Factor which Affect ZSM-5 Acidity

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ABSTRACT

Zeolite is a crystal which have bonding with Silicone and Aluminum with pores inside the crystal and connected in a certain structure. Due to zeolites function, demand of zeolite has been increasing lately. The Acid or active part takes a lead to many chemical processes. Many methods to synthesized Zeolites and form its structure or frameworks. Zeolites' acidity can be affected by the structure itself. Such as the amount of Si/Al molar ratio also cations that fill in the zeolite template. Analysis using IR has been used to determine the absorbance of pyridine by zeolite to determine the acidity of zeolite. Zeolite which used by IR analysis is ZSM-5.

Keywords: Zeolite, Acidity, ZSM-5, Si/Al amount.

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1. INTRODUCTION

Zeolite is a crystal which have bonding with Silicone and Aluminum with pores inside the crystal and connected in a certain structure. The active part for acid and redox-catalyzed reaction and largely use in many chemical processes is the negative charge which could stabilize a whole structure by using metal ion counters species located inside the inner pore volume(Hartanto et al., 2016). Due to the fact that zeolite made by Silicone and Aluminum, zeolite can be synthesized by metakaolin as the main source of Silicone and Aluminum (Hartanto et al., 2016). Many chemical processes using zeolite as their reactant (Hartanto et al., 2019). Zeolite which has many

functions such as alkylation and isomerization reactions, catalytic hydrocarbon cracking as well as for the conversion of ethanol to hydrocarbon, and adsorption of dyes and heavy metal ions (Hartanto et al., 2019). Many dyes used in the industry and throw it away carelessly without any waste treatment and It could also create a serious environmental problem (Iryani et al., 2017). Even though many methods can reduce it regularly. For example, using one of zeolites type like ZSM-5 synthesized from Kaolin Bangka raw material and the result are used as adsorbent for dyestuff waste. And it works for textile base dye waste (Iryani and Hartanto, 2018).

Reaction formed by acid-base react with each other. Bronsted-Lowry have already mentioned the definition of acid and base. Any substance that acts as a proton donor should be classified as an acid, and any substance that acts as a proton acceptor should be classified as a base (Atkins, 2010). Besides Bronsted-Lowry, Lewis also define acid and base. Lewis defined a base as an electron-pair donor and an acid as an electron-pair acceptor (Miessler et al., 2014). In Lewis acid-base concept, there is a theory acid-base hardness and softness. A small cation, which are not easily polarized, are hard and form complexes with small anions. Large cations are more polarizable and are soft. Hard and soft acids and bases are identified empirically by the trends in stabilities of the complexes that they form. Hard acids tend to bind to hard bases and soft acids tend to bind to soft bases. And also, what makes them really different is Hard acid–base interactions are electrostatic and soft acid–base interactions are covalent (Atkins, 2010).

Acid and base properties in Zeolite can be effected by the amount of Aluminium and silica in the structure. Negative charge of AlO_4^- effect the active part of a zeolite. It could control the Bronsted and Lewis acidic strength, increase and decrease of Aluminium can increase or decrease the strength of zeolite acidity. It depends on controllable aluminium siting sites in T-O-T structure to enhance acidity. Also many experiment shows that Si also have dominant role to determine the strength of acidity in zeolites (Hartanto et al., 2016). Furthermore, the aluminum ions act as highly acidic sites that can catalyze a number of chemical reactions (Sahner, Hagen, Schöner, Reiß, & Moos, 2008). So, this review Article show the zeolites acidity.

2. RESULT

2.1 Zeolites Acidity

2.1.1 Multilamellar in zeolites

From the ^1H NMR spectra we can conclude that the Brønsted acidity decreases with increasing multilamellar ZSM-5 template length. For multilamellar zeolites, the acidity decreases when the number of quaternary ammonium centers in the template is increased. For unilamellar zeolites, this trend is less obvious. The acidity was further examined by use of IR spectroscopy of adsorbed pyridine and 2,4,6-collidine. The amount of total Brønsted and Lewis acidities determined after evacuation at 150°C are listed in Table 1. (Leilei Wu, 2013)

Sample	Si/Al Ratio	[Al]	27 Al NMR			Pyridine IR		Collidine IR
		(mmol/g)	[Fal]	[EFAI]	[Fal]NH ₃	[BAS]	[LAS]	[external BAS]
		(mmol/g)	(mmol/g)	(mmol/g)	(mmol/g)	(mmol/g)	(mmol/g)	(mmol/g)
HZSM-5(40)	40	0.41	0.32	0.09	0.39	0.28	0.07	0.022
HZSM-5(27)	27	0.60	0.56	0.04	0.60	0.53	0.11	0.018
MesoMFI(2, Br)	45	0.36	0.24	0.13	0.38	0.20	0.09	0.055
MesoMFI(3, Br)	47	0.35	0.30	0.16	0.46	0.15	0.10	0.079
MesoMFI(4, Br)	46	0.35	0.23	0.20	0.30	0.07	0.10	0.078
MesoMFI(2, OH)	31	0.52	0.28	0.19	0.42	0.23	0.18	0.117
MesoMFI(3, OH)	32	0.51	0.34	0.16	0.46	0.30	0.20	0.127
MesoMFI(4, OH)	41	0.400	0.21	0.09	0.40	0.13	0.23	0.105

Table 1. Si/Al ratio, the concentration of Al ([Al]), framework Al ([FAI]) and extraframework Al ([EFAI]) in HZSM-5 and the meso MFI zeolites as determined from ICP and ^{27}Al NMR, compared to the concentration of Brønsted Acid Sites ([BAS]), Lewis Acid Sites ([LAS]) and external Brønsted acid sites ([eBAS]) from IR measurement with pyridine and 2,4,6-collidine adsorption (Leilei Wu, 2013)

2.1.2 Si/Al Ratio in Zeolites

There are data were analyzed using Infrared with the vibrations between $1422\text{--}1419\text{ cm}^{-1}$ for the pyridine which bound coordinatively with the Lewis acidic site. Meanwhile for the pyridine that adsorbed with the Bronsted acidic site, the vibrations happens within the range between $1548\text{--}1545\text{ cm}^{-1}$ (Li and Wu, 2003). The vibrations within the range between $1650\text{--}1620\text{ cm}^{-1}$ is for the xylanol group as Bronsted acidic sites (Nasikin, et.al. 2013 ; Amin and Anggoro, 2003).

The increasing of xylanol group (Bronsted acid) and the silica defects (Lewis Acid) shows that when the molar ratios of Si/Al were increased, the vibration adsorption bands will also increased. The Bronsted and Lewis acidic sites spectra broadening depends on the increasing of molar ratios Si/Al. Based on the Figure 1, the peak intensities of Si/Al molar ratios 50 and 60 increased rapidly compared to Si/Al molar ratios 30 and 40 (Hartanto, et.al., 2016).

Fig. 1 FTIR spectra of pyridine adsorbed on ZSM-5 zeolite that contained the series of Si/Al molar ratios with (a) Si/Al 30, (b) Si/Al 40, (c) Si/Al 50 and (d) Si/Al 60 (Hartanto, et.al., 2016).

2.1.3 Structure and Bronsted Acidity of Protonic Sites of H-Zeolites

The protonic zeolites acidity of Bronsted is based on the group OH bridge. In the dry zeolites, the acidic protons linked with oxygen atom in covalent bond that connecting aluminium and silicon which called as the “perturbed xylanol group” where a lone pair in the oxygen atom interacts through a Lewis base acid bond to the nearest Al atom where this interactions condition is more liked exothermically and thermodynamically. However, there is no significant results from this interaction in the non-zeolit mixture although it made from silica and alumina. The deposition of silica on alumina doesn’t occur in the strongly acidic bond xylanol, but only happen to the weak one (Finocchio, et.al., 1997 ; Mouat, et.al., 2005). Because the Al ions make strong interaction with three oxygen atoms, a xylanol become in the terminal form which

causing the silicate more stabilized. The stabilization of the OH Bond depends on the total amount of silica because the more silica makes the framework of the silica based zeolite with high covalent becoming rich. The stabilizing contribution can also be given by the weak interaction of protons with OH bond with the other oxygen atoms (Busca, 2017).

There are several factors that affect to the strong protonic activities. The hydrogen bonding activity (occur without real proton jump like in the CO bonding) the interaction between OH an aluminium ion bridging with xylanols is increased strongly cause the hidroxy group brided and the protons become more cationic. That means the Bronsted acid sites become stronger as the more base that is protonated being stabilized and the more deprotonated anionic site is stabilized. The Van der Waals interaction with the walls cavities with the xyloxane bridges in the zeolite cages based on the stabilization of the protonated molecules by the "tridimensional solvation" is the reason why the protonic centers in zeolites has high acidity (Busca, 2017). Figure 2 contain The scheme of adsorption of pyridine on Bronsted acid sites of zeolites. (Busca, 2017).

Fig. 2 The scheme of adsorption of pyridine on Bronsted acid sites of zeolites (Busca, 2017).

3. CONCLUSION

A different structure of zeolites makes a different acidity. The Brønsted acidity decreases with increasing template length for the multilamellar ZSM-5 zeolites. For multilamellar zeolites, the acidity strongly decreases with an

increase of the number of quaternary ammonium centers in the template and also there is correlation between types of ZSM-5 framework lattice vibrations (band wavenumber) with a series of Si/Al molar ratios. The adsorption bands of Bronsted and Lewis acidic sites also become broader with increasing of molar ratios Si/Al.

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