Effect of metal–acid site balance on hydroconversion of decalin over Pt/Beta zeolite bifunctional catalysts

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HIGHLIGHTS

- Hydroconversion of decalin was studied on Pt/Beta catalysts with different metal contents.
- The reaction steps of ring contraction, ring opening and cracking were consecutive.
- Greater hydrogenation activity implies lower availability of adsorbed cracking species.

GRAPHICAL ABSTRACT
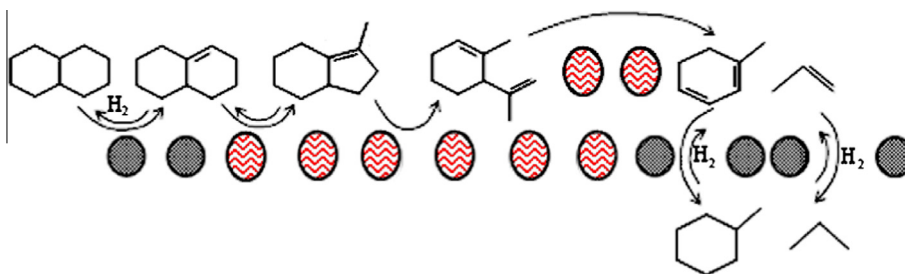
ABSTRACT

The main objective of this work is contributing to the understanding of the ring opening of naphthenic model molecules, an important reaction to improve the cetane number of diesel fuels. Accordingly, the hydroconversion of decalin was studied over a series of Pt/Beta catalysts with different metal contents in order to evaluate the effect of changing the proportion of hydrogenation/acid functions of the catalyst on conversion and products distribution. The overall reaction rate did not change by increasing the hydrogenation activity (metal content) of the catalyst. However, ring contraction and ring opening product yields increased with metal content up to 1.0 wt% and then became constant for higher metal contents, while cracking product yields followed an opposite trend, decreasing with increasing metal content up to 1.0 wt%. This behavior clearly provides evidence of a bifunctional mechanism in the hydroconversion of decalin over Pt/BEA catalysts, since the selectivity depends on the metal/acid function balance. Although decalin is a saturated molecule, its naphthenic character and probably the presence of a tertiary carbon in its structure facilitate activation of the molecule directly on the strong acid sites of zeolite, even at relatively moderate temperatures. Thus, it is not necessary to form an olefin on a metal site, which would undergo subsequent protonation, as in a classical bifunctional mechanism, such as in hydroisomerization and hydrocracking of n-paraffins. However, the hydrogenation component of the catalyst influences the selectivity of the reaction, controlling the process of desorption/adsorption of any intermediate olefins formed. Greater hydrogenation activity implies lower availability of adsorbed carbocations that can be converted to cracking products. This proposition is consistent with the results obtained by varying the content of metal and poisoning of the hydrogenation sites in the catalysts.

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1. Introduction

Environmental laws and stricter quality specifications have driven the development of technologies for reductions in density, sulfur content and (poly)aromatic hydrocarbons present in diesel

oil. The ignition quality of diesel fuel, as measured by cetane number, is negatively affected by the presence of aromatic compounds, and increases with degree of saturation, chain linearity and molecular weight of the diesel oil molecules. Accordingly, in addition to the saturation of (poly)aromatic compounds, responsible for limited gains in density reduction and cetane number, the opening of at least one ring of (poly)cycloalkanes, without loss of yield due to cracking, is a promising strategy for maximizing improvements on these diesel fuel properties [1].

Some studies have demonstrated significant performance of bifunctional catalysts (noble metals supported on acidic zeolites) for the ring opening of naphthenic model molecules, such as 1-methyl-naphthalene, tetralin and decalin [1–4]. The hydroconversion of tetralin and decalin in Pt/Faujasite showed that this catalytic system is more effective for decalin, highlighting the importance of complete saturation of (poly)aromatic compounds before the ring opening reaction step [1–3].

Bifunctional catalysis involving successive chemical steps on two independent types of sites plays an important role in numerous refining processes and production of petrochemicals and fine chemicals. This mechanism has been demonstrated in the investigation of the effect of metal–acid balance on bifunctional catalysts. For low values of metal loading, dehydrogenation becomes the limiting step, which can be verified by the increase of the ratio between dehydrogenation and acid activities. For a high metal content, this ratio is constant, as the acidic function usually associated to the support becomes the rate-limiting step. Examples of such mechanism can be observed in propane conversion and aromatization over mixtures of Ga_2O_3 and MFI [5,6], hydroisomerization of n-heptane over platinum supported on Faujasite and Mordenite [7,8], n-octane transformation over platinum-based Beta zeolite catalyst [9], synthesis of methylisobutylketone (MIBK) from acetone [10] and production of cyclohexylcyclohexanone on palladium supported on Faujasites [11].

The performance of ring opening bifunctional catalysts depends on the metal properties (type and particle size), the acidic support (number and concentration of Brønsted sites, crystallite and pore sizes), the metal-support interaction and balance, and the operating conditions [1,3,12]. However, there are few studies investigating such effects in a systematic way. Arribas et al. [13] performed experiments of hydroconversion of tetralin in Pt/Faujasite catalysts with different acid–metal ratios (metal loading) at high conversions (ca. 100%). According to the authors, the crucial step for obtaining ring opening products was the isomerization (ring contraction) of six-membered rings of decalin, favored at high metal contents, indicating that the decalin dehydrogenation in the metal site was the rate-determining step. The selectivity to ring opening and cracking products followed the same trend, as observed when the Pt content in the catalyst was increased from 0.25 to 4.0 wt%.

Besides the acid–metal site balance, the choice of acid support is essential for achieving activity and selectivity to ring opening products. According to Arribas et al. [14], the formation of ring opening products from tetralin was favored on large-pore zeolites (Beta > Faujasite > Mordenite) in comparison to medium-pore zeolites (ZSM-5, MCM-22). Other researchers also found excellent activity and selectivity using noble metals supported on Beta zeolite for the ring opening of naphthenic compounds [3,15]. As contraction and ring opening of the naphthenic ring are both secondary reactions when tetralin is used as reactant, the analysis of the bifunctional behavior may be influenced by the overall conversion level, as well as by the competition of the aromatic compounds for metallic and acidic sites.

The aim of this study is to investigate the influence of metal–acid sites balance on the activity and selectivity of gas-phase hydroconversion of decalin, achieved through the preparation of Pt/Beta catalysts with different metal loadings in order to assess the domains where metal and acid functions of the catalyst are rate-limiting.

2. Experimental

2.1. Preparation and characterization of the catalyst precursors

The acid support used in this work was Beta (BEA) zeolite with a bulk Si/Al molar ratio of 12.5, purchased from Tricat Zeolites GmbH. The zeolite was previously submitted to three successive ammonium exchanges, in order to eliminate residual sodium, followed by drying at 393 K overnight. Platinum was incorporated by ion exchange method (exchanging efficiency > 99.7%) with appropriate amounts of aqueous solution (5.0 mmol L^{-1}) of $Pt(NH_3)_4Cl_2$ (Tetraammine platinum(II) chloride hydrate, 98% Aldrich Chem. Co.) to obtain catalysts with different metal loadings (0.12, 0.34, 0.50, 0.66, 1.00, 1.97 and 3.95 wt%). In order to avoid a concentration gradient of Pt^{2+} in the zeolite grains, a competitive ion (NH_4^+ from NH_4Cl, 99.5% Vetec) was used during cation exchange with a NH_4^+/Pt^{2+} molar ratio of 10. Then, all materials were dried at 393 K, followed by calcination in two steps: (a) at 393 K (10 K min^{-1} heating rate) for 1 h under 160 mL min^{-1} g^{-1} Argon flow and (b) 573 K (1 K min^{-1} heating rate) for 2 h under 160 mL min^{-1} g^{-1} synthetic air flow. Argon (purity $\geqslant$ 99.9999%) and synthetic air (purity $\geqslant$ 99.999%, O_2 20 ± 5%) were purchased from White Martins (Praxair Inc.). The catalytic precursors were named as Pt(x)/BEA, where x corresponds to the metal content in wt%.

The prepared materials were characterized by X-ray diffraction (XRD), NH_3 Temperature Programmed Desorption (TPD), H_2 pulse chemisorption and Temperature Programmed Oxidation (TPO) of used catalysts.

The powdered samples of catalytic precursors were spread on a hollow glass slide for the X-ray diffraction (XRD) analysis using a Rigaku Multiflex diffractometer and Cu Kα radiation (λCu Kα = 0.1542 nm), 40 kV tension, 40 mA, 2°(2θ) min^{-1}, 5–45°(2θ).

Metallic dispersion was determined with H_2 pulse chemisorption in dynamic mode using a Micromeritics TPD/TPR 2900 analyzer. Previously, the sample was treated by heating at 10 K min^{-1} under argon flow up to 393 K and kept constant at this temperature for 1 h. Then, the sample was reduced in situ at 713 K for 2 h (10 K min^{-1} heating rate). Next, the sample was cooled down under argon flow and kept at room temperature for 30 min. Twenty H_2 pulses (10% H_2/Ar) were injected in a flow passing through the sample with an interval of 2 min for sweeping the weakly adsorbed hydrogen. In order to calculate the metal dispersion, an adsorption stoichiometry of $Pt/H_2 = 2$ was assumed. The metal dispersion of a reference sample was used for checking the procedure.

Determination of the number of acid sites of calcined materials was made by means of anhydrous ammonia TPD. The analysis used a TPD/TPR 2900 Micromeritics equipment coupled to a Pfeiffer Omnistar 422 mass spectrometer. The samples (150 mg) were treated initially at 573 K (10 K min^{-1} heating rate) under a 40 mL min^{-1} Helium flow for 1 h. After the sample was cooled to 308 K, the system was purged under 40 mL min^{-1} Argon flow for 15 min. Then the sample was reduced in situ under a 40 mL min^{-1} flow of 10% H_2 in Argon at 713 K (heating rate of 10 K min^{-1}) for 2 h. After cooling to 308 K, samples were purged under 40 mL min^{-1} Helium flow for 15 min. After heating to 448 K (10 K min^{-1} heating rate), the samples were exposed to anhydrous ammonia. Finally, the samples were heated to 773 K (10 K min^{-1} heating rate) and maintained at this temperature for 2 h. Helium ($\geqslant$99.9999%) and 10% H_2/Ar mixture were purchased from White Martins (Praxair Inc.).