



Effect of metal loading on activity, selectivity and deactivation behavior of Pd/silica–alumina catalysts in the hydroconversion of *n*-hexadecane



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ABSTRACT

Bifunctional catalysts consisting of palladium on amorphous silica–alumina with different metal loadings (0 wt% to 1.2 wt%) were compared in the hydrocracking/hydroisomerization of *n*-hexadecane. The reaction conditions were: pressure = 30 bar; temperature = 310 °C; hydrogen-to-hexadecane feed molar ratio = 10. Metal loading was found to have a remarkable influence on the initial deactivation rate, which could be related to the formation of carbonaceous deposits. The dependence of activity on the metal–acid site ratio was the typical one for bifunctional hydrocracking where, after reaching a threshold value, the catalytic activity does not appreciably increase with increasing metal loading. On the Pd-containing catalysts, the methane space-time-yield showed a strong dependence on conversion, but no clear relationship with metal surface area, indicating that the formation of methane might not proceed by purely metal-catalyzed hydrogenolysis.

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1. Introduction

Due to the growing demand of middle distillate fuels and environmental issues, hydroconversion processes are becoming increasingly important. Hydroconversion is an established technology in refineries, where it is used to improve the value of heavy fractions by lowering their boiling point and removing impurities such as nitrogen, sulfur and heavy metals. One field of application of hydroconversion is the upgrading of primary products of the Fischer–Tropsch (FT) process. The best strategy to yield synthetic diesel in these plants is to maximize FT selectivity towards long chain hydrocarbons (waxes), which are converted by cracking and isomerization into middle distillate fuels in a subsequent hydroprocessing step [1–3]. The conversion of biomass to liquid fuels has been the subject of many studies, as a promising technology for the production of carbon neutral fuels to help reduce CO₂ emissions to atmosphere, even though it has not yet found commercial application [4–9].

Hydrocracking is generally performed on bifunctional metal/acid catalysts, in which the metal sites act as hydrogenating/

dehydrogenating function and the acid sites are responsible for the isomerization and cracking reactions [10]. The waxy products of the FT-synthesis are characterized by the absence of sulfur compounds. For this reason, noble metals such as Pt and Pd or PtPd alloys, which would otherwise be poisoned, can be used in hydrocracking catalysts, and provide high selectivity to middle distillate [11–19]. Due to the high content of linear paraffins in FT-waxes, the resulting fuels are characterized by a high cetane number (good combustion properties). On the other hand, the cold flow properties are detrimentally affected by linear paraffin content, and a high degree of isomerization is required to obtain fuels intended for low-temperature climate or for aviation applications. Catalysts comprised of a strong hydrogenating/dehydrogenating function and a mild acid function were found to satisfy both the requirements of controlled hydrocracking and high isomerization activity [20,21].

The mechanism of alkane hydrocracking has been thoroughly studied [22–28]. The alkane is dehydrogenated on a metal site, producing the corresponding olefin. The olefin diffuses to an acid site where it is protonated to a carbocation, which undergoes successive isomerization steps: mono-branched isomers are formed that can be desorbed as feed isomers after deprotonation and hydrogenation or undergo further branching on the acid site. Di-branched and tri-branched isomers can be cracked into smaller

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Table 1
Textural properties of the fresh catalysts (after calcination at 500 °C for 4 h).

Catalyst	Pd loading (wt%)	BET surface area (m ² /g)	BJH adsorption pore volume (cm ³ /g)	BJH ads. average pore diameter (nm)
Pd0S40	0	440	0.92	8.5
Pd0.18S40	0.18	376	0.90	9.0
Pd0.33S40	0.33	375	0.90	9.1
Pd0.65S40	0.60	377	0.89	8.9
Pd1.25S40	1.20	355	0.84	9.8

olefins which finally migrate to a metal site where they are saturated. According to the classical definition by Weitkamp [24], ideal hydrocracking occurs when the metal function is strong enough to “balance” the acidic function, *i.e.* when the dehydrogenation of the feed molecule and the hydrogenation of the olefinic intermediates are at quasi-equilibrium while the acid catalyzed isomerization and cracking reactions via carbenium ion chemistry are rate determining steps. This theory has been questioned, especially with regards to the importance of the “intimacy” of the two functions and to the role of the metal as the alkane activation function [26]. Alternative theories imply that the alkane can be activated on the acid sites and that the primary role of the metal is to hydrogenate olefinic intermediates to maintain a low steady-state concentration which avoids deactivation by coking [29–31]. Our previous work compared amorphous silica–alumina (ASA) catalysts loaded with platinum and palladium in the hydrocracking/hydroisomerization of *n*-hexadecane at industrially relevant operating conditions. The study pointed out that on Pd/ASA the paraffin reacts according to the classical scheme of successive isomerization steps followed by cracking, while on Pt/ASA a marked contribution of monofunctional, metal-catalyzed hydrogenolysis was observed [32].

To better understand the interactions between the two functions and their role in the complex reaction network, a more detailed study on the effect of the metal loading was required. The present paper addresses the influence of different metal/acid ratios by varying the palladium loading on a mildly acidic silica–alumina support. The purpose of this work is threefold: (1) to find the threshold value of palladium loading required for achieving ideal hydrocracking conditions, *i.e.* for balancing the acidity of the support; (2) to investigate the effect of Pd loading on initial deactivation and selectivity; (3) to assess the potential occurrence and extent of hydrogenolysis at high metal loadings.

2. Material and methods

2.1. Catalysts

The catalysts were prepared by incipient wetness impregnation of amorphous silica–alumina. A commercial silica–alumina (Siral 40, Sasol Germany GmbH) was used as the support material. Siral 40 consists of 40 wt% of SiO₂ and 60 wt% of Al₂O₃. Its characteristics are reported in Table 1. The support was sieved to the desired size (90–200 μm), dried at 120 °C for 6 h and subsequently calcined in air at 500 °C for 2 h, increasing the temperature with a heating rate of 2 °C/min. After calcination the material was kept at 120 °C in order to minimize moisture uptake. The calcined support was impregnated with aqueous solutions of palladium(II) nitrate dihydrate ([Pd(NO₃)₂].2H₂O, Sigma-Aldrich) containing the amount of salt required to achieve the desired weight loading. The amount of added water was calculated from the total pore volume of the support, determined by N₂ adsorption. The impregnated materials were dried at 120 °C for 6 h, and then calcined at 500 °C for 4 h (heating rate 2 °C/min). The catalyst samples were kept in tightly closed containers.

Catalysts with four different palladium loadings were prepared: 0.18%, 0.33%, 0.6% and 1.2%. The non-loaded Siral 40 used in the

catalytic experiments was subjected to the same heat treatment as the Pd-containing catalysts. Throughout this paper, the catalysts are named Pd_wS40, where *w* indicates the nominal weight loading of palladium.

2.2. Catalyst characterization

2.2.1. Surface area and porosity

Nitrogen adsorption measurements were performed using a Micromeritics ASAP 2000 unit. The samples were outgassed by evacuation at 250 °C for a minimum of 4 h prior to analysis. Data were collected at liquid nitrogen boiling temperature (77 K). Surface area was calculated by the BET (Brunauer–Emmett–Teller) method with data collected at relative pressures between 0.06 and 0.2. Total pore volume and average pore size were calculated with the BJH (Barrett–Joyner–Halenda) method using the adsorption isotherm.

2.2.2. Metal surface area and particle size

Metal surface area, dispersion and crystallite size were estimated by volumetric chemisorption of hydrogen using a Micromeritics ASAP 2020C unit. Before the analysis, the samples (0.2–0.4 g) were evacuated for at least 4 h at 250 °C. The samples were subsequently pretreated with the same activation procedure as before the activity testing: *in situ* reduction in flowing hydrogen at 400 °C for 2 h (heating rate 5 °C/min). The samples were then evacuated for 1 h, and thereafter cooled in vacuum to the analysis temperature (35 °C). The analyses were repeated after 30 min of evacuation time. The metal surface area was calculated from the H₂ adsorption value obtained by the extrapolation to zero pressure of the difference between the two adsorption isotherms.

Palladium is known to dissolve hydrogen, forming bulk palladium-hydride. This system has been extensively studied in order to find the optimal chemisorption conditions to estimate Pd surface area [33–36]. Hydride formation can be considered negligible at pressures lower than 2 kPa (15 mm Hg) [36], therefore the part of the isotherms at low H₂ pressure (1–10 mm Hg) was used for the estimation of metal surface area and dispersion of Pd particles.

Average particle diameter (*d_p*) was calculated from the dispersion value (%D), assuming dissociative adsorption of hydrogen (stoichiometric factor = 2) and spherical particles, using the expression: *d_p* [nm] = C1/%D, where C1 has the value of 112 [m × 10⁻¹¹] [37].

The size of the metal particles was also estimated by Transmission Electron Microscopy (TEM) using a JEOL JEM 1400 microscope operating at 120 kV. The samples were mounted on 3 mm holey carbon copper grids by direct contact with the finely ground solids.

2.2.3. Acidity

The acidic properties of the support used and the Pd-containing catalysts were determined by FTIR-spectroscopy of adsorbed pyridine in a ATI Mattson FTIR spectrometer. 15–20 mg of sample was pressed into a self-supported thin wafer and placed in the FTIR-cell. The sample was pretreated in high vacuum at 450 °C for 1 h. The temperature was then lowered to 100 °C and a background spectrum was recorded. Pyridine was adsorbed at its ambient vapor

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