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Application of supported metallic catalysts in catalytic hydrogenation of arenes

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Since arenes generally exist in coals and their derivatives, petroleum, crop stalks and even liquid fuels, such as gasoline and diesel, catalytic hydrogenation of arenes is a very important process both for hydroconverting fossil and biomass resources and for deeply upgrading liquid fuels. Supported metal-catalyzed hydrogenation is still the primary method for reducing arenes and heteroatomic species. Both noble and non-noble metals as well as a variety of alloys have been extensively investigated as the active species of catalysts. The catalytic activity for arene hydrogenation and the sulfur-resistance of catalysts are attributed to the nature of both metals and supports. As widely used supports, zeolites can greatly improve the sulfur-resistance and hydrogenation activity of catalysts due to their distinct channel structure and adjustable acid sites. In addition, some new processes of catalyst preparation have been created to modify the dispersion of metal particles, even to prepare supported metal nanoparticles. The thermodynamics and kinetics of arene hydrogenation have been systematically investigated as well. The hydrogenation order of each aromatic ring is judged by the superdelocalizability and the reaction order greatly depends on the nature of catalyst and the reaction conditions.

1 Introduction

Arenes generally exist in coals[1–3] and their derivatives,[4–6] petroleum,[7–10] crop stalks[11,12] and even liquid fuels, such as gasoline[13,14] and diesel.[15,16] Some of them can be released into the air during incomplete combustion to form aerosols[17] and even haze.[18,19] The released arenes, especially condensed arenes (CAs), are very hazardous due to their teratogenicity, carcinogenicity and mutagenicity.[20–23] On the other hand, perhydroarenes have many important applications. For example, perhydroanthracene is an intermediate for producing jet fuels, steroids and antibiotics,[24] and polycyclic naphthenes, such as decalin and perhydrophenanthrene, are considered to be potential second- and third-generation immersion fluids.[25] Therefore, catalytic hydrogenation of arenes is a very important process both for hydroconverting fossil and biomass resources and for deeply upgrading liquid fuels. Moreover, a rapid increase in the proportion of heavy petroleum, in which more arenes are contained than in the light one, further raises

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the importance of petroleum hydroprocessing using highly active catalysts.[26–31] In fact, the predicted daily output of heavy crude oil over the world will ascend from 8.1 million barrels (MB) in 2005 to 17.5 MB in 2025 while the hydroprocessing capacity is only 8.6 MB (Fig. 1) and more and more countries have legislated to restrict arene levels in fuels as well as sulfur and nitrogen species (Table 1).[32]

In order to reduce arene levels, new hydrotreating technologies have been developed continuously.[33–36] Two-stage hydrogenation process has been widely used since the first two-stage process established by Shell went into operation in 1992.[32,34] The first stage adopts a common hydrotreating catalyst to reduce the levels of sulfur, nitrogen and metal species to avoid poisoning the noble metal catalyst to be used in the second stage, in which the arenes are deeply saturated and sulfur atoms are removed. Using the diesel from FCC of heavy oil as the feedstock, SINOPEC used the two-stage process, in which Pt or Pd catalyst was used in the second stage to produce diesel fitting with the II and III criterion of WWFC (the contents of S and N are lower than 10 ppm and the cetane number is higher than 40).[33] Nippon Oil Company came up with a two-stage process, in which the first stage used Co–Ni, Ni–Mo or Ni–Co catalyst to restrict the sulfur content under 500 ppm and the second stage also used a noble metal catalyst to reduce arene levels to 9 wt%.[35]

As mentioned above, metallic catalysts (MCs), especially noble metal, have been used to saturate arenes.[37] Much work has been done to develop new varieties of supported MCs to increase catalytic efficiency. Metal sulfides, such as Ni–W and Ni–Mo sulfides supported on γ-Al_2O_3, SiO_2, zeolite and multiple oxides, were also used as catalysts to hydrogenate arenes especially in a one-stage process.[38–45] However, the operating conditions of such catalysts were so harsh (*e.g.*, 310–410 °C and 8–14 MPa of H_2 pressure are needed for catalytic hydrogenation over NiMoS/γ-Al_2O_3) that the thermodynamic equilibrium for the saturation of aromatics was severely inhibited. Thus, the metal sulfides would be used in hydrocracking rather than in arene hydrogenation.[32,46–51]

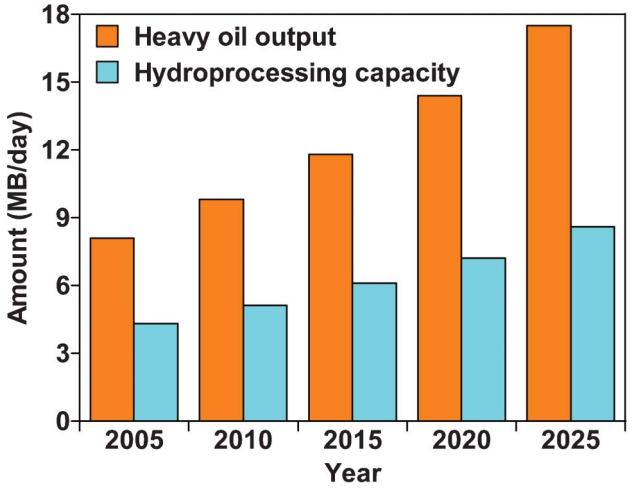

Fig. 1 The trend of international heavy oil output and hydroprocessing capacity.

In this paper, the advances in supported metal-catalyzed hydrogenation of arenes are reviewed. The main factors affecting sulfur-resistance of the supported metals, the thermodynamics and kinetics of arene hydrogenation over the supported metals are discussed.

2 Supported metals

Because of their high turnover frequencies, group VIII metals, especially noble metals, have been prioritized in catalyzing arene hydrogenation without sulfur and nitrogen species or with low concentration of the species.[37,52,53] The temperatures needed for catalytic hydrogenation over the metals are significantly lower than those over the metal sulfides, which benefits the thermodynamic equilibrium motion towards saturated rings. There are two dominant factors determining the catalytic activity of group VIII metals. The first one is chemical bond delocalization amid metal atoms and another

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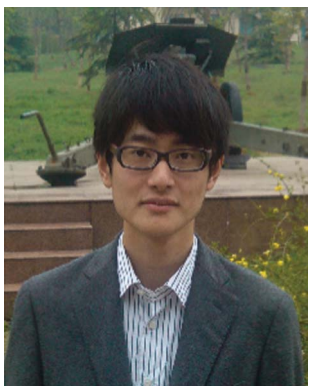

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Table 1 Diesel specification[a]

Diesel	Specification					
	S_{max} (wt%)	D_{20} (g cm^{-3})	TA_{max} (vol%)	PCA_{max} (vol%)	CN_{min}	$t_{95,\ min}$
I	0.5	820–860	none	none	48	375
II	0.03	820–850	25	5.0	53	355
III	0.003	820–840	15	2.0	55	340
IV	0.001	820–840	15	2.0	55	340

[a] TA: total aromatics; D_{20}: density at 20 °C; PCA: polycyclic aromatics; CN: cetane number.

is the electron holes of metal atomic *d* orbits.[54,55] The *d* hole (Table 2) means the energy bands having no electron, and the *d*% denotes the percentage of *d* orbits involved in hybrid orbits. The metals with *d*% from 40 to 50% are usually regarded as appropriate species for catalyzing arene hydrogenation.

2.1 Supported noble metals

According to the multiplet theory of catalysis, noble metals, such as Pd, Pt and Ru, are perfect catalysts for arene hydrogenation since their lattice distances (from 0.36 to 0.38 nm) facilitate the activation of adsorbed arenes. Thus, noble metals, especially Pd and Pt, are most extensively investigated for catalytic hydrogenation of arenes.[56–67]

Ma *et al.* investigated microwave-assisted hydrogenation of anthracene and phenanthrene over Pd/C at temperatures lower than 100 °C.[68] Superdelocalizability (S_r) and resonance energy proved to be proper parameters to interpret the related reaction mechanisms. Ali *et al.* used halogen to modify Pt/Al_2O_3 for catalyzing benzene and toluene hydrogenation at temperatures lower than 150 °C but the detailed mechanism for the modification with halogens was not clear.[69] Kluson *et al.* used Ru/activated charcoal as the catalyst for the hydroconversion of phenol, anisole and benzaldehyde.[70] As a result, phenol and anisole were converted to cyclohexane but benzaldehyde was hydrogenated to cyclohexylmethanol, indicating that the deoxygenation from phenol and anisole and the hydrogenation of carbonyl group in benzaldehyde occurred besides the hydrogenation of the benzene ring in the reactants.

Both monometallic catalysts (MMCs) and bimetallic catalysts (BMCs) were used for catalytic hydrogenation, while BMCs were more likely used because of the synergic effect from supported metals. Pd–Pt BMCs have been studied in detail for a long time.[71–75] Yasuda *et al.*[76] and Fujikawa *et al.*[77] reported that the ionic interaction between Pd and Pt retained the high dispersion of Pd to achieve high catalytic activity and sulfur-resistance when the molar ratio of Pd/Pt was 4 : 1. A series of supported BMCs, such as Pt–Pd, Pt–Re and Pt–Ge on SiO_2–Al_2O_3, were prepared using impregnation-reduction method. Among them, Pt–Pd catalysts are the most highly active and their catalytic activity reached a maximum of *ca.* 0.7 Pd/(Pt + Pd) weight ratio.[78] The detailed characterizations of Pd–Pt catalyst were carried out by Navarro *et al.*,[79] who indicated that the catalytic activity and sulfur-resistance were markedly enhanced by adding Pt species of electron-deficit. Even though majority of the investigations simply considered the synergy between different metals as an important role in enhancing catalytic activity, the preparation methods, in this review, might act as a decider especially for the methods involving the process of hydrogen reduction because of the different reduction temperatures of different metals. Moreover, any processes involving calcination would greatly reduce the specific surface area of the metals. It is well known that metal sintering occurs when the temperature is higher than one third of the melting point.[54]

Table 2 The *d* hole and *d*% of transition metals

Metal	*d* hole	*d*%	Metal	*d* hole	*d*%	Metal	*d* hole
Cr	4–5	39	Rh	1–2	50	Sc	20
Mn	3–4	40.1	Pd	0–2	46	Ti	27
Fe	2–3	39.7	Ag	0–1	36	V	35
Co	1–3	37.5	W	4–6	43	Y	19
Ni	0–2	40	Re	3–5	46	Zr	31
Cu	0–1	36	Os	2–4	49	Nb	39
Mo	4–5	43	Ir	1–3	49	La	19
Tc	3–4	46	Pt	0–1	44	Hf	29
Ru	2–3	50	Au	0	—	Ta	39

2.2 Supported non-noble metals

Because of easier availability, non-noble MCs, especially Ni and its alloys, were also extensively investigated besides the investigations of noble MCs.[80–86] Savva *et al.* investigated benzene hydrogenation over Ni/Al_2O_3 prepared both by the conventional method of dry impregnation and by sol–gel technique.[87] They pointed out that the sol–gel methodology ensured a better compromise between the dispersion of the Ni phase and its interaction with the support than the conventional method. Benzene was completely converted over the Ni/Al_2O_3 prepared by sol–gel technique at 210 °C. Indeed, the calcination for Ni/Al_2O_3 catalyst before H_2 reduction reduced the catalytic efficiency for benzene hydrogenation due to the dispersion decrease of supported Ni. By blending Ni with either noble metals or with non-noble metals, Ni alloys generally showed better catalytic activity than monometallic Ni. Barrio *et al.* impregnated the calcined Ni/SiO_2–Al_2O_3 in $Pd(NO_3)_2$ solution followed by drying, calcination and H_2 reduction to obtain Pd–Ni/SiO_2–Al_2O_3. The catalyst showed a high catalytic activity for naphthalene and toluene hydrogena-

tion when the molar ratio of Pd/Ni was 1 : 8.[88] However, there was no synergy effect between Pd and Ni observed since the stepwise impregnation inhibited the alloy formation.

Although BMCs are generally deemed as more efficient than monometallic ones, some combinations of metals are indeed not ideal catalysts for arene hydrogenation. The number of *d* holes in metals is considered to be an important indicator for catalytic activity, but more *d* holes in metals do not necessarily lead to higher catalytic activity. The metals with too many *d* holes could be too strongly adsorbed by substrates, which is not favorable for catalytic hydrogenation.[54,55] For instance, the *d* holes of Fe are more than those of Ni, but Fe–Ni alloy is not the ideal catalyst for arene hydrogenation.[54] Boudjahem *et al.* prepared Ni–Cu/SiO_2 by aqueous hydrazine reduction to obtain whisker-like shape metallic phase with a mean particle size varying from 25 to 100 nm, however, the presence of Cu decreased the catalytic activity of the Ni.[89] Ni–W or Ni–Mo alloy is still an ideal bimetallic catalyst for arene hydrogenation besides noble metals. Halachev *et al.*[90] investigated the catalytic activity of Ni–Mo and Ni–W supported by Ti-HMS mesoporous material for naphthalene hydrogenation. They found that Ni–W/Ti-HMS catalyst exhibited higher catalytic activity than Ni–Mo/Ti-HMS and decalin yield over Ni–W/Ti-HMS reached 70%.

3 Sulfur-resistant catalysts

Compared with metal sulfides, MCs are much more vulnerable to sulfur-containing species (SCSs).[32,53] According to the investigations on the reaction of di(1-naphthyl)methane over metals or metal–sulfur systems, metals, such as Fe, Ni and Pd, mainly catalyzed arene hydrogenation *via* biatomic hydrogen transfer, whereas metal–sulfur systems tend to hydrocrack the substrate *via* monatomic hydrogen transfer.[47–51,68] SCSs strongly adsorbed on the metal's surface and thereby passivated the MCs for hydrogenation. There are three major routes for enhancing the sulfur-resistance of MCs: changing the composition of alloys, adopting supports of appropriate acidity and modulating the dispersion of metal species.

3.1 Composition of alloys

Many alloys have been investigated to clarify their assistant effect on the sulfur-resistance of the main metal.[91] Hu *et al.* investigated toluene hydrogenation over Pd and Pd–M (M denotes Cr, W, La, Mn, Mo or Ag) supported on HY–Al_2O_3 in the presence of 0.3% thiophene (Fig. 2, in which MCH and DMCP denote methylcyclohexane and dimethylcyclopentane, respectively).[92] Both Cr and W markedly improved the catalytic activity of Pd while other metals inhibited the activity. MCH and cracked products were selectively produced from toluene at lower and higher temperatures, respectively.

Huang *et al.*[93] investigated the sulfur-resistance of Ni/Al_2O_3 modified by Mg, La, Mo, Ti and Th during toluene hydrogenation in the presence of 750 ppm thiophene. Their results showed that all the above metals except Mo enhanced the sulfur-resistance of Ni because there was neither Mo–Ni alloy nor $NiMoO_4$ formed to resist sulfides. The influence from alkali metals was investigated as well.[94] Ferrandon *et al.* impregnated KNO_3 and $Rh(NO_3)_3$ onto La–Al_2O_3 to get Rh–K/La–Al_2O_3.[95] The addition of K significantly enhanced the sulfur-resistance of Rh when the catalyst was used for gasoline reforming with 34 ppm SCSs. Moreover, alkali metals inhibited coke formation, which is the major cause of catalyst deactivation. The assistant species even extended to non-metallic elements.[96] Wang *et al.* investigated boron role in the sulfur-resistance of amorphous Ni–B/SiO_2 catalyst poisoned by CS_2 during cyclopentadiene hydrogenation.[97] They pointed out the higher sulfur-resistance of Ni–B alloy is due to the reversible adsorption of sulfur on the elemental boron prior to adsorption on Ni and the catalyst was deactivated once Ni began to adsorb sulfur.

3.2 Supports

Supports act not only as platforms for the dispersion of active species (ASs) and for catalytic reaction, but also as assistants impacting the performance of the ASs. Indeed, supports themselves also act as ASs.[52,53] Activated carbon (AC) catalyzes monatomic hydrogen transfer, but such a hydrogen transfer did not lead to deep hydrogenation of polycyclic arenes.[98] Acidic supports improved the sulfur-resistance of metallic species and the catalytic activity for arene hydrogenation was modified as well, which was interpreted by the model of electron deficient 'metal-proton' adduct.[52,53,99] The mechanism for the interaction between Pt species and the zeolite was proposed. First, Pt species were linked with the acid sites of zeolite during impregnation or ion-exchange to form (≡Al–O^-)[$Pt(NH_3)_4Cl$], in which '≡Al–O^-' denotes the acid sites of zeolite. Second, the Pt species turned into (≡Al–O^-)$_2Pt^{2+}$ during calcination. At last, the Pt^{2+} species were transformed into small clusters of electron deficient metal during H_2 reduction. The intimate contact between the metal clusters and acid sites promoted electron transfer from metal to acid sites to form electron-deficient metal clusters. Zeolites are most extensively used as appropriate supports of MCs due to their sufficient surface area, good hydrothermal and structural stability, perfect selectivity for products and adjustable acidity. The catalytic activity and sulfur-resistance of metals are markedly improved by zeolites (Tables 3 and 4).[100–108]

The catalytic activity of supported-metals is attributed to two parts: one is the contribution from the metal surface, and the other derives from the acid sites, where the spillover hydrogen could react with the adsorbed arene molecules. The H^+ on zeolites can be exchanged with H_2 easily in the presence of a metal phase, which can adsorb and dissociate H_2. Wang *et al.* investigated the role of interparticle migration of spillover hydrogen in solid acid-diluted catalysts.[109] The H_2 is first adsorbed on Pt sites and then dissociated into H or H^+ (Scheme 1). The hydrogen species are proposed to spillover onto the Al_2O_3 support, cross the interphase between Pt/Al_2O_3 and the solid acid and finally migrate to the acid sites. Meanwhile, benzene molecules adsorbed on the acid sites in the form of carbonium ions are hydrogenated by the spillover hydrogen. There should be no bridge between H_2 and the spillover hydrogen without Pt in the vicinity of the acid sites, and the arene hydrogenation could not take place in the absence of Pt.

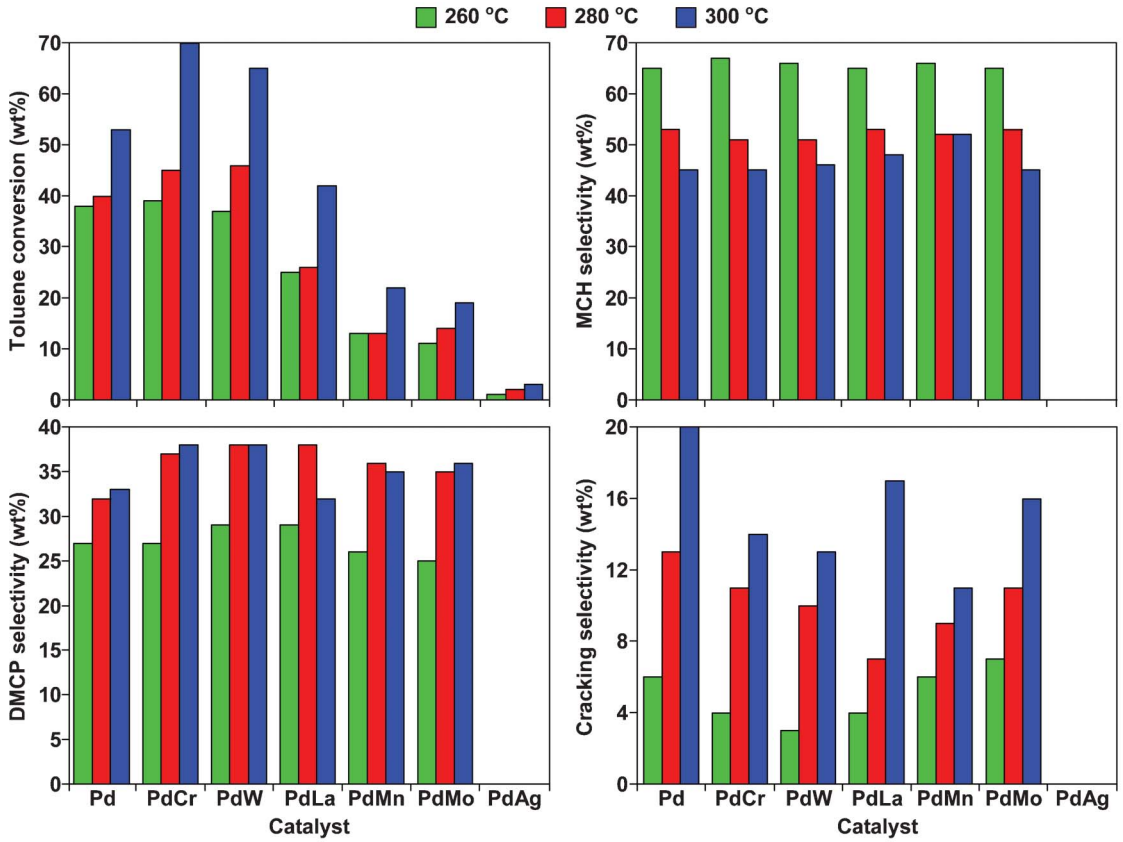


Fig. 2 Toluene conversion over different Pd-containing catalysts.

Weak acid or non-acid supports, such as Al_2O_3, Al_2O_3–SiO_2, B_2O_3–Al_2O_3, MCM-41, F–Al_2O_3, TiO_2 and TiO_2–Al_2O_3, were also researched because of their advantages over zeolites.[110–113] Brønsted acids, the main acid species of zeolites, were strong enough to resist sulfur and to enhance the catalytic activity of supported-metals for arene hydrogenation along with the severe product coking or cracking. Weak acid supports, mainly Lewis acid sites, showed a high selectivity for hydrogenated products and a low yield of coked or cracked products.

Carbon-based supports, such as AC and graphite, were not recommended as supports for non-noble MCs since the resulting carbides have no catalytic activity.[114] However, noble metals supported on carbon-based supports, such as Pd/C, have been used as perfect catalysts for arene hydrogenation. Other carbon-based supports, such as carbon nanotubes (CNT), were also noticed.[115–118] Yoon *et al.* supported Pd and Rh on (or in) CNT to obtain metal nanoparticles and

Table 3 Application of zeolite-supported MMCs in catalytic hydrogenation[a]

Catalyst	Feedstock	Operation condition	Conversion (%)	Main product	Selectivity (%)	Ref.
Pd/USY	Naphthalene with BTP	Mass ratio of feedstock to catalyst 10 : 1, molar ratio of BTP to Pd 0.9–9, P_{H2} 6.89 MPa, 200 °C, 2 h	12–95	Tetralin	95	100
Pt/Mordenite	Benzene	Catalyst 0.45 g, molar ratio of H_2 to benzene 4 : 1,	100	MCP	66.7	101
Pt/ZSM-5		P_{H2} 2.0 MPa, WHSV was 2 h^{-1}, 230 °C	99	Cyclohexane	98.7	101
Pt/Beta			99		50.3	101
Pt/NaH-MOR	Benzene	Catalyst 0.09 g, TP concentration 0 or 50 ppm, H_2 flow	—		70.3–87.9	102
Pt/KH-LTL	with TP	200 mL min^{-1}, 350 °C, 1 h	—		72.3–80.5	102
Pd/H-beta	Naphthalene	Catalyst 0.09 g, TP concentration 0 or 200 ppm,	100	Decalin	15.6–31.7	103
Pd/Al-MCM-41	with TP	P_{H2} 6.2 MPa, 250 °C, 0.3 h or 0.66 h	100	Tetralin	71.5–94.5	103
Ni/SBA-15	Naphthalene	Mass ratio of feedstock to catalyst was 83 : 1, P_{H2} 5.0 MPa, 300 °C, 2 h.	100	Decalin	81.9	104

[a] BTP: benzothiophene; P_{H2}: hydrogen pressure; MCP: methylcyclopentane; TP: thiophene.

Table 4 Application of zeolite-supported BMCs in catalytic hydrogenation[a]

Catalyst	Feedstock	Operation condition	Conversion (%)	Main product	Selectivity (%)	Ref.
PdPt/H-beta	Toluene	Mass ratio of feedstock to catalyst was 1 : 1, molar	100	MCP	100	105
Pt/H-beta		ratio of H_2 to toluene 28 : 1, H_2 flow 50 mL min^{-1},	100		84	105
Pd/H-beta		150 °C	50		84	105
NiRu/ZSM-5 + Al_2O_3	Toluene	Molar ratio of H_2 to toluene 350 : 1,	99	MCP	96	106
Ni/ZSM-5 + Al_2O_3		P_{H2} 3.5 MPa. LHSV 3 h^{-1}, 240 °C	98		100	106
MoNi/Nano-beta	LCO	Catalyst 20 g, P_{H2} 8 MPa, 375 °C, 1 h	92.9	Saturates	22.1	107
WNi/Nano-beta			91.6		27.2	107
PtNi/H-beta	NS	Catalyst 0.75 g, H_2 flow 190 mL min^{-1},	65	Naphthenes	35.1	108
Ni/H-beta		290 °C, 24 h.	45		23.6	108
Pt/H-beta			68		33.2	108

[a] P_{H2}: hydrogen pressure; MCP: methylcyclopentane; LCO: light cycle oil; NS: naphtha stream.

hydrogenated benzene at room temperature.[119] However, the novel supports are generally expensive for practical use.

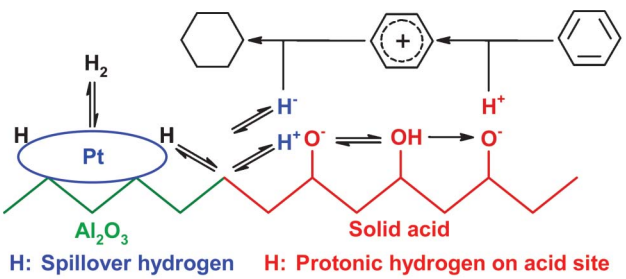
3.3 Preparation method of catalysts

As mentioned above, the interaction between the supported metals and acid sites of the supports enhances both sulfur-resistance and catalytic activity for arene hydrogenation. The size and dispersion of loaded metal particles mainly depend on the preparation method of catalysts. Traditional impregnation-reduction method has been extensively investigated, while there are many novel methods different from traditional processes (Table 5).[89,104,120–125] Highly dispersive supported metals, even metal nanoparticles, can be prepared through such novel methods.

4 Thermodynamics and kinetics of arene hydrogenation

4.1 Thermodynamic aspects

As a foundational theory, the thermodynamics of arene hydrogenation has been well investigated. Stanislaus and Cooper elaborated the thermodynamics of arene hydrogenation.[52,53] There are a few typical arene species in petroleum fractions and a series of related model compounds were used in the research on arene hydrogenation (Table 6).[52,126]



Scheme 1 Benzene hydrogenation *via* hydrogen spillover on acid sites.

Arene hydrogenation proceeds according to the following reaction:

$$A + nH_2 \rightarrow AH_{2n}$$

where A and AH_{2n} denote the arene and its hydrogenated product, respectively.[52] The equilibrium equation is described using parameters Y_A (molar fraction of arene), Y_{AH2n} (molar fraction of the hydrogenated arene), K_a (equilibrium constant), P_{H2} (partial H_2 pressure) and n (equivalent moles of H_2 consumed) as follows:[52]

$$\frac{Y_{AH_{2n}}}{Y_A} = K_a (P_{H_2})^n$$

According to the equation, higher H_2 pressures facilitate arene hydrogenation. The K_a decreases with raising the reaction temperature due to a strong exothermic reaction. Hence, the reaction should be performed at temperatures as low as possible using highly active catalysts.

As for the hydrogenation of CAs, each ring in the substrate is reversibly and successively saturated and the hydrogenation order of each ring is judged by S_r, as shown in Table 7.[68]

Frye measured the constituents of the products after the reaction equilibrium of arene hydrogenation under different conditions and calculated the enthalpies and the equilibrium constants (Table 8).[127]

4.2 Kinetic aspects

Kinetics research has been emerging continuously owing to different substrates and diverse catalysts.[128–133] In order to be easily investigated, the model compounds of arenes were divided into two groups, polyalkylbenzenes (PABs) and CAs.

PABs Arenes display low apparent activation energy (40–60 kJ mol^{-1}) during catalytic hydrogenation over Group VIII metals, and the reaction orders are close to zero.[52] However, the reaction order would increase with raising the reaction temperature. Slioor *et al.* investigated gas phase adsorption and desorption kinetics of toluene on Ni/γ-Al_2O_3 with transient step adsorption-TPD experiments.[131] Their results showed that toluene adsorption was weak and reversible, implying that at least part of the adsorption over Ni was physisorption, and no deactivation was observed. The reaction order of *o*-xylene hydrogenation over Pt/γ-Al_2O_3 ranged from 1.5 (157 °C) to 3.0

Table 5 Unconventional preparation process of supported MCs[a]

Catalyst	Method	Material	Concise process	Ref.
Ni–Cu/SiO_2	AH reduction	Silica, NA, $Cu(NO_3)_2$ and hydrazine	Impregnation was carried out using NA and $Cu(NO_3)_2$ as precursors. Silica was added to the solution to obtain suspension followed by the addition of excess AH at pH = 10.	89
Ni/SBA-15	Pretreatment with NH_3/H_2O vapor	$Ni(NO_3)_2$, SBA-15 and NH_3/H_2O	SBA-15 was impregnated with $Ni(NO_3)_2$ aqueous solution then dried at 100 °C. The dried sample was pretreated by NH_3/H_2O vapor followed by dessication, calcination and reduction in H_2 flow.	104
Ni/Al_2O_3	Sol–gel	ATB, AA and $Ni(NO_3)_2$	ATB was dissolved in isopropanol. AA was added as a chelating agent. $Ni(NO_3)_2$ aqueous solution was added to obtain gel followed by dessication, calcination and reduction in H_2 flow.	120
Ni/SiO_2	Heterophase sol–gel	$Ni(NO_3)_2$, ES-32, ethanol and NH_3 aqueous solution	Precipitation of $Ni(NO_3)_2$ with NH_3 aqueous solution afforded $Ni(OH)_2$, which was calcinated to get NiO. Ni/SiO_2 with desired Ni to SiO_2 ratio was obtained by impregnating NiO with a proper concentration of ES-32 in ethanol followed by dessication and reduction in H_2 flow.	121
Ni–Al	Co-precipitation	$Ni(NO_3)_2$, $Al(NO_3)_3$ and NH_3 aqueous solution	$Ni(NO_3)_2$ was mixed with $Al(NO_3)_3$ and then NH_3 aqueous solution was added until pH = 8. The mixture was aged, dried, calcined and *in situ* reduced under H_2 atmosphere	122
Ni/Al_2O_3	Using NAA as the precursor	NA, benzene and Al_2O_3	NAA was dissolved in benzene and added into Al_2O_3 followed by filtration, washing with benzene, dessication, calcination and reduction in H_2 flow at 400 °C.	123
Nano-Co, Rh and Ir	Using MC as the precursor	MC and an ionic liquid	MC was dissolved in the dried and deoxygenated ionic liquid under argon atmosphere, the solution was heated up to 230 °C to decompose MC into nanoparticles.	124
Pd/SiO_2	Using $PdCl_2(PhCN)_2$ as the precursor	$PdCl_2(PhCN)_2$, CH_2Cl_2 and SiO_2	A solution of $PdCl_2(PhCN)_2$ in CH_2Cl_2 was mixed with modified SiO_2 in a degassed reactor at 48 °C. Then the mixture was cooled, filtered, washed with CH_2Cl_2 and dried in a vacuum.	125

[a] AH: aqueous hydrazine; NA: nickel acetate; ATB: aluminum tri-*sec*-butoxide; AA: acetylacetone; ES-32: ethyl silicate-32; NAA: nickel acetylacetonate; MC: metal carbonyl.

(247 °C).[134] The investigation on the kinetics and stereoselectivity of *o*-xylene hydrogenation over Pd/Al_2O_3 showed that the reaction order with respect to H_2 varied between 1.3 (167 °C) and 2.6 (247 °C), and thermodynamically more stable *trans*-1,2-dimethylcyclohexane was favored. Smeds *et al.* found that the reaction order of mesitylene hydrogenation over Ni/Al_2O_3 increases as a function of the temperature from less than 1 (145 °C) to 2 (220 °C).[135]

The hydrogenation rates of polymethylbenzenes over MCs depend on the amount and distribution of methyls in the following order: benzene > toluene > *p*-xylene ⩾ *m*-xylene > *o*-xylene > mesitylene, which is attributed to the substituent steric and electronic effects.[52,53]

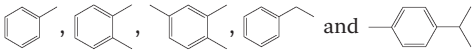
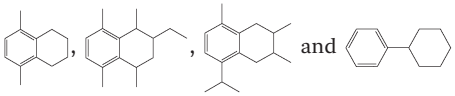
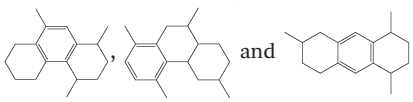
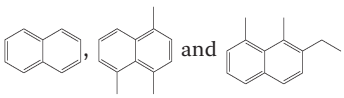
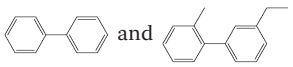
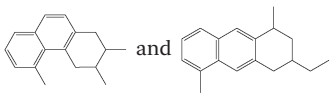
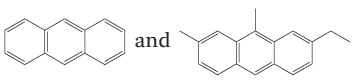
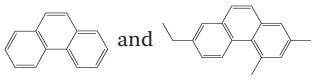
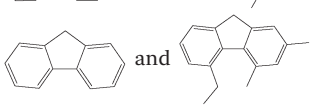
CAs CAs are hydrogenated ring-by-ring in succession. Their hydrogenation reactions generally proceed in first-order. The hydrogenation rate is the fastest for the first aromatic ring and then reduces with the increase in hydrogenation degree, and the last aromatic ring is the most difficult to be saturated. Indeed, the hydrogenation of CAs is eventually ascribed to the saturation of benzene rings. The reactivities of typical arenes toward hydrogenation of the first aromatic ring decrease in the order: anthracene > phenanthrene > naphthalene > benzene.

Zhang *et al.*[136] investigated naphthalene hydrogenation over Pd, Pt and Pd–Pt/SiO_2–Al_2O_3. They found that compared to *cis*-decalin, more *trans*-decalin was produced and *trans*-decalin selectivity increased with prolonging the reaction time. The formation of *cis*-decalin is kinetically controlled due to the adsorption pattern of arenes and H_2 over MCs, while the formation of *trans*-decalin, a thermodynamically stable configuration, is favored at higher temperatures.

According to the investigation on the hydrogenation kinetics of phenanthrene in the presence of Ni catalyst, the slow and fast kinetics based on the adsorption forms of the products on the catalyst surface were calculated (Scheme 2, in which the formation enthalpies are indicated for various species in kJ mol^{-1}).[137] The slantwise and edgewise adsorption with production of strained and unstable structure are stereochemically predicted in the slow production of H_2P and its derived *u*-H_8P. Sterically favored flatwise adsorptions are expected in the rapid formation of H_4P and its derived *s*-H_8P. The low rate constants for both isomerization to *u*-H_8P and irreversible hydrogenation in the direction of stereoisomeric perhydrophenanthrenes have positive implications, since the latter, being a quality factor in coal liquids, does not contribute to hydrogen donation at high temperatures.

The competitive hydrogenation of CAs over MCs was extensively researched as well.[138] Tetralin hydrogenation was severely inhibited by naphthalene added over Pt/TiO_2.

Table 6 Typical structures of arenes present in petroleum fractions

Arene type	Typical structure
Monoarene Alkylbenzenes	
Benzocycloparaffins	
Benzodicycloparaffins	
Diarene	
Naphthalenes	
Biphenyls	
Indenes	
Naphthocycloparaffins	
Triarene Anthracenes	
Phenanthrenes	
Fluorenes	

Similarly, the reactivities of toluene, naphthalene and dibenzothiophene toward hydrogenation over Au–Pd/SiO_2–Al_2O_3, Pd/γ-Al_2O_3, Au/γ-Al_2O_3 and Au–Pd/γ-Al_2O_3 decreased in the order: naphthalene ≫ toluene > dibenzothiophene.[73,139,140]

5 Future outlook

Deep hydrogenation of arenes can be achieved under mild conditions. However, the development of markets for both

Table 7 S_r values of some unsaturated hydrocarbons

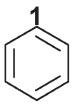
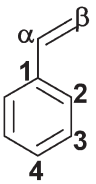
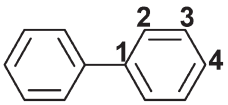
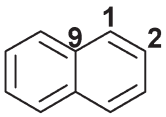
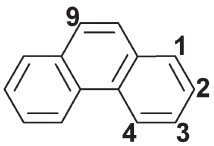
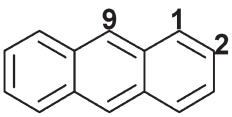
	S_r value						
							
Position							
α	—	—	0.911	—	—	—	—
β	—	—	1.266	—	—	—	—
1	1.000	0.833	0.761	0.772	0.994	0.978	1.073
2	—	—	0.931	0.910	0.873	0.859	0.922
3	—	—	0.829	0.830	—	0.892	—
4	—	—	0.911	0.894	—	0.940	—
9	—	—	—	—	0.703	0.998	1.314

Table 8 The heats and equilibrium constants of polycyclic arene hydrogenation

Substrate	Product	$-\Delta H$ (kJ mol^{-1} H_2)	lgK_p
Naphthalene	Tetralin	—	6460/T − 12.4
Naphthalene	*trans*-Declain	—	16 500/T − 32.88
cis-Declain	*trans*-Declain	—	695/T − 0.301
Biphenyl	Cyclohexylbenzene	75.36	11 750/T − 21.71
Cyclohexylbenzene	Bicyclohexane	75.36	11 750/T − 22.37
Biphenyl	Bicyclohexane	75.36	23 500/T − 44.08
Phenanthrene	9,10-Dihydrophenanthrene	50.24	2600/T − 6.11
Phenanthrene	1,2,3,4-Tetrahydrophenanthrene	62.80	6565/T − 13.25
Phenanthrene	*sym*-Octahydrophenanthrene	62.80	13 030/T − 26.38
Phenanthrene	Perhydrophenanthrene	62.80	23 190/T − 46.49

saturation catalysts and two-stage saturation processes is uncertain. Novel metallic patterns and better sulfur-resistant catalysts should be further investigated.

Amorphous alloys (AAs) markedly improve the dispersion of active sites and the electronic structure of catalysts. The transition metal (such as Ni, Co, Fe and Pd)–metalloids (such as B and P) pattern for AAs will be further investigated. For instance, the adsorption of sulfur on M–B alloy hardly changes the electronic properties of metal atoms, which are the active sites of the catalyst. SCSs prefer to combine with boron rather than metal, thus their ability to poison the active metal atoms decreased greatly. Some kinds of metal nitrides will also be further investigated as their catalytic properties are similar to noble metals, and the catalysts show a good resistance to compounds containing S, N and O atoms in the feedstock. Although the hydrogenation activity and sulfur-resistance of such novel catalysts could be improved after being modified, it is still too early to use them in industry due to the fast or even complete deactivation in the presence of SCSs.

Better sulfur-resistant catalysts might continue centering on the metals supported on zeolites, which have the best industrialized prospect. An ideal designed concept of sulfur-resistant catalysts is proposed in Fig. 3.

There are bore channels with different diameters in zeolites. Metal particles distribute both in large channels ($d > 0.6$ nm) and in small ones ($d < 0.5$ nm). Hydrogen molecules are able to pass through all the channels while the substrates, both arenes and organic SCSs, only react in large channels. Once poisoned by sulfide, the metal particles loaded in large channels are to be refreshed by the spillover hydrogen from small channels. The key for such a model is to ensure that the metal particles remain in the channels of zeolites. Hence, better sulfur-resistant and lower-cost alloys and zeolites which show both shape selectivity and high catalytic activity for large arene molecules will be the hot spots of future investigations. Besides sulfur-resistance, excellent supported MCs for arene hydrogenation should be able to effectively activate both aromatic rings in arenes and H_2.

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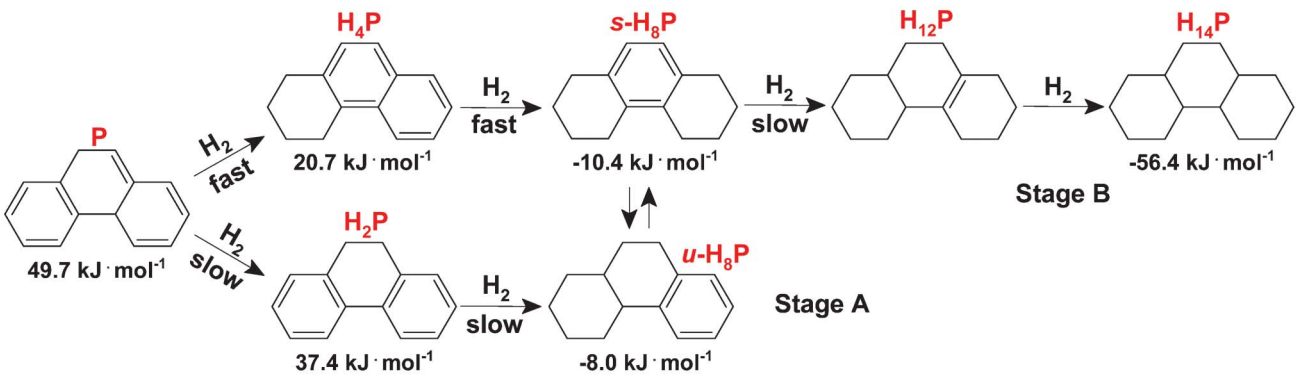

Scheme 2 Reaction rates of phenanthrene hydrogenation and formation enthalpies of the products.

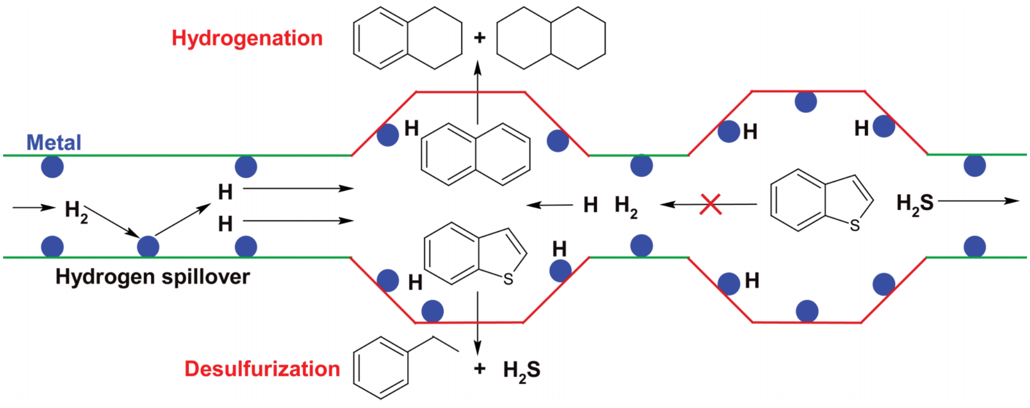

Fig. 3 New concept for sulfur-tolerant mechanism of metal supported on zeolite.

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