# Cracking reactivity of hierarchical catalysts with simultaneous generation of microporous zeolite and mesoporous silica by gel skeletal reinforcement

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**Abstract:** When the gel skeletal reinforcement method using hexamethyldisiloxane (HMDS) was combined in the preparation of ZSM-5, the crystal structure of ZSM-5 and the very large mesoporous structure were simultaneously generated in the prepared catalysts. It was confirmed that these prepared catalysts had the hierarchical structure. The addition of HMDS greatly increased surface area, pore volume and pore size. The highest conversion of 98% was obtained in catalytic cracking of *n*-dodecane by the hierarchical catalyst with both micropores and mesopores. This type of catalyst with both micropores and mesopores showed high values of RON, olefin/paraffin ratio and multi-branched chain/single-branched chain ratio.

**Keywords:** Simultaneous generation of zeolite and mesoporous silica, Gel skeletal reinforcement, Catalytic cracking.

## 1. Introduction

Demands in white oils of gasoline and diesel are increasing year after year. On the other hand, demands in heavy oils such as atmospheric residue and vacuum gas oil are decreasing. Therefore Fluid Catalytic Cracking (FCC), which converts heavy oils to fuels with low molecular weight, is increasing the importance in a field of the oil refining. The general catalyst which is used by FCC is mixed catalysts composed of zeolite, which has strong acid sites and micropores, and matrices, which have weak acid sites and mesopores, are used. Materials for matrices can be produced through drying of precursor gels and successive calcination. However, the significant shrinkage in the gel structure is caused by drying stress or condensation in these steps. In order to avoid the problems above, we found the gel-skeletal reinforcement method to prepare materials with very large mesopores.[1-3)]

In this study, catalysts with hierarchical structure having micropores in the inner side and mesopores in the outer side of a catalyst particle were prepared in one step reaction using gel skeletal reinforcement method and the reactivity in the catalytic cracking was investigated.

## 2. Experimental

In the generation of ZSM-5 crystals (C-ZSM-5), colloidal silica ($SiO_2$) as a silica source, sodium aluminate ($NaAlO_2$) as aluminum source, sodium hydroxide (NaOH) and water ($H_2O$) for an aqueous basic solution, tetrapropylammonium hydroxide (TPAOH) as a structure directing agent under the condition of a hydrothermal synthesis method were mixed. As a gel-reinforcing solution, hexamethyldisiloxane (HMDS) and acetic anhydride ($(CH_3CO)_2O$) were mixed simultaneously. A stainless steel container was used for the sealed drying container, and the calcination was performed at 550 °C for 6 hours under an air atmosphere. In order to obtain H-ZSM-5, cation exchange was carried out using ammonium nitrate ($NH_4NO_3$) and C-ZSM-5. In the notation of GSR-12HS-H-ZSM-5, for example, GSR represents the gel skeletal reinforcement method, 12 is obtained by multiplying the molar ratio of HMDS to $SiO_2$ in colloidal silica by 100, HS means HMDS and H-ZSM-5 $H^+$ exchanged ZSM-5. The catalytic cracking of n-dodecane was performed under the following reaction condition; 500 °C, flow rate of feed = 1.3 ml/min, reaction time =80 s. After this reaction, the liquid products obtained were collected in a cold trap under $N_2$ stream and were analyzed by GC-FID.

## 3. Results and discussion

In the measurement of XRD patterns, the crystal structure of ZSM-5 was not confirmed when the molar ratio of a reinforcing agent of HMDS to $SiO_2$ of colloidal silica was more than 0.13. However, typical peaks of ZSM-5 were observed when gel skeletal reinforcement was not performed or when only a small amount of gel skeletal reinforcing solution was added, that is, the ratios of HMDS to $SiO_2$ were 0.13 and less

**Table 1.** Pore properties of catalysts by nitrogen adsorption-desorption measurement

| Catalyst | BET |  |  | BJH |  |  |
|---|---|---|---|---|---|---|
|  | Surface Area ($m^2/g$) | Pore Volume ($cm^3/g$) | Pore diameter (nm) | Surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Pore diameter (nm) |
| **ZSM-5(24)** | **388** | **0.30** | **3.1** | **34** | **0.14** | **3.7** |
| **H-ZSM-5** | **416** | **0.23** | **2.25** | **36** | **0.043** | **3.7** |
| **GSR-10HS-H-ZSM-5** | **404** | **0.21** | **2.06** | **11** | **0.029** | **3.7** |
| **GSR-12HS-H-ZSM-5** | **348** | **0.25** | **2.87** | **9.4** | **0.093** | **22** |
| **GSR-13HS-H-ZSM-5** | **297** | **0.87** | **11.7** | **72** | **0.77** | **16** |
| **GSR-14HS-H-ZSM-5** | **176** | **1.68** | **38.1** | **170** | **1.70** | **39** |

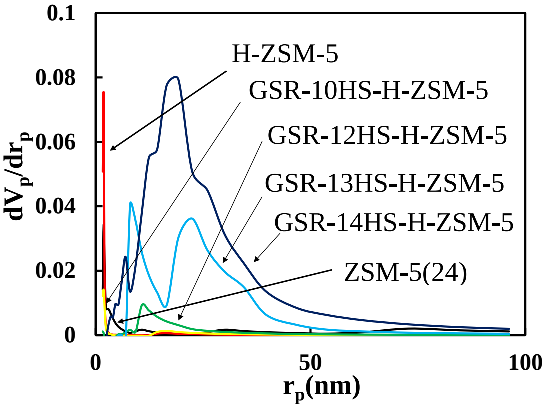

**Fig. 1.** BJH pore size distribution of catalysts

**Table 2.** Product distribution and some parameters in gasoline fraction.

| Catalyst | Product distribution (wt.%) |  |  |  | Parameters in gasoline fraction |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  | C1-C4 | Gasoline (C5-C11) | C12- | Conv. (%) | O/P* | iso-/ n- | m/s* | RON |
| **ZSM-5(24)** | **74** | **25** | **1.03** | **60** | **0.065** | **2.58** | **0.07** | **106** |
| **H-ZSM-5** | **71** | **29** | **0.22** | **67** | **0.98** | **1.34** | **0.38** | **104** |
| **GSR-10HS-H-ZSM-5** | **74** | **26** | **0** | **85** | **1.39** | **1.30** | **0.69** | **108** |
| **GSR-12HS-H-ZSM-5** | **65** | **35** | **0** | **98** | **2.47** | **1.18** | **0.46** | **105** |
| **GSR-13HS-H-ZSM-5** | **84** | **16** | **0** | **79** | **1.42** | **1.01** | **1.39** | **99** |
| **GSR-14HS-H-ZSM-5** | **49** | **50** | **1.13** | **5** | **2.13** | **1.46** | **0.05** | **94** |

*O/ P= Olefin/ Paraffin, m/ s = Multi/ Single branch, HMDS : $SiO_2$ (mol / mol) = 10, 12, 13 or 14 : 100, $SiO_2/Al_2O_3$ ratio 109 ~ 132

than 0.13. Table 1 shows the pore characteristics of catalysts, specific surface areas, pore volumes, pore diameters by BET and BJH methods. The BJH method gives the information about only mesopores. Therefore, when the difference between the surface areas by BET and BJH methods is small like the case of GSR-14HS-H-ZSM-5 catalyst (14HS), it is thought that most of pores in the catalyst consisted of mesopores. In contrast, the 10HS catalyst did not have mesopores. The 12HS and 13HS catalysts included both micopores derived from zeolite and mesopores derived from reinforcing agents. In the BJH pore size distribution (Fig. 1), large mesopores were seen for catalysts with more than 13. On the other hand, there was no distribution for the 10HS catalyst in this plot. In addition, as for the 12HS and 13HS catalysts, the peaks of zeolite crystals were observed in XRD. These results confirmed that catalysts having both zeolite and large mesopores were formed.

Table 2 summarizes the product distribution and some parameters in the gasoline fraction obtained in the catalytic cracking. A high Olefin/Paraffin ratio (O/P) and a high multi-branched/single-branched chain ratio (m/s) were obtained in the catalysts prepared. In addition, a relatively high RON value was confirmed. As compared with the commercially available ZSM-5 (24), the catalysts prepared in the present study decreased paraffins and increased olefins, indicating that the hydrogen transfer capability was suppressed because the distance between zeolite particles became large in the presence of GSR-silica. Although the 12HS catalyst showed the highest conversion of n-dodecane 98%, the selectivity for the gasoline fraction increased, indicating that over-cracking was suppressed using hierarchical catalysts. The 14HS catalyst had a very low conversion of 5%, indicating that this catalyst did not include any crystals of ZSM-5 in the inside of the particles.

## 4. Conclusions

The crystallinities of ZSM-5 in the 12HS and 13HS catalysts, which showed microporous and mesoporous structures simultaneously, were 84% and 42%, respectively. 14HS hardly showed crystals of ZSM-5. The 12HS catalyst showed the high conversion of *n*-dodecane 98%, the high selectivity of gasoline fraction 35% and the O/P ratio 2.47. The 13HS catalyst showed the high m/s ratio 1.39.

## References

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