ELECTRONIC SUPPLEMENTARY MATERIAL (ESI) FOR NEW JOURNAL OF CHEMISTRY. THIS JOURNAL IS © THE ROYAL SOCIETY OF CHEMISTRY AND THE CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE 2015

Supplementary Information, New Journal of Chemistry

Downsizing K-CHA zeolite by a postmilling-recrystallization method for enhanced base-catalytic performance

Chokkalingam Anand,[a] Takeshi Kaneda,[b] Satoshi Inagaki,[c] Sae Okamura,[c] Hiroki Sakurai,[c] Kyosuke Sodeyama,[a] Taiji Matsumoto,[b] Yoshihiro Kubota,[c] Tatsuya Okubo[a] and Toru Wakihara[a]*

[a]Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

[b]Department of Materials Technology, Industrial Technology Centre of Tochigi Prefecture, 1-5-20, Yuinomori, Utsunomiya, 321-3226, Japan.

[c]Division of Materials Science and Chemical Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan.

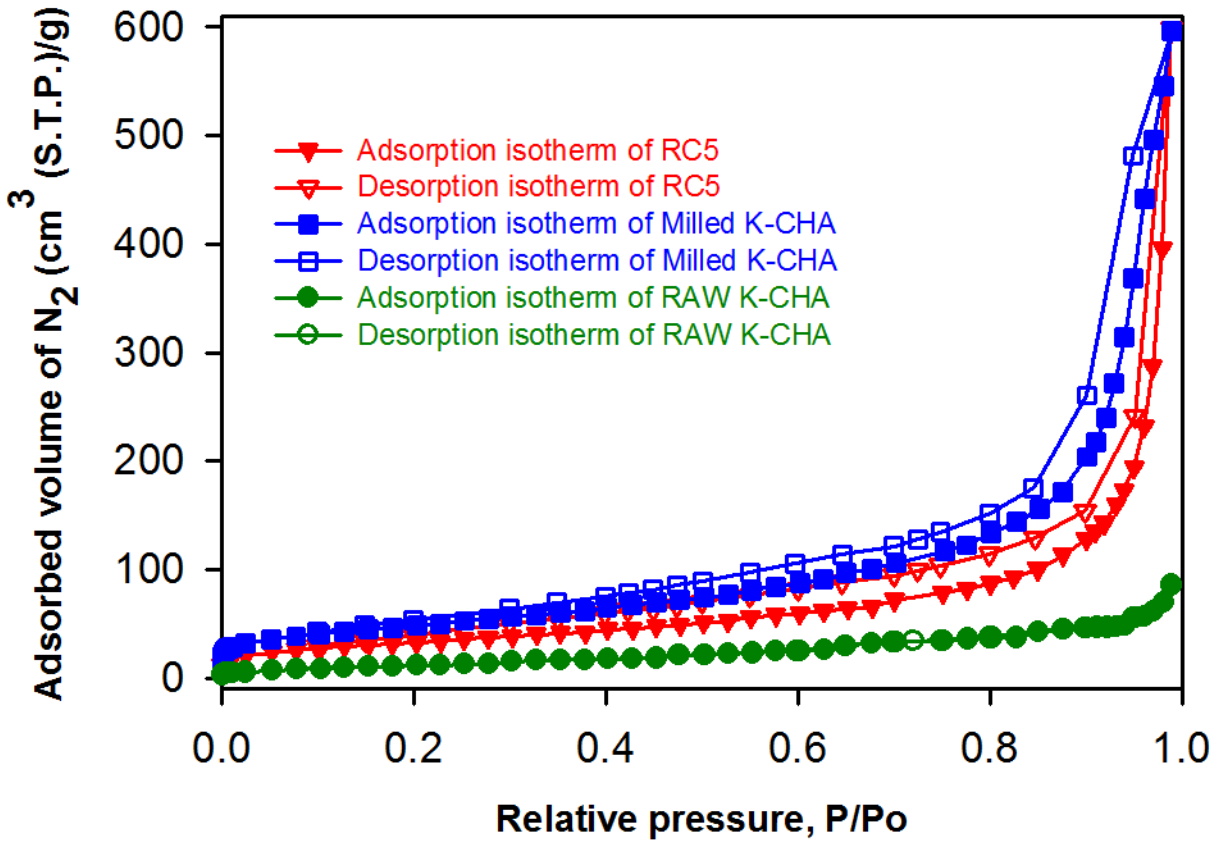

Fig. S1 N_2 adsorption-desorption isotherms of raw, milled and RC5 K-CHA samples.

Table S1. Comparison of catalytic performance of K-CHA samples

Sample	2M KOH added (g)	RC temperature (K)	RC duration (hour)	Crystallinity (%)	Yield (%)	BET surface area ($m^2 g^{-1}$)	Product yield in the catalytic reaction (%)[a]
Raw	0	0	0	100	100	11	35
Milled	0	0	0	11	100	96	46
RC1	0.4	413	5	46	94	110	50
RC4	1.2	413	2	79	92	77	61
RC5	1.2	413	5	80	91	65	80

a. Reaction conditions: catalyst, 30 mg; temperature, 353 K; time, 60 min; benzaldehyde, 1.2 mmol (130 mg); ethyl cyanoacetate, 1.4 mmol (160 mg); solvent, EtOH (ca. 3.0 mL).

Results and Discussion

The average surface area for H-CHA samples is approximately between 500-600 $m^2 g^{-1}$, (see references below) majority of which are confined into their microporous region. However, impregnation of potassium tends to block the microporous entrances of the K-CHA zeolite prohibiting the detection of these surfaces during N_2 adsorption-desorption analysis. Therefore, the surface area of K-CHA samples listed in Table 2 and Table S1, presumably is due to the external surface area as observed from their respective N_2 adsorption-desorption isotherms displayed in Figure S1. In addition, Figure S1 shows a variation in the volume of nitrogen adsorbed (y axis) by K-CHA samples relative to their respective surface areas (Table 2) and particle size differences (Fig. 2).

Table S1 compares the catalytic performances of raw, milled and recrystallized K-CHA samples. The catalytic yield increased from 35 to 80 % as a result of bead-milling and postmilling-recrystallization. The KOH content, time and temperature used for recrystallizing RC5 were found to be optimum as it yielded 80% catalytic product. Further, the lower yield of RC4 (61%), while possessing crystallinity equivalent to RC5, strongly reiterates the fact that the recrystallization conditions (longer RC duration, 5 hours) used for RC5 is highly inevitable for enhanced catalytic performance.

References

1 H.-X. Li, W. E. Cormier, B. Moden, EU Patent 2512988, 2011.
2 F. N. Ridha, Y. Yang, P. A. Webley, *Micropor. Mesopor. Mater.,* 2009, **117**, 497.