



Benzene reduction in gasoline by alkylation with olefins: Comparison of Beta and MCM-22 catalysts

Georgina C. Laredo*, J. Jesus Castillo, Juan Navarrete-Bolaños, Patricia Perez-Romo, Flavio A. Lagos

Programa de Procesos de Transformación, Instituto Mexicano del Petróleo, Lázaro Cárdenas 152, México 07730, D.F., México

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ABSTRACT

The study compares the performance of Beta and MCM-22 zeolites as catalysts for propylene alkylation of benzene present in an enriched sample of reformat heart cut (20 wt% benzene). The experiments were carried out in a batch system with a 2/1 mole ratio of benzene/propylene at 220 °C for 1 h. An MCM-22 zeolite that contained Brønsted/Lewis acid sites in a 2–3/1 ratio proved to be much more resistant to deactivation during these real feed benzene alkylation experiments when compared with the Beta catalyst (Brønsted/Lewis acid site ratio of 0.1–0.3/1). MCM-22 with a 45 wt% benzene conversion presented higher *i*-propylbenzene selectivity than Beta (38 wt% benzene conversion) by reducing the formation of by-products. The outstanding behavior of MCM-22 may be explained by its particular Brønsted to Lewis acid ratio, which could help in the carbonium-ion formation and in the activation of the benzene ring toward electrophilic attack, and to its open crystalline framework that facilitates diffusion of reactants, products and coke precursors. Additional studies regarding experimental conditions for the preparation of MCM-22 and alkylation procedures are required for optimization.

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1. Introduction

The reduction of benzene content in naphtha streams has become the focus of much research over recent years. While benzene is a valuable input for the manufacture of basic products in the chemical and petrochemical industries, its presence in the gasoline pool needs to be minimized because of its known carcinogenic properties. Indeed, the Mobile Source Air Toxics rule, published on February 26, 2007, requires that refiners and importers in the USA produce gasoline that has an annual average benzene content of 0.62 volume percent (vol%) or less, beginning in 2011 [1,2].

Gasoline from the catalytic reforming process contributes with 70–85% of the benzene in the gasoline pool according to the EPA [3]. Pre-treatment and post-treatment technologies have been developed to reduce the benzene content from this source [3–8]. Alkylation technologies offer increases in octane number and gasoline volume, with no hydrogen consumption [6–10], advantages that other technologies do not present. Moreover, in a well-developed technology, benzene present at low levels was successfully alkylated during an olefin oligomerization process using a solid phosphoric acid (SPA) catalyst [11,12]. However, solid catalysts like SPA are being replaced with non-polluting, non-corrosive,

regenerable materials, such as zeolites, to perform the aromatic alkylation procedure. Recommended zeolite catalysts used for the alkylation of pure benzene with short chain olefins include Beta [13–28], MCM-22 [25–36] and ZSM-5 [25–27]. Information regarding zeolitic catalysts used in the reduction of benzene from gasoline feedstocks can only be found in patents: ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, MCM-22, MCM-36, MCM-49, MCM-56, Beta and TEA mordenite [37–48]. The preferred zeolitic materials for this work include ZSM-5 [38–45], ZSM-12 [37], MCM-22 [46,48] and a combination of ZSM-5 and MCM-22 in a two-step process [47].

The preferred product for the alkylation with propylene of pure benzene and benzene present in real feeds is *i*-propylbenzene (IPB), although in the case of gasoline feeds, controlled amounts of di-isopropylbenzene (DIPB) isomers supposedly improve octane number [46]. Excessive amounts of these by-products and other polyalkylated aromatics must be reduced by transalkylation procedures [49–52] because their presence may adversely affect the gasoline pool blending specifications, most notably the end point or T90 [46] (30–225 °C at 0.1 MPa [53]), and they can cause catalyst deactivation from pore blockage [17]. Keeping lightweight oligomers as part of the gasoline pool might increase octane number and volume [48], however, the presence of high molecular weight oligomers may also affect catalyst life by coke deactivation [13,15,19,23,25,26].

The use of olefins to alkylate benzene in real feeds was studied by Laredo et al. [54–56]. By performing propylene alkylation experiments on benzene present in an enriched fraction using Beta

* Corresponding author. Tel.: +52 5591756615; fax: +52 5591758429.

E-mail addresses: glaredo@imp.mx (G.C. Laredo), jcastill@imp.mx (J.J. Castillo), jnavarre@imp.mx (J. Navarrete-Bolaños), pperezr@imp.mx (P. Perez-Romo), flagos@imp.mx (F.A. Lagos).