

## A Study on Silylated Beta Zeolite-Supported NiW Catalysts by TEM Techniques

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Zeolites are crystalline aluminosilicates of various structures containing large active surfaces and ordered micropore network, which accommodate a wide range of industrial applications such as gas adsorption, ion exchange, and separation [1,2]. Especially, the basic structural unit of zeolite frameworks consists of silicon or aluminum atoms tetrahedrally coordinated to four oxygen atoms, but replacing Si<sup>4+</sup> by Al<sup>3+</sup> creates a negative charge on the framework [3]. When zeolite framework charges are neutralized by protons, they create acid sites that can facilitate acid-catalyzed reactions, such as isomerization, alkylation, and cracking for hydrocarbons [4,5].

For this reason, zeolites have been used in refining processes. However, the zeolites require that desirable mono-ring aromatics, hydrogenation and hydrocracking should be properly proceeded to maintain mono-ring aromatics and avoid the loss into excessive cracked fractions for high yield toward. By introducing metal elements into zeolites, not only acidic function from zeolites but also metallic function from metal elements can promote ring opening and aromatic saturation step, respectively, as bi-functional catalytic system. To fully exploit the advantages of bi-functional catalytic system, balancing the functions of metal and zeolites is critical in the way of controlling the ratio of metal to acid sites and the proximity between both sites. In particular, the acid sites on zeolites can influence the catalytic conversion and selectivity depending on being located on the external surface or channels [2,3]. Furthermore, the different metal-support interaction induced by being deposited on these acid sites can alter the electronic properties of metal. Taken together, once the correlation of the catalytic activities according to the distribution of the acid sites and their metal-zeolite interaction is clarified, it will pave an alternative way to give fine control over the bi-functional catalyst system. However, due to the complexity of maneuvering the acid site distribution of the zeolite, the realization of such bi-functional catalysts has been rarely reported.

Here, we report a synthetic strategy to control the acid site distribution of Beta zeolite through the silylation reaction with tetramethyl orthosilicate (TMOS), tetraethyl orthosilicate (TEOS), and tetrabutyl orthosilicate (TBOS) as silylation agents. As the size of alkyl chain group in the silylation agents gets larger, the silylation agents were suppressed to spread into the channels and thus the formation of SiO<sub>2</sub> layer was intentionally occurred on the external surface of the zeolite. Resulting from the selectively deposited SiO<sub>2</sub> layer, NiW metal supported on each silylated Beta zeolite altered the metal distribution and further the balance of metallic and acidic function.

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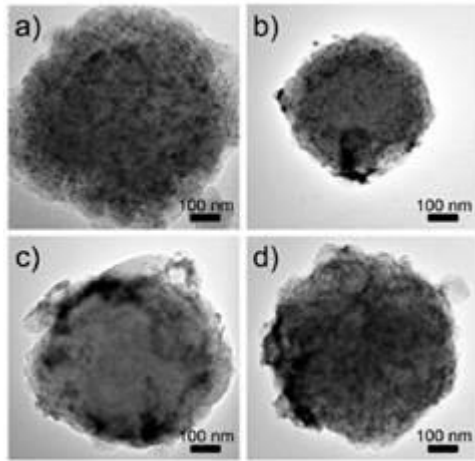


Fig. 1. TEM images of (a) NiW/TMOS-, (b) NiW/TEOS-, (c) NiW/TBOS-silylated Beta, and (d) NiW/Beta.

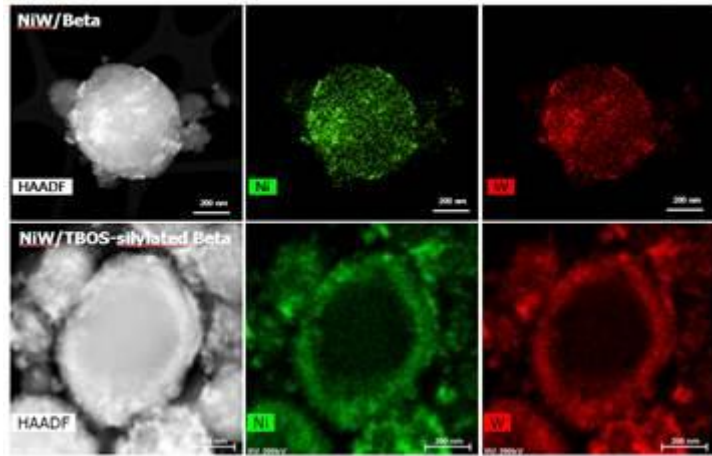


Fig. 2. HAADF image and chemical element distribution maps obtained by STEM-EDS. NiW nanoparticles were concentrated on the outer part of TBOS-silylated Beta.

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