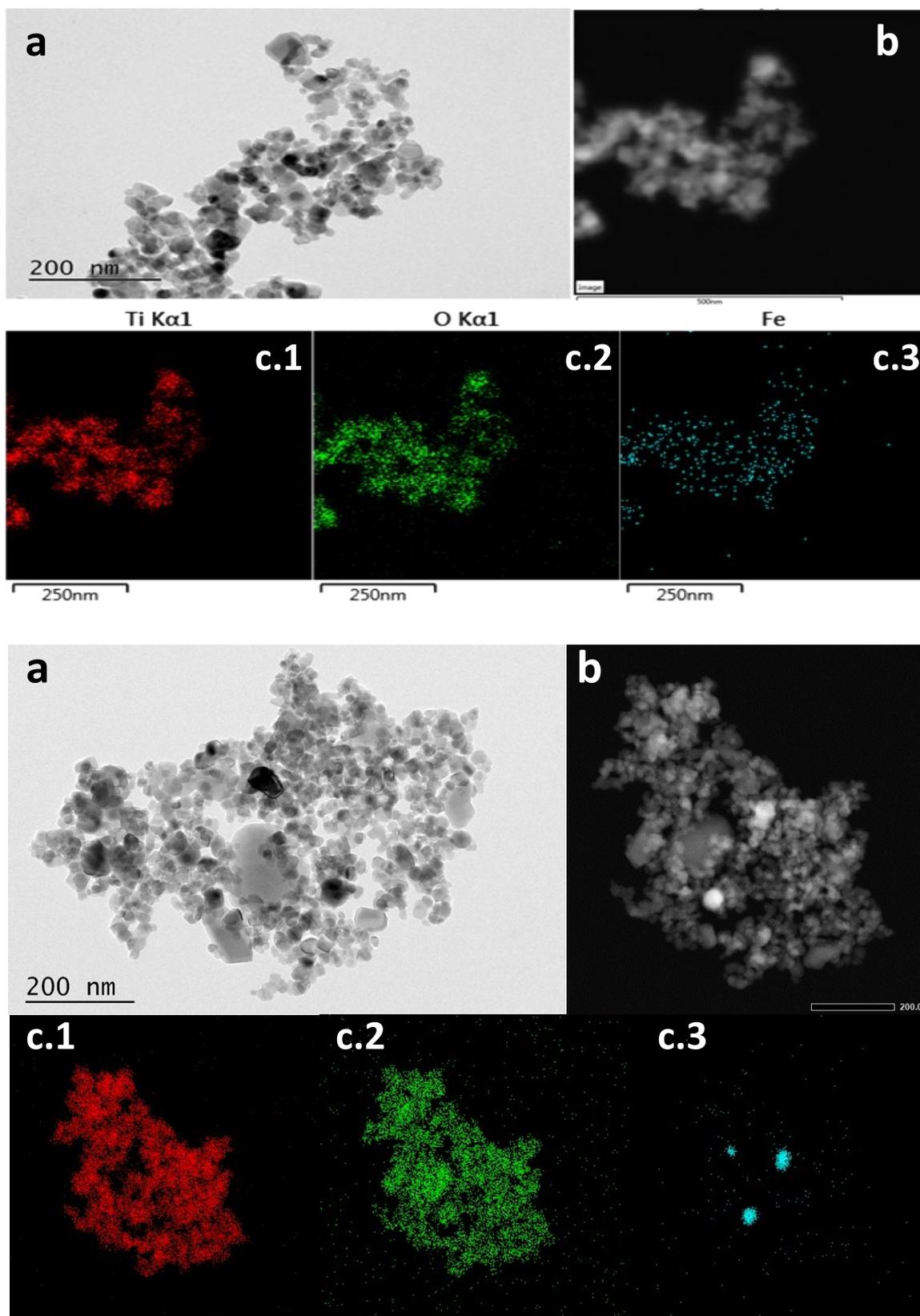


Fig. S2 Fe/TiO₂ reduced at 400 °C (top) and 500 °C (bottom) : a) TEM bright field image b) STEM-HAADF image and c) Elemental mapping of c.1) Ti, c.2) O, c.3) Fe. (A tilt of the image is observed between the bright and dark field modes)

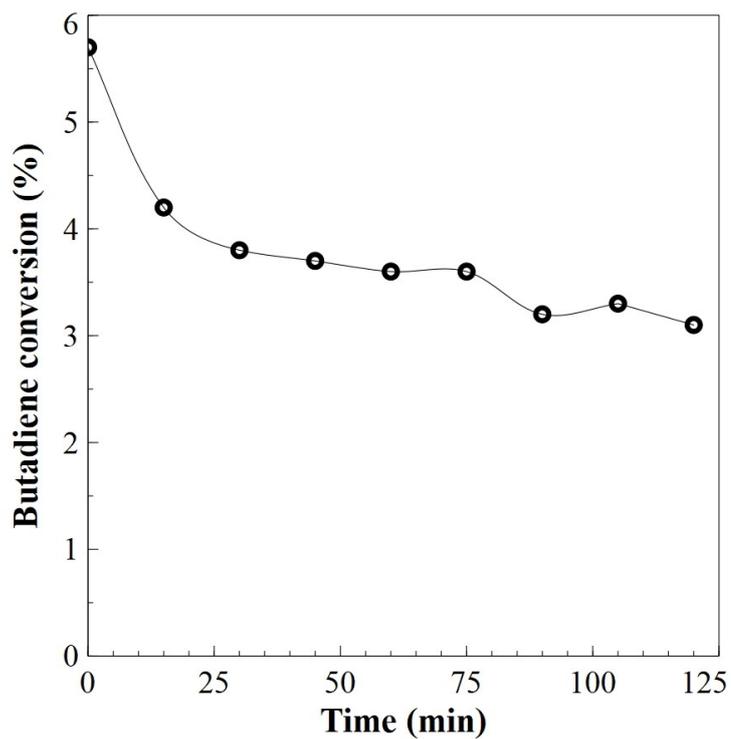


Fig. S3 Evolution of butadiene conversion with time on stream at 200 °C after *in situ* treatment at 400 °C under N₂ for Fe(2.5wt%)/TiO₂ *ex situ* pre-calcined at 400 °C

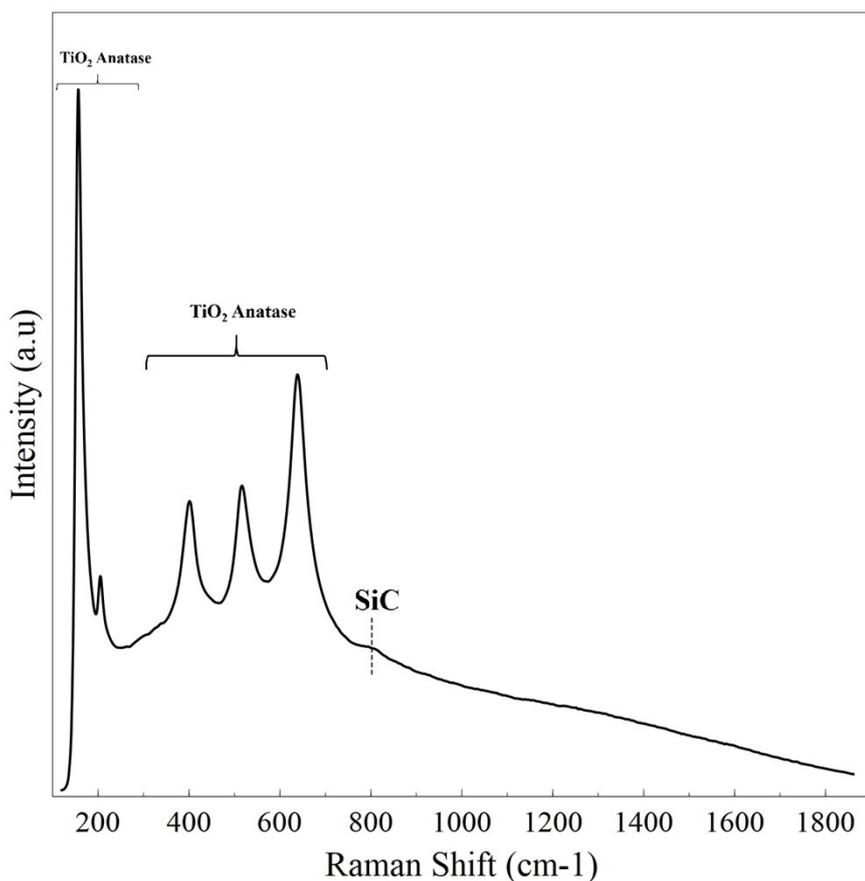


Fig. S4 Raman spectrum of the Fe (2.5 wt%)/TiO₂ catalyst (reduced at 400 °C) after butadiene selective hydrogenation at 50 °C.

The rather fast deactivation observed at 50 °C is not due to a poisoning by carbonaceous deposition since the Raman spectrum does not show the presence of deposited coke species, usually characterized by D and G bands at 1340 cm⁻¹ and 1604 cm⁻¹ respectively, on the surface of the catalyst after reaction^{2,3}.

The observed peaks/bands at 144 cm⁻¹, 195 cm⁻¹, 395 cm⁻¹, 515 cm⁻¹, and 638 cm⁻¹ belong to the Raman active vibrations of TiO₂ with symmetries of Eg(1), Eg(2), B1g(1), B1g(2), and Eg(3), respectively⁴.

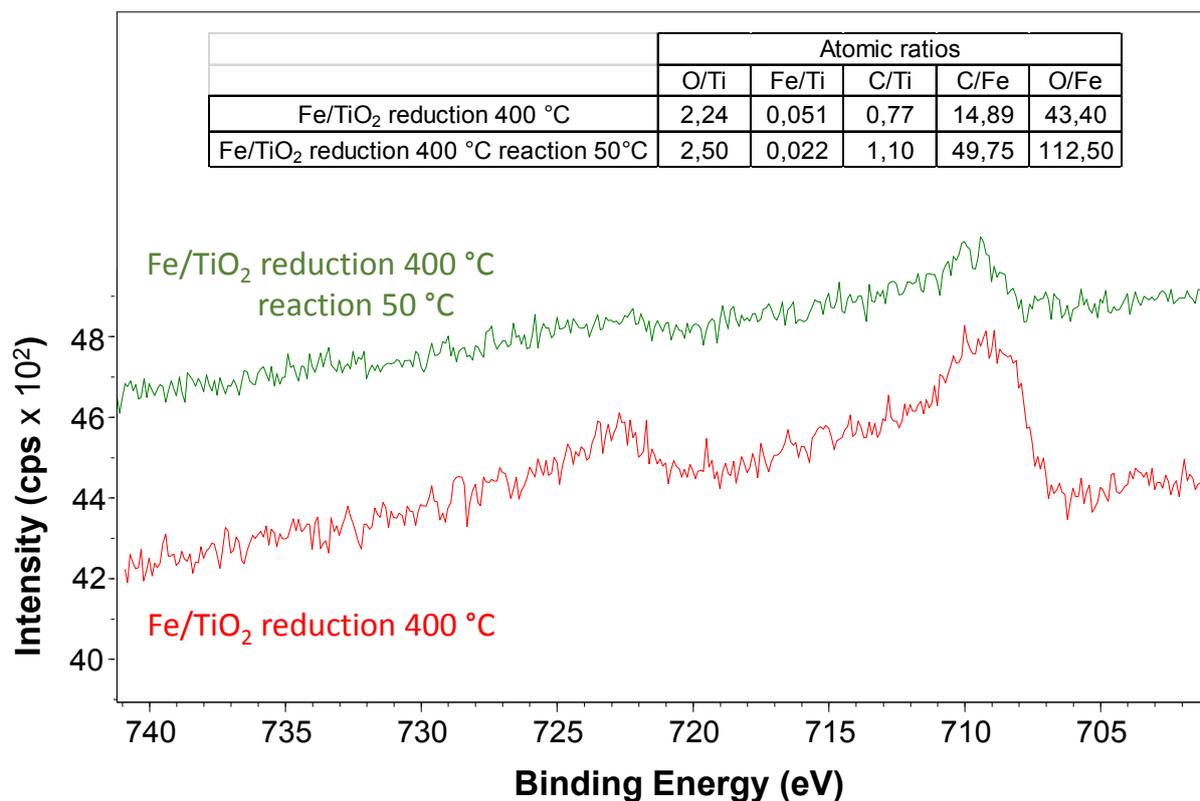


Fig. S5 X-ray photoelectron spectroscopy of the Fe2p region of Fe/TiO₂ catalyst after reduction at 400 °C and after butadiene hydrogenation reaction at 50 °C. The surface atomic ratios in inserted table were calculated using the integration of peaks for iron, titanium, carbon and oxygen.

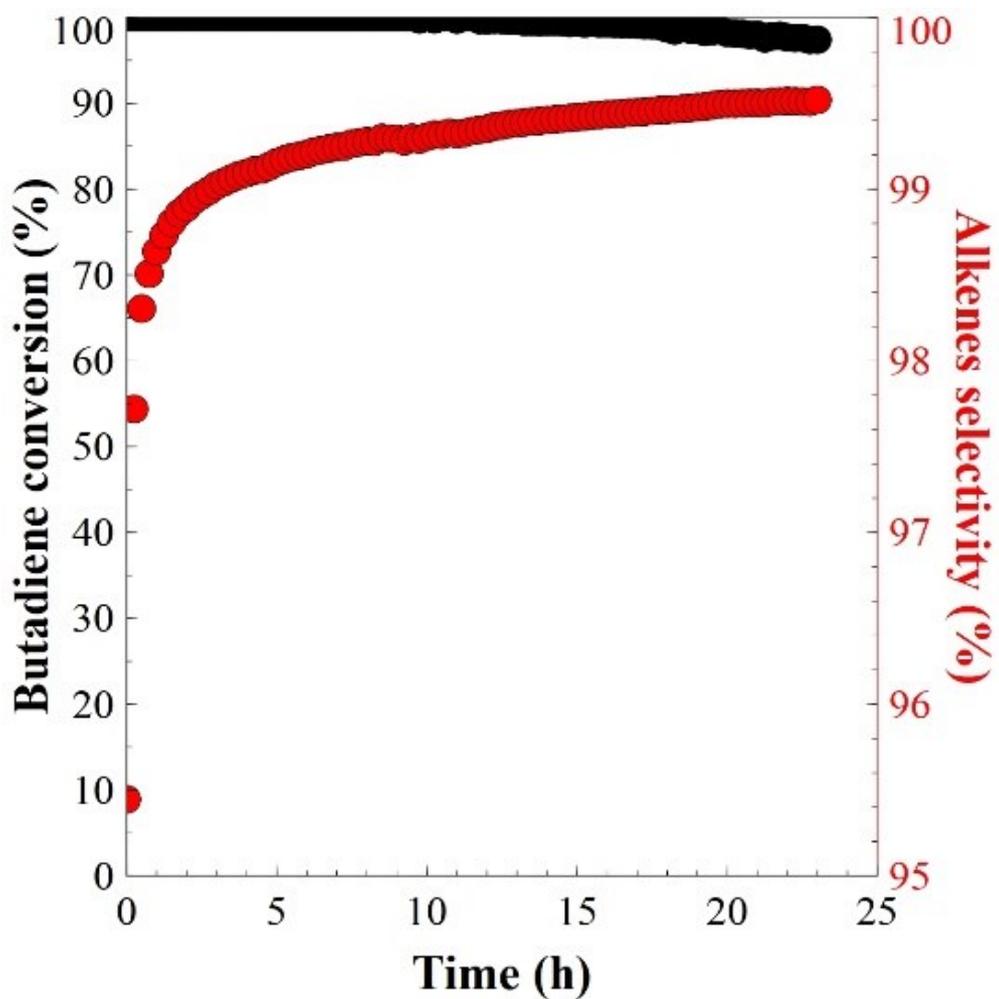


Fig. S6 Evolution of butadiene conversion and alkenes selectivity with time on stream at 200 °C over Fe(2.5wt%)/TiO₂ reduced at 400 °C under H₂

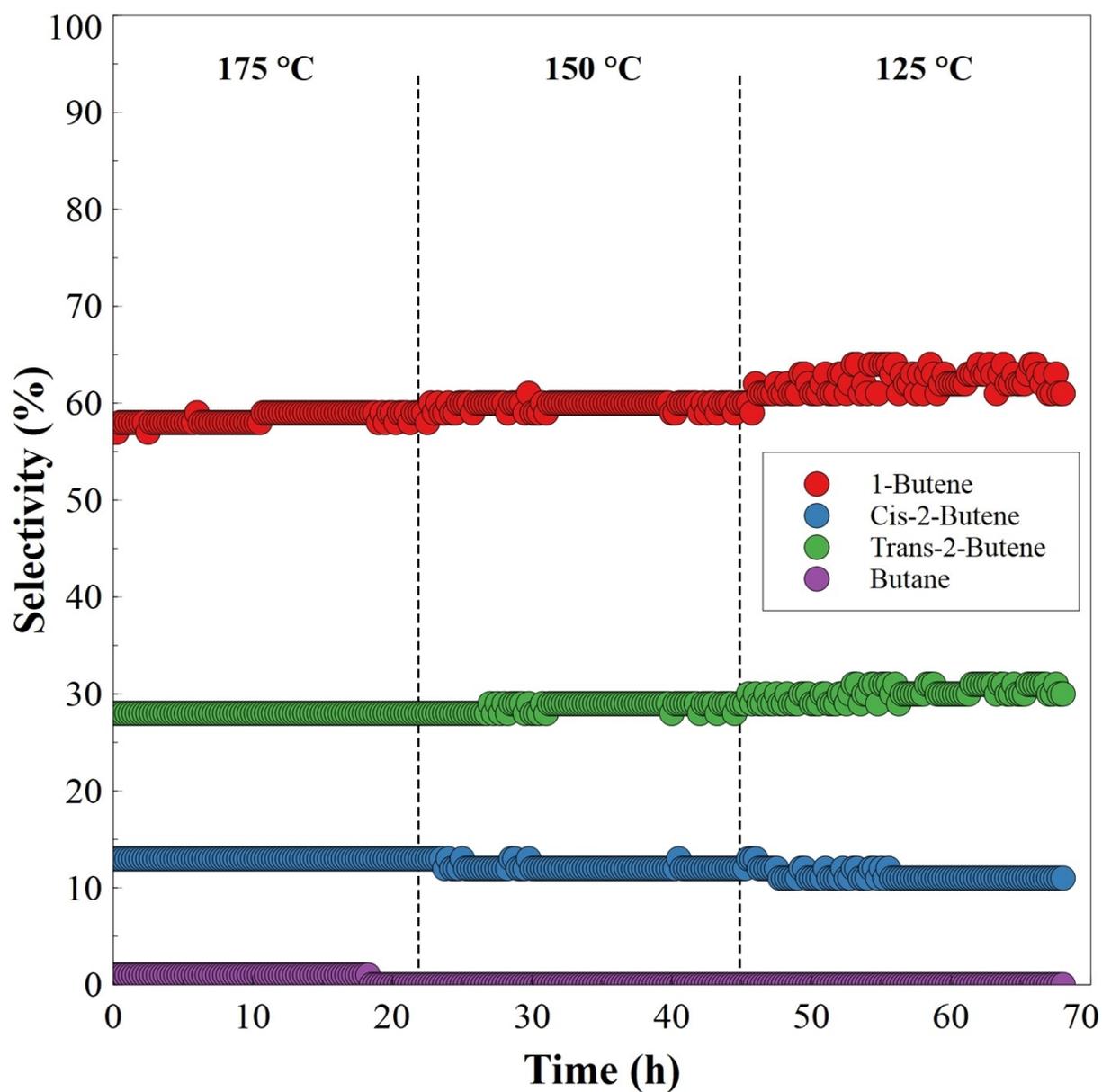


Fig. S7 Evolution of the selectivity to C₄ products with time on stream at 175, 150 and 125 °C for Fe(2.5wt%)/TiO₂ reduced at 400 °C (complement of Figure 5).

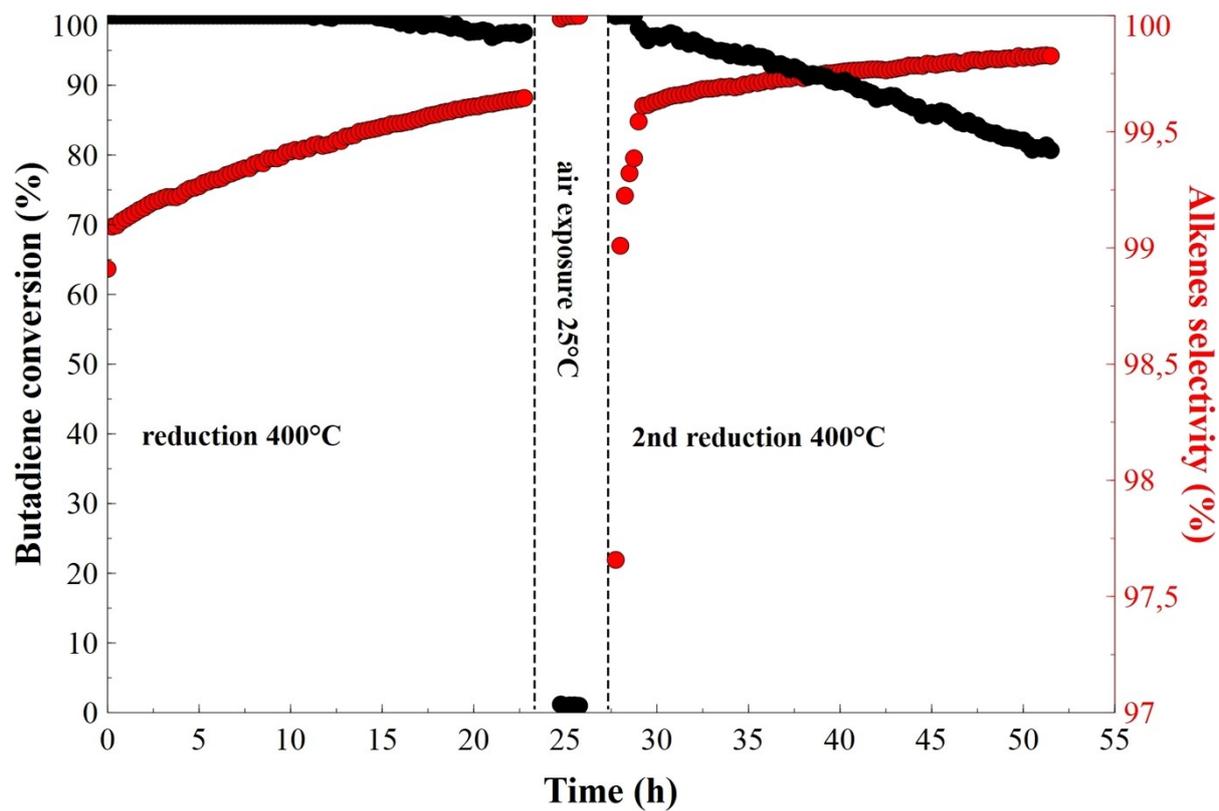


Fig. S8 Evolution of butadiene conversion and selectivity to alkenes with time on stream at 200 °C over Fe(2.5wt%)/TiO₂ after reduction at 400 °C, then after air exposure at RT and finally after second reduction at 400 °C.

References

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