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Synthesis and New Potential Application of Sn-Beta Zeolite in Sugar Industry

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The Sn-beta zeolite (silica zeolite beta inserted in tin atoms) is a new catalytic material with unique properties, which shows its great talent in the industry of petrochemical, fine chemical and sugar industry. In this paper, we briefly introduce the source of its singularity and synthetic methods of the new-style heterogeneous molecular sieve. In addition, we put forward the prospect of the industrial application in the conversion of glucose.

Keywords: Sn-beta zeolite, Catalytic material, Synthetic method, Heterogeneous molecular sieve, Conversion of glucose.

INTRODUCTION

The Sn-beta zeolite is a kind of modified molecular sieves of the highly siliceous beta zeolite whose framework is substituted with tin atoms. Sn-beta zeolite has shown its high catalysis for many conversions of organic compounds which have a carbonyl functional group. When applied into the catalytic reactions, Sn-beta zeolite showed its good thermal stability, high catalytic activity and recovery. Sn-beta was firstly synthesized by Corma *et al.*[1] in 2001 and then applied in many other important organic reactions[2-10]. In recent years, the synthesis method of Sn-beta zeolite has brought a vast interest, which contributes to more environment-friendly and energy saving routings as well as it boosts the Sn-beta applied industry. In this research, a summary and perspective research are reported.

Preponderance of Sn-beta: The zeolite is one of the heterogeneous catalysts which are famous for their easy retrieving and high recovery. The beta zeolite was initially synthesized by Wadlinger *et al.*[11] in 1967, but unfortunately it failed to get attention of the industry owing to the lack of the relative structure determination. It was in 1988 that Higgins *et al.*[12] reveal its unique 3D structure and emphasize beta zeolite is the only one that posses both the 12-member-ring cross channel system and the high content of silicon. Ever since, this special zeolite has always been catching the eyes of scientists.

Many kinds of modified zeolite molecular sieves have been synthesized since Blasco *et al.*[13] successfully introduced tin atoms into the beta zeolite framework and achieved excellent performance in the adsorption experiments[14,15]. Sn-beta showed its preponderance when it came to the organic compounds having the carbonyl function group. The tin atom has the special lowest unoccupied molecular orbital which gives the Sn-beta zeolite the properties of Lewis acid. Besides the good performance in the Meerwein-Ponndorf-Verley reduction and Baeyer-Villiger oxidation[2-10], the Sn-beta has been found to have prominent activities in the isomerization of glucose[16], conversion of carbohydrates to its derivatives[17], the cyclization of citronellal and oppenauer oxidation in quick succession[18]. Compared with Ti-beta zeolite, Sn-beta seemed to be almighty dealing with the carbonyl compounds *via* the shift of hydrogen atom and carbon atom in some cases.

The Lewis acidity is highly determined by the framework of the zeolite beta, which is always considered to be the key of the outstanding catalytic activity. The bonding site of the Sn atom substituted is of much interest. From the early research, we have already known that there are nine different T-sites in the zeolite beta which can be substituted by metal hetero atom[19]. Considering their different topological surroundings, the nine sites are divided into three groups. Group one is the sites without any four-member rings. Group two is the sites group with the only four-member ring. Group three concludes the sites which are involved in two four-member rings. The location of the metal hetero atom substituted have been detected *via* many technique methods such as PXRD, MAS NMR, IR spectroscopy and neutron scattering. Many experiment data shows that there indeed exists some prior site. Shetty *et al.*[20] put forward that T_2 which is associated with the group two has the highest cohesive energy and smallest HOMO-LUMO energies gap, resulting in the most potential site to be substituted.

Synthesis of Sn-beta: Now that Sn-beta zeolite shows its excellent performance in the industry, many scientists devote themselves in the synthesis of the catalyst. Some neotype syntheses have been put forward.

The most common method of the preparation is as reported in the initial syntheses. They get the target product by adding some fluoride ion into the hydrothermal system. It is reported that a certain amount of fluorine ion can make zeolite crystallizing in system close to neutral medium. It is also believed that the fluoride ion can balance the cations of the templates to avoid the defects. The zeolite synthesis in fluoride medium has good hydrophobic property so that it always shows superior performance in the catalytic reactions. The conventional preparation also requires the seed crystals and silicon alkoxides as the removals. Besides long time of syntheses processing, the traditional method run the risk of introducing the hydrofluoric acid to produce some disastrous pollutions. Some researchers also question that the ratio of H_2O to SiO_2 is difficult to control by using the common method.

In 2011, Li *et al.*[21] reported a new syntheses to avoid the deficiency of the traditional method. In his study, the Sn-beta zeolite is obtained *via* a gas-solid reaction on the basis of Al-beta which has been modified by dealumination. Though the whole syntheses process is to certain extent complex, it solves the low reproducibility and gives a good control of the ratio. For improvement this reaction requires at high temperature, which cost much extra energy. Some energy-saving measure should be taken.

In 2012, Kang *et al.*[22,23] introduced a attractive syntheses which is assisted by steam. This new route has some advantages on the time saving and the milder condition. They also studied the factors affecting the syntheses of Sn-beta. The good performance in the Baeyer-Villiger reaction gives it a strong support for scaling up.

The conventional method is still the main method to produce the Sn-beta sample. New method are heading-grabbing thanks to their respective advantages. More experiment data are needed to prove the full performance of sample produced via either new method. The SAC method shows its strong competitiveness in replacing the traditional method mainly because of the shorter duration. New convenient syntheses make Sn-beta more valuable in the application in the industry.

Potential industrial application of Sn-beta in the conversion of glucose: The Sn-beta zeolite was initially known for its outstanding catalytic performance in the Baeyer-Villiger and Meerwein-Ponndorf-Verley reduction as reported by Corma *et al.*[1-10]. Several literatures have reported relevant mechanism. After a long time of deeper study about the tetrahedrally coordinated framework, the catalytic property of isomerizing aldose to ketose in carbohydrates manufacturing catches the eyes.

The specific catalytic activity of Sn-beta in the isomerization of glucose was reported by Ricardo[24] in 2012. Sn-beta zeolite catalyzes isomerization of glucose to fructose in aqueous media, instead isomerizes glucose to mannose in methanol solution. It is also reported that the framework Sn atom seems to be dual-functioned. Researchers further look into the mechanism by using the NMR and isotope-tracer technology. They concluded that the Sn atom triggered a carbon shift between C-1 and C-2 in methanol solvent while in the aqueous solvent, it catalyzed the exchange of hydrogen atom in both C-1 and C-2 positions.

As far as we are concerned, now that the isomerization of glucose is a very important industrial reaction. Fructose is a new type of sugar derived from a variety of fruits and grains with a sweet fragrance. Fructose has attracted more attention for the reason of less likely to lead high blood sugar and fat accumulation, reducing the risk of dental tooth decay. Mannose is the only sugar nutrient in clinical application which are directly used in the glycoprotein synthesis. The common conversion method takes the advantage of isomerase catalyst. This biological conversion has its high requirements on the purity of raw material. However, the cost of the process is high. The side reactions are very complex which lead to greater difficulties in process control and product separation. Researches now show Sn-beta zeolite has the ability to replace the traditional catalysts in this conversion. This heterogeneous catalyst has strong competitiveness in mass production-scale for their apparent advantages in operation control and product separation. In addition, Sn-beta is a kind of environmental friendly catalyst.The catalytic product will not cause any damage to the surroundings.

Conclusion

The Sn-beta zeolite is a active catalyst for many reactions in the petroleum chemical and fine chemical industry. The zeolite attracts much interest *via* its good thermal stability and high recovery. Meanwhile, more and more scientists put their eyes on the new synthesis and potential applications in order to meet the needs of large-scale production. In spite of the obvious convenience, the new synthesis and applications still need much more practice to complete the property verification in order to get the chance to replace the common method.

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