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Sulfur tolerance of Pt/mordenites for benzene hydrogenation
Do Brønsted acid sites participate in hydrogenation?

L.J. Simon [a,b], J.G. van Ommen [b], A. Jentys [a], J.A. Lercher [a,*]

[a] *Technische Universität München, Lehrstuhl für Technische Chemie II, Lichtenbergstrasse 4, D-85748 Garching, Germany*
[b] *Faculty of Chemical Technology, Catalytic Processes and Materials, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*

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Abstract

The comparison of Pt electronic properties studied by in situ XANES and the kinetic study of benzene hydrogenation strongly suggests that the hydrogenation of benzene on Pt/mordenites occurs along two parallel reaction pathways. The routes proposed include (i) the monofunctional hydrogenation of benzene on the metal itself and (ii) the hydrogenation of Brønsted acid bound benzene using hydrogen dissociated on the close metal surface. In the presence of sulfur containing compounds, the activity of solely metal catalyzed route ceases, while the route involving Brønsted acid sites is more sulfur tolerant. The activity and sulfur tolerance of these catalysts for benzene hydrogenation depends upon the vicinity between metallic and Brønsted acidic sites and the concentration of the Brønsted acid sites. Increasing hydrogen partial pressure increases the rates of the reaction and the sulfur tolerance of the catalysts. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Benzene hydrogenation; Sulfur tolerant; Acid sites; Noble metal

1. Introduction

Pt supported on basic zeolites has been shown to be highly active for (de)hydrogenation reactions [1,2]. However, the high sensitivity of noble metals towards sulfur is one of the major drawbacks for the industrial development of such catalysts. For bifunctional reactions, it was reported that catalysts based on Pt–Pd alloys supported on amorphous silica alumina and dealuminated faujasite remain active in the presence of 1000 ppm sulfur in the feed [3]. In general, such sulfur tolerant catalysts are based on highly acidic supports. The positive effect of the acidity on the noble metal sulfur resistance was explained by the changes in the metal electron deficiency induced by metal/support interactions [4–7]. The presence of nucleophilic sulfur compounds results in a high sulfur poisoning of the metal sites, which decreases the metal/support interactions [2], and thus, induces pronounced sintering and migration of particles outside of the zeolite pores.

Although several reviews reported that benzene hydrogenation is a purely metal catalyzed reaction [8–10], the support acidity was shown to have a significant influence on the activity of metal-supported catalysts for the hydrogenation of aromatic molecules. The rate of benzene hydrogenation was reported to increase with increasing acid site concentration, which was generally explained by an increase of the metal electron deficiency [7]. However, Vannice and co-workers [11,12] explained the increase in aromatic hydrogenation activity of Pt and Pd supported on acidic supports compared to catalysts on inert supports by the presence of additional hydrogenation sites

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[*] Corresponding author.
E-mail address: lercher@ch.tum.de (J.A. Lercher).

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in the metal–acid interfacial region, which contribute to the overall rate of benzene hydrogenation.

This study focuses on the potential role of interfacial sites and sites on the support, i.e. Brønsted acid sites, upon the hydrogenation of aromatic compounds and on the consequences for the sulfur tolerance of Pt supported on acid and basic mordenite based catalysts.

2. Experimental

2.1. Catalyst preparation

Mordenites exchanged with alkali (e.g. Cs^+, Li^+ and K^+), ammonium cations and protons were prepared from a commercial Na-mordenite sample (TOSOH, Si/Al $=$ 9.3, reference HSZ-641NAA, lot T960402). The zeolites were loaded with Pt applying liquid phase ion exchange at room temperature using tetraammine platinum hydroxide ($Pt(NH_3)_4(OH)_2 \cdot H_2O$, 59% Pt, STREM) as precursor [13]. The solution containing the precursor was added dropwise to the slurry of zeolite and stirred overnight. The sample was filtered, washed with de-ionized water, dried for 24 h in air, calcined in dry air at 493 K during 1 h (heating rate of 0.5 K min^{-1}) and finally reduced in H_2 at 623 K during 1 h (heating rate of 0.5 K min^{-1}).

Pt supported catalysts containing various alkali/proton ratios were prepared. The samples are designated in this paper as Pt/XH-MOR, Pt/X-MOR and Pt/NH_4^+-MOR with X being the type of alkali cations.

2.2. Catalyst characterization

The chemical composition of the catalysts was determined by X-ray fluorescence spectroscopy. The concentration of acid sites was measured by ammonia TPD. A total of 90 mg of the sample was evacuated at 623 K for 1 h (heating rate of 10 K min^{-1}). After cooling down to room temperature 10^3 Pa of ammonia was adsorbed and allow to equilibrate with the surface for 1 h. Physisorbed ammonia was removed by heating the sample to 423 K for 1 h. TPD was performed up to 973 K with a heating rate of 10 K min^{-1}. A Balzers mass spectrometer was used to detect the desorbing molecules.

The number of accessible Pt atoms was determined by hydrogen chemisorption. The catalyst was reduced in flowing hydrogen (flow rate approximately 50 ml min^{-1}) for 1 h at 623 K and subsequently evacuated (pressure $<$1 MPa) at the reduction temperature for 1 h. After cooling the sample to room temperature, 5×10^4 Pa of hydrogen were admitted into the sample chamber and were allowed to equilibrate with the catalyst overnight. The sorption isotherm was measured with decreasing hydrogen pressure in steps applying equilibrium times of 1 h for each step. The H/Pt ratio was determined by an extrapolation of the flat part of the desorption isotherm to a pressure of 0 Pa.

X-ray absorption spectra were collected on beamline X1 at HASYLAB, DESY, Germany. The Si(3 1 1) double crystal monochromator used was detuned to 60% of the maximum intensity to minimize the intensity of higher harmonics in the X-ray beam. Data were collected at the Pt L_{III} edge (11,564 eV) and analyzed with the WINXAS97 software [14]. The area of the peak above the edge was calculated by fitting the absorption edge using an arctan function [15]. The height of the arctan function was adjusted using a least square fit. The arctan function was then subtracted from the XANES and the main peak above the edge was integrated (area of the white line).

In situ thiophene poisoning (623 K, 0.1 MPa in H_2) and benzene hydrogenation (623 K, 0.1 MPa, H_2/C_6H_6 $=$ 34.2) was followed by XANES in the absence and the presence of thiophene. The same reactions were repeated in the laboratory, where the products were analyzed by an online gas chromatograph HP6890 equipped with a DB-1 column and a FID.

2.3. Benzene hydrogenation measurements

The effect of the pressure on the catalytic activity was studied at 623 K, WHSV $=$ 53 h^{-1} and with H_2/C_6H_6 ratios of 7.6 at 0.1 and 1 MPa and 20.6 at 2.5 MPa. Sulfur contamination was avoided by using a system with two reactors and separated feed lines. For each measurement, between 45 and 90 mg of the catalyst (particle diameters between 0.3 and 0.6 mm) mixed with quartz were reduced in situ in a hydrogen flow of 200 ml min^{-1} at 673 K for 1 h. The solution of benzene and thiophene (Aldrich) was mixed with the hydrogen flow using a high-pressure syringe pump

(ISCO) and injected into the gas stream. The reaction products were analyzed using an on-line HP6890 gas chromatograph equipped with a FID and a DB-1 column.

3. Results and discussion

3.1. Chemical and physicochemical characterizations of the samples

The chemical and physicochemical characterizations of the samples are compiled in Table 1.

Catalysts with a wide range of Brønsted acid site concentrations and similar Pt loading and dispersions were prepared. The Brønsted acid site concentration increased with decreasing alkali content of the zeolite. The results of the EXAFS analysis are compiled in Table 2. Pt–Pt coordination numbers above 8 observed for the reduced samples are in agreement with the moderate values of the Pt dispersion obtained by hydrogen chemisorption. Although Pt–Pt coordination numbers were high, i.e. the diameter of the Pt particles was larger than the pores of MOR (around 20 Å) [16], HREM studies showed that most of the Pt particles were located inside the pores of Pt/H-MOR and Pt/NaH-MOR [17]. The Pt–Pt interatomic distances varied between 2.74 and 2.77 Å for all catalysts.

3.2. In situ XANES study

The effects of the thiophene adsorption on the metal electron properties were studied using XANES on catalysts containing various H^+/Na^+ ratios (see Fig. 1). An increase of the Pt white line intensity with increasing thiophene concentration was observed. The physical cause of the changes in white line intensity after reactant adsorption are still controversially and subject to discussion and can be explained by

Table 2
Pt L_{III} edge EXAFS analysis of the reduced catalysts

Sample	$N_{Pt–Pt}$	$R_{Pt–Pt}$ (Å)	$\Delta\sigma^2_{Pt–Pt}$ (Å^2)
Pt/H-MOR	9.3	2.77	1.3×10^{-3}
Pt/NaH-MOR	9.0	2.75	4.0×10^{-3}
Pt/LiH-MOR	8.6	2.74	5.3×10^{-3}
Pt/KH-MOR	9.6	2.76	3.1×10^{-3}
Pt/CsH-MOR	8.2	2.76	3.2×10^{-3}
Pt/Na-MOR	8.8	2.74	3.5×10^{-3}
Pt/NH_4^+-MOR	9.0	2.74	5.1×10^{-3}

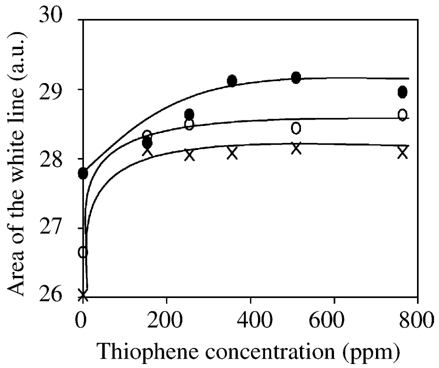

Fig. 1. Influence of the adsorption of thiophene on the Pt white line intensity for (●) Pt/H-MOR, (○) Pt/NaH-MOR and (×) Pt/Na-MOR (623 K, 0.1 MPa, in H_2).

Table 1
Chemical and physicochemical properties of the catalysts

	Si/Al	Alkali exchanged degree (mol%)	Acid site concentration (mol g^{-1})	Pt loading (wt.%)	H_{ads}/Pt
Pt/H-MOR	9.1	2.1	1.3×10^{-3}	1.1	0.56
Pt/LiH-MOR	9.1	56.1	7.4×10^{-4}	1.0	0.62
Pt/NaH-MOR	9.1	70.4	2.6×10^{-4}	1.1	0.59
Pt/CsH-MOR	8.9	85.6	1.9×10^{-4}	1.0	0.52
Pt/KH-MOR	9.0	92.1	1.0×10^{-4}	1.0	0.51
Pt/Na-MOR	9.0	98.2	9.7×10^{-5}	1.0	0.58
Pt/K-MOR	8.9	100.0	3.4×10^{-5}	1.1	0.56
Pt/NH_4^+-MOR	9.0	3.1	1.4×10^{-3}[a]	1.1	0.58

[a] Acid sites covered by ammonium cations.

two mechanisms: (i) an increase of the electron deficiency of the metal surface due to the attraction of electrons by the sulfur species adsorbed on the Pt surface [18] or (ii) a change in the electron orbital energy of the metal due to the formation of Pt–S bonds [19,20]. In both cases, the increase of the Pt white line intensity is proportional to the concentration of sulfur adsorbed on the metal surface. The constant Pt white line intensity for thiophene concentrations above 400 ppm and the constant white line intensity as a function of reaction time (not shown here) indicate that at lower thiophene concentrations sulfur species did not cover the complete metal surface [21]. Therefore, an equilibrium between the gas phase thiophene and the adsorbed sulfur containing species is concluded to exist. After thiophene poisoning, Pt white line intensities remained constant, which indicates that most of the adsorbed sulfur species are irreversibly adsorbed. Our results [22] show that the formation of H_2S by decomposition of thiophene was observed only for acidic MOR based catalysts. The higher increase of the white line intensity observed for Pt/H-MOR was, therefore, attributed to the enhanced thiophene decomposition on Brønsted acid sites of the zeolite, which resulted in a higher H_2S and in a stronger sulfur poisoning of the Pt sites.

For all catalysts a decrease of the Pt white line during benzene hydrogenation compared to the reduced samples was observed (Fig. 2a). This decrease can be attributed to the adsorption of benzene and reaction intermediates on the metal surface during benzene hydrogenation. The adsorption of benzene on Pt (1 1 1) has been shown to be a flat adsorption via the π orbitals [23] with Kekule distortions [24], which results in an electron transfer from the aromatic ring to the unoccupied d-orbitals of Pt [25,26]. These changes in metal electron properties induced by the chemisorption of benzene via π electrons on the Pt particles are clearly reflected in the decrease of the white line intensity during the benzene hydrogenation. However, in the presence of thiophene, an increase of the Pt white line intensity is observed (Fig. 2b), which is attributed to the adsorption of sulfur species on the metal surface as observed with the adsorption of thiophene (see Fig. 1). The increase of the Pt white line was higher in the case of Pt/H-MOR compared to more basic samples, which indicates a higher concentration of sulfur species adsorbed on the metal during benzene hydrogenation and is in agreement with the results shown in Fig. 1. After reaction in the presence of thiophene and flushing with hydrogen, the white line intensity did not reach its initial value indicating an irreversible adsorption of the sulfur species on the metal surface.

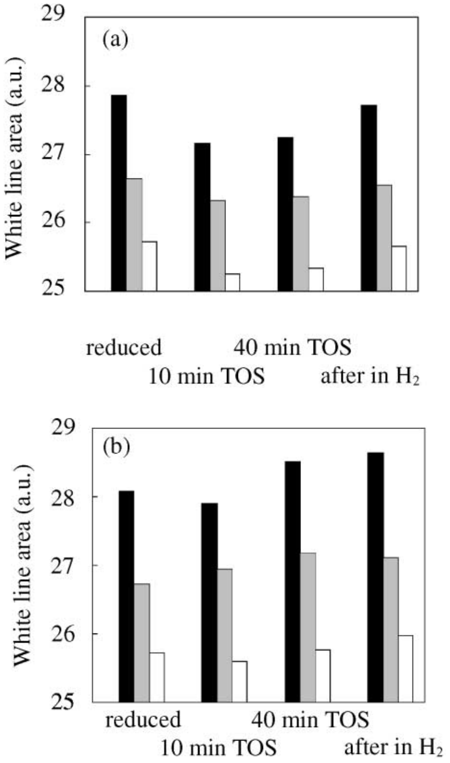

Fig. 2. Changes in the Pt white line intensity during benzene hydrogenation in the absence (a) and the presence (b) of 50 ppm thiophene for (■) Pt/H-MOR, (▨) Pt/NaH-MOR and (□) Pt/Na-MOR (623 K, 0.1 MPa, $H_2/C_6H_6 = 34.2$).

In general, benzene hydrogenation is described as a metal only catalyzed reaction [8–10], where the increase of benzene conversion with increasing acid site concentration is explained by the increase of the Pt electron deficiency [7,27]. In contrast to this, the kinetic results reported in Figs. 3 and 4 show that the activity of Pt supported on more acidic and more basic supports is lower than on Pt/NaH-MOR. A stable activity is observed for all catalysts after 30 min time on stream in the absence and the presence of thiophene (see Fig. 3). Therefore, in agreement with

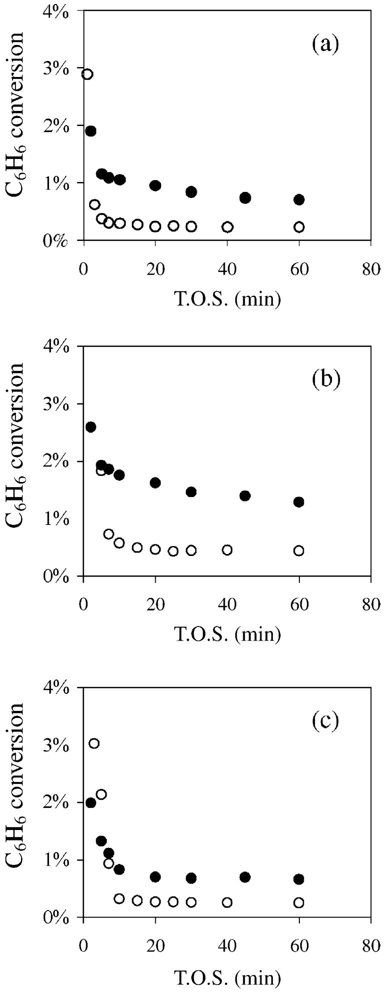

Fig. 3. Time on stream dependence of benzene conversion measured in the XAS cell in the absence (●) and the presence (○) of 50 ppm thiophene for (a) Pt/H-MOR, (b) Pt/NaH-MOR and (c) Pt/Na-MOR (623 K, 0.1 MPa, $H_2/C_6H_6 = 34.2$).

Vannice et al. [11], we propose that benzene hydrogenation occurs on two catalytically active sites (i) on the metal and (ii) on the Brønsted acid sites close to the metal surface. The low benzene conversion for Pt/Na-MOR (Table 2) is explained by the low concentration of Brønsted acid sites, while the low benzene hydrogenation activity on Pt/H-MOR resulted from the higher deactivation by coke formation and from the higher metal sulfur poisoning, which strongly affects the acidic route.

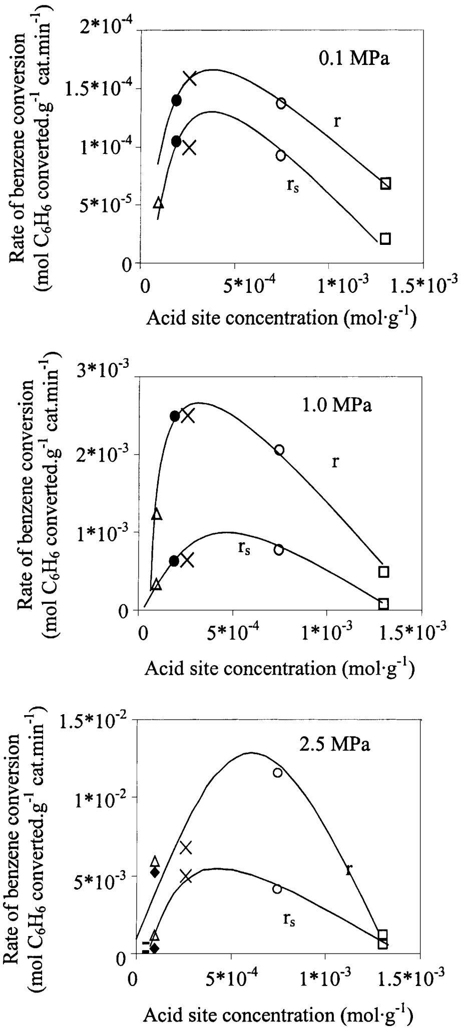

Fig. 4. Effects of acid site concentration on the activity of Pt/XH-MOR ((○) X = Li^+, (×) Na^+, (Δ) K^+, (●) Cs^+), Pt/X-MOR ((◆) X = Na^+, (▬) K^+) and Pt/H-MOR (□) on benzene hydrogenation in the absence (r) and the presence of 50 ppm thiophene (r_s) (623 K, WHSV = 53 h^{-1}).

3.3. Effects of the acid site concentration and hydrogen partial pressure

The effects of acid site concentration and hydrogen partial pressure on the catalyst activity for benzene hydrogenation are illustrated in Fig. 4. Partially alkali exchanged catalysts were more active and sulfur resistant than more acidic and more basic ones. In

Table 3
Ratios between benzene hydrogenation rates in the absence of thiophene (r) and the presence of 50 ppm thiophene (r_s) after 1 h TOS at 0.1, 1 and 2.5 MPa (623 K and WHSV = 53 h^{-1})[a].

	0.1 MPa	1 MPa	2.5 MPa
Pt/H-MOR	3.3	6.5	2.2
Pt/LiH-MOR	1.5	2.7	2.8
Pt/NaH-MOR	1.6	3.9	1.4
Pt/CsH-MOR	1.3	3.9	ND
Pt/KH-MOR	1.7	3.7	5.1
Pt/Na-MOR	ND	ND	17.0
Pt/K-MOR	ND	ND	12.0
Pt/NH$_4$-MOR	ND	ND	24.3

[a] ND: not determined.

the absence of thiophene the increase in pressure to 1 and 2.5 MPa increased the benzene hydrogenation rate, which is explained by a higher surface concentration of reactant molecules on the catalyst. However, in the presence of thiophene, the increase of the total pressure to 1 MPa also increases the thiophene concentration on the metal surface and, thus, the metal sulfur poisoning. Consequently, sites for benzene hydrogenation and for hydrogen decomposition on the metal surface were affected. Due to the smaller metal surface necessary for the adsorption/dissociation of hydrogen compared to benzene and to the changes in electron properties of the metal, one can expect that hydrogen decomposition on the metal was less affected by the presence of sulfur than benzene adsorption. Consequently, the presence of thiophene at 1 MPa strongly reduced the activity on the metal, i.e. increasing the r_s/r ratio (Table 3), while the activity on Brønsted acid sites remained constant (Fig. 4).

The increase of hydrogen partial pressure from 1 to 2.5 MPa increased the hydrogen concentration on the metal surface, which decreased the direct sulfur poisoning and increased the hydrogen dissociation on the metal surface. This led to an increase of the benzene hydrogenation rate via both routes. In the presence of thiophene at 2.5 MPa the high hydrogen partial pressure decreased the Pt sulfur poisoning and increased the concentration of hydrogen available for benzene hydrogenation on the metal and the Brønsted acid sites, resulting in a low r_s/r ratio (Table 3), i.e. a low deactivation by sulfur.

The higher r_s/r ratios (Table 3), i.e. the higher deactivation, observed for Pt/H-MOR compared to Pt/XH-MOR can be attributed to the effect of the enhanced coke formation as shown in Table 4. The coke formed led to the combined effects of a direct blocking of Brønsted acid sites, decreasing the concentration of Brønsted acid sites in relation with metal sites and to a pore blocking as already described in [28]. The higher formation of H_2S by thiophene decomposition on Brønsted acid sites increases the probability of metal sulfur poisoning.

Table 4
Carbon and sulfur content of the catalysts after 2 h benzene hydrogenation in the presence of 50 ppm thiophene (2.5 MPa, 623 K and WHSV = 53 h^{-1})

Catalyst	523 K		573 K		623 K	
	C	S	C	S	C	S
Pt/H-MOR	1.30	0.02	1.27	0.01	1.24	0.01
Pt/NaH-MOR	0.11	0.01	0.12	<0.01	0.20	0.01
Pt/Na-MOR	0.02	0.00	0.02	0.00	0.04	0.00

3.4. Improving the sulfur tolerance of aromatic hydrogenation on Brønsted acid sites

The two routes proposed for benzene hydrogenation on Pt supported MOR suggest a new way to improve the sulfur tolerance of noble metals for aromatic hydrogenation. A model of the overall activity with increasing acid site concentration for the two routes of benzene hydrogenation is shown in Fig. 5. To achieve an optimum for benzene hydrogenation and sulfur tolerance of Pt supported on zeolite-based catalysts, a subtle balance between the Brønsted acid site concentration and the metal availability is necessary. For the metal only catalyzed reaction route, the type of alkali cations present in the zeolite is supposed to influence the Pt electronic properties and, thus, the metal catalytic activity, while for the acid catalyzed pathway the type of counter ion should have little of effect on the activity. Therefore, in the presence of sulfur where the catalytic activity on the metal surface is blocked the type of alkali cation does not play an important role in the catalytic activity of the catalysts. The presence of thiophene mainly affects the activity of the metal surface, but also play a role of coke precursor on Brønsted acid sites. Thiophene molecules decompose on the Brønsted acid sites to form H_2S and coke precursors, possibly via the reverse Paal–Knorr

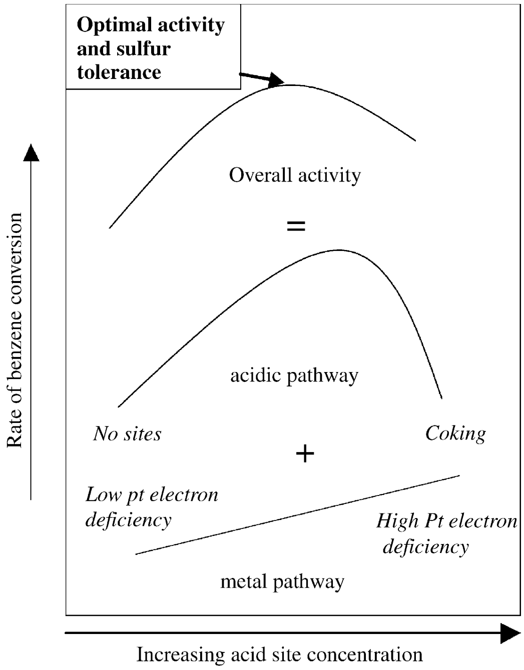

Fig. 5. Model for benzene hydrogenation and sulfur tolerance.

reaction [29]. The high affinity of sulfur for metal indicates that benzene molecules are mainly hydrogenated on Brønsted acid sites in the presence of thiophene.

4. Conclusions

Benzene hydrogenation on Pt supported MOR proceeds via two routes, i.e. hydrogenation (i) on the metal surface and (ii) on the acid sites in the vicinity of Pt particles with hydrogen dissociated on the metal. The latter reaction pathway depends on the concentration of Brønsted acid sites of the zeolite and on the metal and acid site vicinity. An optimal acid site concentration of $4 \times 10^{-4}\,\mathrm{mmol\,g^{-1}}$ for Pt/MOR is required to achieve an optimal benzene hydrogenation activity and sulfur tolerance of the catalysts. In the presence of thiophene, a high benzene hydrogenation activity on Brønsted acid sites is maintained, while the activity on the metal sites is strongly reduced. Therefore, the type of alkali cation used did not have a significant influence on the benzene hydrogenation activity of Pt supported on MOR in the presence of thiophene. The increase of the hydrogen partial pressure to 2.5 MPa increases the sulfur tolerance of the catalysts by decreasing the sulfur poisoning of the metal surface and by increasing the hydrogenation of benzene via both routes.

The model proposed here, i.e. to increase the sulfur tolerance of Pt by adjusting the Brønsted acid site concentration of the support to an optimum value, while increasing the hydrogen partial pressure to increase the rate of hydrogen dissociation, can be applied to a wide variety of macroporous and microporous supports that are more active for aromatic hydrogenation and, thus, has the potential to lead to a highly active and sulfur resistant catalyst.

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