Supplementary Material (ESI) for RSC Advances

Catalytic ketonization of palmitic acid over a series of transition metal oxides supported on zirconia oxide-based catalysts

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1. Reactor set up for ketonization reaction

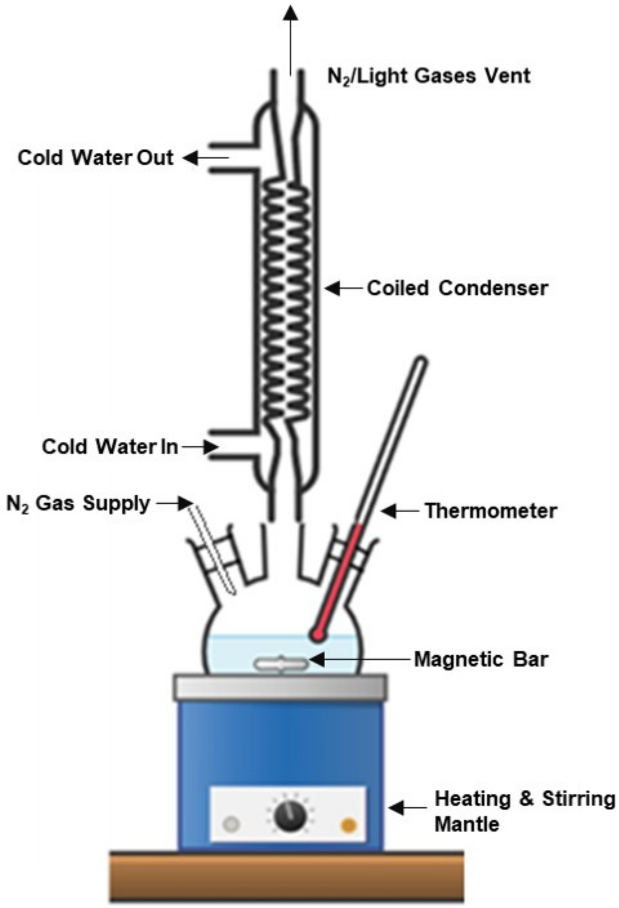

Fig. 1S Reactor set-up for ketonization reaction.

2. TEM Result of fresh MnO_2/ZrO_2

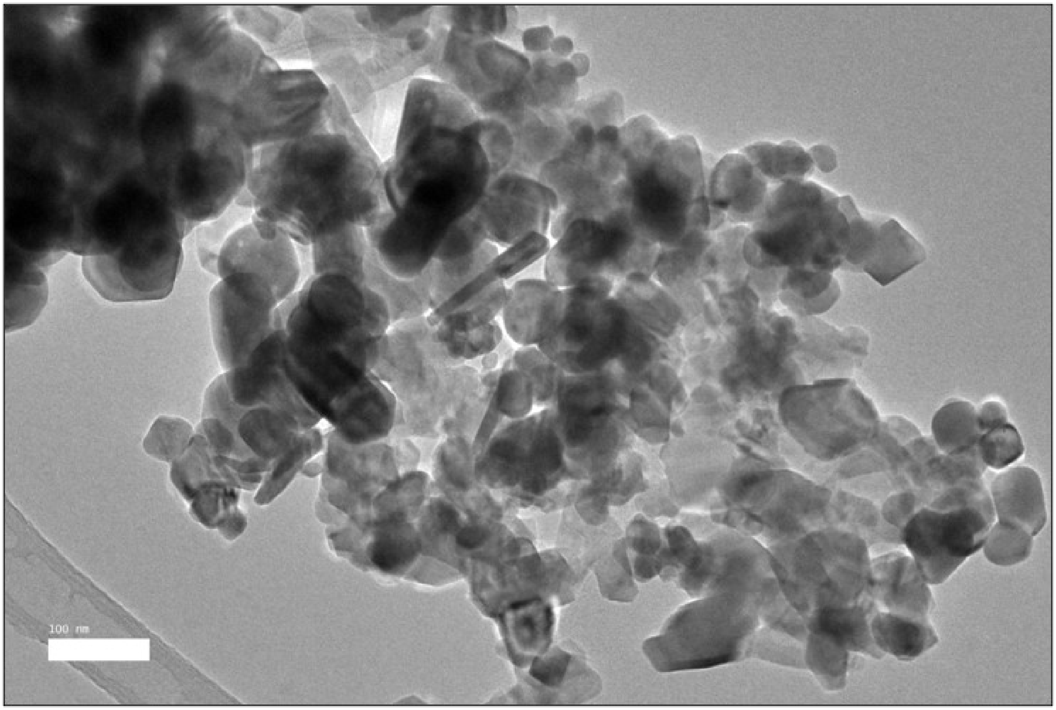

Fig. 2S TEM image of MnO_2/ZrO_2 catalyst

3. XPS Spectra of MnO_2/ZrO_2 catalyst (A) Wide Scan (B) Zr 3d (C) Mn 2p (D) O 1s

In this study, XPS was used to analyse the surface properties of MnO_2/ZrO_2 catalyst and the XPS results are shown in **Fig. 3S**. The XPS results shows the wide scan survey of the catalyst, showing the peaks for Zr, O, Mn and C as the reference peak at 285eV.[1] For Zr, is well known that the Zr 3d spectrum is a doublet Zr $3d_{5/2}$–Zr $3d_{3/2}$. From **Fig. 3S**, the deconvoluted Zr spectra shows ZrO_2 3d spin-orbit doublet peaks at ~182eV and ~184eV that respectively corresponds to the ZrO_2 $3d_{5/2}$ and ZrO_2 $3d_{3/2}$, and this agrees very well in the literature.[1] the integral intensities of both peaks is roughly 3:2 in ratio and the spin energy gap between the peak is ~2.2 eV, which closely corroborates the findings from previous studies.[2,3] Further analysis of the spectra shows a few other peaks which are from the doublet peaks of Zr metal at ~179eV and ~181eV corresponding to the Zr $3d_{5/2}$–Zr $3d_{3/2}$.[4]

For Mn (**Fig. 3S (C)**), it can be seen by the deconvolution of Mn 2p photoelectron spectrum that the high-resolution Mn2p spectrum of the Mn doped ZrO_2 catalyst consists of two main peaks of the spin–orbit couplet. The low binding energy peak at and the high binding energy peak (641.1 eV and 652.2 eV) corresponds to photoelectron states MnO_2 $2p_{3/2}$ states and MnO_2 $2p_{1/2}$ [5,6]. These values match well with the literature values from previous literature as well as NIST Handbook and it is exciting to note that spin energy gap is 11.1 similar to findings by Castillo et al. (2020).[2] The manganese 2p peak was deconvoluted into two other components in small amounts which are components as Mn3+ corresponding to Mn_2O_3 and Mn at binding energies of ~643eV and ~638.8 eV [7,8].

Scrutinizing the O 1s spectra complements the finding from Zr 3d and Mn 2p spectra. The deconvolution of O 1s spectrum resulted in the observation of Zr-O bond at binding energy of ~ 529.4eV and Mn-O bond at binding energy of ~529.8 corresponding to ZrO_2 and MnO_2 respectively. [6,9] From these findings, it can be concluded that MnO_2 is the largest constituent of the Mn species on the catalyst surface as tested by XPS.

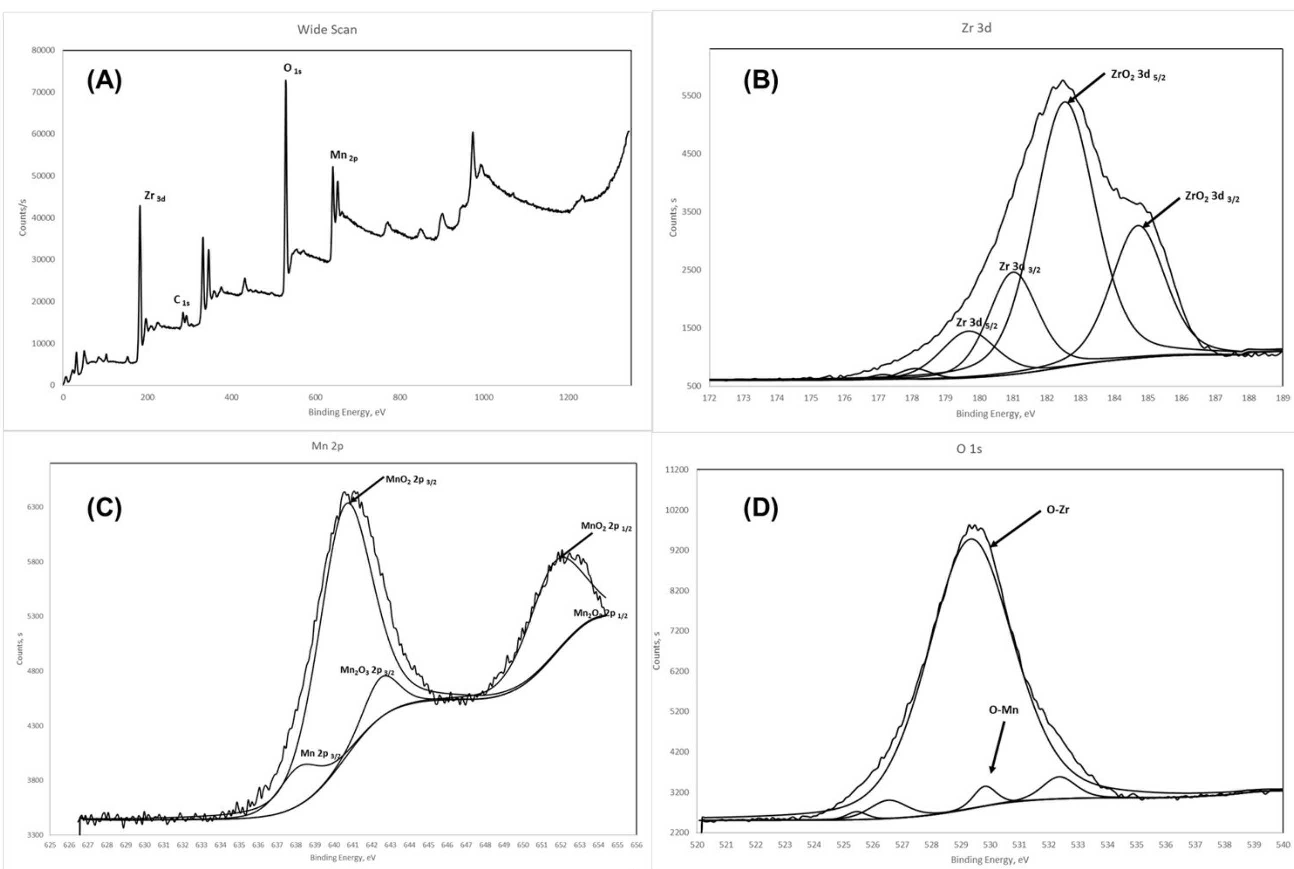

Fig. 3S XPS Spectra of MnO_2/ZrO_2 catalyst (A) Wide Scan (B) Zr 3d (C) Mn 2p (D) O 1s

4. FESEM/EDX Result of spent MnO_2/ZrO_2

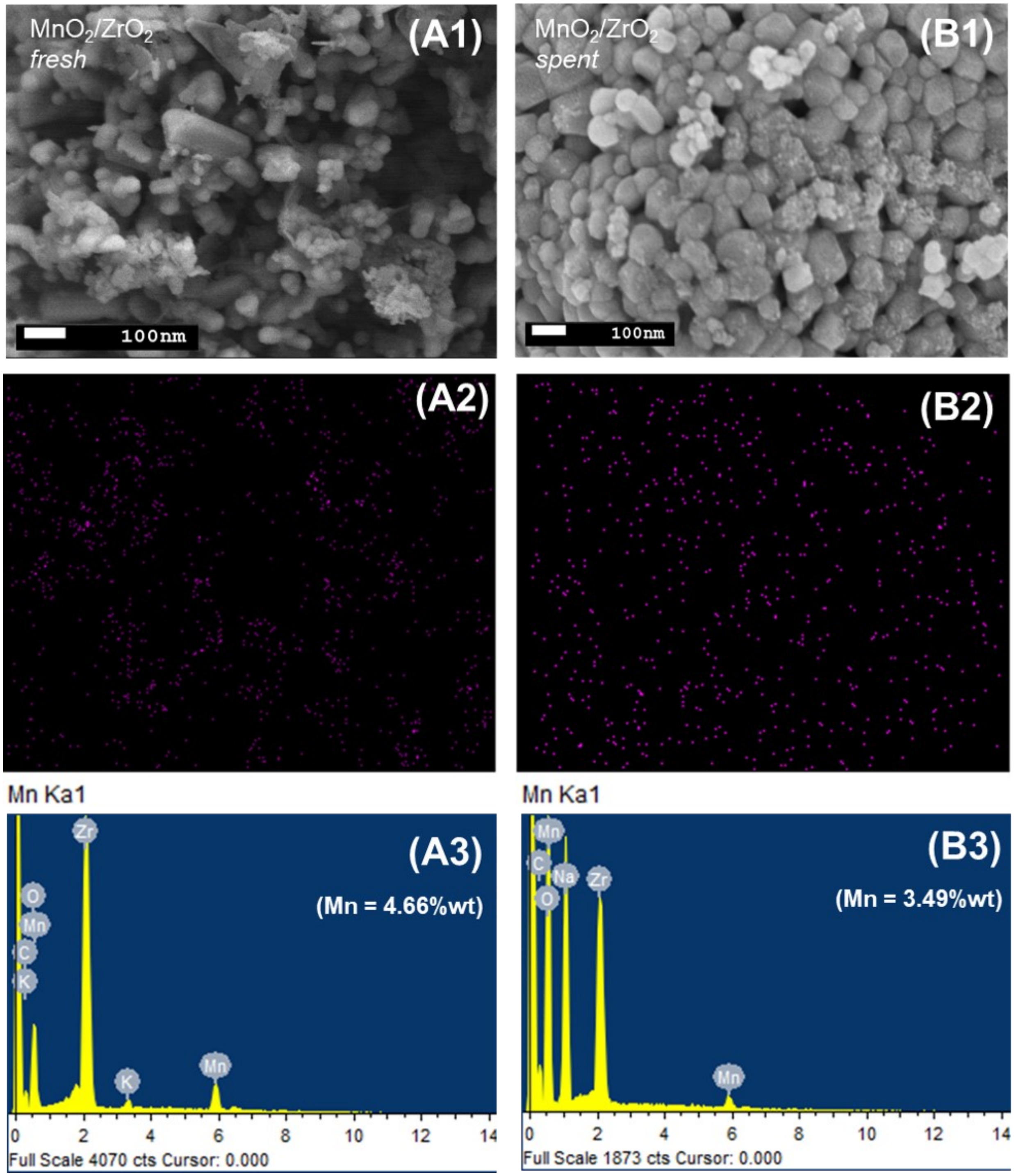

Fig. 4S (A1) FESEM of fresh catalyst, (A2) Elemental dot mapping of Mn in fresh MnO_2/ZrO_2 (A3) Elemental mapping spectra of fresh MnO_2/ZrO_2 (B1) FESEM of spent MnO_2/ZrO_2 catalyst (B2) Elemental dot mapping of Mn in spent MnO_2/ZrO_2 (B3) Elemental mapping spectra of spent MnO_2/ZrO_2 catalyst

5. References

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