# Understanding Anomalous Constraint Index Results for Zeolites

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**Introduction**

For the last two decades, the Constraint Index (CI) test has been utilized as a convenient simple tool to distinguish zeolites with small, medium or large pore structures by the competitive cracking of equimolar amounts of n-hexane and 3-methylpentane. This screening has provided insight into the structure and shape selective properties of zeolites as well as served as a distinguishing characterization of catalyst in many patents. However, Constraint Index values of some zeolites with new structures have been observed to be inconsistent with the trends first reported by Mobil [1] in developing the test. These anomalies have been described recently by Zones and Harris [2].

Zeolites such as SSZ-25 (MWW), SSZ-35 (STF), and SSZ-28 (DDR) have produced CI results reflecting pore sizes that are larger than the actual pores [2]. This is illustrated in Table 1 where several zeolites listed in italics have CI values that would classify them incorrectly based on known pore structure. Also SSZ-25 has shown an unusual increase in the CI value over time on stream [2] whereas the CI values of other zeolites typically maintain constant or slightly decreased value. A common feature of these zeolites are their structures containing pores opening into larger cages as opposed to more channel-like structures of zeolites like ZSM-5 used in the original studies. The large cages in these newer structures have led to several hypotheses as to the anomalous CI results. One suggestion is the larger cages in the structure provide incomplete cages open to the external surface which may provide a higher external surface activity that is not subject to the same size constraint of the pores and as such may reduce the observed CI value for the structure. On another hand, the large cages could provide more room for the bulkier 3-methylpentane to maneuver into the structure or more room for transition states. In this study, we have investigated these materials with atypical CI results for both surface effects and accessibility to better understand their CI results. A better understanding of these CI results may aid in the interpretation of results from other zeolites with know and unknown structures.

**Materials and Methods**

Zeolites used in this study were prepared by reported literature procedures or obtained from commercial sources. Zeolites were characterized by powder XRD, solid state NMR, TGA, $N_2$ adsorption, XPS, TPD, SEM and ICP. Surface modification of the zeolites was performed in an aqueous solution by addition of ammonium hexafluorosilicate in a process detailed by Breck and Skeels [3] except the structure-directing agent was left in the zeolite to act as a pore blockage to prevent internal dealumination. Catalytic tests were performed in a bench-top plug-flow reactor using an argon internal standard an online GC/MS analysis. Adsorption capacities were measured using a Cahn C-2000 balance [4].

**Results and Discussion**

Various reports have suggested the influence of the external surface of zeolite structures on reactivity and selectivity. Particularly for the MWW structure of SSZ-25 the surface has been shown to be covered in hemi-cages [5]. Thus, the role of the external surface in the CI test was investigated. Both surface characterization and isopropanol dehydration limited to the external surface demonstrated a reduction in external surface activity after the ammonium hexafluorosilicate treatment. However, minimal differences were observed between samples before and after treatment suggesting that any surface activity is deactivated before the initial measurements. The external surface of the zeolite does not appear to be responsible for the uncharacteristic CI results. Typically, CI results are presented as a single time point result. Observing the CI results as a function of time on stream demonstrates that structures with two distinct pore structures like SSZ-25, offretite, and mordenite reveals a shift in the CI value as each feature deactivates at a different rate. Where as for structures like ZSM-5, BEA, and Y the CI value remains relatively constant over a period of time on stream. Adsorption studies have also demonstrated the SSZ-35 has less discrimination between n-hexane and 3-methylpentane than ZSM-5. We demonstrate that the CI test when viewed as a single point test (in time) can be quite misleading in pore size determination. However, understanding the changes in CI over time, the products, and the reactivity can provide more insight especially when combined with other simple screens such a adsorption capacity measurements.

**Table 1. Selected Zeolites by CI Pore Size Classification with Anomalies Highlighted**

| Small Pore Classification CI > 12 | | | Medium Pore Classification 12 > CI > 1 | | | Large Pore Classification CI < 1 | | |
|---|---|---|---|---|---|---|---|---|
| Zeolite | Pore Apertures | CI | Zeolite | Pore Apertures | CI | Zeolite | Pore Apertures | CI |
| SSZ-13 | 8-ring | >100 | ZSM-23 | 10-ring | 10.6 | SSZ-31 | 12-ring | 0.9 |
| Erionite | 8-ring | 38 | SSZ-20 | 10-ring | 6.9 | ***SSZ-25*** | ***10-&10-ring*** | ***0.8*** |
| | | | ZSM-5 | 10-&10-ring | 6.9 | ***SSZ-35*** | ***10-ring*** | ***0.6*** |
| | | | ***SSZ-28*** | ***8-ring*** | ***4.0*** | LZY-82 | 12-rings | 0.4 |
| | | | EU-1 | 10-ring | 3.7 | CIT-5 | 14-ring | 0.4 |
| | | | ***SSZ-23*** | ***9-&7-rings*** | ***3.2*** | SSZ-24 | 12-ring | 0.3 |
| | | | ZSM-12 | 12-ring | 2.1 | UTD-1 | 14-ring | 0.3 |
| | | | ***SSZ-36*** | ***8-ring*** | ***1.1*** | | | |

Data from [1,2] and current study

**Significance**

Understanding the reasons resulting in anomalous Constraint Index results for zeolites could provide insight into results on unknown structures. Improving the understanding of the Constraint Index will lead to better structure determination and property prediction.

**References**

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