

Unexpectedly high activity of pure alumina for non-oxidative alkane dehydrogenation

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Experimental methods

Materials

All experiments used alumina Chempur basic (Chempur Karlsruhe) that was calcined for 4 h at 400°C in air.

Catalytic tests

Catalytic tests were carried out in an in-house developed setup containing 15 continuous-flow fixed-bed quartz reactors (3.8 mm inner diameter) operated in parallel and heated in a single oven. Different amounts of alumina samples (0.15 – 2 g, particle size of 315-710 μm) were installed in the individual reactors and heated in air, N_2 or a H_2/N_2 1:1 mixture at 5 K min^{-1} to the respective activation temperature and held at this temperature for the desired time. Then the samples were cooled down to the reaction temperature of 550 °C under nitrogen flow. For catalytic tests a reaction gas mixture (isobutane: N_2 =40:60 or isobutane: N_2 : H_2O =40:10:50) was fed at a flow rate of 10 ml/min and a pressure of 1.23 bar over one of the differently activated alumina samples holding the other samples under a flow of nitrogen. After one hour the feed gas flow was switched to the next reactor and this procedure was repeated until all samples were tested.

The feed and product gas compositions were measured by an on-line gas chromatograph (Agilent 6890) equipped with PoraplotQ (for CO_2 and water), HP-PLOT Al_2O_3 ”KCl” (for methane, ethane, ethylene, propane, propylene, n-butane, isobutane, trans-2-butylene, cis-2-butylene, 1-butylene, isobutylene, butadiene) and Molsieve 5 (for H_2 , N_2 , CO) capillary columns and flame ionization (for hydrocarbons) and thermal conductivity (for other products) detectors. The isobutane conversion and selectivity to gas-phase products were calculated according to Eq. 1 and 2, respectively. Coke selectivity was determined from the difference between unity and the sum of selectivity of all determined gas-phase products (Eq. 3).

$$X(\text{isobutane}) = \frac{\dot{n}_{\text{isobutane}}^{\text{inlet}} - \dot{n}_{\text{isobutane}}^{\text{outlet}}}{\dot{n}_{\text{isobutane}}^{\text{inlet}}} \quad (1)$$

$$S(i) = \frac{\beta_{\text{educt}} \dot{n}_i^{\text{outlet}}}{\beta_i (\dot{n}_{\text{isobutane}}^{\text{inlet}} - \dot{n}_{\text{isobutane}}^{\text{outlet}})} \quad (2)$$

$$S(\text{coke}) = 1 - \sum_i S(i) \quad (3)$$

where $S(i)$ is the selectivity to product i , β_i is a stoichiometric factor, and \dot{n}_i with superscripts “inlet” and “outlet” stand for molar flow of a gas-phase component at the reactor inlet and outlet respectively. Changes in gas volume were accounted for by using N_2 as an internal standard.

Reaction rates were determined from conversions applying a plug flow reactor model as described in detail in [1].

Specific surface area

The specific surface area (S_{BET}) of the differently activated aluminas was determined from N_2 adsorption isotherms measured at 77 K on BELSORP mini II (BEL, Japan) applying the Brunauer, Emmet and Teller (BET) equation for relative pressure range of $0.05 < p/p_0 < 0.30$.

Temperature programmed desorption of ammonia

Acidic sites created during activation of alumina at higher temperature were determined by temperature programmed desorption (TPD) of ammonia in an in-house developed setup containing eight individually heated reactors and a mass spectrometer (Pfeiffer Vacuum Omnistar) for gas analysis. Samples of alumina (50 mg per reactor) were heated in Ar or H_2/Ar 1:1 flow (10 ml/min) to establish the different activation procedures. After cooling down to 120 °C a flow of 1 % NH_3 in Ar was passed over the samples for one hour followed by flushing with Ar flow for two hours at 120 °C and additionally three hours at 80 °C to remove physisorbed ammonia. For TPD the sample was heated in an Ar flow (10 ml/min) with a rate of 10 K/min to the final temperature of 900 °C. Ammonia desorption was monitored by mass spectrometer using AMUs of 15 and 40 for NH_3 and Ar, respectively.

Temperature programmed release of water

Release of water during the different activation procedures was determined by temperature programmed heating of the activated samples in the above mentioned apparatus in an Ar flow (10 ml/min) with a rate of 10 K/min to the final temperature of 900°C (see Fig. S3). Water release was calculated from the difference between the water release of alumina dried at 120°C and those of differently activated aluminas.

References

[1] U. Rodemerck, M. Stoyanova, S. Sokolov, U. Bentrup, D. Linke, E. V. Kondratenko, J. Catal. 338 (2016) 174-183.

Figures

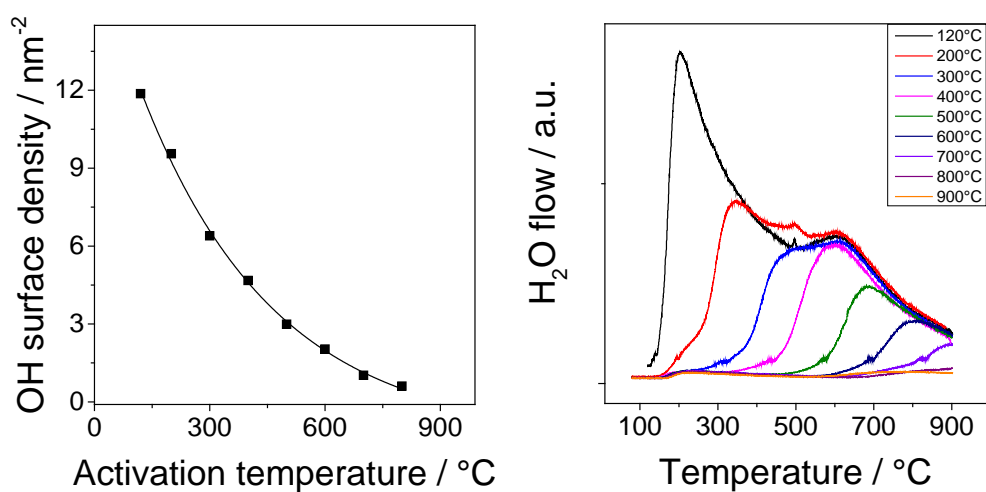


Fig. S 1 OH surface density of alumina (left) determined from temperature programmed release of water (right) from alumina activated for 12 h at different temperature.

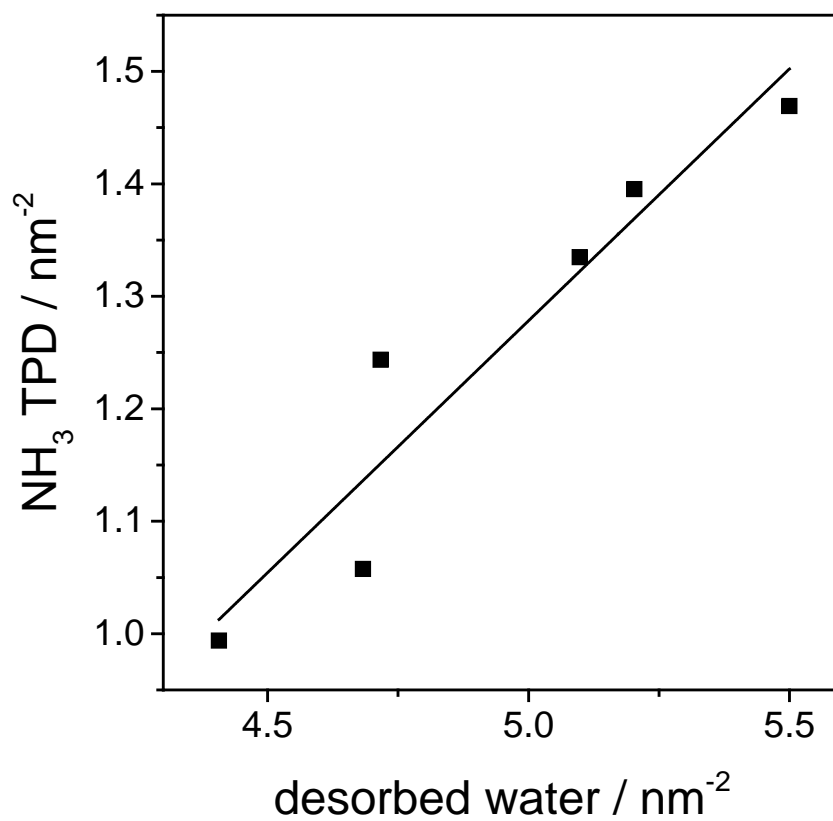


Fig. S 2 Dependence of number of NH₃ molecules desorbed up to 900°C after NH₃ adsorption at 120°C from number of water molecules desorbed during activation of alumina

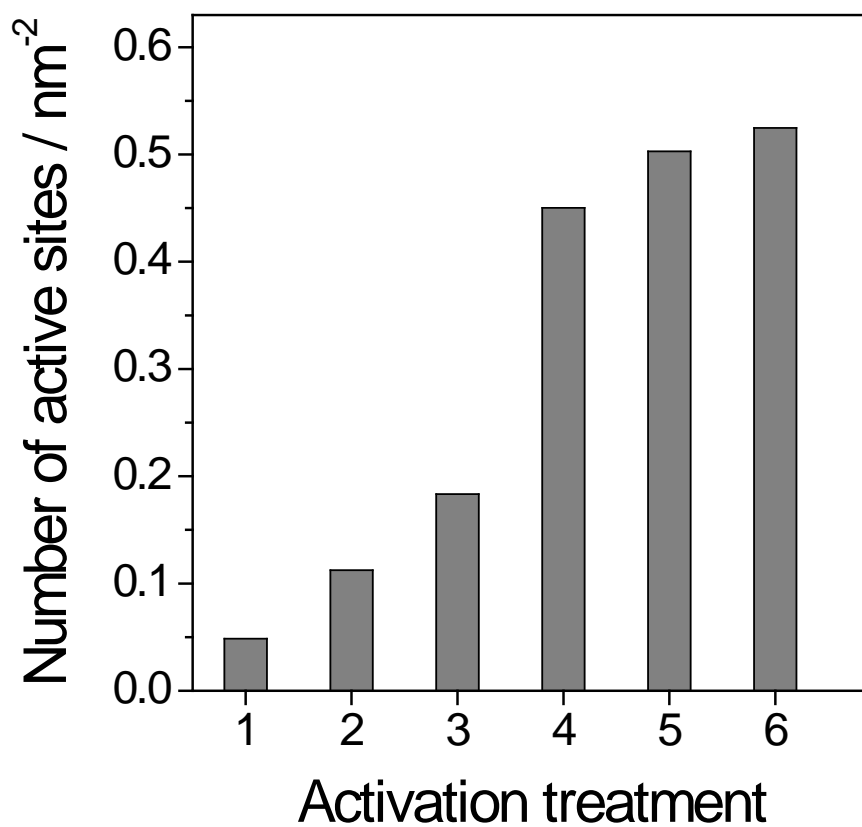


Fig. S 3 Concentration of number of active sites for isobutane DH determined from NH₃ molecules adsorbed on strong Lewis acidic sites formed after different alumina activation treatments: 1 - 10 min 550°C N₂, 2 - 1 h 550°C air, 3 - 10 h 550°C N₂, 4 - 10 h 600°C N₂, 5 - 10 h 600°C H₂/N₂, 6 - 5 h 700°C N₂.