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Cation-anion double hydrolysis derived mesoporous γ-Al_2O_3 as an environmentally friendly and efficient aldol reaction catalyst

Peng Bai, Pingping Wu, Guofeng Zhao, Zifeng Yan and X. S. Zhao*

1. Synthesis

The preparation of DHA samples was according to our previously established procedure with some modification.[3] 3.75 g of $Al(NO_3)_3.9H_2O$ and 4.52 g of Pluronic P123 were dissolved in 65 mL of deionized water under stirring at 40 ^oC for 16 h, then at 70 ^oC for 4 h. Another clear solution containing 2.46 g of $NaAlO_2$ and 10 mL of water was slowly dropped into the former one. White precipitate formed immediately. After further stirring at 70 ^oC for 4 h, the mixture was transferred into an autoclave and heated in an oven at different temperatures for 24 h. The solids were recovered by filtration, washed with deionized water, dried at 80 ^oC in a vacuum oven, and calcined at 500 ^oC for 2 h with a heating rate of 1 ^oC/ min. The final alumina samples are denoted as DHA-X, where X represents the crystallization temperature.

2. Characterization

X-ray powder diffraction (XRD) patterns were recorded on a XRD-6000 (Shimadzu, Japan) system with a Cu Kα radiation of wavelength λ = 0.15418 nm. ^{27}Al solid-state magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were collected on a Bruker DRX400 FT-NMR spectrometer. Nitrogen adsorption/desorption isotherms were measured on a Micromeritics TRISTAR 3000 analyzer at 77 K. The samples were degassed at 573 K for 4 h prior to analysis. The measurement of temperature-programmed desorption of CO_2 (CO_2-TPD) was performed on an automatic apparatus (ChemBET-3000 TPR/TPD, Quantachrome). The samples were pre-treated at 500 ºC for 1 h in a highly pure He atmosphere. After cooling down to room temperature, the samples were exposed to CO_2 for 30 min to allow adsorption of CO_2

to occur, followed by purging with He for another 30 min. Then, the adsorbed CO_2 was desorbed by increasing temperature from room temperature to 500 ^{o}C with a ramping rate of 10 ºC min^{-1}.

3. Catalysis

The self-condensation of cyclohexanone was carried out by stirring a mixture of cyclohexanone and alumina in a three-neck flask with water being continuously carried into a water-separating device in the form of a cyclohexanone-water azeotrope. The water was separated and the unreacted cyclohexanone flowed back to the reactor. The mixture was refluxed at 155 to 165 ºC for 2 h with a stirring rate of 200 rpm. The catalyst loading is 2 wt% and the alumina samples were ground and sieved to 120-140 mesh. For comparison purpose, commercial alumina samples with neutral, basic, and acidic surface properties (Sigma-Aldrich), denoted as C-Al_2O_3-n, C-Al_2O_3-b, and C-Al_2O_3-a, respectively, were also evaluated for comparison purpose. The reaction products were analyzed using a gas chromatograph (HP 6890 series GC) with a mass spectrometer detector (HP 5973 mass selective detector) and a capillary column (HP 5MS, L = 30 m, I.D. = 0.25 mm, Film thickness = 0.25 μm).

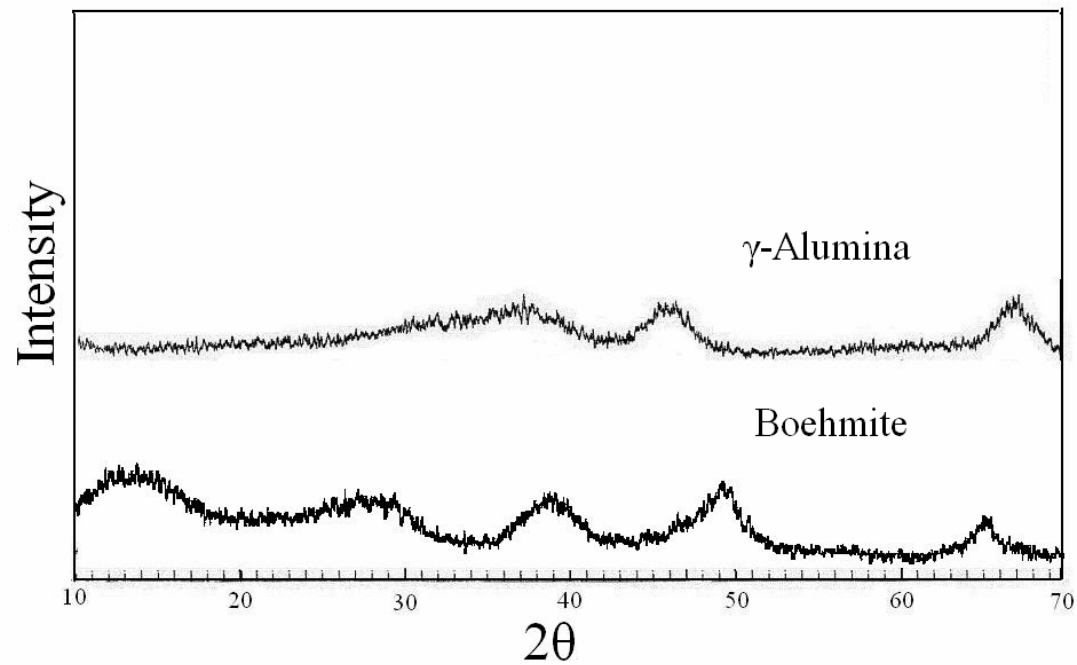

Fig. S1 XRD patterns of the mesoporous alumina before and after calcination reported in our previous work (P. Bai, W. Xing, Z. Zhang and Z. Yan, Mater. Lett., 2005, 59, 3128.).

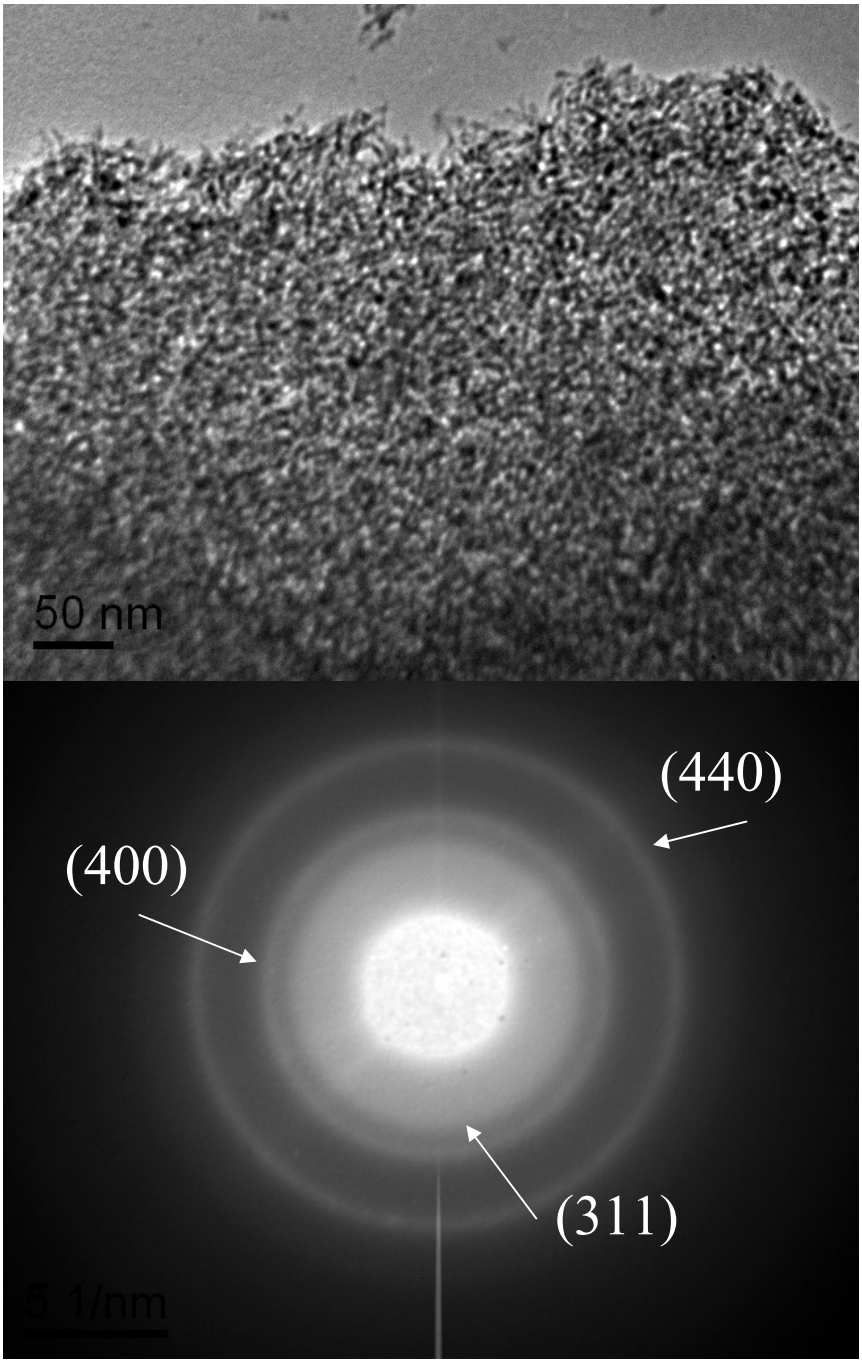

Fig. S2 TEM image and SAED pattern of the sample DHA-110.

Table S1 Structural properties of DHA and C-Al_2O_3 samples.

Samples [a]	S_{BET} (m^2/g)	D_{BJH} (nm)	V (cm^3/g)
C-Al_2O_3-a	203	4.5	0.35
C-Al_2O_3-b	247	4.3	0.43
C-Al_2O_3-n	248	4.3	0.45
DHA-80	471	3.5	0.51
DHA-100	410	7.1	0.81
DHA-110	414	5.2	0.59

[a] C-Al_2O_3-a, C-Al_2O_3-b, and C-Al_2O_3-n represent commercial acidic, basic, and neutral aluminas, respectively.

Table S2 Catalytic performance of the catalysts.

Catalysts	Conv. (wt %) [a]	Dimer yield (wt %)	Selectivity (wt %)			
			CHC [b]	CDC [c]	Dimer [d]	Other products [e]
C-Al_2O_3-a	19.0	18.9	80.7	18.7	99.4	0.6
C-Al_2O_3-n	36.0	35.4	81.6	16.7	98.3	1.7
C-Al_2O_3-b	50.8	49.9	81.1	17.1	98.2	1.8
DHA-80	95.6	82.2	68.6	17.4	86.0	14.0
DHA-100	77.9	71.7	74.4	17.6	92.0	8.0
DHA-110	79.7	73.9	74.6	18.1	92.7	7.3

a Conversion of cyclohexanone. b 2-(1-cyclohexenyl) cyclohexanone. c 2-cyclohexylidene cyclohexanone. d Sum of 2-(1-cyclohexenyl) cyclohexanone and 2-cyclohexylidene cyclohexanone. e Trimers and other products.

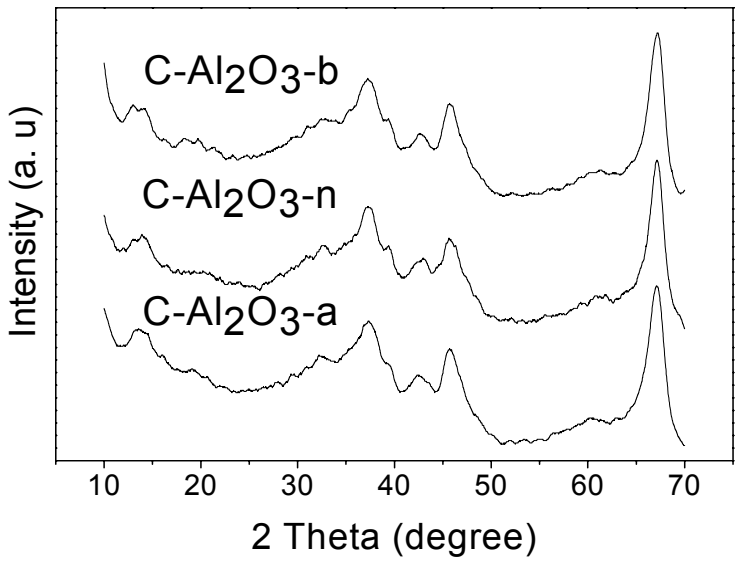

Fig. S3 XRD patterns of commercial alumina samples.

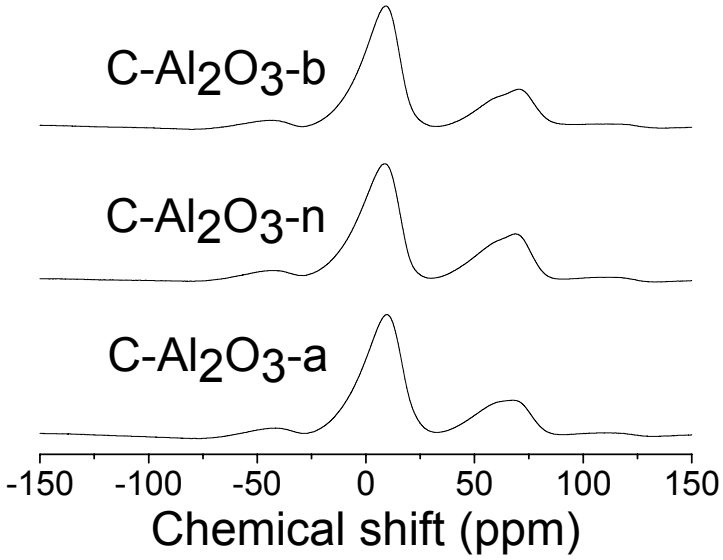

Fig. S4 ^{27}Al MAS NMR spectra of commercial alumina samples.