Applied Catalysis A: General 533 (2017) 28–37

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Superior activity of non-interacting close acidic protons in Al-rich Pt/H-*BEA zeolite in isomerization of *n*-hexane

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ARTICLE INFO

Article history:
Received 12 October 2016
Received in revised form
15 December 2016
Accepted 17 December 2016
Available online 3 January 2017

Keywords:
Isomerization
Alkanes
Hexane
Zeolites
Al-rich beta (*BEA)
Mordenite

ABSTRACT

Skeletal isomerization of linear alkanes, an essential reaction for the production of gasoline, relies on environmentally questionable chlorinated catalysts, whose activity exceeds that of alternative zeolite catalysts. This work describes an attempt to understand relations between the local arrangement of active sites and skeletal isomerization of *n*-hexane in order to adapt the structure of zeolite catalysts to increase the reaction rates. For this purpose, we used a combination of synthesis of zeolites of *BEA structural topology with unique density and distribution of strongly acid sites, analysis of the nature of the acid sites by ^{1}H MAS NMR spectroscopy and FTIR spectroscopy of the OH groups and adsorbed d_3-acetonitrile, UV–vis-NIR spectroscopy of carbocations formed by protonization, and kinetic analysis. We demonstrate that the high density of non-interacting but close and strongly acidic structural hydroxyl groups significantly lower the activation barrier in the isomerization reaction compared to far-distant acid sites. The organotemplate-free synthesized Al-rich Pt/H-*BEA zeolite (Si/Al 4.2) with an unparalleled high concentration of the non-interacting close H$^+$ ions balancing the charge of the Al-Si-Al sequences forming a wall between the two channels yields 6 times higher reaction rates compared to state-of-the-art Si-rich Pt/H-zeolite catalysts.

1. Introduction

Hydroisomerization of linear alkanes into branched alkanes represents a key reaction for the production of automotive fuels. This complex catalytic reaction consists of dehydrogenation of a linear alkane to an alkene on a noble metal, skeletal isomerization of the formed alkene via protonization and a cyclopropyl intermediate on a strongly acidic site and re-hydrogenation of the branched alkene to the alkane (Fig. 1) [1–6]. The dehydrogenation/hydrogenation reactions on a bifunctional catalyst are in thermodynamic equilibrium and practically do not affect the reaction rate of the hydroisomerization [4]. In contrast, the acid-catalysed reaction steps determine the rate of isomerization and require strongly acidic centers [7]. The labile protons of the O—H groups with acid strength strongly enhanced by the presence of chlorine on the traditional chlorinated Pt-alumina catalysts [8] provide sufficient conversion at temperatures as low as 150 °C [9,10]. Since the chlorination occurs by reversible chemical exchange of the surface hydroxyl groups of the alumina support, the use of this catalyst is associated with constant supply and formation of organic chlorines [11], which leads to serious questions about the environmental impact. Zeolite-based acid catalysts, such as Pt-mordenite zeolite with improved texture [12–14] or sulfated Pt-zirconia [15,16] were developed; however, the acid centers of these catalysts facilitate a sufficient rate of isomerization at much higher temperatures. Conversely, low-temperature activity is crucial for achieving sufficient conversion of linear alkanes to branched ones due to the thermodynamic equilibrium of the isomerization reaction, wherein the lower temperatures shift the equilibrium towards the desired di-branched products, whereas higher temperatures hinder their formation. Development of an acidic catalyst for hydroisomerization of linear alkanes, particularly *n*-pentane and *n*-hexane, functional at low temperatures without streams containing low concentrations of chlorine additives, remains a great challenge for heterogeneous catalysis.

Knaeble et al. [7] and Macht et al. [5] documented well that the rate of hexane skeletal isomerization at acid sites with an opened coordination sphere and located in an unconfined space in tung-

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http://dx.doi.org/10.1016/j.apcata.2016.12.016
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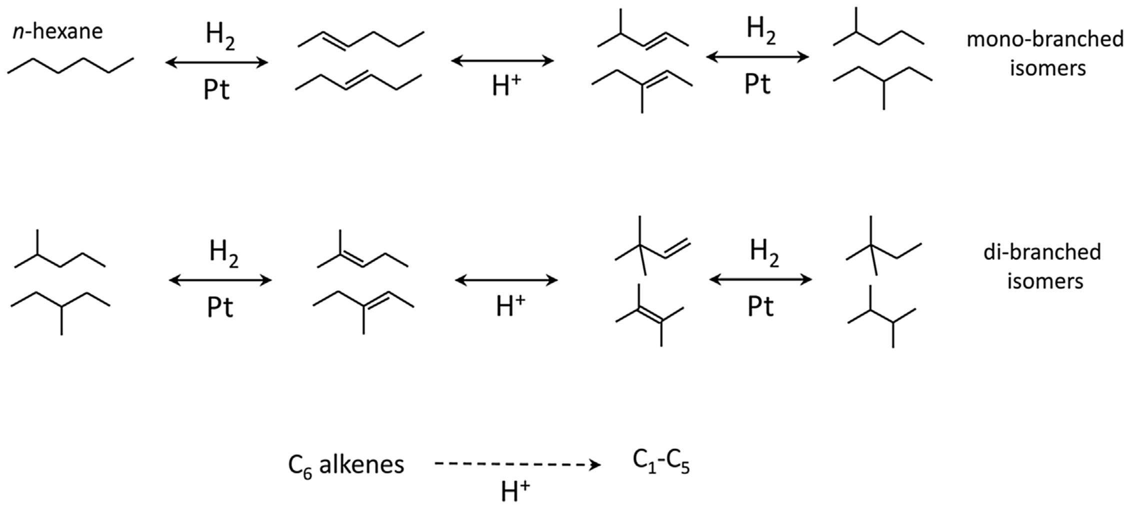

Fig. 1. Reaction scheme for *n*-hexane hydroisomerization on bifunctional Pt/H-zeolite catalysts. The fast dehydrogenation–hydrogenation reactions at Pt sites equilibrate alkanes and all alkene isomers of a given carbon chain structure providing a very low and constant concentration of alkenes. In the acid catalysed reaction steps, the alkene molecules undergo skeletal isomerization and, at high temperatures, also produces lower molecular weight alkanes [5,6].

sten Keggin polyoxometalates supported on silica is proportional to the concentration of acid sites and decreases exponentially with decreasing acid strength. However, in the case of zeolite catalysts, the location of protons in the individual pores of high-silica zeolites and, in addition, the distances between the protons might be also expected to affect their function and reaction pathway in the isomerization reaction. The rate of skeletal isomerization per proton in the 8-member ring (8-MR) side channels of the mordenite structure was reported to be five times higher in comparison with that in the large straight 12-member ring (12-MR) channels [17]. Since the pioneering work of Haag et al. [18], suggesting a linear relationship between the concentration of tetrahedral aluminum in the framework, hence the acid centers, and the reaction rate in the cracking of hexane, it has been well established that, not only the concentration, but also the local spatial arrangement of acidic centers attached to crystallographically different sites in the channels [19,20] and the distance between them [21] fundamentally influence both the reaction rate and the mechanism.

In pursuing the present work on the isomerization of linear alkanes over zeolites, we wanted to specify the role of an increase in the density of the strongly acidic protons countering the negative charge of the framework in the H-forms of zeolites in relation to the occurrence of Al-Si-Al sequences, inevitably formed at high concentration of Al in the zeolite framework. We wanted to determine the effect of variations in the distribution of aluminum providing charge balance for the corresponding high concentration protons located in the close vicinity on the reaction rate and selectivity. We therefore employed zeolite *BEA topology, which can be prepared in a broad range of Al concentrations and which offers fast intra-crystalline diffusion of reactants and products through channels with three-dimensional architecture and 12-MR openings. We exploited recent progress in the synthesis of the beta zeolite that opened a new potential to manipulate the framework aluminum content in a very broad range and employed Al-rich beta zeolites with very high concentration of aluminum (Si/Al ≥ 4) with highly predominant tetrahedrally coordinated Al in the framework [22–34]. This approach enabled us to examine the extent to which the isomerization reaction is affected by close proximity of strongly acidic centers. We found that the high density of non-interacting strongly acidic sites facilitates extraordinarily high reaction rates due to a synergetic effect significantly decreasing the activation barrier of the reaction. This enabled more rational design of isomerization zeolite catalysts providing superior activity.

2. Experimental

2.1. *BEA and MOR zeolites and preparation of Pt/H-catalysts

Al-rich beta zeolite (molar Si/Al 4.2), denoted as *BEA/4.2, was hydrothermally synthesized from aluminosilicate synthesis gel prepared from $NaAlO_2$ and fumed silica (Cabosil) in the absence of an organic structure-directing agent and using seeding of calcined beta crystals (TZB-212, Tricat). Details of the procedure were reported previously [33]. The high-silica zeolites used as standards for comparing the catalytic properties kindly supplied by the Tricat Company (now part of Clariant), (*BEA, Si/Al 11.5, TZB-212) and Zeolyst International (*BEA, CP814B-25, Si/Al 12.5 and MOR, CBV 20A, Si/Al 12.1) were denoted as *BEA/11, *BEA/12, and MOR/12, respectively. A hierarchical mordenite zeolite with optimal micro-mesoporous structure was prepared and used for comparing the catalytic properties of Al-rich beta zeolite with a state-of-the-art hydroisomerization zeolite-based catalyst [12]. The hierarchical mordenite was prepared by treatment of MOR/12 in alkaline solutions (30 ml 0.2 M NaOH per 1 g mordenite stirred in a beaker at 85 °C for 2 h) and subsequently in acid solution (10 ml 0.1 M oxalic acid per 1 g alkaline treated zeolite stirred in a beaker at 85 °C for 20 h). All the zeolites were ion-exchanged with 0.5 mol dm^{-3} NH_4NO_3 at RT (1 g of a zeolite per 100 cm^3 of solution, three times over 12 h).

Pt was introduced into the zeolites by incipient wetness impregnation of pre-dried (105 °C/2 h) powder zeolites with a H_2PtCl_6 solution to yield 1.5 wt.% of Pt. The Pt-impregnated granulated zeolite was activated before the catalytic test in a stream of O_2 at 450 °C for 3 h, then purged by a N_2 stream at 450 °C, then cooled down to 250 °C, and finally activated in a mixture of 80 mol% H_2 and 20 mol% N_2 at 250 °C for 1 h.

2.2. Structural analysis

X-ray powder diffraction (XRD) patterns were obtained with a graphite monochromator and a position sensitive detector (Våntec-1) using a Bruker AXSD8 Advance diffractometer with CuKα radiation in Bragg–Brentano geometry. The porosity of the zeolites was determined by the analysis of the adsorption isotherms of nitrogen at 77 K carried out using an ASAP2010 apparatus (Micromeritics). Before the adsorption experiment the samples were outgassed at 240 °C for at least 24 h. The crys-