Hydroconversion of paraffinic wax over platinum and palladium catalysts supported on silica–alumina

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ABSTRACT

Two bifunctional catalysts consisting of platinum or palladium supported on amorphous silica–alumina were prepared and tested in hydrocracking/hydroisomerization of paraffinic wax. The performance of both noble metals was studied at the following reaction conditions: $P = 35$ bar; $T = 300–330\,^\circ$C; H_2/wax $= 0.1$ wt/wt; WHSV $= 1–4\,h^{-1}$. The platinum sample was more active in hydrocracking of C_{22+} compounds and more selective to middle distillates. On the other hand, the palladium-based catalyst resulted in a higher isomerization degree of the products and lower amounts of methane and ethane. The higher production of light compounds over platinum is attributed to a monofunctional hydrogenolysis mechanism, in addition to the classical bifunctional route. Characterization studies showed that both catalysts had comparable metal and acid site distributions. These observations would indicate that the different catalyst performance is due to the different nature of platinum and palladium as hydrogenation/dehydrogenation function.

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1. Introduction

Reducing fossil fuel dependency and lowering greenhouse gas emissions are the main driving forces in the development of alternative fuels for the transportation sector [1–3]. Additionally, the energy demand is forecasted to increase in the coming years [4]. In this context, the Fischer–Tropsch (FT) technology is a promising alternative to meet the global energy challenge. Depending on the feedstock, the overall process is named coal-to-liquids (CTL), gas-to-liquids (GTL) or biomass-to-liquids (BTL). If biomass is used as feedstock, GHG-neutral fuels can be produced, increasing at the same time the energy security [3].

When diesel is the desired product, the FT process aims at maximizing the selectivity to long-chain hydrocarbons, *i.e.*, FT waxes, which are then selectively converted to middle distillates in a hydroconversion step [5–8]. Middle-distillate yields of about 80 wt% have been reported, but process improvements are still possible [6].

The hydroconversion step serves two purposes, namely selective cracking of the heavy paraffins and increase in the isomer content, thus improving the cold flow properties of the final product [7,9]. The result is a high-quality diesel fuel, which is also virtually free of sulfur, nitrogen and aromatics. Moreover, it is characterized by a high cetane number and, therefore, excellent ignition properties [7,8].

Hydroconversion of FT wax is usually carried out on bifunctional catalysts, containing a hydrogenation–dehydrogenation function (provided by a metal) and an isomerization-cracking function (acidic support). The commonly accepted reaction mechanism consists of the following steps: (1) dehydrogenation of a *n*-paraffin into an olefin on a metal site; (2) protonation of the olefin to form an alkylcarbenium ion on an acid site; (3) skeletal rearrangement and/or cracking by β-scission of the carbenium ion on an acid site; (4) deprotonation of the resulting ion(s) on an acid site; (5) final hydrogenation of the olefin(s) on a metal site [5,10]. The balance between metal and acid sites has a great influence on the catalyst performance [11].

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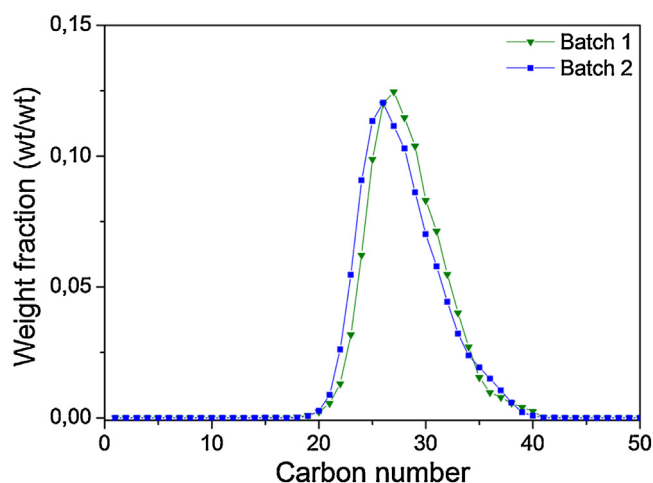 E-mail address: rosp@kth.se (R. Suárez París).

Fig. 1. Carbon number distributions of the wax used in the catalytic tests.

Regarding the metal function, both noble metals (Pt, Pd) and sulfided transition metals (NiWS, NiMoS, CoMoS) have been used, although the former have stronger hydrogenation activity and are usually preferred when processing FT wax [3,5]. Regarding the acid function, a wide variety of solids have been investigated, but materials with weak or medium acid strength (e.g., silica–alumina) are required to maximize middle-distillate production [5].

The performance of platinum supported on silica-alumina for FT wax hydroconversion has been previously studied, showing high middle-distillate selectivities [9,12–14]. Nevertheless, palladium-based catalysts have been mainly examined in batch systems [15,16] or using short-chain paraffins as model compounds [17,18]. To the best of our knowledge, there are no publications comparing platinum and palladium as the metal component of bifunctional catalysts used in wax hydroconversion. The lower cost of palladium compared to platinum suggests the need for performing this comparison under realistic operating conditions.

The aim of this study is to extend our previous work on *n*-hexadecane hydrocracking and hydroisomerization [19] and gain insight into the catalytic behavior of platinum and palladium supported on amorphous silica-alumina in hydroconversion of longer compounds. Paraffinic wax (C_{20}–C_{40}) was used as a model FT wax. The catalytic tests were performed in a continuous reactor at temperatures between 300 and 330 °C and a pressure of 35 bar, conditions analogous to those applied industrially in the Shell Middle Distillate Synthesis process [20].

2. Methods

2.1. Catalyst preparation

Two catalysts with the same molar metal loading were synthetized by incipient wetness impregnation, containing either platinum or palladium as the metal function. The acid function consisted of a commercial amorphous silica–alumina support, Siral 40 (Sasol Germany GmbH). Prior to the impregnation, the support was sieved to the desired fraction (90–200 μm), dried at 120 °C (heating ramp of 5 °C/min) for 6 h and finally calcined in air at 500 °C (heating ramp of 2 °C/min) for 4 h.

The calcined support was impregnated with the corresponding aqueous solution of platinum nitrate (Sigma–Aldrich: $Pt(NH_3)_4(NO_3)_2$, ≥ 50.0% Pt basis) or palladium nitrate (Sigma–Aldrich: $Pd(NO_3)_2 \cdot 2H_2O$, ∼40% Pd basis). The volume of water used was equal to the total pore volume of the support, previously measured by nitrogen adsorption.

The impregnated catalysts were dried and calcined applying the same temperature programs as for the support. The final samples were kept in tightly closed containers and, additionally, dried overnight at 120 °C before the catalytic tests. They are named Pt/S40 and Pd/S40 throughout this paper.

2.2. Catalyst characterization

2.2.1. Elemental composition

The content of platinum or palladium in the catalysts was determined using inductively coupled plasma—sector field mass spectrometry (ICP-SFMS).

2.2.2. Textural characteristics

Nitrogen adsorption measurements were performed in a Micromeritics ASAP2000 unit. The samples were evacuated at 250 °C for a minimum of 4 h before being analyzed. Data were collected at liquid nitrogen boiling temperature (77 K).

Surface area (SA) was calculated using the BET (Brunauer–Emmett–Teller) method with data collected at relative pressures between 0.06 and 0.2. Pore volume and average pore diameter were estimated applying the BJH (Barrett–Joyner–Halenda) model to the adsorption data.

2.2.3. Metallic properties

Metal dispersion, surface area and particle size were estimated by volumetric chemisorption, using hydrogen and carbon monoxide as probe molecules. The samples were first evacuated at 250 °C for a minimum of 4 h. Thereafter, the catalysts were activated *in situ*, by flowing hydrogen at 400 °C for 2 h (heating ramp of 5 °C/min); the same reduction procedure was applied prior to the catalytic tests. The samples were then evacuated for 1 h and, subsequently, cooled in vacuum to the analysis temperature (35 °C). Chemisorption analyses were carried out using a dual-isotherm method: the measurements were repeated after a 30 min-evacuation and the calculations were performed by extrapolating to zero pressure the difference between both isotherms. Average metal particle size (d) was calculated from the dispersion value ($\%D$) using the expression $d = C1/\%D$ [21], where C1 has the value of 113 ($m\,10^{-11}$) for platinum and 112 ($m\,10^{-11}$) for palladium.

The key parameter for a reliable estimation of metallic properties via chemisorption is the adsorption stoichiometry. It is generally assumed that hydrogen adsorbs dissociatively on supported noble metals [22]. Consequently, a stoichiometry of one hydrogen atom per surface metal atom (H:M = 1) was considered in this study, although greater and smaller values have also been reported [22]. Specifically, palladium can adsorb large amounts of hydrogen and form β-palladium hydride at high hydrogen pressures. Therefore, chemisorption measurements on the palladium sample were performed at pressures between 1 and 12 mmHg [23,24].

Different stoichiometry factors were considered for CO chemisorption. In the case of platinum, a CO:Pt stoichiometry equal to 1:1 was used [25]. For palladium, a CO:Pd stoichiometry equal to 1:2 was found to be the most accepted according to various studies [26,27].

The size of the metal particles was also estimated by transmission electron microscopy (TEM) using a JEOL JEM-1400 microscope. All samples were mounted on 3 mm holey carbon copper grids. A minimum of 100 particles were analyzed for each sample.

2.2.4. Acidic properties

The acidic properties of the support and catalysts were studied by FTIR spectroscopy of adsorbed pyridine. Temperature-programmed desorption of ammonia (NH_3-TPD) and thermogravi-