

Catalytic selective oxidation of *isobutane* in a decoupled redox-process

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1 Experimental setup of the periodic reactor

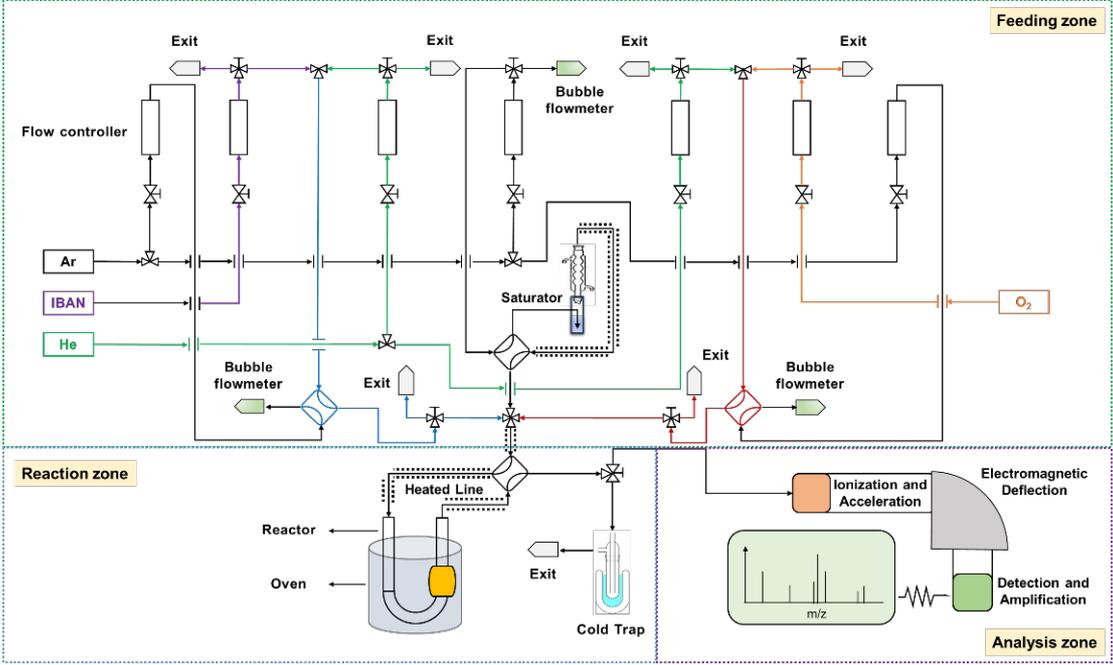


Fig. S1. Schematic diagram for the lab scale periodic feed setup

2 Catalytic evaluation in isobutane oxidation reaction in periodic conditions

Table S1.

Catalytic performance of 40CsV₁ samples with different cycling times and the quantities of O₂ and IBAN consumed in IBAN oxidation.

Cycling time	Molar ratio O ₂ /IBAN	Injected amount per cycle		Converted amounts per cycle		Conversion ^a , %	
		IBAN, μmol	O ₂ , μmol	IBAN, μmol	O ₂ , μmol	IBAN	O ₂
2R-3O	2.14	572.6	1226.9	33.0	49.1	5.8	4.0
2R-2O	1.43	572.6	817.9	32.8	47.5	5.7	5.8
2R-1O	0.71	572.6	409.0	27.0	36.0	4.7	8.8
2R-0.5O	0.36	572.6	204.5	24.3	31.2	4.3	15.3
2R-0.2O	0.14	572.6	81.8	18.1	25.1	3.2	30.8

^a Reaction conditions: Atmospheric pressure, Contact time: 3 s; Reaction temperature: 340 °C;

3 Hydrodynamic behavior of the TZFBR

To study the hydrodynamic behavior of the TZFBR, the support CARiACT Q-10 SiO₂ mixed with the 40CsV₁ catalyst (80 g of SiO₂ support and 20 g of catalyst) was used. The fluidized-bed total height was 14 cm (measured in a glass fluidization column with identical diameter). Hence, the regeneration zone and reaction zone heights were chosen to be equal with a value of 7 cm ($V_{reaction} / V_{regeneration} = 1$). A system of U tube manometers was installed to measure the pressure drop ΔP of the catalytic bed. The minimum fluidization velocity (U_{mf}) was determined by measuring the pressure drop through the catalytic bed (ΔP) as a function of the gas velocity (U), as shown in **Fig. S2**. As can be seen from these figures, the minimum fluidization velocity occurs at the intersection of the pressurized and constant pressure lines, which is the transition point from the fixed-bed to the fluidized-bed. Here, the minimum fluidization velocity (U_{mf}) was found at 5.0×10^{-3} m/s at reaction temperature of 340 °C (U_{mf} does not change during the reaction). From the results of this measurement, it was decided to employ a velocity during the catalytic tests of 1.0×10^{-2} m/s, which is twice the minimum experimental fluidization velocity ($U/U_{mf}=2$), so as to ensure the optimal fluidization and avoid the back-mixing of gas when the flow velocity is too high ($U \geq 2.6 U_{mf}$) [1].

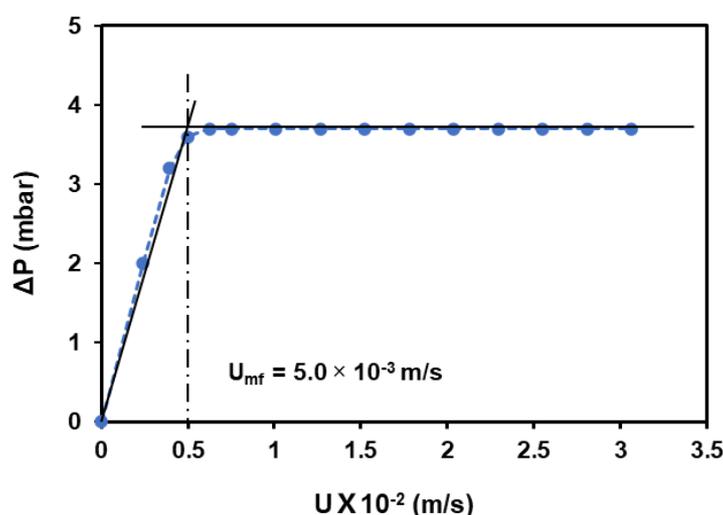


Fig. S2. Pressure drop as function of the gas velocity (measured in decreasing order) for the diluted catalyst at reaction temperature of 340 °C.

According to the pressure drop, it is possible to evaluate the quantity of solid participating to the fluidization in a fluidized bed, calculated by the relation between the theoretical and experimental drop pressure [2]:

$$\alpha = \frac{\Delta P_{experimental}}{(m \cdot g / A)}$$

The value α is referred as “fluidization quality”, ΔP is the pressure drop measured experimentally, m is the mass of diluted catalyst (100 g), g is standard gravity (9.81 m/s²), and A is the surface area of the catalyst bed (cross section of 1.96×10^{-3} m²). According to the above equation, the fluidization quality during the experiment was calculated to 75 %. In a lab-scale fluidized-bed, this fluidization quality (the effect of the column walls) is suitable for catalytic reactions in TZFBR.

4 Evaluation of the mechanical stability of the catalyst employed in TZFBR

4.1 Microstructure of the catalysts

Fig. S3 shows the typical optical microscope images of diluted catalyst 40CsV₁ spheres before and after fluidization. In (B) and (C), the pale white spheres are SiO₂ and the yellow-green spheres are catalysts. As shown in the figures, part of the catalyst turned blue after fluidization by N₂ and after reaction, which indicates that some of the active phase on the SiO₂ surface is reduced during these processes.

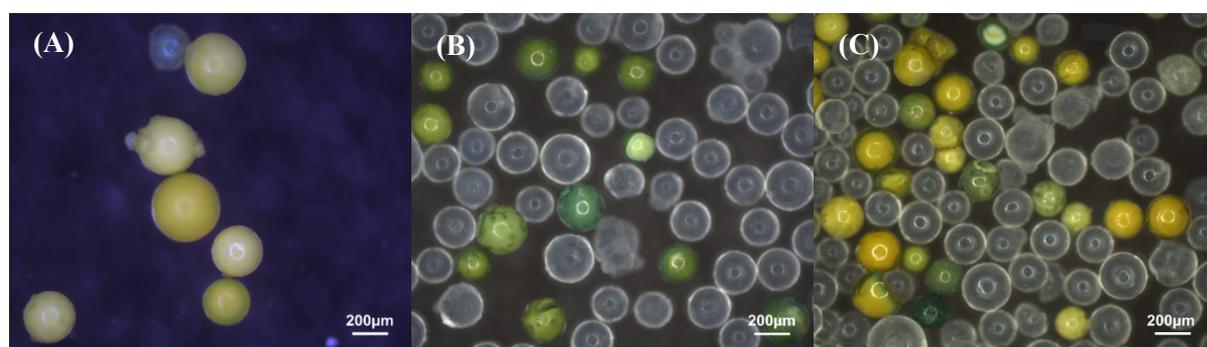


Fig. S3. Typical optical microscope images of 40CsV₁/SiO₂ spheres: (A) fresh, (B) fluidized, (C) spent.

4.2 Crystal phases and structural features analysis by XRD and Raman

Fig. S4 shows the XRD patterns of the diluted catalysts (20 wt.% 40CsV₁ and 80 wt.% SiO₂) before and after the fluidization by N₂ and after reaction. The patterns exhibit diffraction peaks at $2\theta = 26.2^\circ$ and 30.4° assigned to the lattice planes of (222) and (400) belonging to the Keggin-type CsV₁ [3], showing that the catalysts did not decompose into metal oxides during these processes, underlining the good stability of the catalyst under the fluidized reaction conditions.

IR-Raman spectroscopy was used to verify the presence of HPA active phase in fresh, N₂-fluidized and spent catalysts. As shown in **Fig. S5**, the typical Raman spectra bands of Cs₂H₂PMo₁₁VO₄₀ at 983 cm⁻¹, 871 cm⁻¹, 600 cm⁻¹, 255 and 235 cm⁻¹, which can be ascribed to the vibrations of the *vs* Mo=O_d bond, *vas* Mo-O_b-Mo, *vas* Mo-O_c-Mo, δ (Mo-O-Mo), respectively, are still present [4,5]. These results confirm that the catalyst has good mechanical

stability, and the friction of catalyst particles during the fluidization did not lead to abrasion of the active phase from the surface of the catalyst.

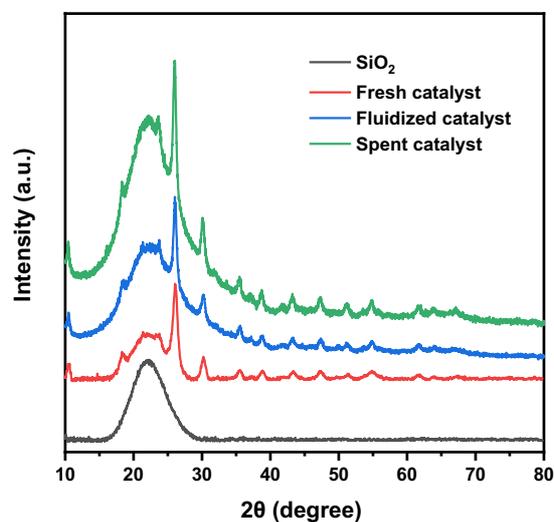


Fig. S4. XRD patterns of fresh, fluidized and spent catalysts.

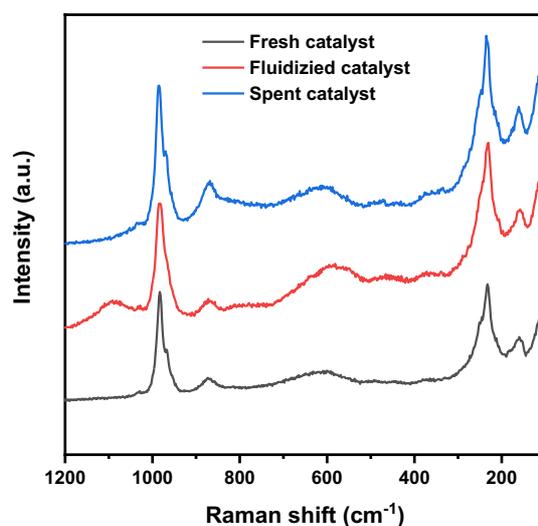


Fig. S5. Raman spectra of fresh, fluidized and spent catalysts.

4.3 Size distribution of the catalysts

The comparison of the particle diameter of the catalysts before and after 24 h of fluidization and after 15 days of reaction. **Fig. S6** indicates that no decrease in particle diameter was observed after a long reaction time and therefore no significant abrasion phenomenon occurred.

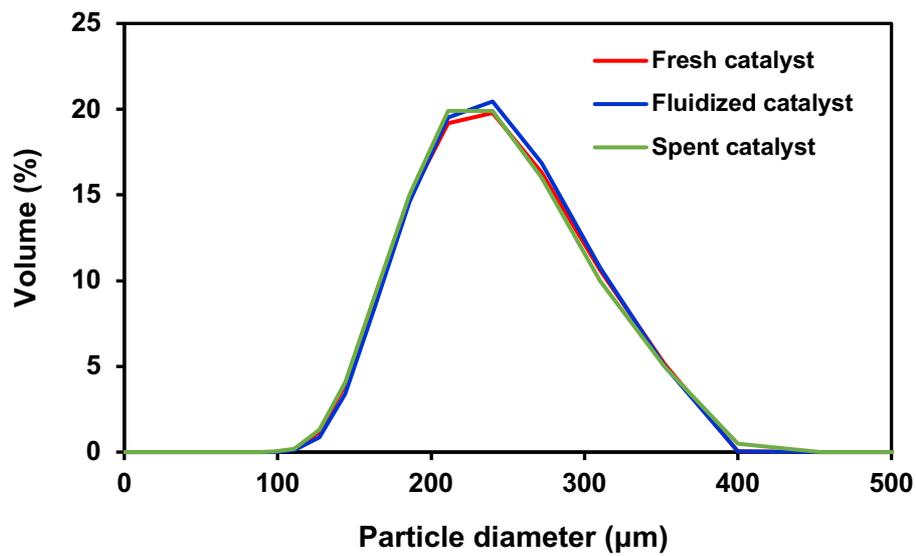


Fig. S6. Size distribution of fresh, fluidized and spent catalysts.

5 Structures of the DFT calculations

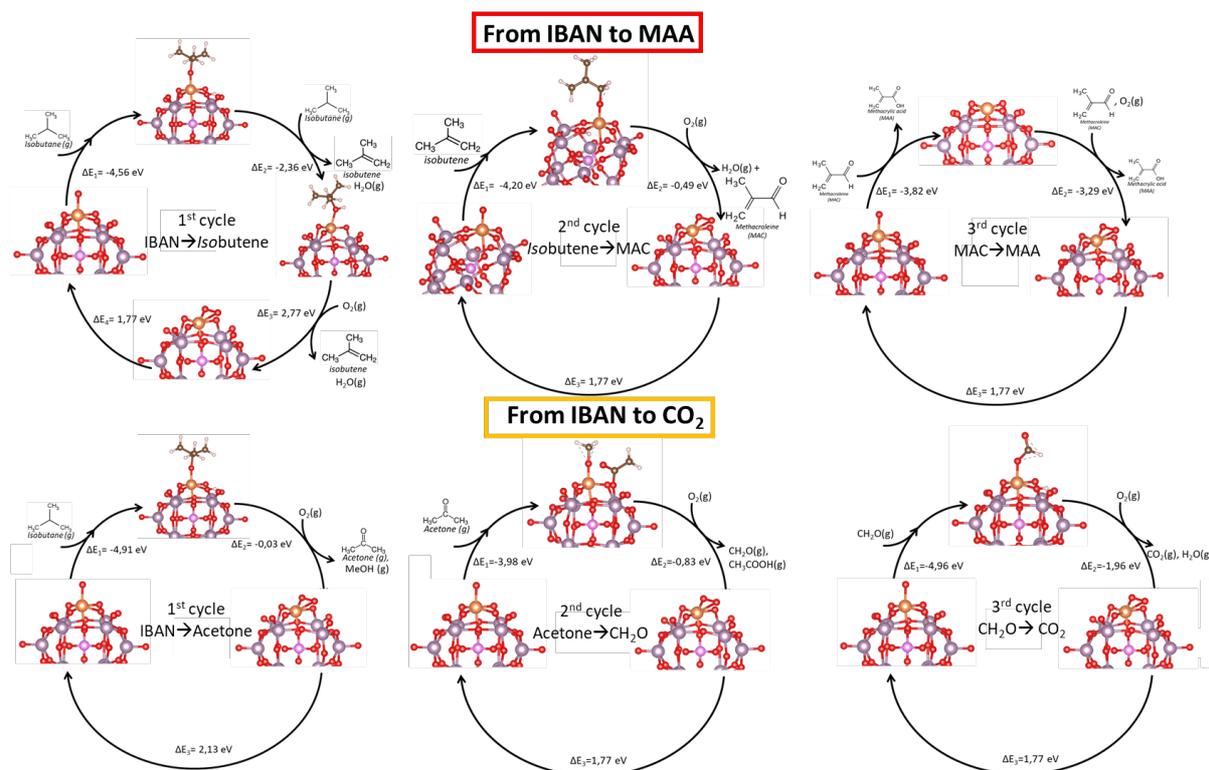


Fig. S7. Ball & stick model structures for the main catalytic cycles implied in IBAN conversion into MAA (top panel), and CO₂ formation from IBAN (bottom panel). Colors: red, O; pinkish, H; brown, C; greyish: Mo; orange, V; pink: P.

References

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