## Supporting Information

## One-step synthesis of hollow Cr(OH)<sub>3</sub> micro/nano hexagonal pellets

## and the catalysis properties of hollow Cr<sub>2</sub>O<sub>3</sub> structure

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Figure S1 the TGA (thermal gravimetric analysis) curve of as-prepared product from Room Temperature to 700 °C

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Figure S2 XRD patterns of the products after different time of reaction. (a)1 second, (b)15 seconds, (c)1 day ,(d)5 days



**Figure S3** TEM images of Cr(OH)<sub>3</sub> hexagonal pellets after different reaction times. (a)0.5day, (b)1 day, (c)2days, (d)3 days, (e)4 days, (f)5days.



Figure S4 SEM images of Cr (OH)<sub>3</sub> product.

The product was obtained by the reaction of a 50 ml 5.6 mM  $CrCl_3$  solution and a 50 ml 16.8 mM  $NaBH_4$  solution for a day, two drops of 0.1M hydrochloric acid were added into the solution after an hour of reaction.



Figure S5 TEM image of hollow  $Cr(OH)_3$  hexagonal pellet prepared by the reaction of 50 ml 10 mM  $CrCl_3$  solution and 0.064g NaBH<sub>4</sub>(solid) for 12 hours





**Figure S6** Cr(OH)<sub>3</sub> micro/nano structures obtained by the similar synthesis strategy (a) 50 ml 20 mM CrCl<sub>3</sub> solution react with 50 ml 50 mM NaBH<sub>4</sub> solution for an hour, (b) 50 ml 20 mM CrCl<sub>3</sub> solution react with 50 ml 40 mM NaBH<sub>4</sub> solution for an hour, (c) 50 ml 33 mM Cr(NO<sub>3</sub>)<sub>3</sub> solution react with 50 ml 50 mM NaBH<sub>4</sub> solution for an hour, hour,

(d) 50 ml 5.6 mM CrCl<sub>3</sub> solution react with 0.096g NaBH<sub>4</sub> (solid) for 3 days

Since the direct dehydrogenation data is also important for studying the dehydrogenation of alkanes, a control experiment that without  $CO_2$  was tested for comparison (Fig. S7). The direct dehydrogenation were carried out in the same fixed-bed flow type quartz reactor packed with 0.15 g of the catalyst and 1 g of quartz sand at atmospheric pressure, the average height of catalyst pellets is 212 nm. The reactant stream consisting of 20 % isobutane and 80 % Ar was introduced into the reactor at a flow rate of 2000 mL/(h•g). The reaction temperature varied from 823 K to 973 K.

It can be found that isobutane conversion in oxidative dehydrogenation (ODH) reactions is higher than that in direct dehydrogenation (DH) reactions from 823K to 943K. Isobutene selectivity in ODH is also higher than that in DH when the reaction temperature higher than 853K. The results indicate that oxidative dehydrogenation is more efficiency than direct dehydrogenation over the similar catalyst.



**Figure S7** Isobutane conversion (a) and the Isobutene selectivity (b) of  $i-C_4H_{10}$  as a function of temperature in oxidative dehydrogenation (ODH) and direct dehydrogenation (DH) reactions.

Sample	Total (BET) specific surface area (m <sup>2</sup> /g)
Cr <sub>2</sub> O <sub>3</sub> -203	102.64
Cr <sub>2</sub> O <sub>3</sub> -284	86.58
Cr <sub>2</sub> O <sub>3</sub> -396	53.06
Cr <sub>2</sub> O <sub>3</sub> -510	28.72
commercial nano Cr <sub>2</sub> O <sub>3</sub>	31.63

Table S1 BET specific surface area of hollow  $\mbox{Cr}_2\mbox{O}_3$  and commercial  $\mbox{Cr}_2\mbox{O}_3$  nanoparticle