ELECTRONIC SUPPLEMENTARY INFORMATION

Exceptional activity of mesoporous β-MnO_2 in the catalytic thermal sensitization of Ammonium Perchlorate

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1. Experimental details

1.1 Catalyst preparation

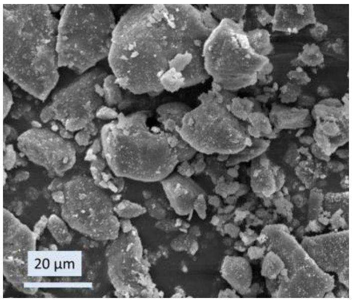
The mesoporous silica template, KIT-6 was prepared according to the procedure reported by Ryoo and coworkers.[1] For the synthesis of mesoporous β-MnO_2, 6 g of $Mn(NO_3)_2.4H_2O$ was dissolved in 25 ml of ethanol. To impregnate the silica template with the metal nitrate, 1 g of KIT-6 was added to the solution and stirred overnight. The impregnated template was separated by centrifugation and calcined at 350 °C for 5 hours. A slow heating rate was employed during calcination. The mesoporous silica framework was then removed selectively using a NaOH (2 M) solution. The replica mesoporous structure of β-MnO_2 was washed several times with distilled water and ethanol, and dried to obtain the final catalyst. For a comparative study, micron-sized β-MnO_2 was prepared by direct calcination of $Mn(NO_3)_2.4H_2O$ at 350 °C for 5 hours.

1.2 Catalyst characterization

The crystal phases of the catalysts were identified by Powder X-Ray Diffraction (PXRD). The analysis was carried out with a Philips diffractometer (model: X'PERT PRO) using monochromatized Cu Kα (λ = 1.5406 Å) radiation. The nanostructural morphology of the catalyst was characterized using a Technai T20 Transmission Electron Microscope (TEM).The N_2 adsorption-desorption measurements were conducted at 77 K using a Micromeritics surface area analyzer (model: ASAP 2020). The specific surface areas of the synthesized catalysts were calculated using the Brunauer-Emmett-Teller (BET) method, and the average pore sizes and pore volumes were estimated using the Barett-Joyner-Halenda (BJH) method.

1.3 AP-catalyst composite preparation

Ammonium Perchlorate (AP) was re-crystallized twice in distilled water. AP crystals collected after double re-crystallization were ground using an Agate mortar and pestle, and then sieved through a BS 200 mesh (75 µm openings). The fine white AP crystals collected after sieving were used in this study. From the SEM pictures, AP crystals were seen to be of irregular morphology. Comparable characteristic lengths of individual particles in all three dimensions showed that the particles were not homogeneously stretched in any particular dimension, and thus, were closer to spherical geometry. Particles with characteristic lengths from few hundred nanometers to up to approx. 60 micrometers were observed in the SEM images. The volume/mass based mean length was estimated as approx. 33 µm.



AP-catalyst composites for the thermal decomposition studies were prepared by mechanically mixing AP with various catalysts (according to the desired % *w/w*), in the presence of acetone as the dispersing agent.

1.4 Evaluation – thermal analyses

Thermo-Gravimetry (TG) and Differential Thermal Analyses (DTA) of pure AP and various AP - catalyst composites were carried out under a flowing nitrogen atmosphere (50 ml/min, model: Schimadzu DT-40). Differential Scanning Calorimetric (DSC) analyses were performed at a heating rate of 5 °C/min using Mettler Toledo DSC, STARe System. Samples of approximately 10 mg and 1.5 mg were taken for the TG-DTA and DSC experiments respectively. As a customary practice in the evaluation of novel propellant formulations, the repeatability of thermal analyses data was verified by multiple experiments. Results reported in the main article are 'median' values of triplicate experiments. Dispersion of data was quantified by its 'range' = 'highest value' – 'lowest value'. Dispersion of 'specific heat release' values calculated from DSC curves was observed to be higher. Measurement errors in initial sample mass and particularly, the selection of baseline for integration possibly contribute to this observation.

1.5 Kinetics

The kinetics of the thermal decomposition reactions were quantified using the Kissinger method (DTA; heating rates – 2,3,4,5 and 6 °C/min). This method is independent of the reaction order or conversional function, and is based on the principle that, if a reaction proceeds at a rate varying with temperature-i.e., possesses activation energy-the position of the DTA/DSC peak varies with the heating rate. Some major assumptions made by this method are –

- The order of reaction remains constant throughout the part of reaction in study.
- The order of reaction does not vary with heating rate.
- Rate constant follows the Arrhenius law.
- The reaction rate is maximum at peak temperature.

The correlation between peak temperatures and heating rates allows the determination of apparent activation energy using equation

$$(\frac{E_a}{R}) = -(d(\frac{\ln\phi}{T_p^2}))/(d(\frac{1}{T_p}))$$

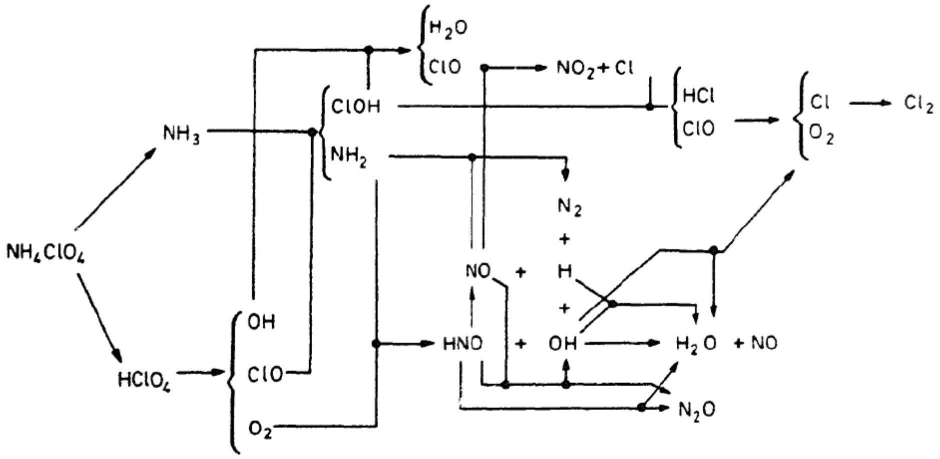
where *Ea* is the apparent activation energy, *A* is the heating rate employed, *Tp* is the peak temperature and R is the universal gas constant. The slope (-Ea/R) is estimated by plotting the values of $(\ln\varphi/Tp^2)$ vs $(1/Tp^2)$ and fitting a straight line through these data points. In our case of AP decompositions with and without catalysts, the R^2 correlation coefficient was found to be greater than 0.98. The apparent frequency factor, *A*, at HTD peak temperature (T_p), is then calculated from the equation

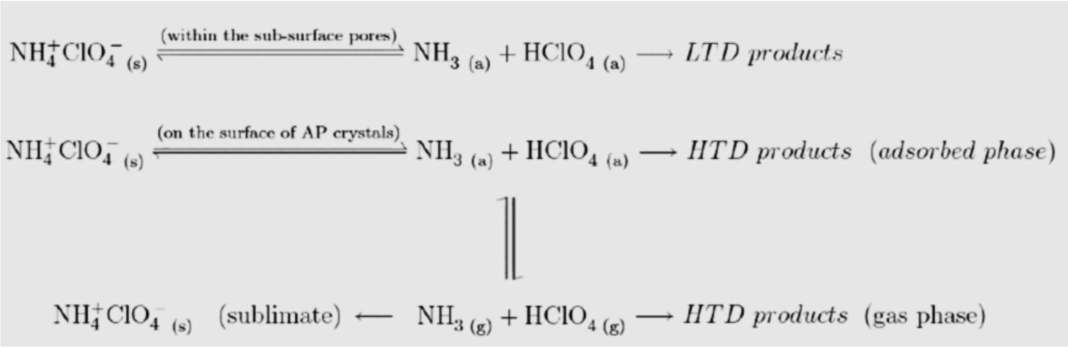
$$A = (\phi E_a e^{\frac{E_a}{RT_p}})/(RT_p^2)$$

Subsequently, the specific rate of reaction, *k,* at Tp, is estimated from the *Arrhenius* equation

$$k = A\ e^{-\frac{E_a}{RT_p}}$$

2. Schematics of AP decomposition



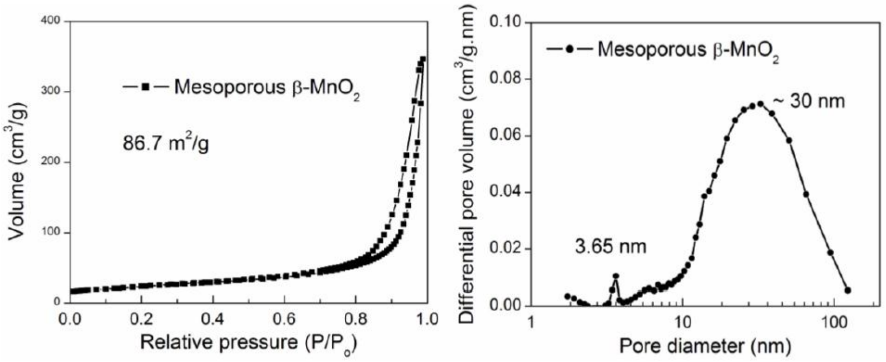


Schematic representations of the processes involved in the thermal decomposition of Ammonium Perchlorate (adapted from ref. 2,3).

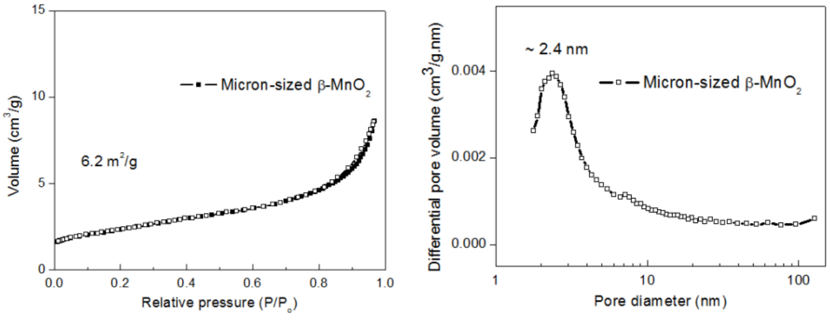
References:
1 F. Kleitz, S. H. Choi and R. Ryoo, *Chem. Commun.*, 2003, **17**, 2136.
2 P. W. M. Jacobs and G. S Pearson, *Combust. Flame*, 1969, **13**,419.
3 P. W. M. Jacobs and H. M. Whitehead, *Chem. Rev.*, 1969, **69**, 551.

3. Additional characterization and evaluation data

3.1 N_2 adsorption-desorption isotherms and pore size distribution

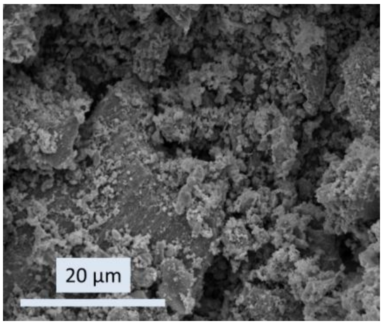


N_2 adsorption-desorption isotherms and pore size distribution of the prepared β-MnO_2 mesoporous catalyst



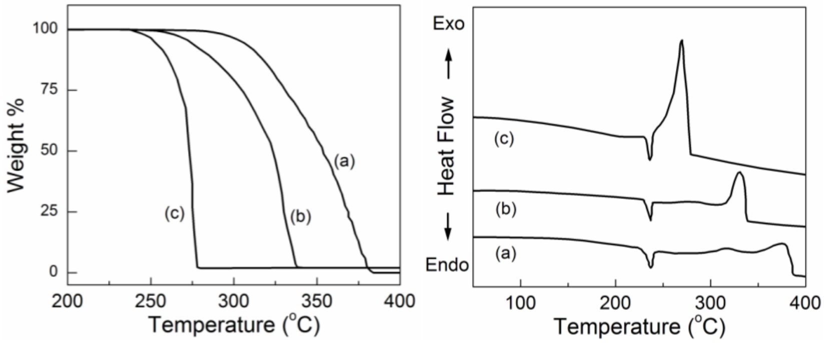
N_2 adsorption-desorption isotherms and pore size distribution of the micron-sized β-MnO_2 catalyst

3.2 SEM of micron-sized MnO_2 catalyst



SEM of micron-sized MnO_2 catalyst; particles are of irregular morphology; agglomerates of few hundred nanometers to tens of microns.

3.3 Non-Isothermal TG and DTA curves



Non-Isothermal TG and DTA curves of (a) pure AP, (b) AP + 2% w/w micron-sized β-MnO_2 and (c) AP + 2% w/w mesoporous β-MnO_2.

3.4 Additional DSC data

DSC data for the thermal decomposition of pure AP and AP +catalysts (heating rate – 5 °C/min)

Sample	HTD peak temperature/°C	Apparent specific heat release/J g^{-1}
Pure AP	**426.3**	**386**
AP + 2 % *w/w* micron-sized α-Fe_2O_3	351.4	972
AP + 2 % *w/w* mesoporous α-Fe_2O_3	317.3	1214
AP + 2 % *w/w* micron-sized β-MnO_2	**341.2**	**821**
AP + 0.25 % *w/w* mesoporous β-MnO_2	301.0	517
AP + 0.5 % *w/w* mesoporous β-MnO_2	295.5	801
AP + 1% *w/w* mesoporous β-MnO_2	287.8	1316
AP + 2% *w/w* mesoporous β-MnO_2	**273.1**	**1696**
AP + 3% *w/w* mesoporous β-MnO_2	270.3	1236
AP + 4% *w/w* mesoporous β-MnO_2	266.7	1171
AP + 5% *w/w* mesoporous β-MnO_2	265.0	1152

3.5 Comparison with related published work

Ref.	Catalyst characterization			AP decomposition					
	Catalyst	Morphology	Surface area/m^2 g^{-1}	Method	Heating rate/ ^{o}C min^{-1}	Catalyst conc./% *w/w*	HTD peak temperature/^{o}C	Apparent specific heat release/J g^{-1}	Apparent activation energy/kJ mol^{-1}
[z1]				DSC	5	-	426.3 (1.8)	386 (23)	161 (3.1)
	β-MnO_2	mesoporous; KIT-6 template	86.7			2	273.1 (0.9)	1696 (19)	159.2 (4.3)
						4	266.7	1171	-
[z2]				DSC	20	-	467	910	165
	Mn–O	octahedral molecular sieves	112			2	322	1570	120
[z3]				DSC	-	-	> 450	-	-
	ZnO	hollow single cages	-			2	285	-	-
[z4]				DTA	10	-	397	584	154.0 ± 13.9
	ZnO	AP core-ZnO shell nano-composite	-			2	276	1131	96.5 ± 15.0
						4	272	1137	93.7 ± 22.4

[z1] Present work; ‘median’ values from triplicate experiments are reported; range of data is given in parentheses.

[z2] F. Tingming, L. Feiquan, L. Lin, G. Liwei and L. Fengsheng, *Cat. Comm.*, 2008, **10**, 108.

[z3] J. Yin, Q. Lu, Z. Yu, J. Wang, H. Pang and F. Gao, *Cryst. Growth Des.*, 2010, **10**, 40.

[z4] Z. Zhou, S. Tian, D. Zeng, G. Tang and C. Xie, *J. Alloy Compd.*, 2012, **513**, 213.