Supplementary Information

Meerwein-Ponndorf-Verley reduction of α,β-unsaturated aldehydes over metal-doped mesoporous zirconia catalysts: Correlation of surface properties and performance

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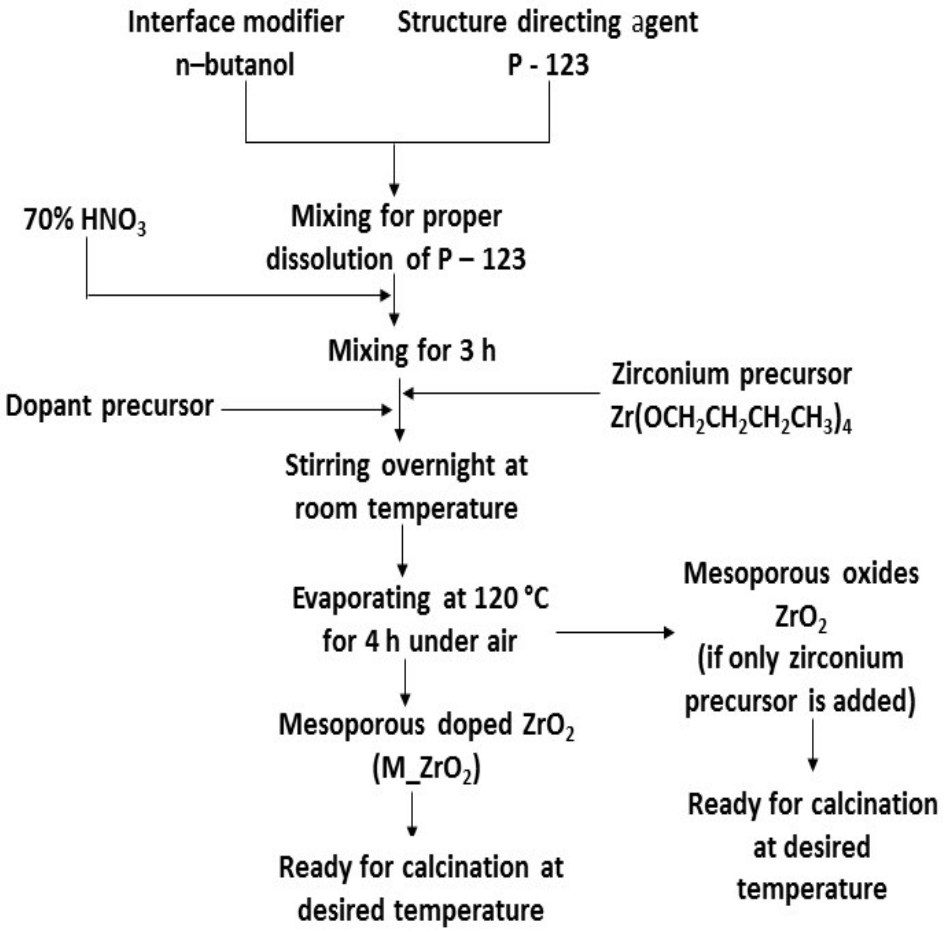
1. Experimental

1.1 Synthesis of mesoporous zirconium oxides

The flow diagram in Scheme S1 was followed for the synthesis of the mesoporous zirconium oxides. For the metal-doped zirconia samples, an appropriate ratio w/w% of the metal precursor is added to the solution containing the zirconium precursor.



Scheme S1: Steps involved in the synthesis of the mesoporous zirconium oxides.

1.2 Structural characterization of the mesoporous metal-doped zirconia

Debye-Scherrer equation:

$$\gamma = \frac{k\lambda}{\beta \cos\theta} \qquad \text{Equation S1}$$

where γ is the particle size (nm), k = 0.89 (dimensionless shape factor), λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) and θ is the angle derived from 2θ values corresponding to maximum intensity peak in the XRD diffractogram.

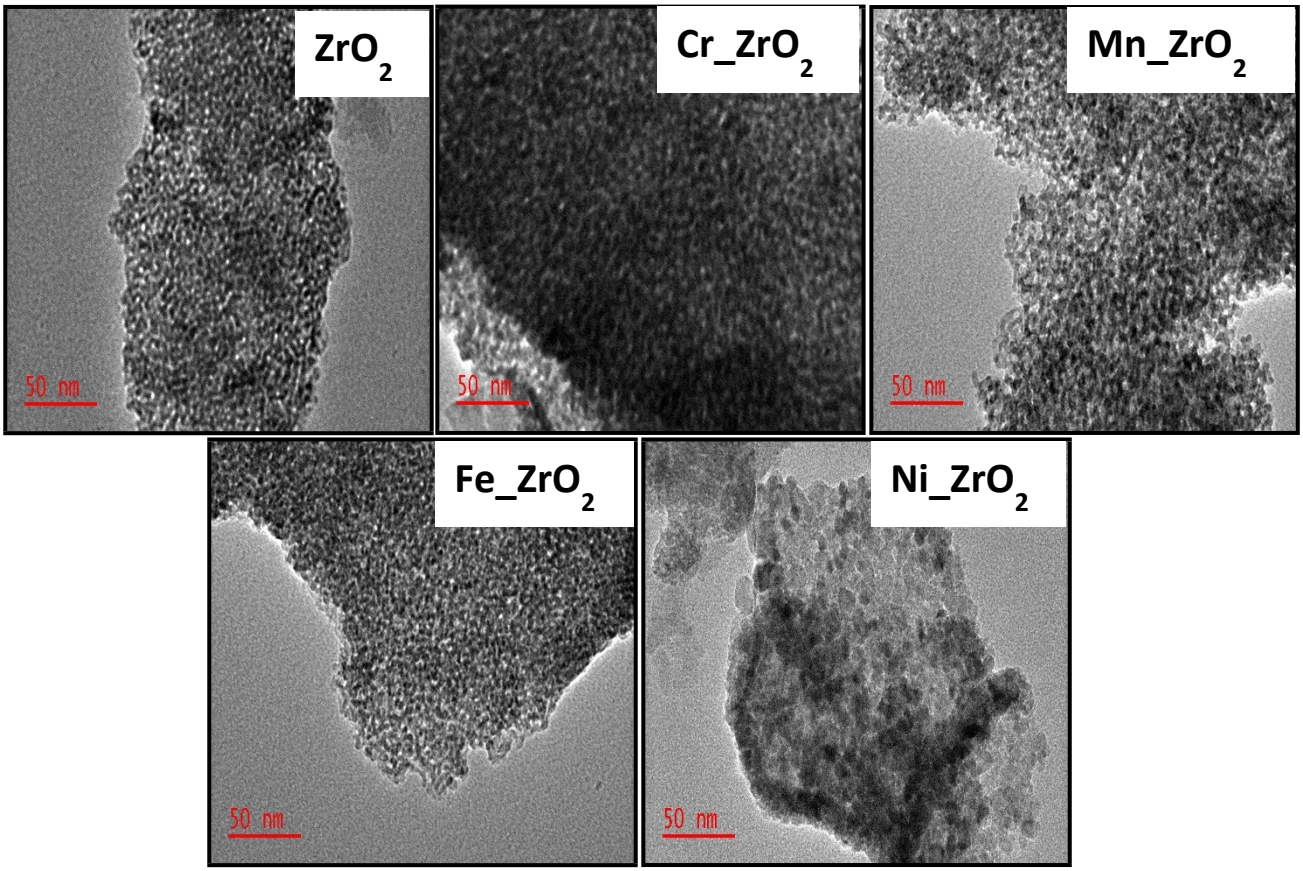


Fig. S1. TEM images of the as-synthesized mesoporous catalysts.

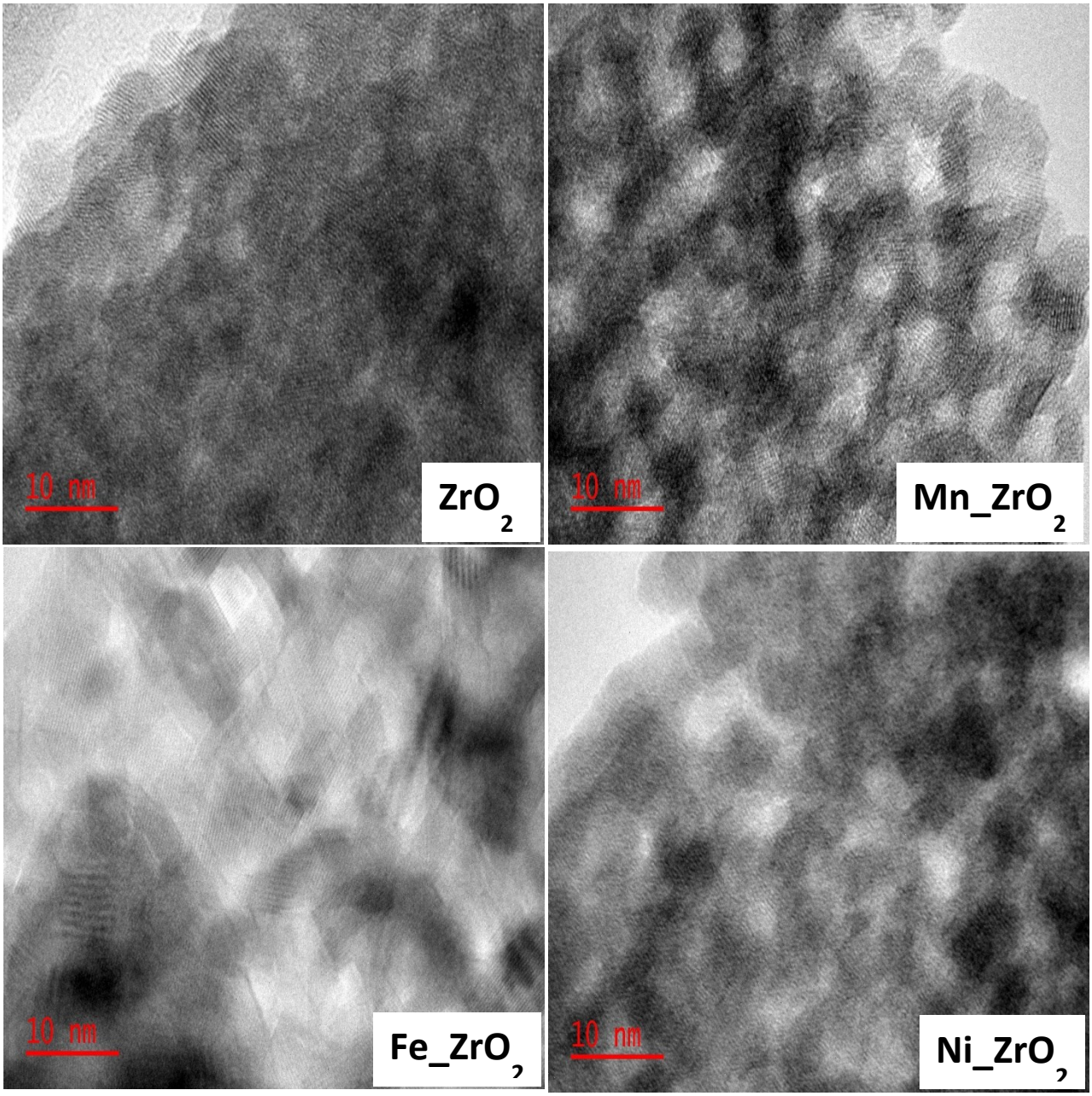


Fig. S2. HRTEM images of the as-synthesized mesoporous catalysts

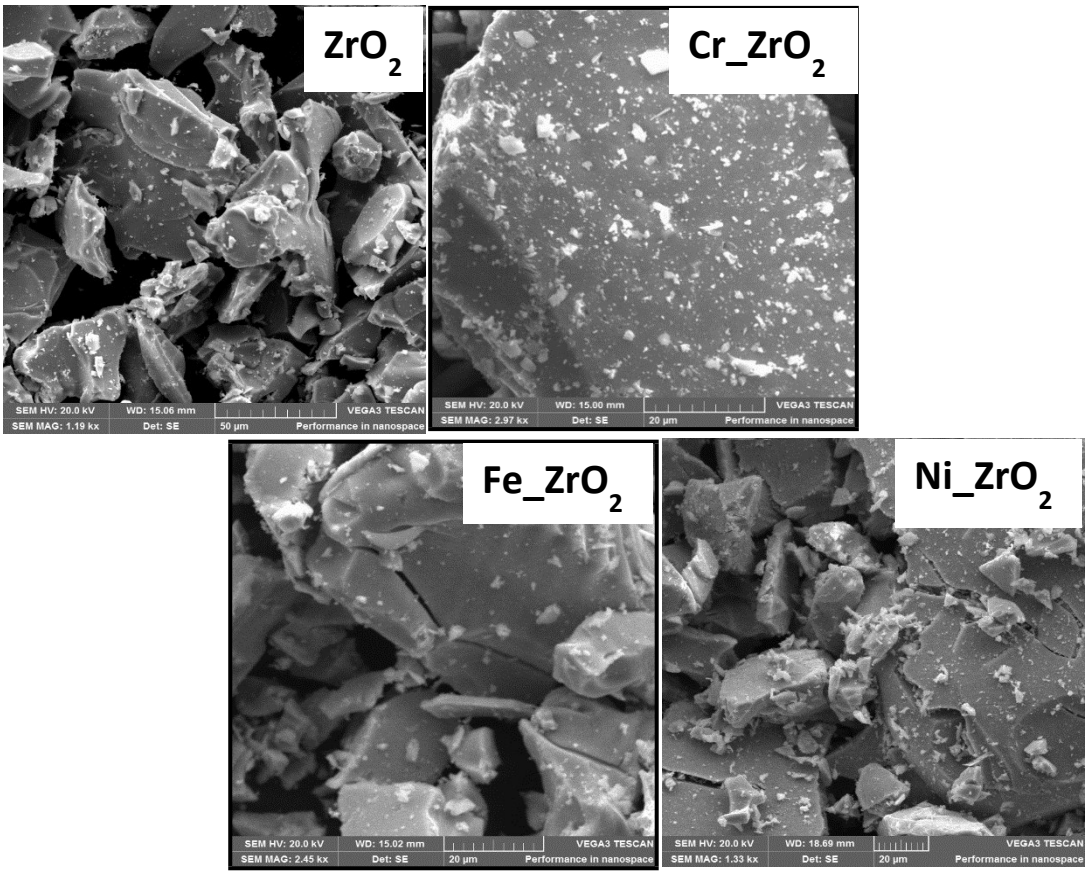


Fig. S3. SEM images of the as-synthesized mesoporous catalysts.

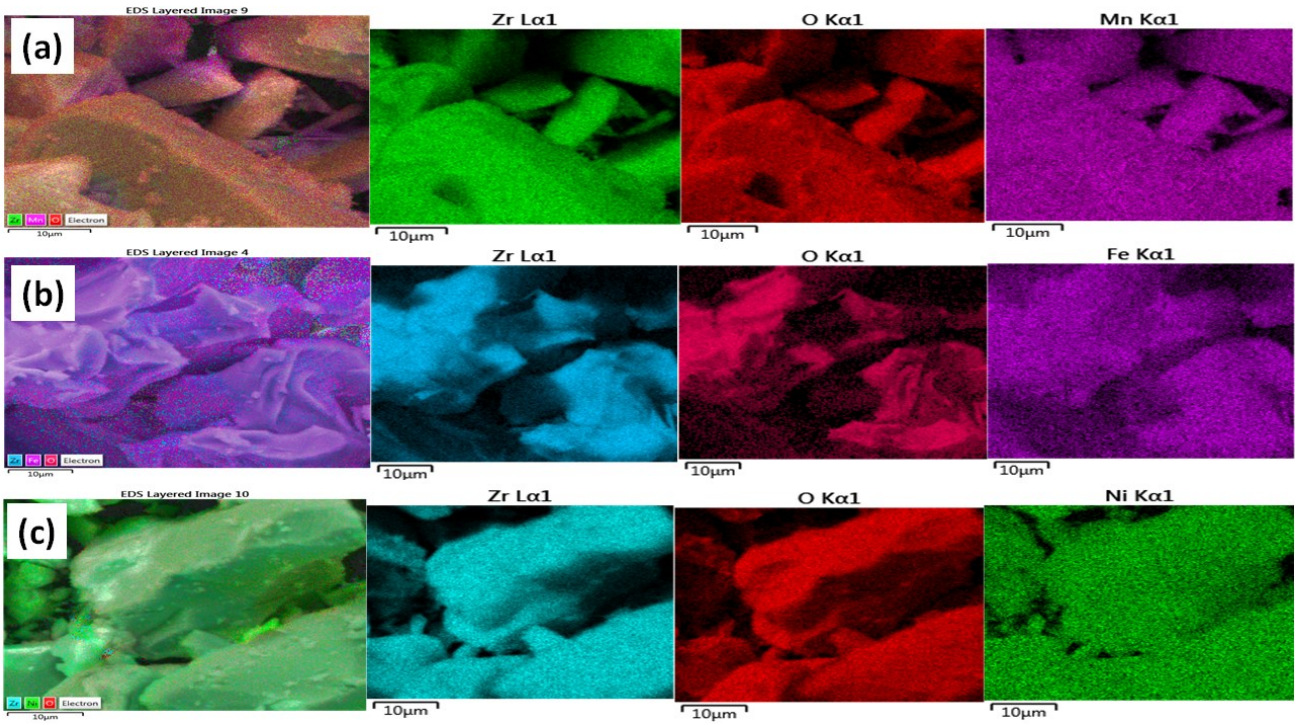


Fig. S4 (a-c) EDX mapping of the mesoporous M_ZrO_2 catalysts showing the metal distribution.

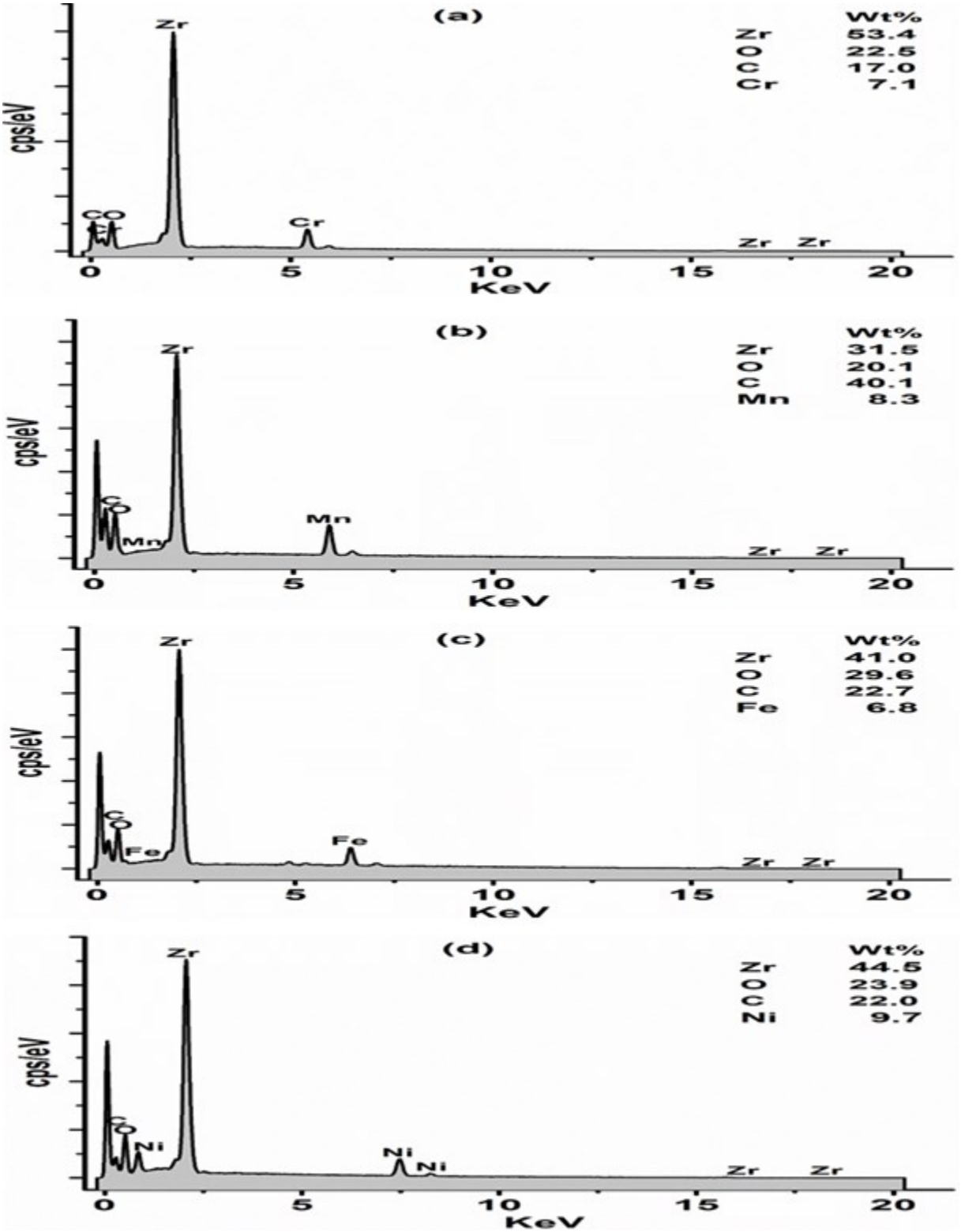


Fig. S5 (a-d) SEM-EDX images of the mesoporous M_ZrO_2 catalysts showing the respective metal content.

1.3 Catalytic activity of mesoporous zirconia in MPV reduction of carbonyl compounds

1.3.1 Preliminary tests

Based on the data obtained in Fig. S4, the thermal treatment of 350 °C was chosen as the optimized calcination temperature for the preparation M_ZrO_2 catalysts. To avoid random selection of an aldehyde for optimizing the reaction conditions, a quick probe of all the pure zirconia prepared with various calcination temperature in the MPV reduction of cinnamaldehyde, citral and benzaldehyde were performed under the starting reaction conditions as reported in the literature [1–3]. As shown in Fig. S4, cinnamaldehyde and citral gave products over all the catalysts variation with the latter having higher conversion while a product was only formed in the conversion of benzaldehyde over ZrO_2 calcined at 350 °C. Hence, citral was the chosen substrate for the model reaction ZrO_2 catalysts.

The basis for the choice of citral is illustrated in Fig. S4. The MPV process variables such as the agitation rate, required catalyst amount, concentration of substrate, reaction temperature and time were studied over pure ZrO_2. The optimal reaction conditions were adopted in the comparative study of the catalytic activity of the synthesized M_ ZrO_2. It was observed that the experiment performed without catalyst did not proceed even after 24 h. The reactivity of the reduction process under different reaction conditions was monitored by calculating their observed rate constant k_{obs} using Kinetic studio version 2.08 software. The k_{obs} is the slope derivative of the graph Y = -A * exp(-R * X) + C. The substrate conversion, product selectivity and normalized activity of the catalysts were also calculated.

$$\text{Conversion (\%)} = \frac{(Substrate_{in} - Substrate_{out}) \times 100}{Substrate_{in}} \quad \text{Equation S2}$$

$$\text{Selectivity (\%)} = \frac{Product_a}{Product_a + Product_b} \times 100 \quad \text{Equation S3}$$

$$\text{Activity}_{\text{normalized}} = \frac{mol\ converted\ (mmol)}{BET_{SA}\left(m^2 g^{-1}\right)\ or\ catalyst\ amount\ (g)} \quad \text{Equation S4}$$

$$\text{Mol converted (mmol)} = \frac{Conversion\ (\%) \times Substrate_{in}}{100} \quad \text{Equation S5}$$

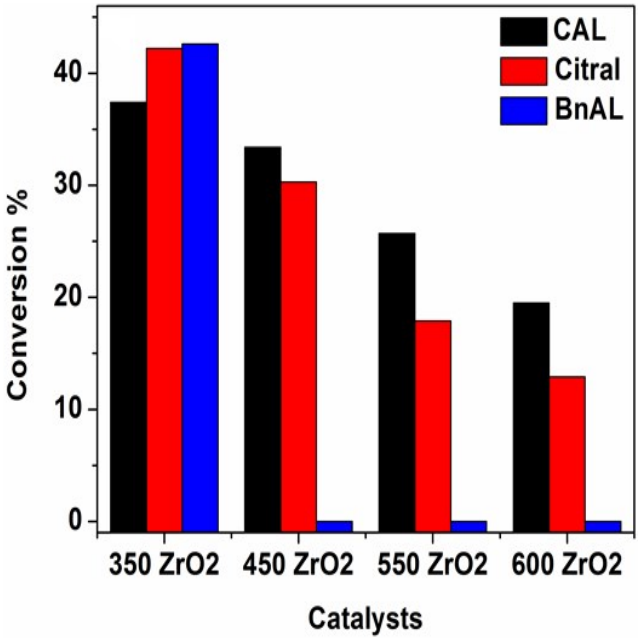


Fig. S6. Indicating the preliminary probe of the catalysts as well as substrates (CAL = cinnamaldehyde, BnAl = benzaldehyde).

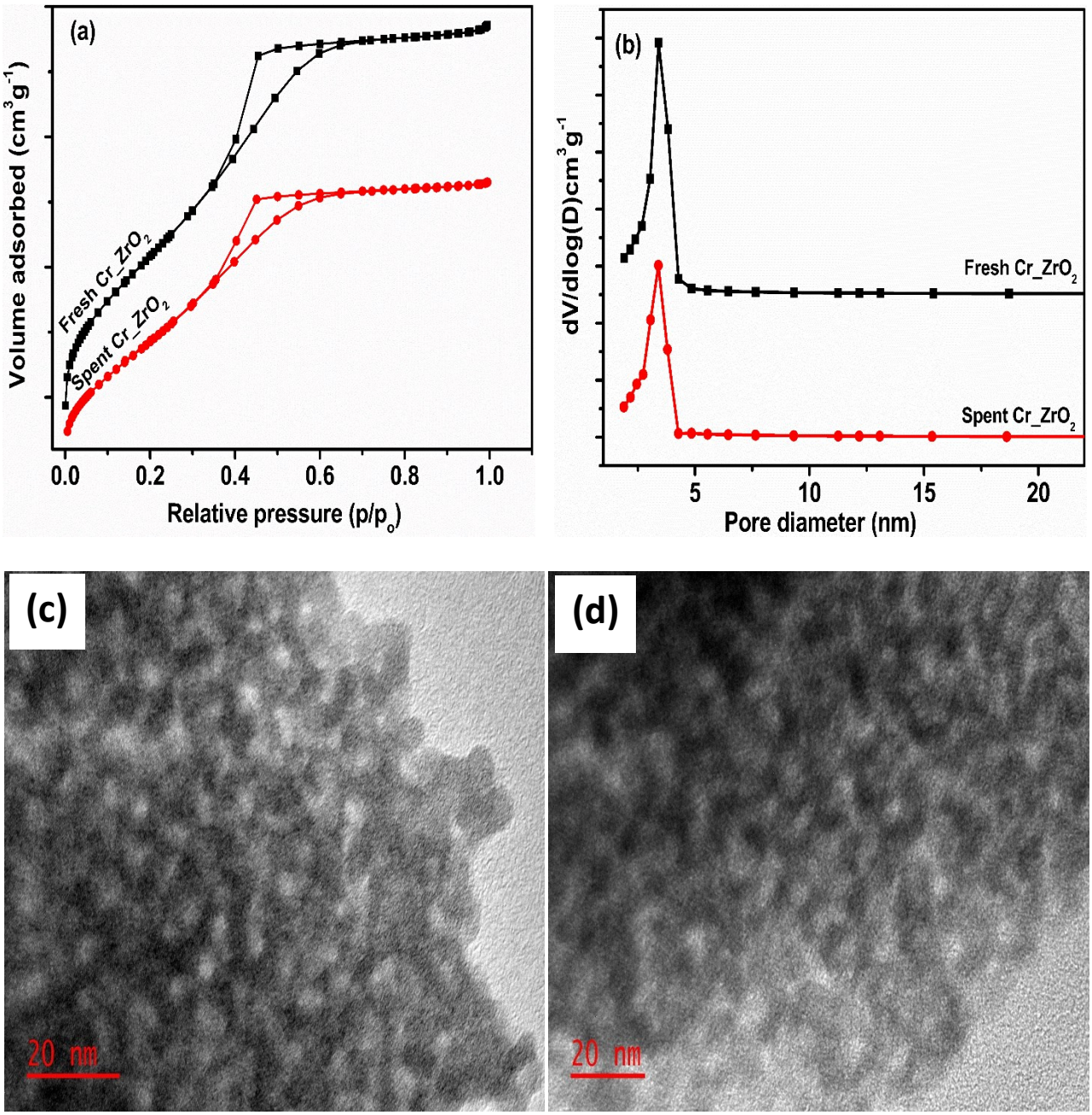


Figure S7. N_2 adsorption-desorption isotherms (a), pore size distribution (b); TEM images of fresh (c) and spent (d) of Cr_ZrO_2 catalysts.

1.3.2 GC details for both FID and MS except otherwise stated

Column: Restek RTX-5; length 30.0 m, inner diameter 0.25 mm ID, film thickness 0.25 µm

Injector temperature: 200 °C

Column oven temperature program

Rate	Temperature (°C)	Hold time (min)

0	0	40.0	2.00
1	20.00	280.0	5.00
2	0.00	0.0	0.00

Total program time: 19 min

Carrier gas: nitrogen, 25.0 ml/min

Flow control mode: linear velocity

Injection mode: split

Split ratio: 20:1

Purge flow: 3.0 ml/min

FID temperature: 350 °C

MS ion source temperature: 200 °C

MS interface temperature: 250 °C.

1.3.4 GC chromatograms of reactivity of Cr_ZrO_2 in the MPV reduction of citral under optimum reaction conditions

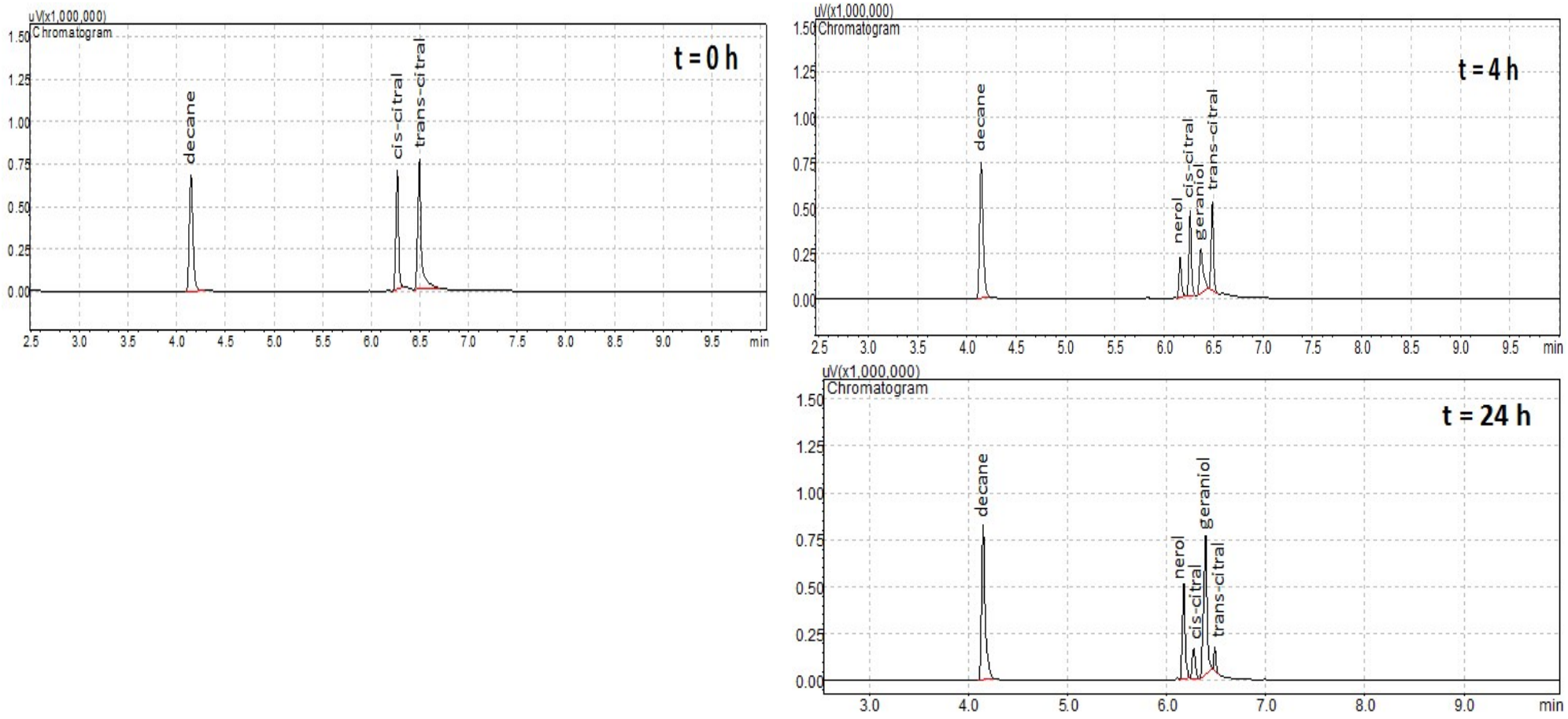


Fig. S8. GC-FID chromatogram under optimum reaction conditions at t = 0, 4, 8 and 24 h. The conversion of citral increased with reaction time.

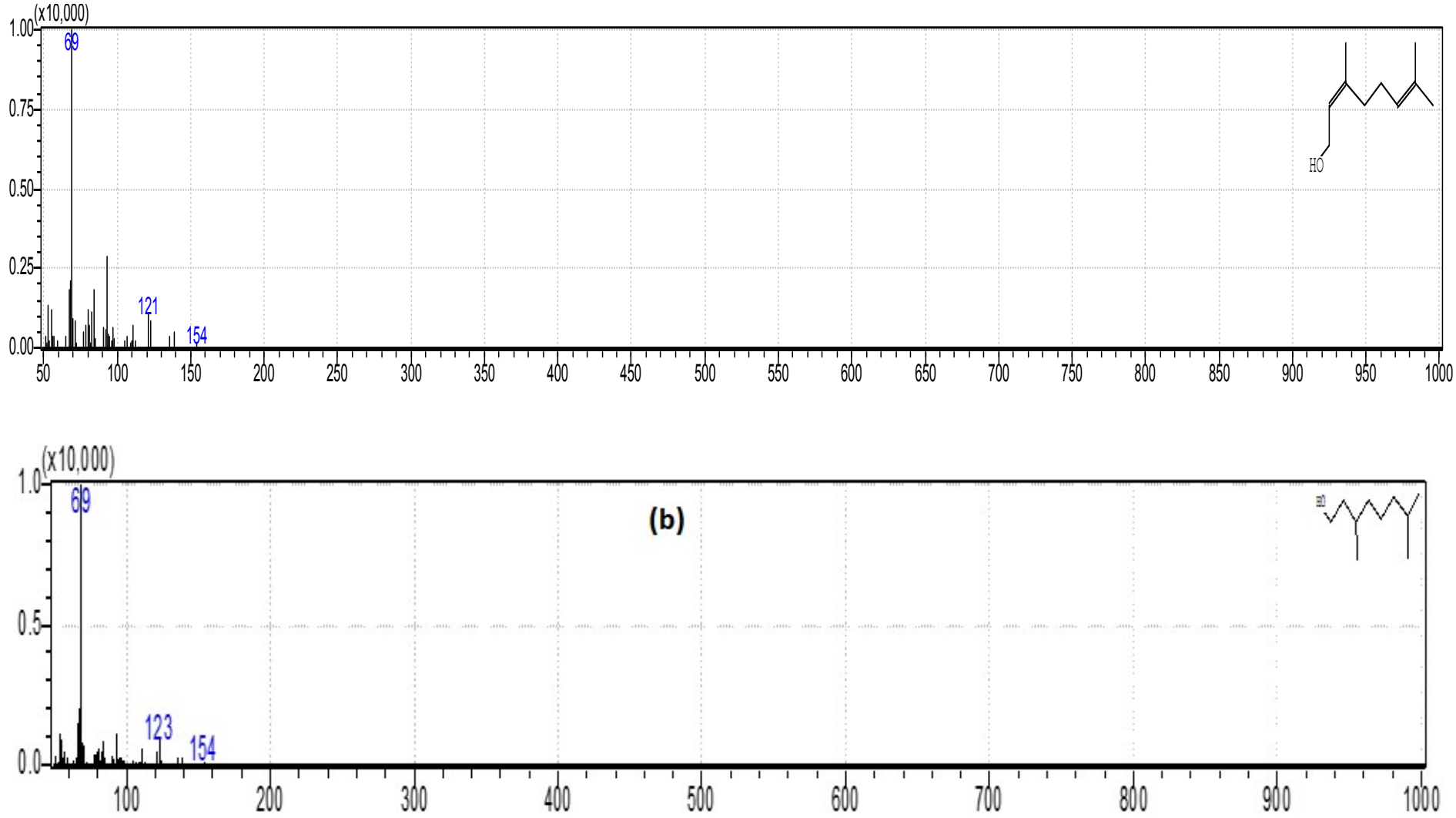


Fig. S9. GC-MS chromatogram confirming the products (a) nerol and (b) geraniol.

References

(1) Urbano, F. J.; Aramendía, M. A.; Marinas, A.; Marinas, J. M. An Insight into the Meerwein–Ponndorf–Verley Reduction of α, β-Unsaturated Carbonyl Compounds: Tuning the Acid–Base Properties of Modified Zirconia Catalysts. *J. Catal.* **2009**, *268* (1), 79–88.

(2) Zhang, B.; Minhui, T.; Jian, Y.; Lei, W. U. Support Effect in Meerwein-Ponndorf-Verley Reduction of Benzaldehyde over Supported Zirconia Catalysts. *Chinese J. Catal.* **2012**, *33* (4–6), 914–922.

(3) Wang, F.; Ta, N.; Shen, W. MgO Nanosheets, Nanodisks, and Nanofibers for the Meerwein–Ponndorf–Verley Reaction. *Appl. Catal. A Gen.* **2014**, *475*, 76–81.