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Producing high quality biofuels: Pt-based hydroisomerization catalysts evaluated using BtL-naphtha surrogates

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ABSTRACT

A series of low loading, platinum-containing catalysts was successfully synthesized impregnating three different acid zeolitic supports of similar SiO_2/Al_2O_3 ratio (~20) but various structure and acidic characteristics (mordenite, ZSM-5, BETA) with an aqueous H_2PtCl_6 solution. All catalysts were thoroughly characterized (ICP, XRD, N_2 physisorption, FTIR-pyridine adsorption and HR-TEM) and studied as candidate hydroisomerization catalysts. In order to accomplish the above purpose, the Pt-loaded zeolites were tested using surrogate naphtha feeds focusing on the effect of the zeolite support, as well as the nature of the feed (additionally examining heavier feeds (>C6), such as BtL-naphtha) on the activity and selectivity of the catalysts. Both Pt/MOR and Pt/ZSM-5 materials contain large numbers of total and Brönsted acidity. However, Pt/ZSM-5 slightly prevails over Pt/MOR concerning acidity strength; thus exhibiting the highest catalytic activity (highest conversion). The same Pt/ZSM-5 catalyst was also able to successfully isomerize heavier hydrocarbons with limited cracking side reactions. Besides acidity, the efficiency of Pt/ZSM-5 is possibly attributed to the faster mobility of carbocation intermediates through its more interconnected structure and the formation of homogeneously dispersed, cubic-shaped and highly crystalline Pt particles along with highly dispersed Pt species on the zeolite surface.

1. Introduction

The Biomass-to-Liquids (BtL) process, which involves the gasification of lignocellulosic biomass to syngas and its conversion to hydrocarbons via Fischer–Tropsch, constitutes one of the most promising technologies for the production of high quality 2nd generation biodiesel fuels. Although the light by-product of FT-synthesis is not a suitable fuel for conventional engines, BtL-naphtha has the potential to become the best suited fuel for future power-trains like HCCI (Homogeneous Charge Compression Ignition). Preliminary tests however indicated that further upgrading of the naphtha fraction is needed for optimized engine performance, targeted toward mild reduction of its cetane number [1], which can be achieved via hydroisomerization of BtL-naphtha.

Hydroisomerization is a very important catalytic process in the petroleum industry, which converts linear alkanes to their corresponding branched isomers. Hydroisomerization of C4–C7 hydrocarbons is applied for the production of gasoline with a high octane number, while isomerization of C7–C15 paraffins is employed for the production of diesel fuel with improved cold flow properties, such as viscosity, pour point and freezing point [2]. Several variables, including operating conditions such as reaction temperature, contact time, pressure and H_2/hydrocarbon ratio [3] as well as catalytic properties, like the distribution of metal and acid sites [4,5] play an important role in this process and have been extensively studied [3–5].

Isomerization requires bifunctional catalysts, containing both metallic sites for hydrogenation/dehydrogenation and acidic sites for the skeletal re-arrangement via carbenium ions reactions, respectively. The isomerization reaction proceeds via the dehydrogenation of alkanes on the metallic sites, while the produced olefins are protonated on the Brönsted acid sites to the corresponding alkylcarbenium ions. These carbenium ions can undergo skeletal rearrangement and b-scission, followed by de-protonation and hydrogenation over metal sites to produce the isomerization and cracking products. During this mechanistic pathway, it is very important to minimize the secondary reactions and to ensure a satisfactory reaction rate. To achieve this, it is necessary to have a defined ratio between the metal and acid sites [6]. Lin, Zhang and Liang [7–9] showed that the higher the acidity of the support, the more enhanced are the cracking reactions at the expense of the selectivity to hydroisomerization. They also suggest that metal sites and catalyst support interact forming a “hybrid” active site, which seems to enhance the hydrogenation activity constraining undesired cracking reactions.

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Currently the industrial catalysts are Pt-based supported either on chlorinated alumina or zeolites, mainly mordenites, and are designed for the isomerization of light feeds (C_5/C_6) [10]. Catalysts supported on chlorinated alumina are highly active at low temperatures (130 °C), but suffer from extreme sensitivity to feed contaminants, such as water and sulfur traces (<0.5 ppm and <0.1 ppm), which poison the catalyst and lower its activity. Furthermore, the pressure of the hydrogen in the reactor results in the elution of chlorine from the catalyst as hydrogen chloride, causing corrosion problems. Finally, the catalysts must be activated, periodically injecting CCl_4 or C_2Cl_4 in the feed [11–13].

Zeolite-supported catalysts although less active, are characterized by their outstanding tolerance to feed poisons (sulfur and water) and therefore do not require feed pretreatment. Moreover, they are more resistant to the presence of aromatics, while they simultaneously have the advantage of a well-defined porous structure, which allows one to select the most suitable structure for the process [6]. However, zeolite-based catalysts exhibit lower activity and thus the reaction must be performed at higher temperatures (250 °C), favoring unwanted cracking side reactions [2,14]. Great efforts have been directed to modify zeolite supports in these catalysts via strengthening or creating stronger acid sites, compared to the traditionally used-alumina support, as well as modifying the metal sites via incorporating metallic promoters [14–16].

It is noteworthy that longer n-alkanes are more easily converted to isoalkanes and/or cracked alkanes than shorter n-alkanes. Unfortunately, multibranched alkanes are susceptible to hydrocracking. If the pore size is made small enough to restrain multibranched isoalkanes from being further converted at inner acidic sites, the isomerization selectivity can be increased. Therefore, shape selectivity of zeolites is probably their most significant and advantageous property, which can be used to suppress the formation of multibranched isoalkanes and thus inhibit hydrocracking reactions, finally improving isomerization selectivity [17,18]. When referring to shape selectivity, we address the fact that the hydroisomerization performance of a zeolite depends on several parameters such as the zeolite topology, pore size, window size and dimensionality of the pore system. For example, it is reported that the methyl branching is favored with small pore zeolites and that the ethyl and/or propyl branchings are favored with wide pore openings and large cavities [19].

An additional approach toward improved catalytic performance is to use catalysts either with weak acidity for suppressing the hydrocracking of multibranched alkylcarbenium ions or with high metal dispersion for enhancing the hydrogenation of desorbed multibranched alkenes [19]. The balance between the two catalytic functions, i.e. the density and the strength of the Brönsted acid sites (H^+) and the amount and the dispersion of the metal [20–25] is what determines the desired selectivity. When the hydrogenating function is highly active, the activity and the selectivity of the bifunctional catalyst will depend only on the acidic function, which is the rate-limiting step in the absence of diffusion limitations. A decrease in acidity would decrease cracking [19,26], but also the global activity since the acidic step is rate-limiting [19,27]. Metal content in the hydroisomerization catalysts has also a crucial effect on the catalytic activity and selectivity [28–31]. However, the optimum Pt content in the majority of modern industrial light naphtha hydroizomerization catalysts is in the range of 0.40% [11].

Summarizing all above, an ideal hydroisomerization catalyst should provide a high yield of isomerization and should have shape-selectivity to react only with n-paraffins. To achieve these characteristics, the catalyst should have suitable compositional and structural characteristics, mainly: proper balance between metal and acid sites, medium pore size, high dispersion of metal on the catalyst surface, mild acidity and strength distribution of acid sites [2]. Thus, for a well balanced (with a strong hydrogenating function) catalyst the product distribution will depend essentially on its acidic properties and its pore structure [32,33]. Finally, the step of chemical transports of intermediates between sites is of the greatest importance [34–36].

Aim of the current work is the study and development of Pt-based hydroisomerization catalysts supported on various zeolitic carriers (ZSM-5, mordenite and beta zeolite). The effect of zeolite support on the activity and selectivity of the catalysts in naphtha hydroisomerization is discussed in view of detailed physicochemical characterization of the materials, aiming to correlate acidic and shape selectivity characteristics to the differentiating hydroisomerization activity and selectivity. The same Pt/zeolite catalysts were also tested for the isomerization of heavier feeds (>C6), such as BtL-naphtha. As the selective isomerization of heavy n-alkanes is much more difficult due to the rapid cracking of long chain alkanes, the investigation focused on developing catalytic systems with high selectivity to isomerization rather than cracking. Thus, results are also presented on the effect of the nature of the feed (aromaticity, heaviness), investigated with experiments conducted with surrogate naphtha feeds.

2. Experimental part

2.1. Catalyst preparation

Three different commercial zeolites (mordenite: MOR, BETA and ZSM-5) with similar SiO_2/Al_2O_3 ratio (∼20) were used as supports. All zeolites [MOR(20), ZSM-5(23), BETA(25), where the numbers in brackets denote the respective SiO_2/Al_2O_3 ratio] were purchased from Zeolyst Int. (refs. CBV21A, CBV2314 and CP814E, respectively). The supports were calcined in air at 500 °C for 3 h prior to impregnation to convert from the ammonium to the H^+-form. Impregnation followed using an aqueous solution of H_2PtCl_6 in order to achieve a 0.1 wt% Pt loading on the final material. Excess distilled water was used as solvent for this precursor. The derived catalysts were dried and calcined at 400 °C for 3 h under air using a synthetic air stream.

2.2. Catalyst characterization

The elemental composition (Al, Na and Pt content) of all samples was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with a Perkin-Elmer Plasma 40 instrument.

X-ray diffraction (XRD) measurements were also performed using a SIEMENS D-500 diffractometer employing CuKα_1 radiation ($\lambda = 0.15405$ nm) and operating at 40 kV and 30 mA. The XRD patterns were accumulated in the 2θ range of 5–80° with a 0.02° step size and a counting time of 2 s per step.

Surface areas of the samples were determined by N_2 adsorption at 77 K, using the multipoint BET analysis method, with an Autosorb-1 Quantachrome flow apparatus. Prior to the measurements, the samples were dehydrated in vacuum at 250 °C overnight. The Brunauer–Emmet–Teller (BET) equation was used to calculate the apparent surface area (SBET), while the micropore volume (Vmicro) and the external surface (Sext) were calculated from t-plot method.

To examine the tendency of catalyst to form coke (related with hydrocracking reactions) C content was determined by elemental analysis using a LECO-800 CHN analyzer on all catalytic samples; Pt/MOR(20), Pt/ZSM-5(23) and Pt/BETA(25) after the hydroisomerization reaction.

The total acidity, type and acid strength distribution of the acid zeolites were measured by the FTIR-pyridine adsorption technique. IR spectra were collected using a Nicolet 5700 FTIR spectrometer (resolution 4 cm^{-1}) by means of OMNIC software. Data processing was carried out via the GRAMS software. All the samples were