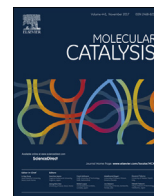




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Analysis and interpretation of acidic nature of aluminosilicates

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ABSTRACT

Aluminosilicate solid acid catalysts, especially zeolites, have been widely utilized in petroleum refinery and environmentally benign chemical processes. The acidic property of aluminosilicates has been a subject of advanced studies. Recently an ammonia IRMS-TPD (infrared/mass spectroscopy temperature-programmed desorption) method, an application of operando technique, has been developed to quantify the number and strength distribution of each of Brønsted and Lewis sites on a solid. With an aid of quantum chemistry, relationships among the composition, structure and acidic property are being unveiled to totally understand the chemistry of SiOHAl unit in the aluminosilicates.

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1. Importance of analysis of solid acidity

Nowadays, we recognize that Brønsted and Lewis acids are different concepts, although they show similar behaviors. The similarity had confused the interpretation of acid base chemistry until 1920's, when Brønsted [1], Lowry [2], Lewis [3] and other researchers discussed and established the definition of acid and base. A number of literatures published in this period evidencing the presence of serious discussion tell us that practical importance of acid base chemistry had already been recognized in this period. It is supposed that they did not discuss on the definition of materials which changed the color of a specific moss, but they discussed for proper understanding of a series of materials which showed important function such as catalysis.

After 100 years, we still have similar discussion on solid surfaces. Throughout the petroleum era, solid acid catalysts, mainly zeolites and other aluminosilicates, have been utilized in many processes such as fluid catalytic cracking (FCC) [4–6], hydrocracking/hydrotreatment [7] and skeletal isomerization [8] in petroleum refinery (Fig. 1) [9,10]. Mainly later than 1980, replacement of liquid acid catalysts with solid acid catalysts realized various environmentally benign chemical processes [11–13], e.g., alkylation-dealkylation of mono-cyclic aromatic compounds [14–18], hydration [19], amination of alcohols [20,21] and phenol [22], Chichibabin condensation [23], and Beckmann rearrange-

ment [24]. Many of materials are now called solid acids, and they are industrially important due to their usage of catalysts, but the type of acid sites, Brønsted or Lewis, or, in some cases, even the presence of acid sites is unclear. However, many kinds of materials are called solid acids, because they show catalytic functions like those of acidic ion exchange resins and H-form zeolites, in which the protons have been clarified to act as Brønsted acid sites. Even on zeolites, relationships among the composition, structure and acidic property have been subjects of serious discussion for finding principles controlling the nature and role of acid sites [25].

To solve energy and environmental problems, development of efficient solid acid catalysts is strongly demanded. The catalysis of solid acid is fundamentally owing to the chemical action of acid sites, in many cases Brønsted acid sites, and therefore it should be necessary to investigate the acidic properties of solid acid catalysts especially aluminosilicates.

In addition, the aluminosilicates, especially zeolites, are utilized as catalyst supports of transition metals and ion exchangers. These functions are also generated by ion exchange ability of aluminosilicates, which may be related with the Brønsted acidic property in their proton forms [26]. Degree of stabilization and electronic nature of transition metal species in atomic dimension held by the ion exchange site are related with the Brønsted acid strength in the H-form of zeolite [27,28]. Such mono-atomically dispersed metal species shows chemical function which is never seen on bulk materials [29].

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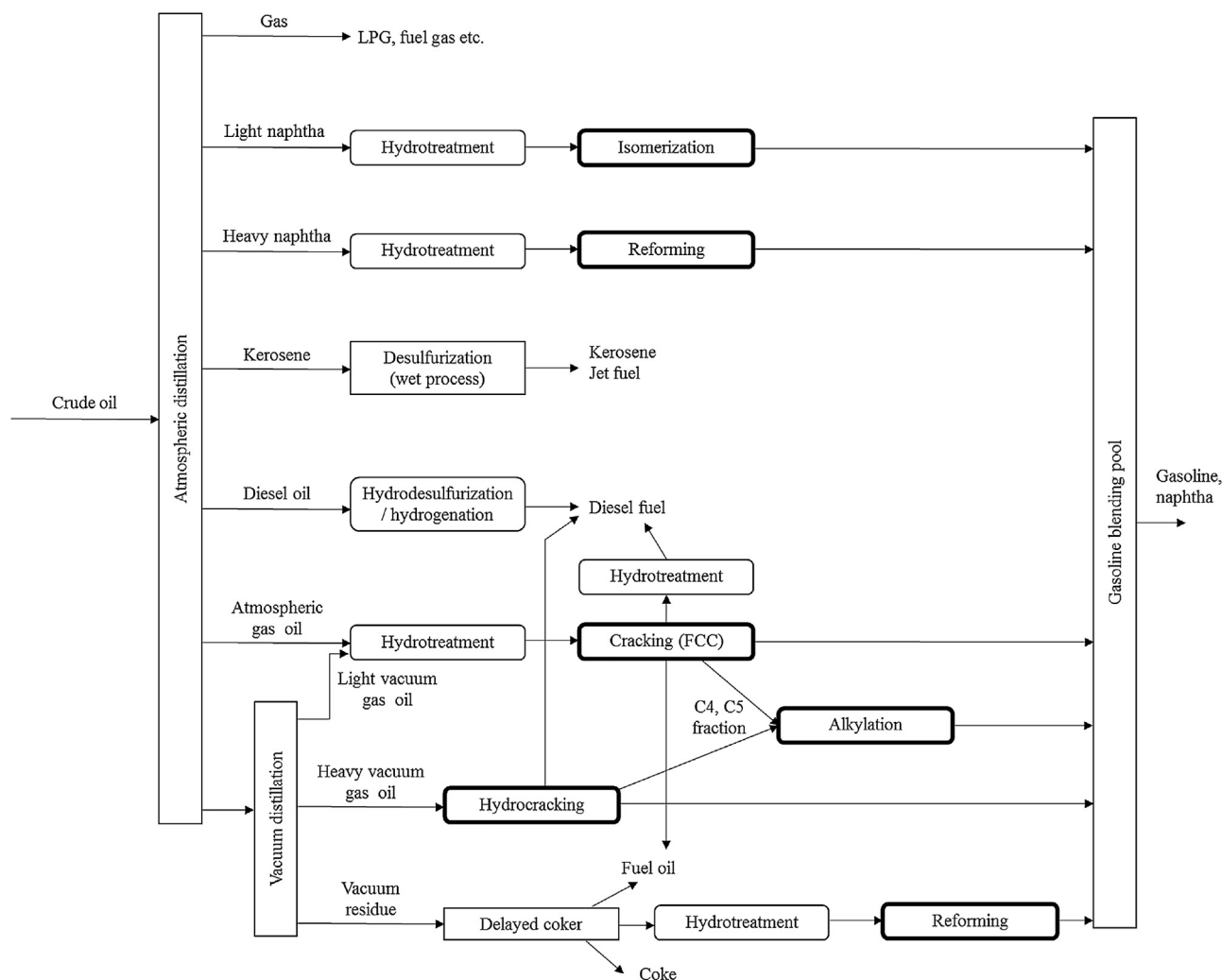


Fig. 1. Schematic drawing of hydrocarbon flow in typical petroleum refinery. Thick rectangles show the processes where aluminosilicates are used as solid acid catalysts.

From these backgrounds, we believe that the analysis of Brønsted acidic property is an important subject. One distinct feature of zeolites is microporosity, and most of commercial amorphous silica alumina catalysts are mesoporous. Therefore, identification of the effects of porosity and acidic property is necessary for fundamental understanding of the catalysis. Nowadays, the analysis of porous nature has been established, but the analysis of acidic properties of solids have been under development. This short review as a proceeding of the plenary lecture in Acid-Base Catalysis 8 describes advances in the measurements and interpretation of acidic properties of zeolites giving new insights on relationships among the composition, structure and acidic property.

2. Advances in measurements of acidic properties of solids

The acidic property of a solid is described by the number (amount), strength and type (Brønsted or Lewis) of acid sites on it. According to the definition by Brønsted, the strength of Brønsted acid site on a solid surface should be shown by some parameters describing the position of equilibrium of the following reaction, i.e., protonation of a probe base:



where $\text{H}-\text{A}$ is the discussed Brønsted acid site, and $\text{B}(\text{g})$ is vapor of probe base. Similarly, the strength of Lewis acid site should be

shown by those of the following reaction, i.e., coordination of a probe base [13]:



where L shows the Lewis acidic species, and $:$ shows a pair of electron. As the parameters, equilibrium constant and standard Gibbs energy at a specific temperature such as 298 K, or, a set of standard enthalpy (reaction heat) and standard entropy can be used.

Table 1 lists methods typically used for the measurements of acidic properties of solids. They are classified into [i] titration-based techniques to mainly quantify the number and strength of acid sites such as indicator and ammonia temperature-programmed desorption (TPD) methods, including H/D exchange [30], and [ii] spectroscopy-based techniques to mainly identify Brønsted and Lewis acid sites such as infrared spectroscopy (IR) of adsorbed pyridine and carbon monoxide. By combining these two principles, Niwa et al. developed a method of ammonia infrared/mass spectroscopy temperature-programmed desorption (IRMS-TPD) [31]. It is noteworthy that the IR measurement of adsorbed pyridine can give a way of quantification of the Brønsted and Lewis acid sites on the assumption that the molar extinction coefficient is constant as proposed by Emeis [32].

It should be noted that, apart from the techniques, amines like ammonia and pyridine are protonated by the Brønsted acid site and chemically coordinate to Lewis acid site giving parameters related to the equilibrium, whereas such molecules as argon, car-

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