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Synthesis of methyl isobutyl ketone using Pt–H[Al]ZSM5 bifunctional catalysts. III. Effect of the nPt/nA parameter on the xPt–H[Al]ZSM5(y) catalysts

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Synthesis of 4-methyl-2-pentanone, better known as methyl isobutyl ketone (MIBK), from propanone (Ac) was studied in a fixed-bed and a flow reactor at 160 °C, 1 atm and an H_2/Ac molar ratio equal to 0.33, using Pt–H[Al]ZSM5 bifunctional catalysts with variable platinum percentage and Si/Al ratio. The results show that initial total activity to all measured products at $t = 0$, per acidic site (A_o/nA), residual activity ($A_r = A_{265}/A_0$, ratio of activity after 265 min of stream and the initial total activity to all measured products at $t = 0$) and initial formation rate of each product per acidic site (R_o/nA) largely depend on the relationship between the number of hydro–dehydrogenating metallic sites and the number of theoretical acidic sites (nPt/nA) present in the catalysts used.

Keywords: bifunctional catalysis, zeolite, Pt–H[Al]ZSM5, acetone, methyl isobutyl ketone

1. Introduction

The acetone aldolization reaction can be carried out over amorphous solids (acid and/or basic) [1] or over crystalline solids such as aluminosilicates [2]. However, the solid to be used will be determined by the products desired from the reaction. For instance, when $MgO–Al_2O_3$ is used as a catalyst [1], the products obtained are mostly (80%) isophorone and isosylitone, which is completely logic, because the active centers of these solids are surrounded by large cavities that can accommodate voluminous transition states which normally lead to the formation of macromolecules. The same behavior can be observed when zeolitic catalysts with a large pore size are used, such as HY, HMOR, etc. [3]. Studies carried out by Biaglow et al. [2] on medium pore catalysts of the H[Al]ZSM5 type, show the formation of a number of low voluminous products, mesityl oxide being the product which is predominantly formed. This product serves as an intermediary for the methyl isobutyl ketone (MIBK) synthesis. MIBK is of high industrial importance, because it can be used as a solvent in the manufacturing of paints, lacquers, etc. [4]. This substance can be obtained from acetone through three successive stages, as shown in reaction scheme 1. However, it has been experimentally proven that MIBK can be obtained from acetone in a hydrogen atmosphere and in one apparent stage, using bifunctional catalysts of the Pt/[Al]ZSM5 type [5,6].

The first stage corresponds to the aldolization of two acetone molecules to form 4-hydroxy-4-methyl-2-pentanone (DA), catalyzed by centers of high acidic strength [7]; the second stage corresponds to DA dehydration to form 4-methyl-3-penten-2-one (MO), which can be catalyzed by sites with low acidic strength [7]; and the last stage is the selective hydrogenation of the double olefinic bond (C=C) of MO; this reaction would take place over the metallic centers dispersed in the zeolite and would produce 4-methyl-2-pentanone (MIBK). In summary, complex processes can be carried out over multifunctional catalysts, involving different stages such as aldolization, dehydration, hydrogenation, isomerization, and rearrangements, in only one apparent stage [4]. A previous paper showed the effect that the variation of the relationship between the number of accessible metallic sites and the number of theoretical acidic sites (nPt/nA) had on the catalytic properties of the Pt–H[Al]ZSM5 solids, in which the metal percentage was modified and the density of the catalyst acidic sites remained constant [8]. This paper presents the effect of the parameter (nPt/nA) on the global initial activity per acidic site (A_o/nA) as well as on the residual activity ($A_r = A_{265}/A_0$) of the catalyst and the initial formation rate per acidic site (R_o/nA) for the products of the acetone transformation over xPt–H[Al]ZSM5(y) bifunctional catalysts, with varying platinum percentages (x) and Si/Al ratio (y). The results show that the aforementioned catalytic properties largely depend on the nPt/nA ratio.

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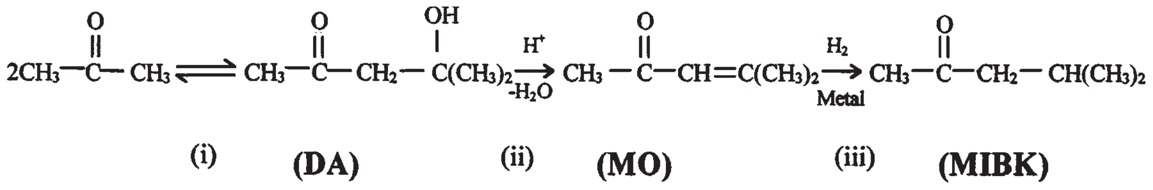


$$2CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{OH}{|}}{C}(CH_3)_2 \xrightarrow[-H_2O]{H^+} CH_3-\overset{\overset{O}{\|}}{C}-CH=C(CH_3)_2 \xrightarrow[Metal]{H_2} CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH(CH_3)_2$$

Scheme 1.

2. Experimental

A series of aluminosilicates of the MFI type with an Si/Al ratio between 22 and 106 was synthesized using the method developed by Guth at al. [9]. The solids obtained, once washed and calcined, were characterized by means of X-ray diffraction (XRD), scanning electronic microscopy (SEM), solid-state nuclear magnetic resonance (^{27}Al-NMR) and nitrogen adsorption at $-196\,^{\circ}$C. Elemental composition of these solids was determined by atomic absorption spectroscopy, which allowed us to establish for each case their respective mesh formulas and calculate the number of theoretical acidic sites per gram, which are considered representative of the active acidic sites of the solids [10] (table 1).

Using these solids with a varying Si/Al ratio (y), several xPt–H[Al]ZSM5(y) bifunctional catalysts were prepared with platinum weight percentages (x) between 0.03 and 0.54% (table 2). The metallic phase was introduced into the zeolites by means of cationic exchange of the $Pt(NH_3)_4^{2+}$ precursor, in the presence of the competitor NH_4^+ ion, according to the method established by Ribeiro et al. [11]. Once prepared, these catalysts were calcined under dry air at 300 °C and then treated in a hydrogen atmosphere at 500 °C. Subsequently, the hydrogenating activity of all of the prepared catalysts was evaluated and was determined by the toluene hydrogenation reaction in a dynamic reactor at 110 °C, 1 atm, an H_2/toluene molar ratio of 9 and a WWH value (grams of reactant injected per hour and per gram of catalyst) of 21.5 h^{-1}. Likewise, three of these catalysts (0.14, 0.31 and 0.54 weight percentage of platinum) were assessed by means of transmission electronic microscopy (TEM), which enabled the dispersion of the supported metallic phase and the number of metallic centers accessible to the reactant to be estimated (table 2).

Propanone reaction was run in a reactor similar to the one used in the toluene hydrogenation, but at 160 °C, 1 atm, an H_2/acetone molar ratio of 0.33 and WWH between 4.7 and 66.4 h^{-1}. These reaction conditions are the ones that lead to a maximum selectivity to MIBK and a higher residual activity [12]. The products obtained in the acetone transformation under the aforementioned operation conditions are: 4-methyl-2-pentanone (MIBK), light hydrocarbons (Hc, basically made up of propane), 4-methyl-3-penten-2-one (MO), 2-methylpentane (2MP), and 2,6-dimethyl-4-heptanone (DIBK). Product analysis, both in the toluene hydrogenation as well as in the acetone transformation, was carried out by the on-line injection of the effluents from the reactor into chromatographs equipped with squalane and CP-Sil-5-CB capillary columns 50 and 25 m in length, respectively.

Table 1
Chemical formulas per unit cell for each of the synthesized H[Al]ZSM5 zeolites, and respective densities of theoretical acidic sites.

Unit cell formula	Si/Al[a]	nA × 10^{20} sites/g[b]
$H_{4.00}Na_{0.20}Al_{4.20}Si_{91.80}O_{192}$	22	4.20
$H_{2.00}Na_{0.30}Al_{2.30}Si_{93.70}O_{192}$	41	2.10
$H_{1.50}Na_{0.10}Al_{1.57}Si_{94.40}O_{192}$	60	1.57
$H_{1.00}Na_{0.01}Al_{1.01}Si_{95.00}O_{192}$	95	1.00
$H_{0.90}Na_{0.01}Al_{0.91}Si_{95.10}O_{192}$	106	0.95

[a] Atomic structure relationship between Si and Al.
[b] Number of theoretical acidic sites per gram of catalyst.

Table 2
Physico-chemical characteristics of the xPt–H[Al]ZSM5(y) catalysts.

Catalysts	Pt[a] (%)	A_H^0 [b] (mmol/h g)	D[c] (%)	nPt/nA[d]
0.14Pt–HZSM5(22)	0.14	5.5	40	0.0041
0.03Pt–HZSM5(41)	0.03	1.3	40	0.0017
0.31Pt–HZSM5(41)	0.31	12.1	35	0.0160
0.54Pt–HZSM5(41)	0.54	27.0	45	0.0357
0.40Pt–HZSM5(60)	0.40	13.4	30	0.0235
0.08Pt–HZSM5(95)	0.08	3.5	42	0.0103
0.07Pt–HZSM5(106)	0.07	3.0	38	0.0086

[a] Percentage of platinum deposited over solids.
[b] Initial activity in toluene hydrogenation.
[c] Dispersion percentage of deposited platinum.
[d] Relationship of metallic sites accessible to theoretical acidic sites.

3. Results and discussion

Characterization by XRD, SEM and nitrogen adsorption to the different synthesized MFI zeolites show that all of the solids have high purity and high crystallinity. ^{27}Al-NMR analysis provided confirmation that all of the aluminum is incorporated into the crystalline structure, because the ^{27}Al-NMR spectra obtained showed a single band at 46 ppm, which is characteristic of tetrahedral aluminum [13]. The results obtained using TEM and toluene hydrogenation suggest the existence of a linear relationship between the number of accessible metallic centers (nPt) and the initial activity of toluene hydrogenation (A_H^0). This correlation between A_H^0 and nPt allowed an estimation of the dispersion percentage (D (%)) of the metallic phase for the rest of the catalysts, which varies between 30 and 50% (table 2). Through this characterization we could determine the ratio between the number of accessible metallic centers and the

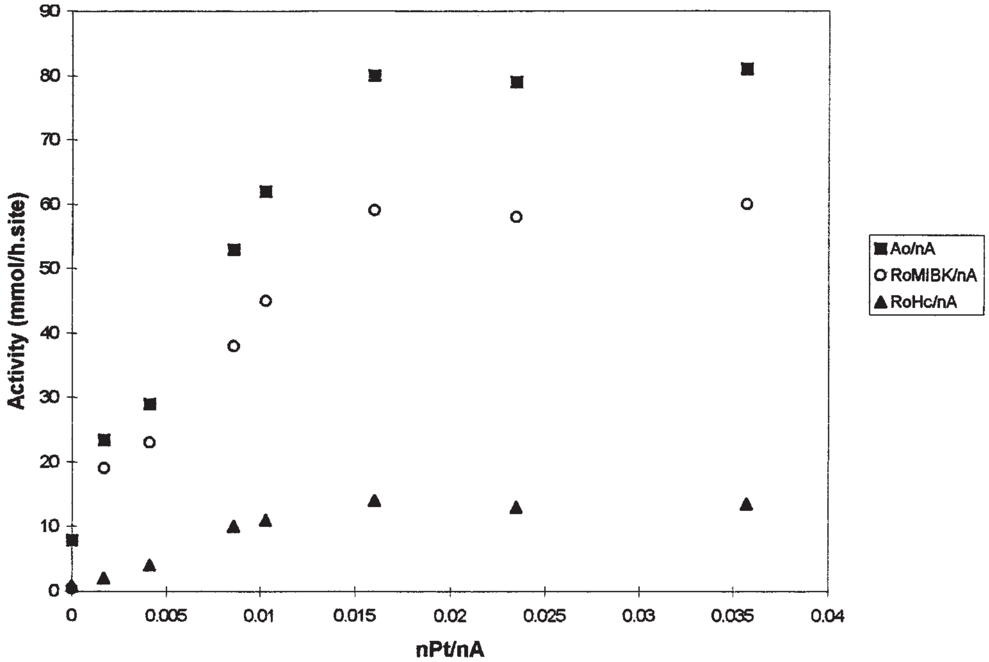
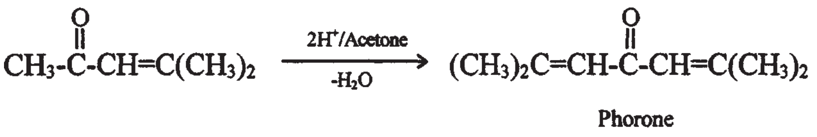
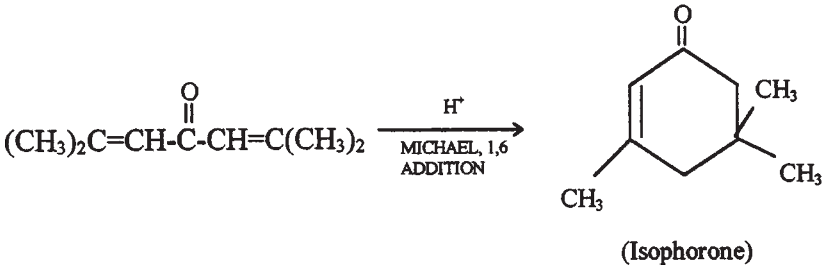


Figure 1. Total initial activity per acidic site (A_o/nA) and initial formation rate for major products per acidic site (R_o/nA) as a function of the catalysts' nPt/nA ratios.



Scheme 2.



Scheme 3.

number of theoretical acidic sites (nPt/nA) of all of the catalysts (table 2).

The acetone transformation reaction under operation conditions and over Pt–H[Al]ZSM5 bifunctional catalysts actually takes place in three stages: stages (i) and (ii) are catalyzed by acidic sites, and stage (iii) by the hydro–dehydrogenating centers, as shown in scheme 1. No relationship between the global initial activity (A_o), the initial formation rate of the different reaction products (R_o), the residual activity (A_r) and the number of theoretical acidic sites (nA) or the number of hydro–dehydrogenating centers (nPt) is observed in the results obtained. However, a clear dependence of the catalytic properties per acidic site (A_o/nA, R_o/nA and A_r) as a function of the relationship between the number of accessible metallic centers and the number of theoretical acidic sites (nPt/nA) can be seen.

Figure 1 shows how the global initial activity per acidic site (A_o/nA) increases as the nPt/nA ratio also increases, with a maximum value of approximately 80 molecules h^{-1} $site^{-1}$ being reached, which remains unchanged from nPt/nA $\geqslant$ 0.015 on. These results suggest that propanone transformation over this type of catalyst takes place through a bifunctional mechanism, where over catalysts with a low nPt/nA ratio (<0.015), the kinetically limiting stage takes place over the metallic centers (nPt). This stage, under operation conditions, could be basically MO hydrogenation to form MIBK (stage (iii) of scheme 1). This reaction does not seem to be favored in these catalysts due to the reduced number of metallic sites (nPt) with respect to the number of acidic sites (nA), which means that a large fraction of the MO produced is not hydrogenated and favors the aldolization reaction between MO and the non-

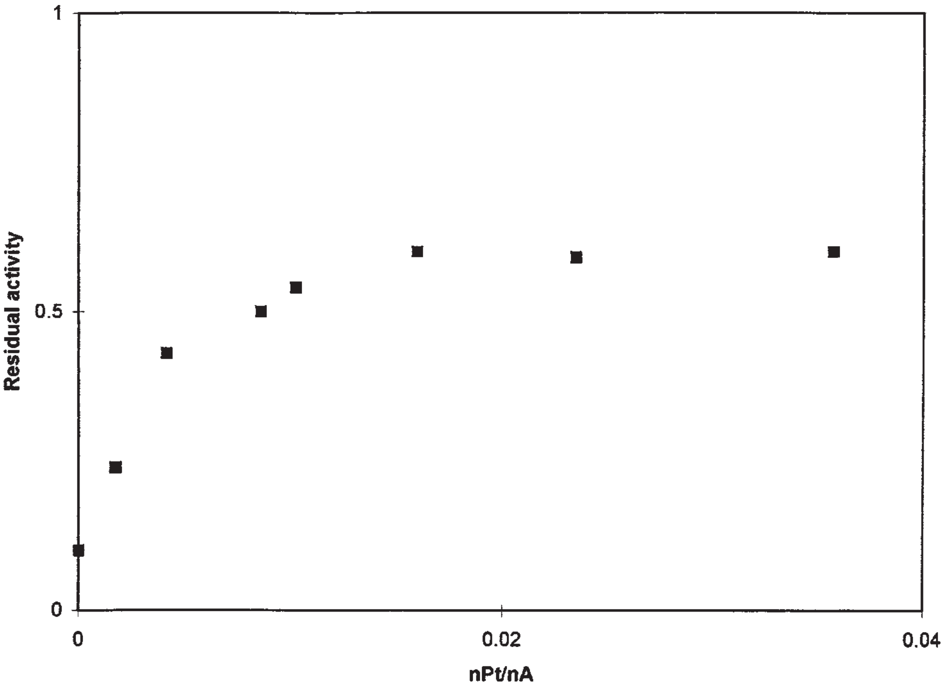
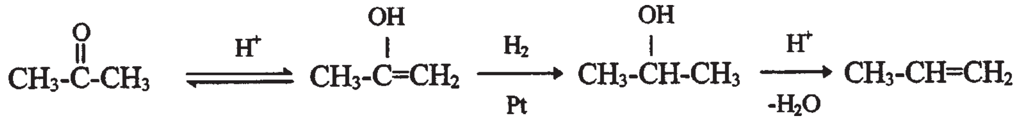


Figure 2. Residual activity (A_r) as a function of the catalysts' nPt/nA ratios.

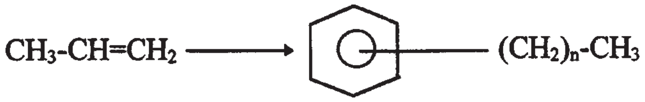


Scheme 4.

transformed acetone, which is catalyzed by the protonic sites of the zeolite support [8]. This generates molecules of high molecular weight and volume, such as isophorone, which would be formed through phorone, a reaction intermediate, as explained in schemes 2 and 3.

Isophorone is a low volatility substance ($T_{\mathrm{boiling}} = 214\,^{\circ}\mathrm{C}$) with a kinetic diameter larger than the pore size of the zeolite used in this work. Therefore, it could be held in the internal structure of the solids, bringing about a rapid deactivation of the catalysts, as demonstrated in previous works [8].

Over catalysts with a high nPt/nA ratio (15 or more metallic centers every 1000 acidic sites), transformation of acetone into MIBK occurs through its passing through a kinetically limiting stage, which takes place over the acidic sites (nA), due to the fact that the global initial activity per acidic site (A_0/nA) does not vary when nPt increases, with respect to nA, for catalysts with an nPt/nA ratio $\geqslant 0.015$ (figure 1). Under the reaction conditions applied, DA is invoked as a reaction intermediate in this transformation, although this has not been observed in the reaction products. The absence of DA and the presence of MO traces in the reaction products can be explained if the DA dehydration rate is higher than that of the MO hydrogenation, and this, in turn, is higher than the aldolization rate at which the acetone molecules form DA [14]. Dehydration of a tertiary keto-alcohol like DA may occur rapidly over the same acidic centers where it is generated. Similarly, MO hydrogenation is a fast reaction, which only permits the accumulation of this intermediary in its balance concentrations. This is not the case with acetone aldolization, which is a stage that requires catalysis by highly acidic sites [7], which would be the first ones deactivated in this type of solid. Therefore, we think that the limiting stage in this transformation is acetone aldolization (stage (i) of scheme 1). In this case, bifunctional catalysts with nPt/nA $\geqslant 0.015$ are balanced and deactivated in a similar manner but much less than the rest of the series, and residual activity, A_r, remains at 0.60, as can be seen in figure 2. The coke contributing to the 40% loss of the initial activity of these catalysts consists basically of isophorone and hydrocarbons of the polyalkylbenzene type ($T_{\mathrm{boiling}} > 200\,^{\circ}\mathrm{C}$), and it is very likely that the formation of these hydrocarbons through reactions involving the reaction intermediaries isopropanol and propene is followed by the oligomerization reaction of the latter [8], which means that the acidic and hydro–dehydrogenating functions of the bifunctional catalyst are involved in the formation of these carbon residues, as shown in schemes 4 and 5.



Scheme 5.

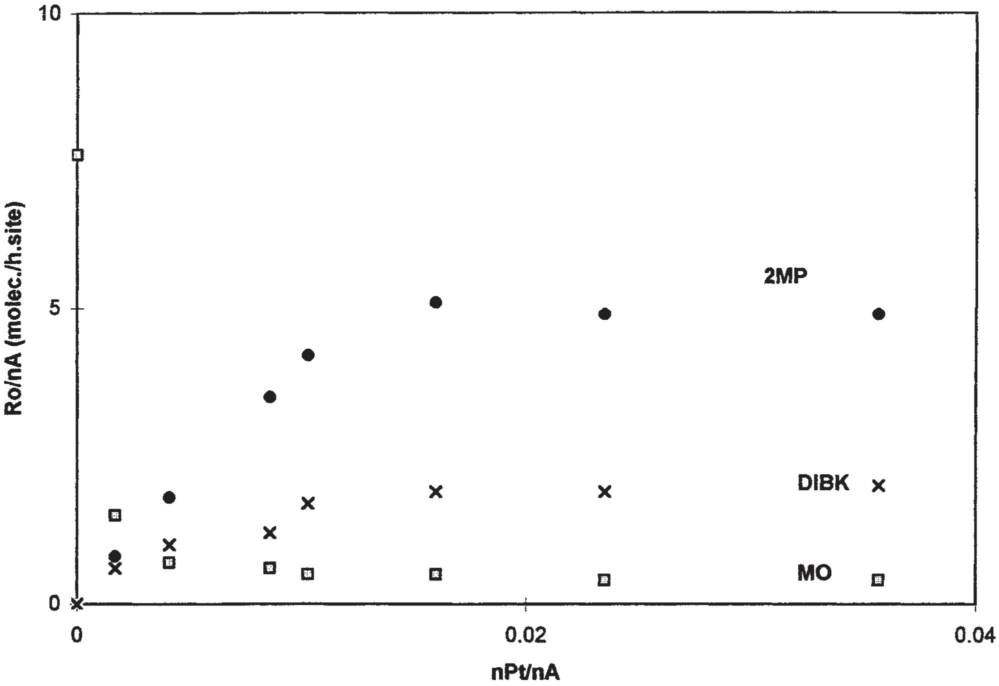


Figure 3. Initial formation rate per acidic site (R_o/nA) for the minor products as a function of nPt/nA.

Finally, figures 1 and 3 show the evolution of the initial formation rates per acidic site as a function of nPt/nA for the major products (MIBK and Hc) and for the minor ones (2MP, DIBK and MO), respectively. Figure 1 shows that the formation rates per acidic site (R_o/nA) for MIBK and Hc initially increase as the nPt/nA ratio increases, but from the moment when catalysts have an nPt/nA ratio $\geqslant$0.015, the R_o/nA parameter for both products reaches its maximum value, which is approximately 60 and 12 molecules h^{-1} site^{-1} for MIBK and Hc, respectively. Figure 3 shows that the behavior of the minor products (2MP and DIBK) is similar to that of the major products. This suggests that each one of these products (MIBK, Hc, 2MP and DIBK) is formed through a bifunctional mechanism, where the stage-controlling reaction kinetics (nPt/nA < 0.015) takes place initially over the metallic centers; subsequently, the limiting stage would occur over the acidic sites of the bifunctional catalyst (nPt/nA $\geqslant 0.015$). In contrast, MO formation takes place through a different mechanism, because only acid catalysis is required; this was proven by the fact that when H[Al]ZSM5(41) and H[Al]ZSM5(106) without platinum are used as catalysts, propanone transformation leads mainly to MO formation.

4. Conclusions

Propanone transformation over bifunctional catalysts of the Pt–H[Al]ZSM5 type and under hydrogen flow generates the following products: MIBK, Hc, 2MP, DIBK, and MO, the first four being formed through bifunctional catalysis, and MO by means of acid catalysis. Similarly, the acidic sites present in each aluminosilicate of the MFI type used (with different Si/Al ratio) have similar acidic strength, given that all catalysts are capable of catalyzing the aldolization stage of this process. Additionally, the catalytic properties per acidic site (activity, stability and selectivity) of the solids used as catalysts, largely depend on the relationship of the number of hydro–dehydrogenating centers accessible to the number of theoretical acidic sites (nPt/nA).

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