

Hydrogenation of Condensed Aromatic Compounds over Mesoporous Bifunctional Catalysts Following a Diels–Alder Adduct Pathway

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Pt(0.5 wt %)-Al-SBA-15 and Pt(0.5 wt %)-Al-MCM-41 bifunctional catalysts were prepared by wet impregnation and investigated in the hydrogenation of anthracene and the hydrogenolysis/ hydrogenation of a series of synthesized Diels–Alder adducts with anthracene and anthracene derivatives. The mesoporous texture of the investigated catalysts allowed the hydrogenation of these substrates to a large extent. In direct correlation with the size of the Pt particles, Pt-Al-SBA-15 exhibited

a higher activity. Both catalysts exhibited a strong Lewis acidity associated with the presence of the Al extra-framework species. The acidity of these catalysts afforded the esterification of the reaction byproduct, that is, succinic anhydride, with methanol or ethanol, and the hydrocracking/decyclization of one hydrogenated ring to lead to 1,2,3,4-tetrahydronaphthalene derivatives. A good correlation with the calculated values of the reaction Gibbs free energy has been evidenced.

Introduction

In the past decades, the depletion of the fossil reserves has orientated oil processing towards heavier petroleum crudes that include polycyclic aromatic molecules.^[1] The presence of these components in diesel products raises important environmental concerns, and the public demands cleaner fuels.^[2] Therefore, a solution to decrease/eliminate the content of polycyclic aromatic molecules, that is, to decrease the aromatic content, is the hydrogenation of these feedstocks.

However, the hydrogenation of these molecules is not simple and is influenced strongly by the nature of the catalyst. Among other factors, it is controlled by the inhibition of different aromatic compounds, which has been demonstrated for both noble^[3] and nonmetal catalysts.^[1b,4] As an effect of competitive adsorption, three-ring aromatic compounds inhibit the

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hydrogenation of two- and one-ring aromatic compounds considerably.

The interaction of anthracene with metal surfaces during hydrogenation has been investigated by both IR spectroscopic studies^[5] and theoretical calculations.^[6] IR spectroscopy^[5] showed that the surface complexes diminish gradually in amount during successive hydrogenation and dehydrogenation cycles, and the spectra of stable partially dehydrogenated species are consistent with the rearomatization of only one end ring. DFT calculations of polycyclic aromatic hydrocarbons on transition metal surfaces support these findings and revealed that the best adsorption structure is associated with aromatic rings on bridging sites with increasing adsorption energies per molecule. Upon adsorption, the molecules are distorted, which implies a modification of the energy level and the shape of molecular orbitals, and hence ensures a better molecule-surface stabilizing interaction.^[6] Calculations performed on Pt(111) suggested that this competition is dominated by the electronic interaction and hence a stronger distortion is obtained for a strong interaction.

The catalysts reported to date for the hydrogenation of anthracene are diverse. Monometallic silica-supported Pt,^[5] hydroprocessing presulfided CoMo/Al₂O₃,^[4] and NiMo/Al₂O₃ and NiW/Al₂O₃^[1b,7] are among the most utilized, the selectivities of which are controlled by the factors discussed above. NiMo/ Al₂O₃ and NiW/Al₂O₃ have the advantage of bifunctionality, in which the metal function promotes hydrogenation and the acidic function promotes isomerization, ring opening, and dealkylation. Ni-MoS₂ supported on carbon nanofibers has also been investigated as a hydrogenation catalyst for this reaction.^[8] Catalysts prepared with the support functionalized by a less severe treatment led to short and defective MoS₂ slabs and a higher hydrogenation activity, whereas a harsher func-



tionalization treatment led to the formation of long stacked ${\sf MoS}_2$ slabs and lower performance towards anthracene hydrogenation.

Homogeneous reactions that use Ru-based catalysts and a series of anthracene derivatives occurred under mild conditions and led to the hydrogenation of only the external rings.^[9] The introduction of ring substituents at C-9 did not impede the hydrogenation of the external aromatic rings. In contrast, substitution of one of the external rings with a functional group (at least a methyl group) makes this ring unattractive for coordination to the metal center, and hence resistant to hydrogenation. Very close conclusions with regard to the selectivity for the preservation of an interior benzene ring were drawn with hydrogen activated by lithium and potassium organoamides, in which the catalytic properties of the strong bases depend on the nature of the organic ligands in the dialkylamide and the corresponding metal cations.^[10] Other studies in which active carbon afforded hydrogen transfer using molecular hydrogen indicated that it is possible to change the reaction pathway to provide the hydrogenation of the central ring to a high extent.^[11]

The effect of the hydrogen source has also been demonstrated by several authors. Zhang et al.^[12] investigated the hydrogenation of anthracene using hydrogen gas or the hydrogen donor tetralin as hydrogen sources and the combination of both in the presence of activated carbon and Ni/C as catalysts. An apparent improvement in both the conversion and product distribution was determined if tetralin and hydrogen gas were used together. In the absence of hydrogen gas, the active carbon facilitates hydrogen transfer from tetralin to anthracene, whereas the metal mainly transferred hydrogen from the gas phase to anthracene. Research on Au and Ag nanoparticles (NPs) emphasized the role of the hydride anions in the same reaction.^[13] Hydride formed from NaBH₄ was trapped by surfactants that stabilized the NPs and was then transferred to the NPs surface. Spectroscopic investigations demonstrate that the metal NPs play a nanoelectrode role by storing electrons from hydrides, and the resulting hydrogen radical then reacts with anthracene. This mechanism is supported by theoretical calculations that indicate that the gold cluster hydride anion is of lower energy than the corresponding neutral cluster.^[14] However, this process requires an optimum size of Au (3-5 nm) and Ag (\approx 3 nm). The effect of the particle size was also confirmed for Rh NPs. Although 5 nm tetrahedral Rh NPs on charcoal provided the hydrogenation of the external rings of anthracene, the commercial Rh/C catalyst led to a high extent of internal-ring hydrogenation.^[15] The deposition of Rh NPs (3-5 nm) onto silica-coated magnetite NPs (Fe₃O₄@SiO₂) did not change this behavior but improved the recoverability.^[16]

A very similar behavior was exhibited by carbon-supported Pd (5 nm) NPs.^[17] Pd NPs (2–10 nm) stabilized in high-densitypolyethylene were also investigated in the catalytic hydrogenation of anthracene in supercritical CO₂ (200 atm with 10 atm of H₂) by in situ UV/Vis spectroscopy. Kinetic studies confirmed that in the presence of the NPs the initial hydrogenation occurs mainly at the external rings.^[18] However, the deposition of Pd on γ -alumina led to a different behavior to that of Rh. In this case, the terminal rings were hydrogenated more rapidly than the interior ring. $^{\left[19\right] }$

In another direction, almost 80 years ago, Diels and Thiele noted the unusual stability of the maleic anhydride cycloadduct and employed this feature to scavenge anthracene generated in a retro-[4+2] reaction.^[20] The Diels–Alder cycloaddition reaction (see, for example, Ref. [21] and references therein) of anthracene with dienophiles is a reversible, temperature-dependent reaction,^[22] and the hydrogenation of the resulting adduct was considered to prevent the pyrolytic reversal reaction and to produce compounds of a higher thermal stability. Indeed, experiments performed with Ru/Al_2O_3 and Raney-Ni catalysts led to the hydrogenation of the external rings, which thus left the adduct unaltered.

The aim of this study was to investigate the processing of the polycyclic aromatic molecules contained in heavy petroleum crudes by combining the Diels–Alder synthesis of a cycloadduct with successive hydrogenation. The fragmentation of these heavy molecules to small cycloalkanes represented a secondary goal. For this purpose, anthracene and substituted anthracene derivatives were considered as probe molecules, and new bifunctional mesoporous Pt-Al-SBA15 and Pt-Al-MCM-41 were used as catalysts.

Results

Textural characterization

The textural characteristics of the investigated catalysts are presented in Table 1. The measured values for the pure supports are typical for such materials. The deposition of Pt had different effects. For MCM-41, the deposition of Pt led to a decrease of the surface area that occurred at the level of micropores (Figures S1 and S2). A small decrease of the pore volume was also evidenced. For the SBA-15 support, the decrease of the surface area was less important and merely associated with the decrease of the surface of the surface of the pore size was determined. Moreover, the deposition of Pt led to a bimodal pore distribution with mesopores of 39 and 62 Å, respectively (Figures S3 and S4).

XRD characterization

Diffractograms of the investigated catalysts are presented in Figure 1. In the absence of Pt, the XRD patterns showed typical reflections for these materials. No reflections of Pt were detect-

Table 1. Textural characteristics of the investigated catalysts.							
Sample	BET surface area [m ² g ⁻¹]	<i>t</i> -plot micropore surface area [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]	Pore size [Å]			
Al-MCM-41 Pt-Al-MCM-41 Al-SBA-15 Pt-Al-SBA-15	912 822 697 684	748 673 289 255	1.14 0.90 1.04 0.79	29 28 90 39, 62			



ed in these patterns after its deposition, which suggests the presence of small particles that are highly dispersed.

H₂ chemisorption

The H₂ chemisorption and H₂ temperature-programmed desorption (TPD) results are given in Table 2. These results demonstrate that the deposition of Pt occurs with a different dispersion and the formation of particles with a different average diameter. On Al-MCM-41 the dispersion is very high (83%), which corresponds to particles with diameters smaller than 2 nm. Differently, on SBA-15 the dispersion is much lower (15.6%) and the average diameter is approximately five times higher. However, there were no differences in the H₂-TPD results that may account for the presence of some hydrogen spillover facilitated by the acid sites generated by Al.

TEM measurements

TEM pictures of the investigated catalysts confirm the conclusions drawn from the results of XRD and H_2 chemisorption (Figure 2). Pt is better dispersed on Al-MCM-41 than on Al-SBA-15 (Figure 2). The histograms presented in Figure 2 show that over 80% of the analyzed particles are smaller than 3 nm. For Pt-Al-SBA-15, the frequency of the particles larger than 4 nm is almost 30%.

The FTIR spectra with absorbed pyridine (Py) as a probe (Figure 3) show typical absorption bands assigned to the 8a and 19b vibration modes of adsorbed Py that forms Lewis-type adducts (Py–L) with bands at $\tilde{\nu} = 1622$ and 1453 cm⁻¹. The band at $\tilde{\nu} = 1453$ cm⁻¹ is very sensitive to the chemical composition^[23] and, for the materials that contain Al, is typical of the extra-framework species.^[24] Absorption bands assigned

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to the 8a and 19b modes of Py in interaction with Brønsted acid sites (Py–B) were detected at $\tilde{\nu} = 1636$ and 1540 cm⁻¹. Compared to that of the bands assigned to Py–L species, the intensity of the bands assigned to Py–B was low for both catalysts. Clearly, the intensity of the band at $\tilde{\nu} = 1542$ cm⁻¹ is also sensitive to the chemical composition, and the low intensity of these bands reflects a very small population of OH groups. The two other bands at $\tilde{\nu} = 1576$ and 1490 cm⁻¹ are assigned to Py adsorbed (Py-ad) on either Lewis or Brønsted acid sites.^[23] Generally, the band located at around $\tilde{\nu} = 1490$ cm⁻¹ is not discussed in the literature because it characterizes the interaction of Py with both Lewis and Brønsted acid sites. However, the variation of this band with temperature parallels that of Py–L, which confirms the acidity generated by the presence of the extra-framework Al species.

X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) spectra are shown in Figure 4, and the binding energies (BEs) of the investigated levels are compiled in Table 3. The Pt4f_{7/2} level overlaps the Al2p level, and the deconvolution of the band led to the values presented in Table 3 (Figure 4A). According to the literature, the deconvoluted binding energies correspond to Pt^{0[25]} and Al^{III.[26]} Deconvolution of the oxygen band (Figure 4B) revealed the presence of three components (Table 3), the first at BE=532 eV, typical of oxygen in molecular sieves,^[27] the second at BE=533 eV, typical of oxygen incorporated into SiO₂,^[28] and the last at BE=530 eV, which better approaches the binding energy of oxygen in dispersed aluminum oxide.^[29] The Si band was also deconvoluted into three components (Figure 4C, Table 3) that all correspond to Si bound to O species.^[30]



Figure 1. XRD patterns of A) Al-SBA-15, B) Pt-Al-SBA-15, and C) Pt-Al-MCM-41.

Table 2. H ₂ chemisorption and H ₂ -TPD results.							
Sample	Metal dispersion [%]	H_2 chemisorption Metallic surface area $[m^2g_{sample}^{-1}]$	Metallic surface area [m²g _{metal} ⁻¹]	Active particle diameter [nm]	$H_2\mbox{-}TPD$ Chemisorbed H_2 desorbed at 130 $^\circ C$ [µmol]	Interfacial H₂ desorbed at 240 °C [µmol]	
Pt-Al-MCM-41 Pt-Al-SBA-15	83.0 15.6	2.05 0.38	205.09 38.48	1.4 7.3	11 11	0.4 0.3	

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Figure 2. TEM pictures and particle size distribution of Pt-Al-SBA-15 (top) and Pt-Al-MCM-41 (bottom).

Catalytic behavior

The results of the catalysis of the hydrogenation of anthracene over Pt-Al-SBA-15 and Pt-Al-MCM-41 are presented in Table 4.

The reaction occurred with a high selectivity to dihydroanthracene. To small extents, 1,2,3,4,5,6,7,8-octahydroanthracene and 1,2,3,4,4a,9,9a,10-octahydroanthracene were produced as well. The hydrogenation of 1,2,3,4,5,6,7,8-octahydroanthracene and 1,2,3,4,4a,9,9a,10-octahydroanthracene continued to perhydroanthracene only in traces on Pt-Al-SBA-15.

The results of the catalysis of the hydrogenation of substrates 3a-e are compiled in Table 5. The reaction proceeded with the formation of succinic anhydride and a mixture of hydrogenated di-, octa-, and perhydroanthracene derivatives. Dihydroanthracenes were the major compounds in these hydrogenations. Under the investigated reaction conditions, the total conversion of the cycloadducts was achieved. However, the degree of hydrogenation of the investigated molecules depended on the catalyst. Thus, Pt-Al-SBA-15 afforded a more advanced hydrogenation of the aromatic rings than Pt-Al-MCM-41. In the case of **3a**, besides perhydroanthracene, tetralin was also produced, although with a low selectivity (13.3%). For the other substrates, the hydrogenation stopped at the octahydroanthracene derivatives. The exception was 3e on Pt-Al-MCM-41, for which the reaction stopped at the dihydroanthracene.

Except substrate **3 d**, in all the other cases, the octahydroanthracene derivatives suffered a hydrocracking/decyclization reaction with the formation of tetrahydronaphthalene deriva-



Figure 3. Py-FTIR spectra of A) Pt/Al-SBA-15 at a) RT under vacuum, b) 150 °C, c) 250 °C, and d) 350 °C and B) Pt/Al-MCM-41 at a) 150 °C, b) 250 °C, and c) 350 °C.



Figure 4. A) XPS spectra of the investigated catalysts at the $Pt4f_{7/2}$ and Al2p levels. B) XPS spectra of the investigated catalysts at the O1s level. C) XPS spectra of the investigated catalysts at the Si2p level.

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Table 3. Bin	Table 3. Binding energies of the $Pt4f_{7/2}$, Al2p, O1s, and Si2p levels.							
Catalyst BE [eV]								
	$Pt4f_{7/2}$		O 1s		Al 2p		Si 2p	
Pt-SBA-15	71.1	530.4	531.8	533.5	73.5	100.8	102.2	103.7
Pt-MCM-41	71.1	530.4	532.1	533.3	73.8	100.8	102.2	103.7

tives. However, decyclization reactions on Pt/Al_2O_3 catalysts were reported a long time ago.^[31] Besides this, the Pt-Al-SBA-15 catalyst is able to continue hydrocracking/decyclization, to a small extent, with a hydrocracking step. No further decyclization or coking was determined on these catalysts. Elemental analysis of the spent catalysts indicated a carbon content lower than 1 wt%.

The time evolution of the conversion and selectivity in the hydrogenation of anthracene and Diels–Alder adducts over Pt/ Al-SBA-15 and Pt/Al-MCM-41 catalysts is presented in Figure 5. This evolution confirms that 9,10-dihydroanthracene derivatives are the first intermediate in the hydrogenation of both kinds of substrates. A similar tendency was determined for the other adducts as well.

The hydrogenation of substrates 3a-c led to the formation of succinic anhydride as a byproduct. However, to make the composition of the hydrogenated feedstock more compatible with fuel characteristics, it was further reacted with either methanol or ethanol to generate the corresponding diesters.^[32] This reaction took the advantage of the acidity of the Al-SBA-15 and Al-MCM-41 supports (Figure 3).

The analysis of the reaction products evidenced that esterification occurred with total conversions and some differences were generated by the nature of the alcohol. With methanol, the esterification led to selectivities to succinate dimethyl ester in the range of 70–90%, whereas with ethanol, the esterification was almost totally toward the diethyl ester.

Discussion

The mesoporous texture of the investigated catalysts allowed the hydrogenation of both anthracene and the hydrogenolysis/hydrogenation of various Diels–Alder adducts.

The routes of the hydrogenation of anthracene and the hydrogenolysis/hydrogenation of intermediate Diels–Alder adducts in connection to the calculated reaction Gibbs free energies are depicted in Schemes 1–3.^[33] Irrespective of the extent of hydrogenation, the Diels–Alder route is energetically more favorable to achieve the hydrogenated products, which is also in perfect agreement with the catalytic results obtained in this study. Although the hydrogenation of the condensed aromatic compounds proceeded in a first step through a parallel reaction both on the inner and outer rings,^[4] the Diels–Alder adduct route corresponds to a consecutive pathway in which the inner ring undergoes hydrogenation first.

In all cases, Pt-Al-SBA-15 was superior to Pt-Al-MCM-41 to afford not only the hydrogenolysis of the adducts but also the hydrogenation of the resulting aromatic rings to a higher extent. Although it was deposited using an identical procedure, Pt had different dispersions and particle sizes on the two supports (Table 2, Figure 2). On Al-SBA-15, the particles were larger and the dispersion lower than those on Al-MCM-41. XPS



Scheme 1. Hydrogenation of anthracene to 9,10-dihydroanthracene by two parallel routes.

H ₂ , 12 h).						
		m/z=1 79 (([M+H]*, 15.4); 178 (M*, 100); 179 (94.5 100); 177 (10.8); 176 (12.2); 152 (5.5); (7.5); 176(10.6 151 (4.5) 89 (20.5); 76(1	+H] ⁺ ,14);180 (M ⁺ , m [/] z=);178 (50.9);177 100););165 (19.5);152 (8.1); (34.1) 2.9) (36.2)	: 187 ([M+H]+, 14.9); 186 (M+, 158 (77.9); 157 (23.4); 145); 143 (31.4); 130 (20.4); 129); 128 (33.4)		
		$(1)) \rightarrow (1)$	+):		
		m ² z = 187 ([M+H] ⁺ , 11.7); 186 (M ⁺ , 84.5); 143 (11); 129 (24.4); 128 (26.07); 115 (20.7); 105 (32.1); 104 (100); 103 (12.7); 95 (15.1); 91 (12.9); 81 (14.8); 80 (12); 75 (14.9)	$D \rightarrow \bigcirc$	$ \begin{array}{c} m/z = 192 \; (M^* \; 100); \\ 150 \; (22.6); 135 \; (82); \\ 121 \; (27.2); 96 \; (41.8); \\ 95 \; (35.6); 94 \; (13.9); \\ 93 \; (21.3); 81 \; (47.3); \\ 93 \; (21.3); 81 \; (47.3); \\ 67 \; (77.22); 55 \; (39.1); \\ 54 \; (13.4); 53 \; (13.8); \\ 41 \; (52.3); 39 \; (16.5) \end{array} $		
Catalyst	Conversion [%]		Selectivity [%]			
		9,10-Dihydroanthracene	1,2,3,4,5,6,7,8-Octa- hydroanthracene	1,2,3,4,4a,9,9a,10-Octa- hydroanthracene	Perhydroanthracene	
Pt-Al-SBA-15	100	71.7	7.2	20.9	0.2	
Pt-Al-MCM-41	100	91.3	4.7	4.0	0	

Table 4. Hydrogenation of anthracene over Pt-Al-SBA-15 and Pt-Al-MCM-41 (0.1 mg Pt, substrate/Pt molar ratio of 20:1, 5.0 mL heptane, 100°C, 100 bar H₂, 12 h).









investigation of these catalysts (Figure 4) confirmed the extensive reduction of Pt to Pt^0 .

In addition to the hydrogenation of the aromatic rings of anthracene and of fragments that resulted from the hydrogenolysis of the Diels–Alder adducts, because of their bifunctional character, the investigated catalysts were able to catalyze the direct esterification of the succinic anhydride byproduct to either mono- or diesters. The detected acidity also favored the disruption of one cycle by a hydrocracking/decyclization reaction with the formation of hydronaphthalene derivatives. No other alkyl derivatives of hydronaphthalene were identified in the reaction products, but analysis of the gas phase in the autoclave identified C_4 fragments.

The acidic function of these catalysts was allowed by the insertion of Al in both the SBA-15 and MCM-41 networks. Py-FTIR spectra indicated that this process generated enough strong Lewis acid centers to be detectable after the desorption of Py at 350 °C.

None of the analyses performed (chromatographic or spectroscopic) indicated the formation of any tarry phase. The catalysts were recycled three times after washing with *n*-hexane. No changes in the performances were detected, and this be-



Figure 5. Time evolution of the conversion and selectivity in the hydrogenation of A, B) anthracene and C, D) Diels–Alder adducts over A, C) Pt/Al-SBA-15 and B, D) Pt/Al-MCM-41 (0.1 mg Pt, substrate/Pt molar ratio of 20:1, 5.0 mL heptane, 100 °C, 30 bar H₂).



Scheme 2. Hydrogenation of anthracene to 1,2,3,4,5,6,7,8-octahydroanthracene by two parallel routes.



Scheme 3. Hydrogenation of anthracene to tetradecahydroanthracene (perhydroanthracene) by two parallel routes.

havior could be associated with the absence of repolymerization. However, it is clear that three times is not enough, and therefore, these catalysts are still under investigation in related reactions in which we are looking for long-term recycling.

Conclusions

The deposition of Pt (0.5 wt%) on Al-SBA-15 and Al-MCM-41 supports led to bifunctional catalysts with different metal dispersions. Pt-Al-SBA-15 contained larger Pt particles than Pt-Al-MCM-41. Both catalysts exhibited a quite strong Lewis acidity associated with the presence of the Al extra-framework species. To evaluate these catalysts, in addition to anthracene, we synthesized a series of adducts according to the Diels-Alder protocol. The mesoporous texture of the investigated catalysts allowed the hydrogenation of anthracene and the hydrogenolysis/hydrogenation of various Diels-Alder adducts. In direct correlation with the size of the Pt particles, Pt-Al-SBA-15 afforded higher conversions in the hydrogenation of both anthracene and the Diels-Alder adducts. The strong Lewis acidity of these catalysts also afforded the esterification of the reaction byproduct, that is, succinic anhydride, with methanol or ethanol and a hydrocracking/decyclization reaction.

The results obtained in the hydrogenation of anthracene and its various Diels–Alder adducts confirmed the values of the reaction Gibbs free energy, which indicates that the adduct route is more energetically favorable.

Experimental Section

Synthesis and characterization of cycloadducts 3

Cycloadducts **3a–e** were prepared in good-to-excellent yields (90– 93%) by the Diels–Alder reaction between anthracene derivatives **1a–e** and maleic anhydride (**2**) according to a modification of a described procedure.^[34] The analytical and spectroscopic data of the known products were identical to those reported previously (Table 6).



A suspension of 1 (1 mmol) and 2 (1.1 mmol) was heated to reflux in xylene (mixture of isomers; 3 mL). The reaction was followed by TLC, and after completion the reaction mixture was cooled. The precipitated solid was collected by filtration, washed with MeOH, and dried. The crude products 3a-e were recrystallized from appropriate solvents. Melting points were determined by using a Kofler micro hot stage. ¹H NMR spectra were recorded by using a Bruker Avance Ultrashield 500 plus spectrometer at 29°C and 500 MHz using TMS as an internal standard. ¹³C NMR spectra were recorded by using the same instrument at 125 MHz and are referenced against the central line of the solvent signal ([D₆]DMSO septet at $\delta =$ 39.5 ppm). The coupling constants (J) are given in Hz. NMR peak assignments are based on HSQC and HMBC 2D NMR spectra. IR spectra were obtained by using a Bruker FTIR Alpha Platinum attenuated total reflectance (ATR) spectrometer. MS spectra were recorded by using an Agilent 6224 Accurate Mass TOF LC/ MS system. Elemental analysis (C, H, N) was performed by using a PerkinElmer 2400 Series II CHNS/O Analyzer. TLC was performed with Fluka silica gel TLC cards.

Characterization of products

9,10-Dihydro-9,10-[3,4]furanoanthracene-12,14-dione (3 a)[35]

Yield: 249 mg (90%) as a white solid; m.p. 274–275 °C (from EtOAc), lit. m.p. 260–262 °C (benzene),^[Sa] IR (ATR): $\tilde{\nu}_{max}$ =3069,





3045, 3021, 2977, 1834, 1767, 1465, 1457, 1234, 1218, 1077 cm⁻¹; ¹H NMR (500 MHz, [D₆]DMSO): δ = 3.66 (s, 2 H, 11-H, 15-H), 4.88 (s, 2H, 9-H, 10-H), 7.18 (m, 4H), 7.33 (m, 2H), 7.47 ppm (m, 2H) (1-H, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H); ¹³C NMR (125 MHz, [D₆]DMSO): δ = 44.3 (9-C, 10-C), 47.9 (11-C, 15-C), 124.5 (Ar), 124.8 (Ar), 126.5 (Ar), 127.1 (Ar), 139.1 (Ar), 141.1 (Ar), 171.5 ppm (CO); MS (ESI+): m/z=277 [M+H]⁺; HRMS calcd for C₁₈H₁₃O₃: 277.0865 [M+H⁺]; found: 277.0857.

9-Methyl-9,10-dihydro-9,10-[3,4]furanoanthracene-12,14-dione (3 b)^[36]



Yield: 261 mg (90%) as a white solid; m.p. 269–271 °C (xylene), lit. m.p. 269–270 °C (xylene),^[36] IR (ATR): $\tilde{\nu}_{max}$ =2963, 1860, 1829, 1771, 1458, 1231, 1210, 1068 cm⁻¹; ¹H NMR (500 MHz, [D₆]DMSO): δ = 2.16 (s, 3 H, Me), 3.33 (d, *J*=9.0 Hz, 1 H, 11-H), 3.70 (dd, *J*₁=3.3 Hz, *J*₂=9.0 Hz, 1 H, 15-H), 4.85 (d, *J*=3.3 Hz, 1 H, 10-H), 7.22 (m, 4 H), 7.33 (m, 2 H), 7.41 (m, 1 H), 7.49 ppm (m, 1 H) (1-H, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H); ¹³C NMR (125 MHz, [D₆]DMSO): δ = 14.6 (Me), 44.2 (10-C), 44.3 (9-C), 49.3 (15-C), 51.7 (11-C), 122.05 (Ar), 122.08 (Ar), 124.1 (Ar), 124.8 (Ar), 126.40 (Ar), 126.44 (Ar), 126.9 (Ar), 127.0 (Ar), 139.1 (Ar), 141.3 (Ar), 141.6 (Ar), 143.6 (Ar), 170.5 (CO), 171.4 ppm (CO); MS (ESI+): *m/z*=291 [*M*+H]⁺; HRMS calcd for C₁₉H₁₅O₃: 291.1021 [*M*+H⁺]; found: 291.1024.

9-Vinyl-9,10-dihydro-9,10-[3,4]furanoanthracene-12,14-dione (3 c)



Yield: 281 mg (93%) as a white solid; m.p. 247–248 °C (xylene); IR (ATR): $\dot{\nu}_{max}$ =2965, 1857, 1776, 1465, 1457, 1221, 1211, 1068, 1054 cm⁻¹; ¹H NMR (500 MHz, [D₆]DMSO): δ =3.71 (dd, J_1 =3.0 Hz, J_2 =9.0 Hz, 1H, 15-H), 3.90 (d, J=9.0 Hz, 1H, 11-H), 4.90 (d, J= 3.0 Hz, 1H, 10-H), 5.79 (d, J=17.8 Hz, 1H, CH₂=CH), 6.06 (d, J= 11.3 Hz, 1H, CH₂=CH), 6.77 (d, J_1 =11.3 Hz, J_2 =17.8 Hz, 1H, CH₂=CH), 7.23 (m, 4H), 7.36 (m, 3H), 7.52 ppm (m, 1H) (1-H, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H); ¹³C NMR (125 MHz, [D₆]DMSO): δ =44.4 (10-C), 48.8 (11-C), 49.0 (15-C), 51.4 (9-C), 121.6 (CH₂=CH), 123.0 (Ar), 123.6 (Ar), 124.2 (Ar), 125.1 (Ar), 126.3 (Ar), 126.8 (Ar), 127.0 (Ar), 127.1 (Ar), 132.1 (CH₂=CH), 138.6 (Ar), 140.3 (Ar), 141.0 (Ar), 142.6 (Ar), 169.7 (CO), 171.2 ppm (CO); elemental analysis calcd (%) for C₂₀H₁₄O₃ (MS (ESI +):

m/*z* = 302 [M + H]⁺): C 79.46, H 4.67; found: C 79.48, H 4.44.

12,14-Dioxo-9,10-[3,4]furanoanthracene-9(10 H)-carbaldehyde (3 d)^[37]



Yield: 283 mg (93%) as an off-white solid; m.p. 246–247 °C (xylene), lit. m.p. 238–239 °C (benzene);^[37] IR (ATR): $\tilde{\nu}_{max}$ =3061, 2947, 2883, 2769, 1863, 1767, 1716, 1457, 1224, 1215, 1068 cm⁻¹; ¹H NMR (500 MHz, [D₆]DMSO): δ =3.79 (dd, J_1 =3.3 Hz, J_2 =9.2 Hz, 1 H, 15-H), 4.31 (d, J=9.2 Hz, 1 H, 11-H), 4.95 (d, J=3.3 Hz, 1 H, 10-H), 7.14 (m, 1H), 7.20 (m, 1 H), 7.28 (m, 3 H), 7.42 (m, 1 H), 7.58 (m, 1 H), 7.70 (m, 1 H) (1-H, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H), 10.83 ppm (s, 1 H, CHO); ¹³C NMR (125 MHz, [D₆]DMSO): δ =44.6 (10-C), 48.4 (15-C), 48.7 (11-C), 57.0 (9-C), 122.9 (Ar), 123.4 (Ar), 125.2 (Ar), 125.5 (Ar), 126.6 (Ar), 127.2 (Ar), 127.4 (Ar), 127.6 (Ar), 136.9 (Ar), 138.77 (Ar), 138.81 (Ar), 141.0 (Ar), 170.85 (CO), 170.94 (CO), 201.6 ppm (CHO); MS (ESI+): m/z=305 [M+H]⁺; HRMS calcd for C₁₉H₁₃O₄: 305.0814 [M+H⁺]; found: 305.0819.





Yield: 277 mg (91%) as a white solid; m.p. 257–258 °C (toluene), lit. m.p. 256–257 °C (benzene),^[38] IR (ATR): $\tilde{\nu}_{max}$ =2964, 2928, 2867, 1847, 1771, 1472, 1231, 1212, 1075 cm⁻¹; ¹H NMR (500 MHz, [D₆]DMSO): δ =1.10 (t, *J*=7.6 Hz, 3 H, CH₂CH₃), 2.54 (q, *J*=7.6 Hz, 2 H, CH₂CH₃), 3.64 (m, 2 H, 11-H, 15-H), 4.83 (s, 2 H, 9-H, 10-H), 7.02 (m, 1 H), 7.16 (m, 3 H), 7.23 (m, 1 H), 7.46 ppm (m, 2 H) (1-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H); ¹³C NMR (125 MHz, [D₆]DMSO): δ =15.6 (CH₂CH₃), 27.9 (CH₂CH₃), 44.0, 44.4 (9-C, 10-C), 47.9, 48.0 (11-C, 15-C), 124.29 (Ar), 124.33 (Ar), 124.4 (Ar), 124.7 (Ar), 126.2 Ar), 126.4 (Ar), 126.5 (Ar), 136.4 (Ar), 139.1 (Ar), 141.2 (Ar), 141.4 (Ar), 142.7 (Ar), 171.55 (CO), 171.59 ppm (CO); MS (ESI+): *m*/*z*=305 [*M*+H]⁺; HRMS calcd for C₂₀H₁₆O₃: 305.1178 [*M*+H⁺]; found: 305.1176.

Catalyst synthesis

Al-SBA-15 was synthesized according to the following procedure. P123 (3.5 g) was dissolved in $1.5 \,\text{m}$ HCl (100 mL) under vigorous stirring. Then, aluminum sulfate (0.6 g) was added, and the solution was stirred for 1 h. Tetraethyl orthosilicate (TEOS; 8.5 g) was added dropwise, and the solution was maintained at RT for 15 h and then at 40 °C for 24 h. The resulting suspension was transferred into an autoclave and crystallized at 90 °C for 48 h. The obtained solid product was collected by filtration, washed with doubly distilled water, dried, and calcined at 550 °C for 6 h (heating rate of 1 °C min⁻¹). Al-MCM-41 was synthesized according to a procedure reported by Beck et al.^[39]



The deposition of Pt (0.5 wt%) on these supports was performed by a wet impregnation methodology. H_2PtCl_6 (0.11 g) dissolved in water (10 mL) was added to a suspension of the support (1 g; Al-MCM-41 or Al-SBA-15) in doubly distilled water (100 mL), and the mixture was stirred for 48 h at 60 °C. The solid was separated by centrifugation and washed with doubly distilled water until free of chlorine. Then it was dried at 95 °C for 90 min, calcined at 350 °C for 12 h with a heating rate of 1 °C min⁻¹, and reduced under a flow of hydrogen (30 mL min⁻¹) at 450 °C for 6 h.

Catalyst characterization

N₂ adsorption-desorption isotherms were recorded at -196 °C by using a Micromeritics ASAP2020 automated instrument. Before analysis, the catalysts pretreated under H₂ at 400 °C were firstly exposed to Ar and then degassed for 15 h at 150 °C and 1.3× 10⁻⁹ atm. The surface areas were estimated according to the BET model, and the pore size dimensions were calculated using the Barrett–Joyner–Halenda (BJH) method. Powder XRD patterns were recorded by using a Phillips PW 1830 diffractometer using CuK_a radiation. Patterns were collected in steps of $2\theta = 0.02^{\circ}$ over the angular ranges $2\theta = 1-20$ or $10-80^{\circ}$ for 25 s per step.

H₂-pulse chemisorption measurements were performed by using an ASAP AutoChemll 2920 station from Micromeritics. Prereduced catalysts (~20 mg) were introduced into a U-shaped quartz reactor with an inner diameter of 0.5 cm, heated under He at 200 °C, cooled to RT under a He flow of 50 mL min⁻¹, and then exposed to pulses of H₂ at RT until surface saturation. To determine the irreversibly adsorbed hydrogen, the samples were then heated under He at 60 °C. The hydrogen consumption to form the monolayer was calculated by extrapolating the linear portion of the adsorption isotherm to zero pressure. The number of exposed metal atoms was calculated by assuming an atomic stoichiometry H/Pt=1:1. The average metal particle size was estimated by assuming a spherical particle model. $^{\rm [40]}$ Subsequently, $\rm H_2\mathchar`-TPD$ experiments were performed by using the same instrument once saturation was reached at a heating rate of 5 $^{\circ}$ Cmin⁻¹ up to 350 $^{\circ}$ C. The amount of H₂ evolved in the gas phase was quantified using a calibration curve.

Py-FTIR spectra were recorded by using a Thermo Electron Nicolet 4700 FTIR spectrometer with a resolution of 4 cm⁻¹. Before the adsorption of the base, the powder samples were calcined at 450 °C for 2 h under an air flow of 30 mL min⁻¹. Self-supporting wafers obtained by compression ($\approx 12 \text{ mg cm}^{-2}$) were outgassed in the IR cell at 400 °C at a residual pressure of 1 atm. After the adsorption of the probe, the samples were purged for 2 h with He at RT to remove the weakly sorbed species and then heated to each measuring temperature.

TEM was performed by using a JEOL JEM-1010 microscope with an accelerating voltage of 100 kV. Samples were prepared by powder dispersion in ethanol and subsequent deposition on a gold grid with a carbon support.

XPS spectra of both fresh and used catalysts were recorded at RT by using a SSX-100 spectrometer, Model 206 from Surface Science Instrument. To limit reoxidation, the reduced samples were transferred from the reduction setup to the Raman and XPS apparatus under isooctane.^[41] The pressure in the analysis chamber during the analysis was 1.33 MPa. Monochromatized AlK_{\alpha} radiation (h\nu = 1486.6 eV) generated by bombarding the Al anode with an electron gun operated at a beam current of 12 mA and acceleration voltage of 10 kV was used. The spectrometer energy scale was calibrated using the Au4f_{7/2} peak centered at BE=83.98 eV. Charge

correction was made with the C1s photopeak of adventitious carbon (C–C or C–H bonds) located at BE=284.8 eV. The atomic surface compositions were calculated using the sensitivity factors provided with the apparatus software, applied to the surface below the corresponding fitted XPS signals. An estimated error of \pm 0.1 eV of the BE values was assumed for all measurements.

Catalytic tests

The catalytic tests were performed in batch experiments under stirring conditions by using a Teflon-lined autoclave (16 mL) from HEL starting with 0.1 mg Pt (in Pt(0.5 wt%)-Al-MCM-41 or Pt(0.5 wt%)-Al-SBA-15 catalyst) and a substrate/Pt molar ratio of 20:1 dispersed in heptane (5.0 mL). The reactions were performed at 100 °C under a pressure of 30 bar H₂, and reaction times in the range of 1.5–12 h were used. The autoclave was charged in a N₂-filled dry box with the catalyst and then flushed several times with H₂ before pressurization. The reactants and products were analyzed by GC–MS by using a TraceGOLD-5SilMS 2000 column coupled with DSQ MS from Thermo Electron Corporation. The hydrogenation pathways of the products are described in detail in Tables 4 and 5. The structures of the resulting products were confirmed by ¹H and ¹³C NMR spectroscopy by using a Bruker Avance Ultrashield 500 spectrometer in DMSO solvent with TMS as the internal standard.

A TRACETM Ultra Gas Chromatograph fitted with a TraceGOLD column was used. The data were acquired and processed using Thermo Scientific Xcalibur data handling software.

The content and leaching of Pt was checked by inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent Technologies, 700 Series) after the instrument was calibrated with standard solutions. Carbon elemental analysis was performed by using a EuroEA 3000 automated analyzer. The sample (less than 1 mg) was weighed into a tin container and burned in a vertical reactor (oxidation tube) in the dynamic mode at 980 °C in an He flow with the addition of O₂ (10 mL) at the instant of sample introduction. Portions of the sample in tin capsules were placed in the automated sampler and were transferred to the oxidation tube at regular intervals. The concentration of carbon was calculated using the Callidus program supplied with the analyzer.

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