Supplementary Information for

Fe_2O_3, a cost effective and environmentally friendly catalyst for generation of NH_3 – a future fuel with a new Al_2O_3-looping based technology

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2. Experiments

2.1 Raw materials

Pure AlN power was purchased from Advanced Technology & Materials Co. Ltd., (N>32.5%, 5.0um of partial size). Other chemical reagents, including CaF_2, CaO, CuO, Fe_2O_3, K_2CO_3, MgO, Na_2CO_3, ZnO were obtained from Sinopharm Chemical Reagent Co., Ltd (purity >99.0%). Each sample was prepared by mixing predetermined amounts of AlN and catalysts in a mortar and grinded for half an hour.

2.2. Characterization

The N-desorption performances of AlN were characterized using a thermogravimetric analyzer (TGA, STA449F3, NETZSCH, Germany). 30 mg sample was used for each N-desorption test. N-desorption of AIN were evaluated through temperature programmed experiments and started with heating the sample to 700^{o}C at 20^{o}C min^{-1} within 500 sccm Ar environment to purge the moisture in the reactor, followed by introducing 250 sccm Ar and 250 ml sccm H_2O vapor into the reactor and heating it to 1,200^{o}C at the rate of 20 ^{o}C min^{-1}. During the isothermal tests, each sample was heated to a desired reaction temperature at 20 ^{o}C min^{-1} within 500 ml min^{-1}Ar to purge the moisture in the reactor, then 250 ml min^{-1}Ar and 250 ml min^{-1} H_2O vapor was introduced into the reactor. Each N-desorption was ended when the no mass change was observed. The conversion of AlN was calculated by using Eq.1

$$X = \frac{(w_0 - w_t)/M_{\Delta m}}{(w_0 - w_c)/(2M_{AlN})} \times 100\% \qquad \text{S1}$$

where w_0 is the initial mass of Fe_2O_3 and AlN, mg; w_t is the mass of Fe_2O_3 and unreacted AlN measured by the TGA at the end of reaction, mg; w_c is the mass of catalyst or Fe_2O_3, mg; $M_{\Delta m}$ is the mass difference between 1 mole of AlN and 2 moles of Al_2O_3 in R2, 20 g mol^{-1}, and M_{AlN} is the mass of per mole of AlN, 41g mol^{-1}. The blank tests, which are through the same condition as the temperature programmed experiments, were conducted to make sure the stability of the catalysts during the reaction, and the results are shown in Fig. S1.

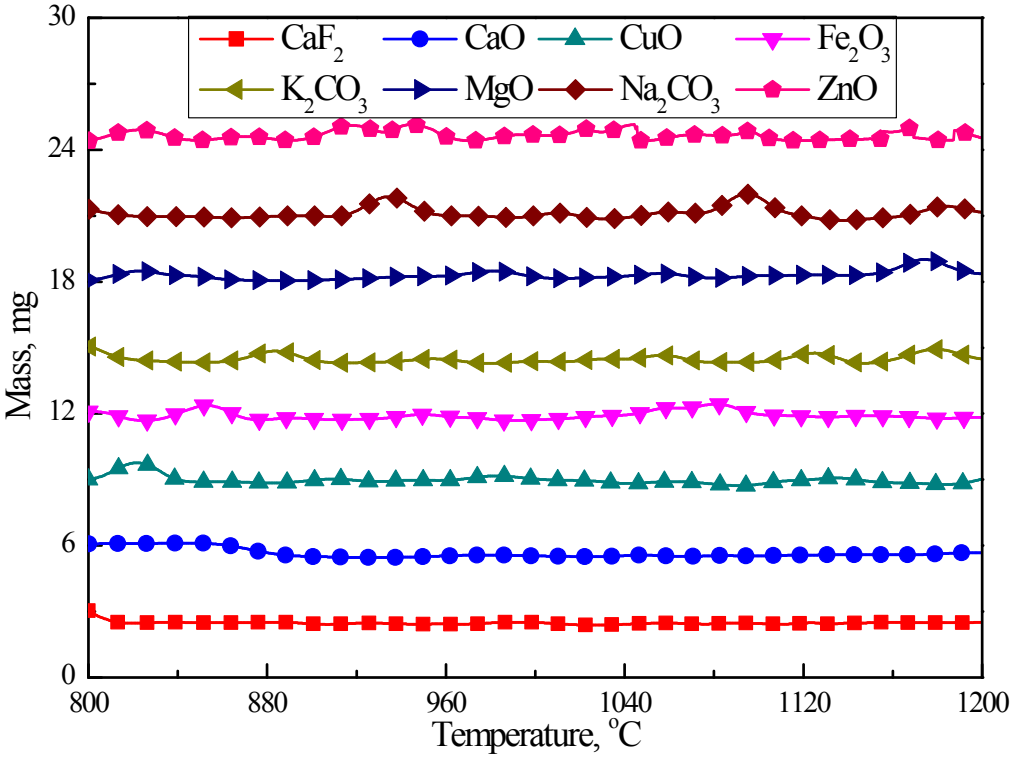

Fig.S1 The blank tests of different catalysts with TGA (sample loading: 30 mg; catalyst loading: 5 wt%; gas flow: 0.5 L min^{-1}; heating rate: 20 ^oC min^{-1}

X-ray diffraction (XRD) data for AlN with Fe_2O_3 were collected using a SCINTAG XDS2000 automated powder diffraction system equipped with a θ-θ XRD goniometer and a solid-state X-ray detector.

2.3 NH_3 generation

In order to verify the catalytic effect of the Fe_2O_3, the produced gas, mainly containing NH_3,[S1] was produced with the ammonia generation setup and collected with a contained 200 ml deionized water (DI) beaker, the details of the setup are shown in Fig. S2. 0.425g AlN or 0.425 g AlN catalyzed with 0.025g Fe_2O_3 was loaded and heated to 1000 ^oC within 250 ml min^{-1}Ar to purge the moisture in the reactor, then 250 ml min^{-1}Ar and 250 ml min^{-1} H_2O vapor was introduced into the reactor.

The resulting DI water was detected with a pH meter in 5mins to verify the catalytic effect of the Fe_2O_3. For clarification, NH_3 is easy to be dissolved into the water and the resulting water is alkalinous. The higher alkalinous of the water, more NH_3 is generated in the limited time. The pH of the pure DI water is 6.96.

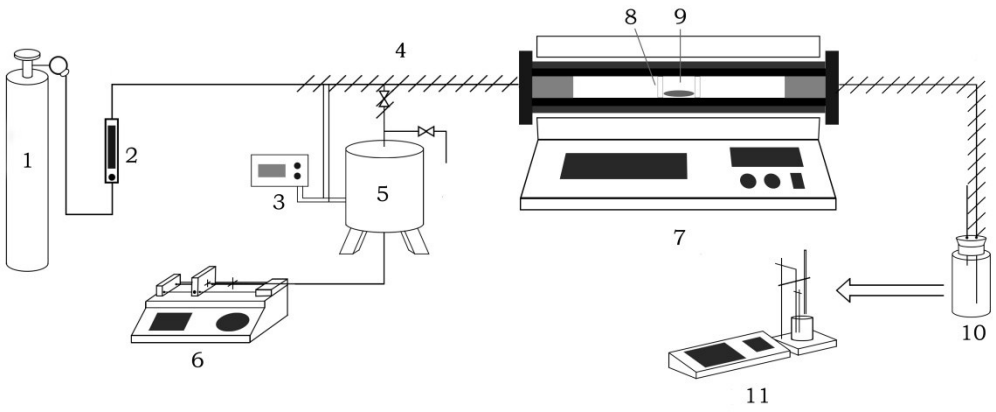

Figure S2. Schematic diagram of the AlN hydrolyzation setup: 1, Nitrogen cylinder; 2, flow meter; 3, thermoregulator; 4, heat type; 5, steam generator; 6, syringe pump; 7, tube furnace; 8,silica wool; 9, AlN and catalyst; 10, water; 11, pH meter.

References

S1. M. E. Galvez, A. Frei, M. Halmann and A. Steinfeld, Ind Eng Chem Res, 2007, 46, 2047-2053.