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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.

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:

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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 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 mmHg) [36], therefore the part of the isotherms at low H₂ pressure (1 - 10 mmHg) 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 [$m \cdot 10^{-11}$] [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 pressure in flowing helium at 100 °C for 30 min. Spectra of adsorbed pyridine were recorded at 100 °C for 50 min, after evacuation for 1 h at 150, 250 and 350 °C. Spectral bands at 1545 cm⁻¹ (Brønsted) and 1450 cm⁻¹ (Lewis) were considered for the estimation of acid site concentration, using the correlation constants of Emeis [38].

2.2.4. Analysis of coke deposits by TPO

The carbonaceous deposits on the spent catalyst were characterized by means of temperature-programmed oxidation (TPO) using a Micromeritics Autochem 2920 coupled to a ThermoStar™ Balzers quadrupole mass spectrometer. Approximately 100 mg of sample was pretreated by flowing 50 Nml/min of helium while heating the sample from room temperature to 250 °C (heating rate 10 °C/min) and holding the final temperature for 1 h. The sample was cooled to 50 °C before starting the TPO measurement. A mixture of 5% O₂ in He (30 Nml/min) was passed on the sample and the temperature was increased to 700 °C with a heating rate of 10 °C/min. The sample temperature and the signal of released CO₂ ($m/z = 44$) were recorded at 3 s intervals. A blank test was performed on one fresh catalyst sample. The corresponding CO₂ signal, which was indeed very low and originated presumably from air or impurities present on the samples, was subtracted from the other measurements. The system was calibrated by performing the same treatment on a sample consisting of carbon nanopowder (Aldrich, 99.95%). The quantitative amount of deposited carbon was obtained by integrating the total peak area in the signal/temperature profiles. For comparative purposes, the amount of deposited carbonaceous species was converted into a hypothetical monolayer of pure carbon. Its surface area was then related to the surface area of Pd, using an atomic cross sectional area of $1.86 \cdot 10^{-20}$ m².

2.3. Catalytic testing

2.3.1. Reactor and analysis systems

The reactor system, the analysis system and the experimental procedures have been described in detail in a previous publication [32], and are only briefly presented here. The catalysts were tested on the hydroisomerization/hydrocracking of n-hexadecane (for synthesis, 99%, Merck 820633) performed in a fixed bed tubular reactor, operated in co-current down flow mode. The reaction products were separated in two consecutive traps, the first kept at room temperature and the second at 5 °C. The gaseous products were analyzed on-line using a Perkin Elmer Clarus 500 GC equipped with an Elite-Alumina PLOT column (30 m x 0.53 mm x 10 µm) and a FID detector. Liquid products were analyzed off-line using an Agilent 6890 GC equipped with a HP-5 (5%-Phenyl)-methylpolysiloxane (60 m x 0.320 mm x 0.25 µm) column and a FID detector. The quantitative results of the gas and liquid analyses were merged in order to obtain a full distribution of the cracking and isomerization products. The carbon mass balance obtained was typically > 95%. For each run, the reactor was loaded with approximately 3 g of catalyst which was subsequently activated in flowing hydrogen (50 Nml/min/g_{cat}) at 400 °C for 2 h (heating rate 5 °C/min). The system was then stabilized at the desired reaction temperature and pressurized in pure hydrogen, before starting the n-hexadecane feed. A set of runs with short time-on-stream (ToS) was performed in order to study the effect of Pd loading on catalytic activity and their initial deactivation behavior. The operating conditions were as follows: after activation of the catalyst and stabilization of temperature to 310 °C and pressure to 30 bar, the n-hexadecane feed was started with a liquid weight hourly space velocity (WHSV) of 3 h⁻¹. The hydrogen flow was set to obtain an inlet molar ratio of 10. Two liquid samples were taken after 1 hour on stream and 2 hours on stream respectively. Thereafter the WHSV was changed in order to get selectivity data in a broader conversion range at ToS between 3 - 8 hours.

At the end of each run, the flow of n-hexadecane was stopped and the catalyst was left under hydrogen flow at the reaction

temperature and pressure for several hours. The system was then depressurized to atmospheric pressure and left to cool overnight. The spent catalyst samples were then recovered for characterization.

2.3.2. Activity and selectivity calculations

Conversion of n-hexadecane was defined as $1 - F_{n-C16,out} / F_{n-C16,in}$ where F_i indicates the molar flow. The hydroconversion activity is reported as the pseudo- first-order reaction rate constant for the decomposition of n-hexadecane, calculated assuming plug flow behavior. The products of n-hexadecane hydroisomerization/hydrocracking were grouped into three lumps: mono-branched hexadecanes (MB), di- or multi-branched hexadecanes (DB), and cracking products (CP). Selectivities (S_i) are defined on a carbon atom basis, as moles of C in product i per mole of C of converted n-hexadecane. In this way the sum of selectivities to the product lumps at a given conversion is always equal to unity. The reported space time yields were calculated as the molar flow of a specific product per unit mass of catalyst.

3. Results and discussion

3.1. Physical characterization

The textural properties of the fresh catalyst samples are presented in Table 1.

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

Catalyst	Pd loading	BET surface area	BJH ads. pore volume	BJH ads. average pore diameter
	(wt%)	(m ² /g)	(cm ³ /g)	(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
Pd0.6S40	0.60	377	0.89	8.9
Pd1.2S40	1.20	355	0.84	9.8

Impregnation with palladium lowered the surface area of the silica-alumina support, but did not alter significantly the porous structure. The loss of surface area was probably caused by blockage of smaller pores by the metal particles. Any effect of the calcination treatment was ruled out by subjecting the non-loaded silica-alumina

to the same heat treatment as Pd-loaded catalysts. No appreciable differences in the textural properties of the support were observed, except for the catalyst with the highest metal loading (1.2-wt%), for which the surface area and pore volume were further reduced.

The Pd particles of the Pd1.2S40 sample have an average diameter (see Table 3) comparable to the size of the pores; therefore a higher extent of pore blockage is to be expected.

The textural properties of the catalyst samples after reaction are presented in Table 2.

Table 2

Textural properties of the spent catalysts (after outgassing in vacuum at 250 °C).

Catalyst	Pd loading (wt%)	BET surface area (m ² /g)	BJH ads. pore volume (cm ³ /g)	BJH ads. average pore diameter (nm)
Pd0S40	0	398	0.89	8.6
Pd0.18S40	0.18	372	0.91	9.1
Pd0.33S40	0.33	375	0.89	9.0
Pd0.6S40	0.60	362	0.89	9.2
Pd1.2S40	1.20	322	0.76	9.0

A graphical comparison of BET surface areas for the fresh and spent catalysts can be seen in Figure 1.

Figure 1. BET surface area vs. palladium loading for the fresh (○) and spent (■) catalysts (ToS = 8 h).

It can be observed that a marked decrease in surface area, pore volume and average pore diameter occurred, after 8 hours on stream, for the sample containing 1.2-wt% of Pd. A possible explanation is the presence of larger Pd particles,

partially blocking the pores (see §3.2). Practically no changes in surface area and pore volume were observed for the catalysts with lower loadings (0.18-wt% and 0.33-wt%), while the 0.6-wt% sample showed a slight decrease of the BET surface area. A large loss of BET surface area was also observed for the Pd-free Siral 40, without any significant change in pore volume and average pore diameter. From this basis and from the results of the analysis of the carbonaceous deposits (see Fig. 5 and §3.4), it could be inferred that the harder, less hydrogenated coke species formed on Pd0S40 affect surface area to a larger extent than the softer ones present on the Pd-containing samples.

3.2 Metal particle size

Table 3 and 4 show the results of hydrogen chemisorption measurements performed on the fresh and spent catalysts. Hydrogen chemisorption was also performed on the non-loaded support and proved to be negligible. The metal surface area of the samples is summarized in graphical form in Figure 2.

Figure 2. Metal surface area vs. palladium loading for the fresh (○) and spent (■) catalysts (ToS = 8 h).

Results of the mean particle size estimation by TEM imaging are also reported for all the catalyst samples except the 0.6-wt%. TEM images of Pd0.33S40 and Pd1.2S40 are shown in Figure 3 and histograms of size distribution are shown in Figure 4.

Table 3
Physicochemical properties of the fresh catalysts.

Catalyst	Pd loading	H ₂ uptake @ 35 °C	Pd surface area	Pd dispersion	Mean particle size (d _p -chemi) (nm)	Mean particle size (d _p -TEM) ⁽¹⁾ (nm)
	(wt%)	(cm ³ STP/g cat)	(m ² /g _{cat})	(%)		
Pd0S40	0	0	-	-	-	-
Pd0.18S40	0.18	0.054	0.226	28.2	4.0	4.7±1.7
Pd0.33S40	0.33	0.102	0.430	29.2	3.8	4.4±2.6
Pd0.6S40	0.60	0.170	0.718	26.9	4.2	-
Pd1.2S40	1.20	0.149	0.628	11.8	9.5	7.8±5.4

⁽¹⁾ Mean and standard deviation.

Table 4
Physicochemical properties of the spent catalysts (after 8 h on stream).

Catalyst	Pd loading	H ₂ uptake @ 35 °C	Pd surface area	Pd dispersion ⁽¹⁾	Mean particle size (d _p -chemi) ⁽¹⁾ (nm)	Mean particle size (d _p -TEM) ⁽²⁾ (nm)
	(wt%)	(cm ³ STP/g cat)	(m ² /g _{cat})	(%)		
Pd0.18S40	0.18	0.009	0.038	4.7	23.9	7.4±2.3
Pd0.33S40	0.33	0.022	0.091	6.2	18.0	5.1±2.3
Pd0.6S40	0.60	0.030	0.126	4.7	23.8	-
Pd1.2S40	1.20	0.024	0.103	1.9	58.3	10.0±7.2

⁽¹⁾ Calculated assuming no influence of coke deposits on Pd particles; reported for comparison purposes only.

⁽²⁾ Mean and standard deviation.

Figure 3. TEM images for fresh Pd0.33S40 (A), spent Pd0.33S40 (B), fresh Pd1.2S40 (C), spent Pd1.2S40 (D).

No size distribution is reported for Pd0.18S40, due to the limited amount of images taken on this sample. The metal dispersion was similar (~30%) for the fresh samples up to 0.6-wt% loading, while the Pd1.2S40 sample showed considerably lower dispersion (~12%). Mean particle size estimation by TEM confirmed the hydrogen chemisorption measurements on the fresh catalysts; the presence of larger particles and a much broader size distribution was observed on the 1.2-wt% sample (Fig. 4 B).

Figure 4. Particle size distribution for Pd0.33S40 (A) and Pd1.2S40 (B); fresh (empty bars) and spent (patterned bars).

A remarkable drop in H₂-uptake was observed on all the spent catalysts, which can only partly be explained by sintering of the metal particles. TEM results indicate that sintering of Pd particles occurred, but the mean Pd-particle size on the spent catalysts was still much lower than the corresponding estimation by hydrogen chemisorption (see Table 4). This indicates that coverage of the metal particles by carbonaceous deposits is the main cause of the observed loss in hydrogen uptake. The loss of BET surface area observed on Pd1.2S40 can be explained by pore blockage due to the larger Pd particles present on this sample.

3.3 Acidity measurements

The concentrations of Brønsted (BAS) and Lewis (LAS) acid sites of different strength, determined by IR-spectroscopy of adsorbed pyridine, are presented in Table 5. The addition of palladium clearly modifies the acidic properties of the silica-alumina support. Lewis

acidity is decreased with the lowest Pd loading and increased with higher Pd loadings. Both low and medium strength BAS are increased by addition of low amounts of Pd, while an increase of weak Brønsted sites and a decrease of medium strength BAS was observed for Pd1.2S40. The reasons behind these observations are due to non-trivial metal-support interactions. Kubicka et al. [39] observed similar effects when loading different solid acids with Pt. They speculated that metal crystallites can blanket Lewis acid sites of the support but also act themselves as electron acceptors, while the observed increase in BAS was attributed to modification of the support during impregnation. An alternative explanation could be that the metal particles, acting as Lewis acids, polarize the OH bonds of the Si-OH groups, giving rise to BAS of lower strength. The medium strength BAS (measured after desorption of pyridine at 250 °C) were used in the calculation of the metal/acid site ratio of the catalysts.

Table 5
Acid properties of the fresh catalysts, determined by pyridine adsorption FTIR.

Catalyst	Brønsted acid sites ($\mu\text{mol/g}$)			Lewis acid sites ($\mu\text{mol/g}$)		
	150 °C	250 °C	350 °C	150 °C	250 °C	350 °C
Pd0S40	44	31	4	114	54	12
Pd0.18S40	56	43	0	69	24	0
Pd0.33S40	58	52	0	88	38	0
Pd0.6S40	51	39	0	149	72	0
Pd1.2S40	62	27	0	139	37	0

3.4 Temperature-Programmed Oxidation

In order to assess the formation of carbonaceous deposits, the spent catalysts were characterized by means of temperature-programmed oxidation (Fig. 5). All the carbon could be removed from the samples after oxidation treatment up to 700 °C. The most apparent difference is the high temperature peak, centered at ~540 °C, for the non-loaded catalyst (Pd0S40), implying that a much larger amount of hard-to-remove carbon was formed compared to the Pd-containing catalysts. On the non-loaded sample no low-temperature carbon is present, thereby indirectly confirming that possible adsorbed hydrocarbon species were successfully removed by the post-reaction

treatment on the spent samples. Among the Pd-containing catalysts, some differences can be noted: the CO₂ evolution profiles present at least three features, indicating the presence of different carbonaceous species. The sample with the lowest Pd loading (Pd0.18S40) presents a larger high temperature peak, at ~480 °C, which for the 0.33-wt%, 0.6-wt% and 1.2-wt% samples is centered at lower temperature (~450 °C).

Figure 5. Temperature-programmed oxidation (TPO) profiles for the spent catalysts after ToS = 8 h.

The position of the low temperature peaks follows the metal loading, moving from $\sim 270^\circ\text{C}$ for 0.18-wt%, through $\sim 250^\circ\text{C}$ (0.33-wt%), $\sim 215^\circ\text{C}$ (0.6-wt%), and finally to a peak centered at $\sim 160^\circ\text{C}$ for the 1.2-wt% sample. This implies that more reactive coke deposits, presumably with higher hydrogen content were formed on the samples with higher Pd loadings and less reactive, “harder”, species on lower Pd loadings. This situation is in line with the findings about selectivity of the catalysts, where increasing hydrogenating activity was observed with increasing metal loading.

Figure 6. Carbon-to-metal surface-area ratio, calculated assuming monolayer coverage of pure carbon

The total amount of carbonaceous species deposited on the catalysts shows a clear dependency on metal loading. Figure 6 shows the ratio between the surface area occupied by carbon species (calculated assuming monolayer coverage of pure carbon) and the Pd surface area

(calculated by H_2 -chemisorption on the fresh samples) plotted against the metal-acid site ratio. The formation of carbon is favored on the 0.18-wt% sample, while the difference in carbon-to-metal surface ratio is much smaller between the 0.33-wt% and 1.2-wt% samples. The absolute values were very high for all the catalysts (between 32 and $138 \text{ m}^2_{\text{C}}/\text{m}^2_{\text{Pd}}$) indicating that the carbon was probably mostly located on the support.

3.5 Effect of palladium loading on initial activity and initial deactivation

The initial activities of the four tested catalysts, expressed as the pseudo-first-order rate constant for the conversion of n-hexadecane, are shown in Figure 7.

Figure 7. Total hydroconversion activity vs. metal/acid site ratio in the initial reaction period, after ToS = 1 h (■) and ToS = 2 h (▲). Conditions: 310°C , 30 bar, $\text{H}_2/\text{n-C}_{16}\text{H}_{34} = 10 \text{ mol/mol}$, $\text{WHSV} = 3 \text{ h}^{-1}$.

Two sets of data are presented, comprising activity values after approximately 1 hour on stream and 2 hours on stream respectively. The dependence of initial activity on metal-acid site ratio is the typical one for the classical bifunctional hydrocracking mechanism [40], for which activity increases up to a given value, where the number of metal sites is sufficient to balance the activity of the acid function for the transformation of the intermediate alkenes. This threshold value for Pd loading was found to lie between 0.33-wt% and 0.6-wt%.

The stability of the catalysts was also found to be dependent on the metal loading. The second set of activity values in Figure 7 shows a similar pattern as the first set, but a considerable

activity drop is apparent, especially at low Pd loading.

Figure 8 shows the relative activity loss per hour on stream versus metal-acid site ratio. The deactivation rate is higher at lower Pd loadings and flattens out at higher metal contents. This can be explained by the occurrence of secondary reactions on the acid sites, such as dehydrocyclization and alkene condensation, finally leading to the formation of coke.

Figure 8. Relative activity loss during the initial reaction period as a function of the metal/acid site ratio. Conditions: 310 °C, 30 bar, $H_2/n\text{-C}_{16}H_{34} = 10$ mol/mol, WHSV = 3 h⁻¹.

Steady-state alkene concentration on the acid sites is influenced by the amount of metal sites

available for alkene hydrogenation; at lower metal loadings, the “residence time” of alkene intermediates on the acid sites is longer, favoring the formation of coke precursors. This is even more apparent in the unloaded silica-alumina catalyst (Pd0S40). The initial activity (ToS = 1 h) is only a fraction of the activity measured for the Pd loaded catalysts, but it is by no means negligible. This indicates that activation of alkanes can occur on acid sites, but that the high concentrations of olefins, which, in absence of metal sites, are not readily hydrogenated, cause a fast deactivation. This behavior is confirmed by the analyses of carbonaceous deposits discussed in §3.4 above.

3.6 Effect of palladium loading on selectivity

Selectivity data are presented in Table 6. Although the catalytic activity was not stable, the deactivation rate after the first few hours on stream was low enough to get comparable results. Selectivity depends strongly on conversion level, and, even though activity varies due to ongoing deactivation, a relevant comparison of product distribution data at varying n-hexadecane conversion can be obtained.

Table 6

Initial activity and selectivity for the Pd/Siral 40 catalysts (310 °C, 30 bar, $H_2/n\text{-C}_{16}H_{34} = 10$ mol/mol, WHSV = 3 h⁻¹).

Catalyst	ToS	n-C ₁₆ H ₃₄ conv.	K ⁽¹⁾	S _{CP} ⁽²⁾	S _{MB} ⁽²⁾	S _{DB} ⁽²⁾	STY _{CH₄} ⁽³⁾	i/n in CP ⁽⁴⁾	o/p in CP ⁽⁵⁾	molCP/ mol cracked ⁽⁶⁾
	(h)	(%)	(h ⁻¹)	(C%)	(C%)	(C%)	(μmol/h/g _{cat})	mol/mol	mol/mol	mol/mol
Pd0S40	1	6.7	0.21	86.9	4.5	8.6	7.1	6.81	0.23	2.42
	2	3.9	0.12	92.9	1.7	5.4	5.5	7.21	0.34	2.58
Pd0.18S40	1	47.1	1.91	6.7	58.5	34.8	3.7	2.37	-	2.01
	2	38.6	1.46	4.7	64.3	30.9	4.7	2.03	-	2.03
Pd0.33S40	1	50.8	2.14	6.3	59.1	34.6	6.1	2.15	-	2.00
	2	45.2	1.80	4.3	65.4	30.3	6.4	1.91	-	2.03
Pd0.6S40	1	51.5	2.17	6.8	61.9	31.3	6.6	2.07	-	2.01
	2	47.0	1.90	4.8	66.1	29.1	6.2	1.98	-	2.02
Pd1.2S40	1	53.0	2.26	6.2	60.6	33.1	7.8	1.66	-	1.99
	2	48.2	1.97	3.9	65.5	30.6	7.9	1.64	-	2.02

⁽¹⁾ Pseudo-first-order rate constant for n-C₁₆H₃₄ conversion.

⁽²⁾ Carbon based selectivities to product lumps. (CP = cracking products, MB = mono-branched hexadecanes, DB = multi-branched hexadecanes).

⁽³⁾ Methane Space Time Yield (moles of methane produced per unit time per unit mass of catalyst).

⁽⁴⁾ Iso-to-normal alkane ratio in cracking products.

⁽⁵⁾ Olefin-to-paraffin ratio in cracking products (calculated on products with n_C < 6).

⁽⁶⁾ Moles of cracking products per mole of cracked n-hexadecane. A value of 2 indicates pure primary cracking.

Due to the low activity and fast deactivation of the unloaded silica-alumina, selectivity data for this catalyst were collected only at low conversion. It could be observed that a high amount of unsaturated hydrocarbons were produced on the unloaded sample, while no olefins could be detected in the products for the Pd-containing catalyst, even at the lowest metal loading. The ratio between the moles of cracking products and the moles of cracked hexadecane is very close to 2, showing that no secondary cracking occurred on the metal-loaded catalysts.

3.6.1 Hydroisomerization/hydrocracking selectivity

Selectivities to the three main different product lumps (mono-branched hexadecanes, multi-branched hexadecanes and cracking products) are presented in Figure 9. All the tested Pd/ASA catalysts follow the expected pattern of consecutive reactions in which the feed alkane undergoes successive isomerization steps before cracking, with the assumption that mono-branched isomers cannot crack. Cracking selectivities are indeed low (< 10% on a carbon atom basis) up to 80% conversion.

Figure 9. Selectivity/Conversion plots for the different product lumps (MB = mono-branched hexadecanes, DB = multi-branched hexadecanes, CP = cracking products) on Pd/ASA catalysts: Pd0.18S40 (●), Pd0.33S40 (▲), Pd0.6S40 (■), Pd1.2S40 (★). The lines were obtained by fitting the experimental data (△) considering consecutive successive first-order reaction steps on a stable Pd0.33S40 catalyst [32]. Conditions: 310 °C, 30 bar, $H_2/n\text{-}C_{16}H_{34} = 10$ mol/mol, WHSV = 0.75–18 h⁻¹.

The differences among the Pd-containing catalysts with this product lumping are subtle and may seem to fall within the experimental error. Nevertheless, deviations can be seen for the 0.18-wt% sample and, to a lesser extent, for

the 0.33-wt% sample. Compared to the other catalysts, the selectivity to mono-branched hexadecanes is lower, while multi-branched feed isomers and cracking products are formed in slightly larger amounts. This can be explained by the classical bifunctional mechanism: the lower the available metal surface area, the longer is the average lifetime of the olefinic intermediates on the acid sites before being hydrogenated. These intermediates are thus subjected to further transformations on the acid sites leading to more multi-branched isomers and eventually to cracking products.

The differences become more appreciable looking at another parameter influenced by the metal/acid site balance, i.e. the degree of branching in the cracking products. In Figure 10 the iso-to-normal molar ratios for butanes and pentanes are plotted versus the metal-acid site ratio. At higher metal-acid ratios the degree of branching is lower, a further indication of the larger availability of the hydrogenation function. On the metal-free catalyst these values are up to 5 times larger. One should note that the data in Figure 10 were collected at the same operating conditions and time-on-stream, resulting in slightly different conversion levels for the Pd-containing catalysts (38.6% – 48.2%), with conversion decreasing with metal loading.

Figure 10. Iso-to-normal molar ratios for butanes (■) and pentanes (●). (T = 310 °C; P = 30 bar; $H_2/n\text{-}C_{16}H_{34} = 10$ mol/mol; ToS = 2 h).

The iso-to-normal ratio is affected by total conversion, but the trend would be further enhanced if the catalysts were compared at the same n-hexadecane conversion. A plot of the branched-to-linear alkane ratio in cracking

products versus total conversion is shown in Figure 11.

Figure 11. Iso-to-normal paraffin ratio in the cracking products as a function of n-hexadecane conversion for Pd0S40 (x), Pd0.18S40 (●), Pd0.33S40 (▲), Pd0.6S40 (■), Pd1.2S40 (★).

The increase in the total isomer content in the cracking products with conversion is apparent, and it can be observed that the iso-to-normal ratio is generally higher on the catalysts with the lowest metal loadings. The values of iso-to-normal ratio range from below 1 at low conversion to 3 at high conversion; these figures are in line with the classical hydrocracking mechanism and arise from different contribution from the β -scission modes at different total conversion. Type A β -scission requires a tri-branched carbenium ion and produces two branched fragments, while type B scission events occur on di-branched intermediates and give one branched and one linear fragment. Type C β -scissions, which give two linear fragments from a monobranched carbenium ion, are much slower [26]. At higher conversion, the higher degree of isomerization of the hexadecane intermediates will increase the concentration of tri-branched carbenium ions, which can be cracked by type A β -scission, thus increasing its relative contribution and consequently the content of branched isomers in the cracking products. Values of the iso-to-normal ratio lower than one, which are observed at conversion around 10%, imply that type C β -scissions occur to some extent.

The relative abundance of intermediates with different branching degrees could account for the observed differences in the iso-to-normal ratios on the catalysts with different metal

loadings; on a catalyst with a weaker hydrogenating function, isomerization of the intermediates will proceed further, giving rise to a higher concentration of tri-branched isomers which are required for type A β -scission to occur.

3.6.2 Methane selectivity

According to the classical bifunctional hydrocracking mechanism, the formation of methane proceeds via type D β -scission, which is by far the slowest of the hydrocracking modes and is usually termed “forbidden”, due to the highly unstable primary carbenium ion intermediate required [26]. The yields of methane are indeed very low on all the Pd/ASA catalysts. Nevertheless, it is interesting to understand if the methane produced originates from a small contribution of type D cracking or from a hydrogenolytic route catalyzed by the metal sites alone. Rates of formation of methane can be used to assess the extent of the monofunctional hydrogenolysis mechanism, as we have reported before when comparing platinum and palladium on a similar support [32]. Therefore, we investigated the dependence of the methane yield on palladium loading. In Figure 12, the methane space time yield (mmol CH₄/g_{cat}/h) is shown as a function of total conversions of n-hexadecane.

Figure 12. Space time yield of methane as a function of n-hexadecane conversion for Pd0S40 (x), Pd0.18S40 (●), Pd0.33S40 (▲), Pd0.6S40 (■), Pd1.2S40 (★).

On all the Pd-containing catalysts, the methane yield was highest at low conversion and declined strongly at higher conversion. In a reaction scheme accounting for direct hydrogenolysis of the alkane on the metal sites

superimposed to the classical bifunctional hydrocracking mechanism, this pattern could indicate that methane is formed by hydrogenolysis. At higher conversion two factors would reduce the contribution of this mechanism: (1) the rising population of branched alkanes decreases the number of “free ends” that can undergo demethylation; moreover, (2) the increasing amount of olefinic intermediates from the bifunctional isomerization/cracking reactions being hydrogenated would reduce the Pd-site vacancies where hydrogenolysis takes place. Hence, as was observed, the rate of formation of methane would be much lower at high conversion. On the other hand, if hydrogenolysis on the Pd sites is the main source of methane, a dependence of methane yield on the available metal surface area would be expected. Significant differences between the tested catalysts are not immediately apparent from the plots in Fig. 12. In Figure 13 the specific methane yield per unit exposed metal surface area (site time yield) is plotted against n-hexadecane conversion.

Figure 13. Specific methane yield per Pd surface area (calculated by H₂ chemisorption on the fresh samples) as a function of n-hexadecane conversion. Pd0.18S40 (●), Pd0.33S40 (▲), Pd0.6S40 (■), Pd1.2S40 (★).

If methane is produced by monofunctional hydrogenolysis, its site time yield should be the same for all catalysts and only depend on conversion. If the interplay between the acid and the metal functions is accounted for, the excess metal present on the samples with the highest metal surface area (Pd0.6S40 and Pd1.2S40), would increase the specific rate for hydrogenolysis, while on metal-poor catalysts

the observed methane yield would be lower. This does not seem to be the case; on the contrary, the highest specific methane yields are observed on the low metal-surface-area catalysts. These results indicate that the metal function is not the main responsible for the formation of methane, and that a role of the acid function cannot be ruled out. Further and more specific work is required to confirm this hypothesis.

4. Conclusions

Pd/silica-alumina bifunctional catalysts with different metal loadings, ranging from 0-wt% to 1.2-wt%, were prepared and compared in the hydroconversion of n-hexadecane. The metal loading influenced the acidic properties of the support and the metal-acid site ratio was found to affect initial activity, rate of deactivation and selectivity. The initial activity showed a strong dependence on the metal-acid site ratio up to a Pd loading of 0.33-wt%, while the increase in activity at higher metal loadings was limited. This led us to conclude that a Pd loading between 0.33-wt% and 0.6-wt% is required to balance the acid function of the Siral 40 support and thus achieve the ideal hydrocracking regime at the reaction conditions used in this study. The initial deactivation rate could be correlated to the metal-acid site ratio; catalysts with the lowest metal content showed a faster rate of deactivation. TPO analyses of the spent catalysts confirmed that coking was the main cause of deactivation, although a limited extent of sintering of the metal particles was observed by TEM imaging.

Hydroconversion of n-hexadecane was shown to proceed through the typical bifunctional hydroisomerization/hydrocracking reaction steps on all the palladium containing catalysts. The unloaded catalyst showed high selectivity to cracking products with a high content of branched alkanes and alkenes, while no alkenes were present in the products on the metal-containing catalysts.

Pd loading affected the selectivity to isomerization and cracking and the content of branched alkanes in the cracking products. At Pd loadings below 0.6-wt%, the selectivity was shifted towards more multi-branched feed

isomers and cracking products. Moreover, on low Pd-loading catalysts the iso-to-normal alkane ratio in the cracking products was higher.

Methane yield was shown to strongly depend on the total conversion of n-hexadecane, being highest at low conversion and decreasing markedly at higher conversion. A surprising dependence on Pd loading was also observed: the rate of formation of methane per metal surface area (i.e. per metal site) seemed to be highest on catalysts with low Pd loadings and lowest at high Pd loadings. This behavior indicates that methane might not be formed by direct hydrogenolysis of the alkane molecules on the metal sites.

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