

Electronics Supporting Information

Efficient oxidation of hydrocarbons over nanocrystalline $\text{Ce}_{1-x}\text{Sm}_x\text{O}_2$ ($x=0-0.1$) synthesized using supercritical water

Sandip Kumar Pahari,^a Provas Pal,^a Apurba Sinhamahapatra,^a Arka Saha,^a Chiranjit Santra,^b Subhash Ch Ghosh,^a Biswajit Chowdhuri,^{b,*} Asit Baran Panda,^{a,*}

^aDiscipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (Council of Scientific and Industrial Research), G.B. Marg, Bhavnagar-364021, Gujarat, India.

^b Department of applied chemistry, Indian School of Mines, Dhanbad, India.

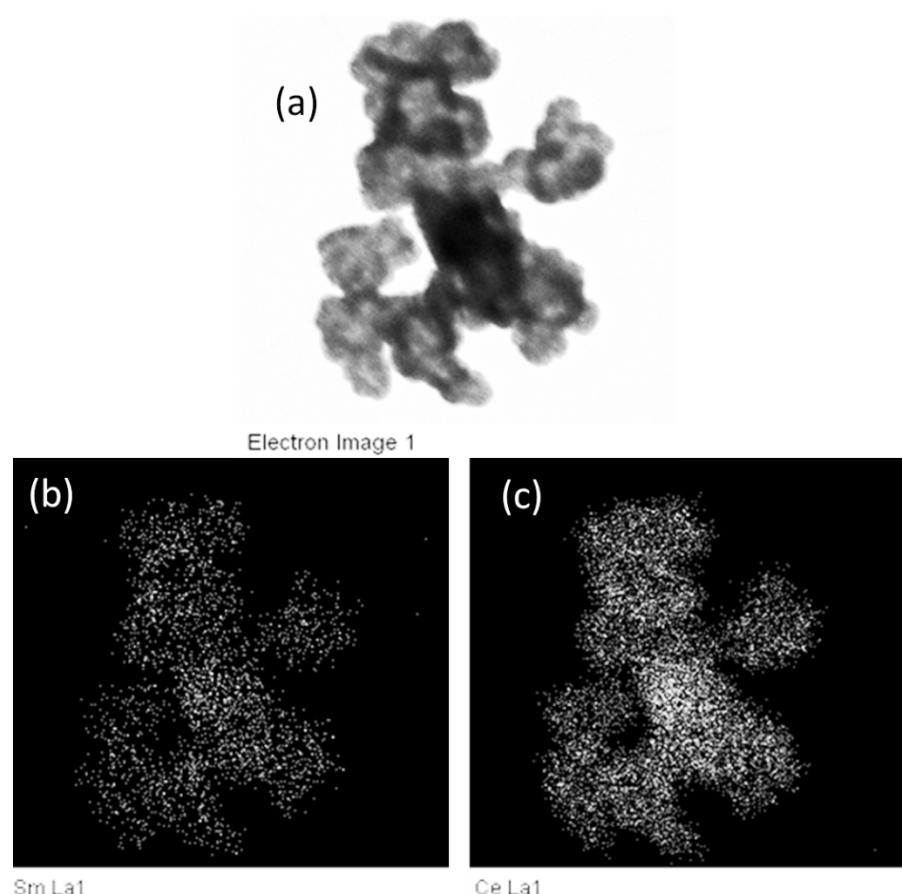


Fig. S1. (a) bright field image and corresponding STEM XEDS elemental maps of (b) Ce-L_α , (c) Sm-L_α of the synthesized $\text{Ce}_{0.95}\text{Sm}_{0.05}\text{O}_2$.

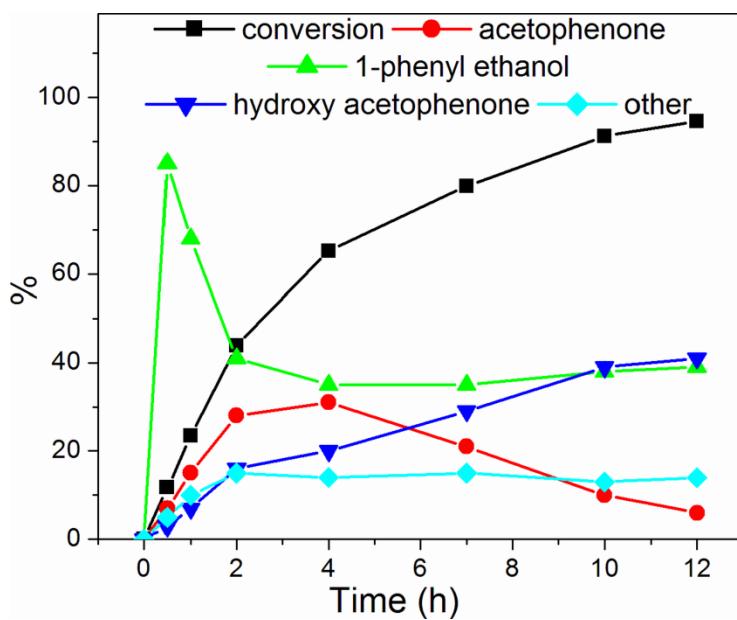


Fig. S2. Reaction profile (conversion of ethyl benzene and selectivity of different products) obtained for the allylic oxidation of ethyl benzene over the prepared pure CeO_2 catalyst.

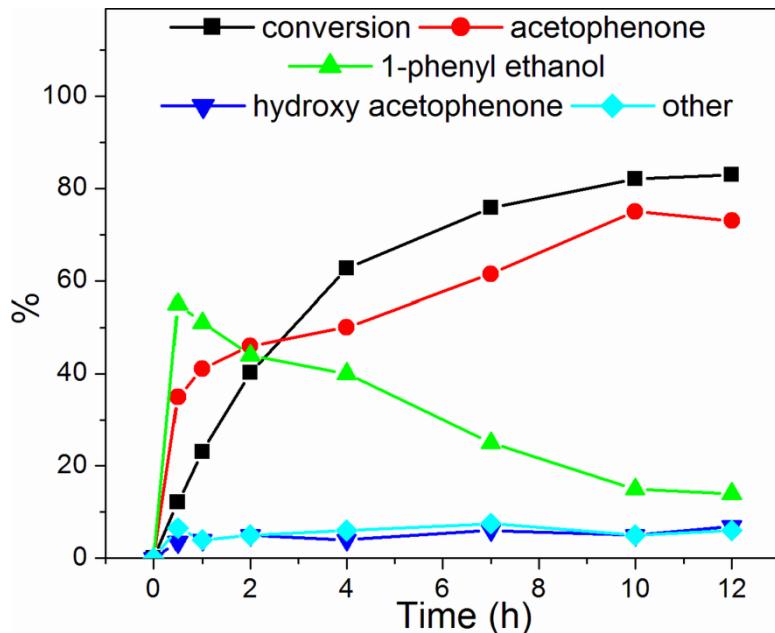


Fig. S3. Reaction profile (conversion of ethyl benzene and selectivity of different products) obtained for the allylic oxidation of ethyl benzene over the prepared pure $\text{CeO}_2 - 2.5\%$ Sm catalyst.

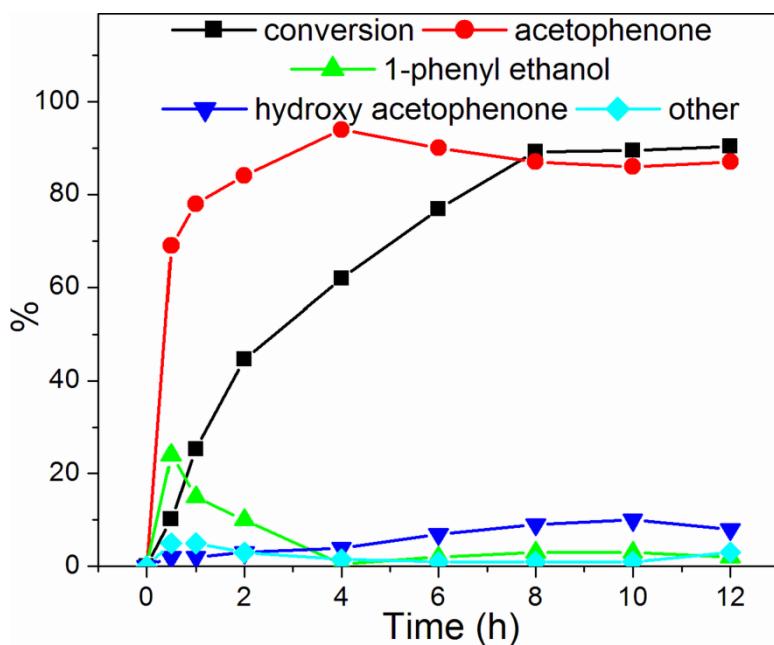


Fig. S4. Reaction profile (conversion of ethyl benzene and selectivity of different products) obtained for the allylic oxidation of ethyl benzene over the prepared pure CeO_2 - 5%Sm catalyst.

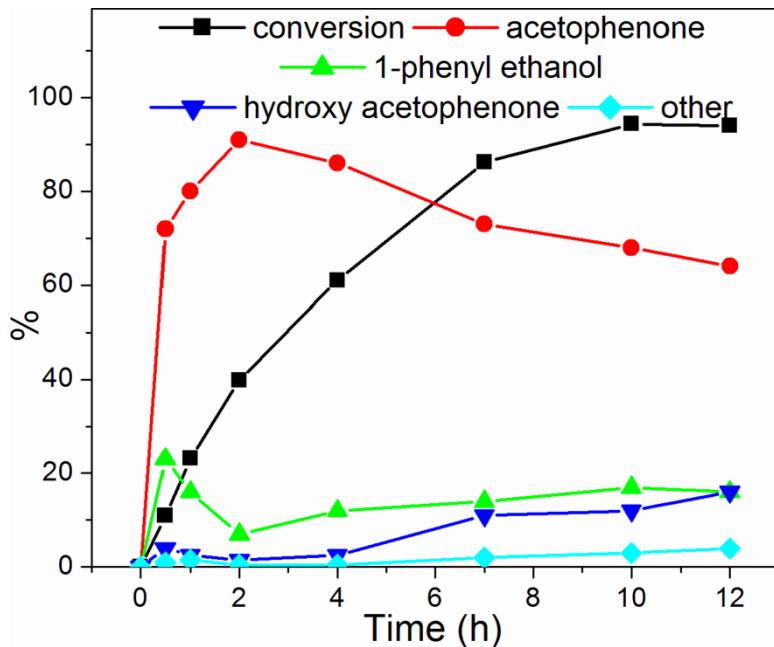


Fig. S5. Reaction profile (conversion of ethyl benzene and selectivity of different products) obtained for the allylic oxidation of ethyl benzene over the prepared pure CeO₂ - 7.5%Sm catalyst.

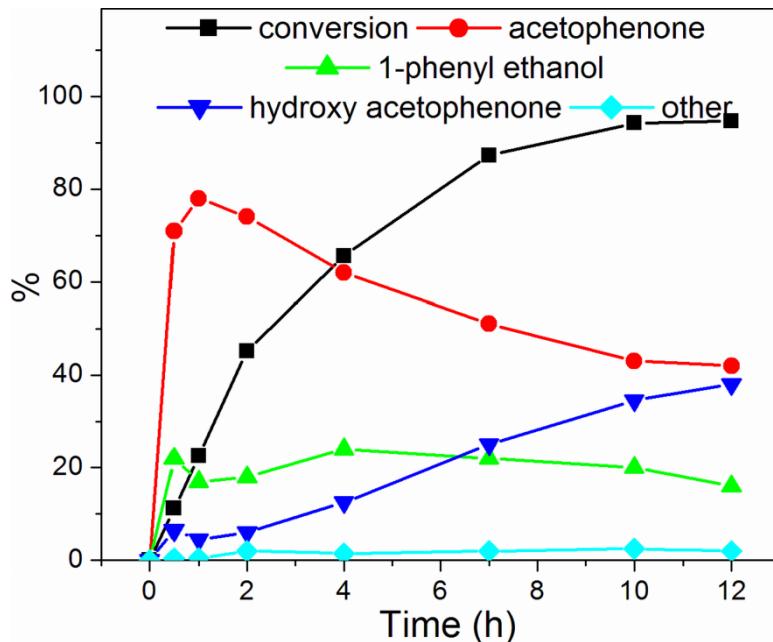


Fig. S6. Reaction profile (conversion of ethyl benzene and selectivity of different products) obtained for the allylic oxidation of ethyl benzene over the prepared pure CeO₂ - 10%Sm catalyst.

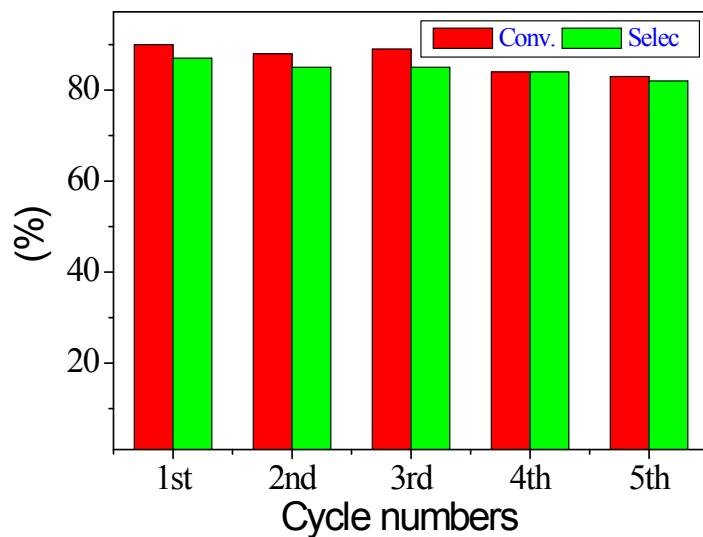


Fig. S7. Reusability (conversion of ethyl benzene and selectivity of Acetophenone) obtained for the allylic oxidation of ethyl benzene over the prepared pure CeO_2 -5%Sm catalyst.

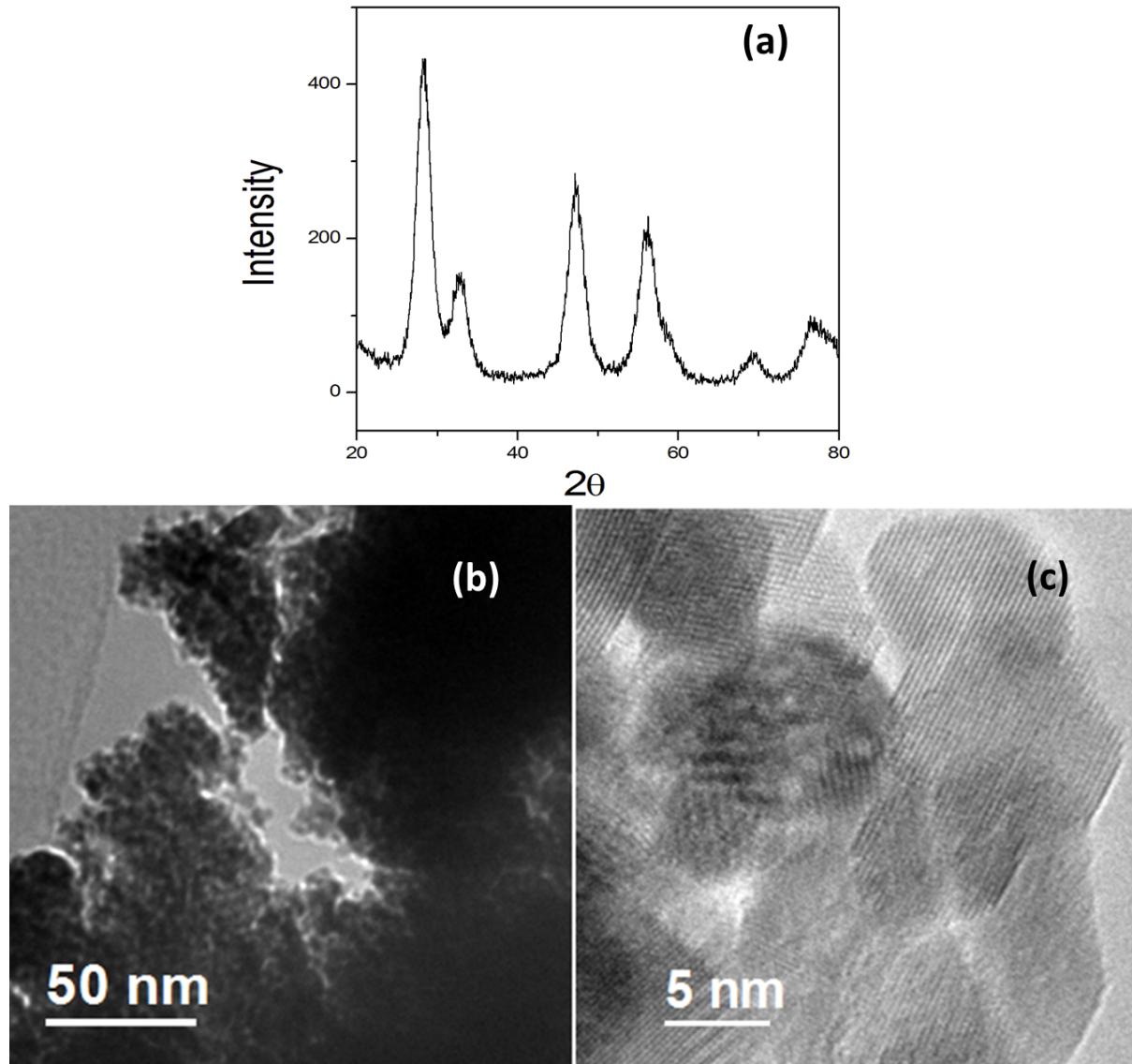


Fig. S7. (a) XRD pattern, (b) TEM and (c) HR-TEM of the reused (after 5 time) catalyst.

From the TEM image it looks like the porosity has been decreased compared to the fresh catalyst. It is most probably due to the adsorbed organic substrate. However, from the HR-

TEM image it is evident that the crystallinity and morphology remained same as fresh catalyst.

Table S1 Comparative study of catalytic activity of the synthesized $\text{Ce}_{0.95}\text{Sm}_{0.05}\text{O}_2$ catalyst with other reported catalyst towards ethyl benzene oxidation.

Catalyst	Oxidant	Conversion (%)	Selectivity (%)	Yield (%)	Ref.
$\text{Ce}_{0.95}\text{Sm}_{0.05}\text{O}_2$	30 wt.% aqueous H_2O_2	90	87	78.3	Present work
Supported cobalt (II) Salen complex	oxygen/acetic acid	84 ^(a)	90	76	1
Ti-MCM-41	30 wt.% aqueous H_2O_2	12	80	9.6	2
V-MCM-41	30 wt.% aqueous H_2O_2	18	21	3.7	2
Metalloporphyrin covalently bound to silica	30 wt.% aqueous H_2O_2	30.3	95.1	28.8	3
Pd (0) and Pd (II) nanotubes and nanoparticles on modified bentonite	tert-butylhydroperoxide(80%)	92.3	95.5	88.1	4
Mn catalyst supported on a modified nanosized $\text{SiO}_2/\text{Al}_2\text{O}_3$	tert-butylhydroperoxide(80%)	84	86	72.2	5
Ni/13USY	molecular O_2	21.5	76.4	16.3	6
Manganese containing MCM-41	tert-butylhydroperoxide(80%)	57.7	82	47.3	7
Vanadia supported on ceria	30 wt.% aqueous H_2O_2	20.5	72.2	14.8	8
MnO_4^{-1} exchanged Mg-Al	molecular O_2	22.6	98.4	22.2	9

hydrotalcite					
Ni-Al hydrotalcite	molecular O ₂	47	99.3	46.6	10
Nanocrystalline CeO ₂ (hydrothermal)	30 wt.% aqueous H ₂ O ₂	85	77	65.4	11

^(a) The conversion has been calculated based on selectivity and yield.

References:

- [1] F. Rajabi, R. Luque, J. H. Clark, B. Karimi, D. J. Macquarrie Catal. Commun. 12 (2011) 510–513
- [2] R. K. Jha, S. Shylesh, S. S. Bhoware, A. P. Singh Micropor. Mesopor. Mater. 95 (2006) 154–163
- [3] M. Ghiaci, F. Molaie, M. E. Sedaghat, N. Dorostkar Catal. Commun. 11 (2010) 694–699
- [4] M. Ghiacia, Z. Sadeghib, M. E. Sedaghata, H. Karimi-Maleha, J. Safaei-Ghomib, A. Gilc Appl. Catal. A: Gen. 381 (2010) 121–131
- [5] M. Arshadia, M. Ghiacia, A. Rahmaniana, H. Ghaziaskara, A. Gil Appl. Catal. B: Environ. 119– 120 (2012) 81– 90
- [6] G. Raju, P. Shiva Reddy, J. Ashok, B. Mahipal Reddy, A. Venugopal J. Natural Gas Chem. 17 (2008) 293–297
- [7] K. M. Parida, S. S. Dash J. Mol. Catal. A: Chem. 306 (2009) 54–61
- [8] T. Radhika, S. Sugunan Catal. Commun. 8 (2007) 150–156
- [9] V. R. Choudhary, J. R. Indurkar, V. S. Narkhede, R. Jha J. Catal. 227 (2004) 257–261
- [10] S. K. Jana, P. Wu, T. Tatsumi J. Catal. 240 (2006) 268–274
- [11] N. Sutradhar, A. Sinhamahapatra, S. K. Pahari, M. Jayachandran, B. Subramanian, H. C. Bajaj, A. B. Panda, J. Phys. Chem. C 115 (2011) 7628-7637