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COMMUNICATION

Effect of Aluminum Distribution in ZSM-22 Zeolite on Ethylene Oligomerization

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Olefin oligomerization is a crucial process for fuel and chemicals production. Here, we report in ZSM-22 zeolite, paired aluminum sites are more effective than isolated aluminum sites in ethylene oligomerization, giving higher conversion and forming heavier oligomers. This highlights the importance of modulating aluminum organization in zeolite for catalysis.

Zeolites are the catalytic workhorses of a variety of reactions, because of their inherent acidity generally associated with aluminum[1,2]. Recently, there was a growing interest from academy in exploring the proximal Al sites or paired Al sites to tune the catalytic performance[3,4]. To date, most studies have been focused on three-dimensional or two-dimensional zeolites, including ZSM-5[5,6], ferrierite[7], mordenite[8], beta[9], and SSZ-13[10]. However, the uneven distribution of Al among different channels could have an additional influence on catalytic performance, which cannot be completely excluded.

In light of this, one-dimensional (1D) zeolites should be more suitable for such investigation due to the presence of unique microporous and non-intersecting pore channel[11]. Besides, 1D zeolites have been found to be effective for isomerization and oligomerization, due to their exceptional shape-selectivity[12,13]. In this report, we chose ZSM-22 (1D) as study subject, which possesses TON-type framework and 10-membered ring channels. We prepared a series of H-ZSM-22 zeolite samples with comparable Al content, crystal size and morphology, but varying the number of Al pairs. We then evaluate their performance in the ethylene oligomerization reaction. The results reveal a clear relationship between the abundance of aluminum pairs and the oligomerization behavior of this zeolite.

Three zeolite samples, named HZ-25(19%), HZ-27(10%), HZ-34(17%), were synthesized in our laboratory based on a previous literature report[14], and the fourth sample named HZ-35(12%) was purchased. All samples have TON topology, as confirmed by X-ray diffraction (**Fig. 1**). Samples were prepared in their H-form *via* a typical NH_4^+ ion-exchange followed by calcination procedure. The Si/Al ratio of zeolite was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), as indicated in the sample code HZ-x, where x is the Si/Al ratio. In general, based on Si/Al ratios, four samples can be classified into two groups: Group I with a ratio around 25-27, and Group II with a ratio around 34-35.

Fig. 1 Powder XRD patterns of samples.

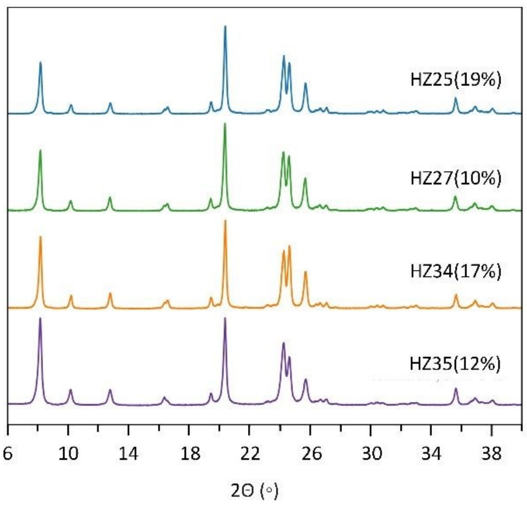

Fig.2 shows the electron micrographs, where typical rod-like morphology was observed in all samples. All crystals are nanosized, showing similar sizes of ~50 nm in [100] and [010] dimensions, with different lengths in [001] direction. The crystals for the two samples of Group I fall within the same length range of 100~350 nm, while the Group II crystals possess larger sizes of 150-500 nm in [001] direction. The acidity was probed by pyridine-IR, and the quantities of Brønsted acid sites (BAS) and Lewis acid sites (LAS) were estimated and listed in **Table 1**. Given that BAS are predominant across all the samples, the influence of LAS on catalytic performance is likely minimal. For zeolites with similar Si/Al ratio, the BAS concentration is

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relatively similar. For example, the BAS concentrations for HZ-25(19%) and HZ-27(10%) are 179 and 161 μmol g^{-1}, respectively. No significant difference in the acid properties was observed based on temperature-programmed desorption (TPD) of NH_3 (**Fig. S1**). Also, these two samples do not differ much in external surface acidity (**Fig. S2**). **Table S1** lists the elemental textural properties, where HZ-25(19%) and HZ-27(10%) exhibit similar surface areas (~160-170 m^2 g^{-1}), micropore volumes (~0.05 cm^3 g^{-1}) and total pore volumes (~ 0.2 cm^3 g^{-1}).

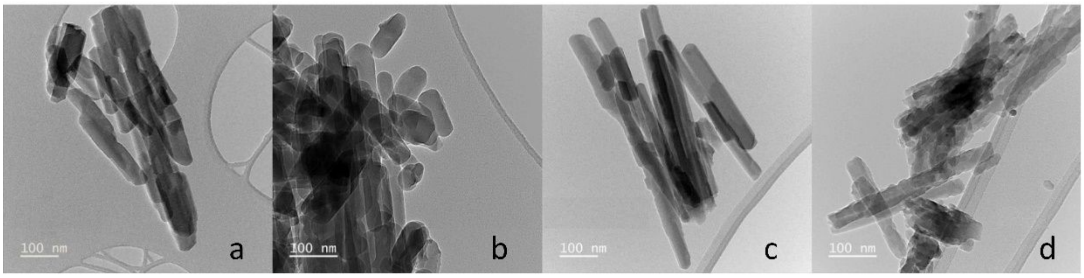

Fig. 2 Transmission electron microscopy images of samples. (a) HZ-25(19%). (b) HZ-27(10%). (c) HZ-34(17%). (d) HZ-35(12%).

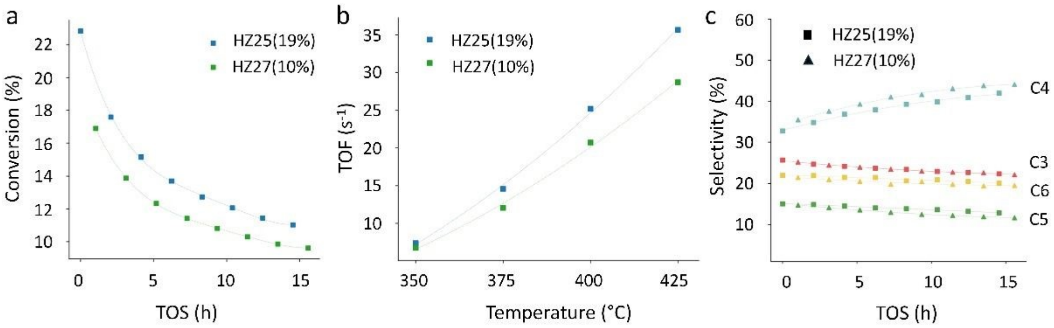

Fig. 3 (a) Conversion of ethylene at 400 °C. (b) TOF at different temperatures (c) Product selectivities at 400 °C. Reaction conditions: 1 bar, WHSV = 5 h^{-1}.

Table 1. The concentrations of BAS and LAS probed by pyridine-IR.

	Samples	BAS (μmol g^{-1})	LAS (μmol g^{-1})	Si/Al	Al-pair percent
Group I	HZ-25(19%)	179	7	25	19%
	HZ-27(10%)	161	10	27	10%
Group II	HZ-34(17%)	155	13	34	17%
	HZ-35(12%)	136	17	35	12%

To investigate the proximity of aluminum atoms, a titration method using Co^{2+} cations as probe was employed[15]. In principle, two negative AlO^- charges in close proximity are required at the cationic site to balance the positive charge of Co^{2+}. Therefore, only two paired Al sites located in one zeolite ring can accommodate the Co^{2+} hexaaqua complexes. In contrast, the Al atoms located far from each other cannot accommodate Co^{2+} hexaaqua complexes or bare Co^{2+} cations after dehydration and should be regarded as isolated Al sites. The amount of Co after the ion-exchanging process using a cobalt acetate solution was determined by ICP-OES (**Table 1**). It is observed that the ZSM-22 samples with similar Si/Al ratios exhibited different percentages of paired Al, as indicated in the sample code HZ-x(y), where y is the percentage of paired Al sites in total Al sites. The feasibility of experimentally determined Co-exchangeable Al fraction was also confirmed by Monte-Carlo calculation.

After confirming that the samples possess comparable compositions and textural properties but differ in the abundance of aluminum pairs, the catalytic performance of two H-ZSM-22 zeolites, namely HZ-25(19%) and HZ-27(10%), was extensively examined and compared in ethylene oligomerization, owing to the pronounced difference of their Al pairs fractions. The reaction was conducted at 350-425 °C and atmospheric pressure, with a weight hourly space velocity (WHSV) of 5 h^{-1}. Ethylene conversion decreased with reaction time for both samples, most likely as a result of coke formation. However, at all temperatures, HZ-25(19%) exhibited higher conversions compared to HZ-27(10%), as shown in **Fig. 3a** and **Fig. S3**. To normalize the activity of per Brønsted acid site, turnover frequency (TOF), defined as the mole of ethylene converted per mole of BAS per second, was also calculated (**Fig. 3b**). The higher activity of BAS associated with HZ-25(19%) was also observed. The main products of reaction were C3-C6 olefins, and their selectivities with time were plotted in **Fig. 3c** and **Fig. S4**. Interestingly, a higher fraction of heavier olefins were produced over the sample with more acid pairs (HZ-25(19%)), particularly C5 and C6 olefins, which likely arise from consecutive oligomerization steps occurring at paired sites. In contrast, a higher selectivity to C4 olefins was observed over HZ-27(10%), which was produced by one-step dimerization of two ethylene. We expect the above differences in activity and selectivity should be related to the amount of paired Al sites. Such trend was also observed for HZ-34(17%) and HZ-35(12%) samples (**Fig. S5**).

To elucidate the activity difference between paired and isolated Al sites, we resort to DFT calculations. We first considered the possible influence of acidic strength, since ethylene oligomerization is mainly catalyzed by BAS in zeolites. The deprotonation energy (DPE) is a widely used indicator for acidic strength, which is defined as the energy needed to remove a bonded proton from the anionic zeolite structure (Z^-) to an infinite, non-interacting distance ($ZH \rightarrow Z^- + H^+$). Our calculation results suggest that the energy difference over isolated and paired acid modes is quite small (**Fig. S6**). This observation is consistent with previous reports showing no significant difference in the acid properties of isolated Al sites and Al pairs[16,17].

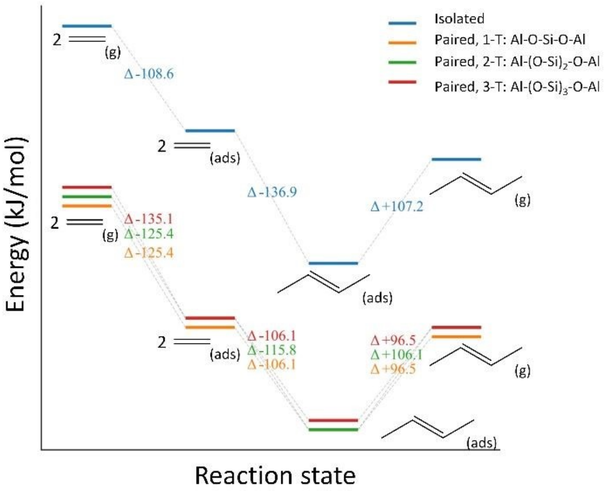

Fig. 4 The energy profile diagrams for ethylene to butene. The number in the legend represents the number of T-sites (Si atoms) between paired Al sites.

To further elucidate the reaction energetics, static calculations were employed to quantify adsorption and reaction energies along the ethylene-to-butene pathway. The model comprises the unoccupied zeolite with ethylene, the ethylene-adsorbed zeolite, the butene-adsorbed zeolite, and the regenerated zeolite with desorbed butene (**Fig. 4**). The results indicate that the adsorption of two ethylene molecules is more favorable in models with closely located aluminum sites, being more exothermic and more feasible by ~16-26 kJ/mol. After adsorption, the molecules undergo the oligomerization reaction, which produces a single butene molecule. Slight difference for total energies were observed between isolated (-138.3 kJ mol^{-1}) and paired acid sites (-135.0 ~ -144.7 kJ mol^{-1}). Accordingly, we conclude that the ethylene adsorption ensured by the paired acid site case is stronger than in the isolated models, which promotes the reaction proceeding. We expect that the oligomerization intermediates are also more likely to stabilize close to paired acid sites, which facilitates the occurring of further reactions, as observed experimentally. These observations also validate previous experimental work which reported that the oligomerization of propene over proximal acid sites was higher in turnover rates per Al(H^+) than over those with isolated acid sites in H-ZSM-5[18].

In summary, we show that in one-dimensional ZSM-22 zeolite, the paired Al sites are more active than isolated Al sites in ethylene oligomerization. Our work also illustrates how to develop high-performing zeolite catalysts for olefins oligomerization by controlling acid size distribution at the nanoscale.

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Author contributions

Teng Li: Conceptualization, Validation, Data curation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. Yazeed Alfawaz: Validation, Data curation, Formal analysis, Investigation. Stefan Nastase: Validation, Data curation, Formal analysis, Investigation. Juan Carlos Navarro de Miguel: Validation, Data curation. Luigi Cavallo: Conceptualization, Supervision, Writing – review & editing, Investigation. Javier Ruiz-Martinez: Conceptualization, Supervision, Writing – original draft, Writing – review & editing, Funding acquisition, Investigation.

Conflicts of interest

The authors declare no conflict of interest.

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Data availability

Data will be made available on request

Notes and references

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Data Availability Statement

Data will be made available on request.