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Sulfur-Tolerant Pt-Supported Zeolite Catalysts for Benzene Hydrogenation

I. Influence of the Support

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Benzene hydrogenation was investigated over a series of Pt-supported MOR and LTL zeolites in the presence of varying thiophene concentrations. Higher activity and a higher sulfur resistance were observed for Pt supported on partially alkali-exchanged zeolites compared to completely alkali-exchanged and purely acidic zeolites. This is attributed to the contribution of catalytically active sites on the metal and on Brønsted acid sites in the vicinity or at the perimeter of the metal particles. Increasing temperature and hydrogen partial pressure increased the sulfur tolerance of the catalysts. Although the deactivation of Pt by thiophene during benzene hydrogenation was higher for Pt/KH-LTL compared to Pt/NaH-MOR, the higher overall hydrogenation activity for benzene in the presence of thiophene was observed for Pt/KH-LTL. This is attributed to the high Pt dispersion and the closer vicinity of Pt and Si(OH)Al groups in LTL. As a consequence, the benzene hydrogenation route on Brønsted acid sites with spillover of hydrogen from Pt is more effective on Pt/KH-LTL than on Pt/NaH-MOR. © 2001 Academic Press

Key Words: **sulfur tolerance; high pressure; benzene hydrogenation; LTL; acid sites; noble metal.**

INTRODUCTION

Pt supported on LTL has been shown to be highly active for hydrogenation and dehydrogenation reactions (1–3). However, the major drawback for its industrial implementation is its high sensitivity toward sulfur-containing feeds. For dehydrocyclization of *n*-heptane to benzene, Pt supported on basic supports such as K^+- and Ca^{2+}-exchanged zeolite LTL was reported to be extremely sensitive to sulfur and may be poisoned by the presence of a few ppm of sulfur in the feed (4). Pronounced sintering and migration of metal particles outside of the zeolite pores in the presence of nucleophilic sulfur compounds were identified as the main causes of catalyst poisoning. The anchoring of Pt in LTL using Ni has been shown to increase activity and stability in the presence of sulfur compared to conventional LTL-based catalysts (5, 6).

Nevertheless, most of the sulfur-tolerant noble metal catalysts reported are supported on acidic silica-alumina or zeolites (7). The positive effect of acidity on the sulfur tolerance has been explained primarily *via* influencing the electronic properties of the noble metal (8, 9). An increase of the Pt electron deficiency with increasing acid site concentration was related to the increase of activity and to the sulfur tolerance of the catalysts (10).

Benzene hydrogenation has generally been described as a monofunctional reaction on metal surfaces (11–13). The noted influence of the support acidity upon the hydrogenation of benzene was attributed to the presence of Brønsted acid sites influencing the electronic properties of the metal (14). Alternative models have also been presented to explain the higher activity of Pt on acidic supports involving hydrogenation sites at the interface between the Pt and the support (15–19).

In order to explore these concepts and their potential impact on designing robust aromatic hydrogenation catalysts, benzene hydrogenation over Pt/LTL was studied in the absence and the presence of thiophene and compared to the activity and sulfur tolerance of Pt/MOR-based catalysts.

EXPERIMENTAL

Preparation

Pt supported on K-LTL (LTL, TOSOH, Si/Al = 6, Ref. HSZ500KOA, Lot 1041) and Na-MOR (TOSOH, Si/Al = 9.3, Ref. HSZ-641NAA, lot T960402) were prepared by liquid-phase ion exchange at room temperature using platinum tetraaminehydroxide ($Pt(NH_3)_4(OH)_2 \cdot H_2O$, 59% Pt, STREM) as precursor (20). The volume of the precursor solution required to obtain a platinum loading of 1 wt% Pt was

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added dropwise at a rate of 12 ml min^{-1} to the zeolite suspended in deionized water. The suspension containing the zeolite and the precursor was stirred overnight. The sample was filtered, washed with deionized water, dried 1 day in air at room temperature, calcined in a flow of air of 40 ml min^{-1} per gram catalyst at 493 K for 2 h (heating rate of 0.5 K min^{-1}), and finally reduced with H_2 in a flow of 35 ml min^{-1} per gram catalyst at 623 K for 1 h (heating rate 0.5 K min^{-1}).

To obtain fully alkali-exchanged Pt-loaded zeolites, parent Pt/NaH-MOR and Pt/KH-LTL samples were ion-exchanged at 323 K with a solution of 0.033 M of $NaNO_3$ and KNO_3, respectively. After filtering, the catalysts were washed with deionized water and dried in air.

Prior to Pt ion exchange, H-MOR was prepared by ion exchanging 20 g of Na-MOR with 300 ml of a 0.1 M solution of NH_4NO_3 (Merck) at room temperature. The procedure was repeated three times. After each step, the zeolite was filtered and washed with 50 ml of deionized water. Subsequently, the material was calcined in dry air with a flow of 100 ml min^{-1} per gram zeolite at 723 K for 3 h (heating rate of 5 K min^{-1}).

Characterization

Chemical compositions of the catalysts were determined by X-ray fluorescence spectroscopy (21).

The concentration of strong acid sites was measured by NH_3 temperature-programmed desorption (TPD). For this experiment, 90 mg of the sample was evacuated at 623 K for 1 h (heating rate of 10 K min^{-1}). After cooling to room temperature ammonia was adsorbed for 1 h with a partial pressure of 10 mbar. 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 mass spectrometer was used to detect the desorbing molecules.

The concentration of accessible Pt atoms was determined by volumetric hydrogen chemisorption. After reduction of the catalyst in a hydrogen flow of 50 ml min^{-1} for 1 h at 623 K, the system was evacuated ($p < 1.10^{-5}$ mbar) at the reduction temperature for 1 h. After cooling the sample to room temperature, 500 mbar of hydrogen was adsorbed and allowed to equilibrate with the catalyst overnight. The sorption isotherm was obtained by lowering the hydrogen pressure in equilibrating time steps of 1 h per point.

HRTEM pictures were obtained using a Phillips CM30 T electron microscope with a LaB6 filament as the source of electrons operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at room temperature.

EXAFS spectra were obtained on beamline B-2 at CHESS (Ithaca, NY) and beamline X1 at HASYLAB, DESY (Hamburg, Germany). The Si (111) double crystal monochromator (CHESS) and the Si (311) double crystal monochromator (DESY) were detuned to 60% of the maximum intensity to minimize the presence of higher harmonics in the X-ray beam. The weight of the sample was chosen to obtain a total absorption of 2.5. The samples were reduced *in situ* at 623 K for 1 h prior to benzene hydrogenation in the absence and the presence of thiophene (623 K, 1 bar, $H_2/C_6H_6 = 34.2$). Data were collected at the Pt L_{III} edge (11564 eV) and analyzed with the WINXAS97 software (22).

Benzene Hydrogenation Measurements

Benzene hydrogenation in the absence and presence of thiophene was performed using two parallel fixed-bed reactors. One reactor was used for reactions in the absence of thiophene and the other in the presence of thiophene. For each temperature and pressure, between 25 and 90 mg of the catalyst (particle diameters between 0.3 and 0.6 mm) mixed with quartz was reduced *in situ* in a hydrogen flow of 200 ml min^{-1} at 673 K for 1 h. A solution of benzene and thiophene (Aldrich) was mixed with a hydrogen flow using a high-pressure syringe pump (ISCO) and injected into the gas stream. The reaction products were analyzed using an on-line gas chromatograph with a FID detector and a DB-1 column.

RESULTS

Characterization of the Catalysts

Results of the chemical and physicochemical characterization of the catalysts are summarized in Table 1. The acid site concentration decreased with increasing alkali content for both zeolites. Due to the lower Si/Al ratio of LTL compared to Na-MOR, i.e., 6 and 9.3, respectively, Pt/KH-LTL and Pt/NaH-MOR had a similar acid site concentration. The theoretically expected acid site concentration is in good agreement with the values obtained from NH_3 TPD. The Pt dispersion was higher for Pt supported on LTL compared to MOR, i.e., 80 and 55%, respectively, which is in agreement with previous reported studies (23).

HRTEM pictures of reduced Pt/NaH-MOR and after 2 h of benzene hydrogenation in the absence and the presence of 50 ppm thiophene are shown in Fig. 1. From the particle size distribution between 0.5 and 2.5 nm, an average particle size of 2 nm was determined. HRTEM of the catalyst investigated during tilting of the sample holder under the electron beam showed that Pt particles were mainly located inside the zeolite pores and only a small fraction was present on the surface of the zeolite crystals. Changes in Pt particle size were not detected after 2 h of benzene hydrogenation in the absence and presence of 50 ppm thiophene. Also for Pt/H-MOR a significant increase in Pt particle size

TABLE 1

Chemical and Physicochemical Characterizations of the Catalysts

	Formula[a]	Acid site concentration (mol g^{-1})		Pt loading (wt%)	H/Pt
		Theoretical	Measured		
Pt/H-MOR	$Na_{0.11}H_{4.64}\,[Al_{4.75}Si_{43.25}\,O_{96}] \cdot 24\,H_2O$	1.6×10^{-3}	1.3×10^{-3}	1.1	0.56
Pt/NaH-MOR	$Na_{3.35}H_{1.41}\,[Al_{4.75}Si_{43.25}O_{96}] \cdot 24\,H_2O$	4.7×10^{-4}	2.6×10^{-4}	1.1	0.59
Pt/Na-MOR	$Na_{4.71}H_{0.09}\,[Al_{4.80}Si_{43.20}O_{96}] \cdot 24\,H_2O$	2.9×10^{-5}	1.1×10^{-5}	0.9	0.53
Pt/KH-LTL	$K_{4.42}H_{0.79}\,[Al_{5.22}Si_{30.78}O_{72}] \cdot 21\,H_2O$	3.0×10^{-4}	4.4×10^{-4}	1.1	0.80
Pt/K-LTL	$K_{5.12}H_{0.17}\,[Al_{5.29}Si_{30.71}O_{72}] \cdot 21\,H_2O$	6.6×10^{-5}	9.3×10^{-5}	1.1	0.86

[a] Calculation based on AAS.

after benzene hydrogenation in the absence and presence of 50 ppm thiophene was not observed.

XAFS spectra were taken before and after 1 h of benzene hydrogenation in the absence and presence of 50 ppm thiophene on all catalysts. Pt–Pt coordination numbers and interatomic distances calculated from the EXAFS analysis are compiled in Table 2. Significant changes in the Pt–Pt coordination numbers after 1 h of reaction were not observed for all alkali-exchanged catalysts. In contrast, an increase of the Pt–Pt coordination number after 1 h of benzene hydrogenation in the presence of thiophene was observed for Pt/H-MOR. From Pt–Pt coordination numbers between 8 and 10, particles containing between 60 to 1000 atoms were estimated indicating an average particle sizes between 1.5 and 4 nm. For fresh Pt-supported MOR, coordination numbers for Pt–Pt around 9 were observed, indicating Pt particles of 2 nm, which contain 150 atoms were observed (24). For Pt supported on LTL Pt–Pt coordination numbers were lower than those for MOR, which is in accordance with earlier observations (23).

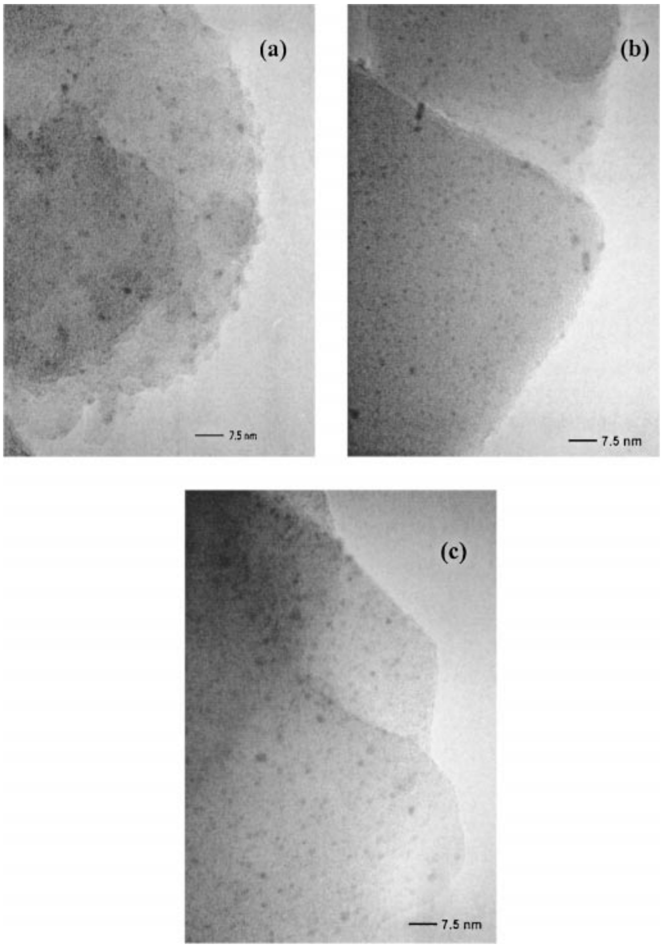

FIG. 1. HREM pictures of Pt/NaH-MOR (a) reduced, (b) after 2 h of benzene hydrogenation, (c) after 2 h of benzene hydrogenation in the presence of 50 ppm thiophene (623 K, 25 bar, WHSV = 53 h^{-1}).

Benzene Conversion and Catalyst Stability

The activity for benzene conversion in the presence and absence of thiophene is shown in Fig. 2 for Pt/KH-LTL,

TABLE 2

Results of the EXAFS Analysis of the Reduced Catalysts, after 1 h of Benzene Hydrogenation and after 1 h of Benzene Hydrogenation in the Presence of 50 ppm Thiophene (623 K, 1 bar, $H_2/C_6H_6 = 34.2$)

Catalyst	Status	$N_{Pt–Pt}$	$r_{Pt–Pt}$(Å)	$\Delta\sigma^2_{Pt–Pt} \times 10^{-3}$(Å^2)
Pt/H-MOR	H_2	9.3	2.77	1.3
	$H_2 + C_6H_6$	9.1	2.76	3.1
	$H_2 + C_6H_6 + C_4H_4S$	10.7	2.76	2.3
Pt/NaH-MOR	H_2	9.0	2.75	4.0
	$H_2 + C_6H_6$	10.5	2.75	4.4
	$H_2 + C_6H_6 + C_4H_4S$	10.7	2.75	4.6
Pt/Na-MOR	H_2	8.8	2.74	3.5
	$H_2 + C_6H_6$	8.1	2.73	3.6
	$H_2 + C_6\ H_6 + C_4H_4S$	8.1	2.73	5.9
Pt/KH-LTL	H_2	5.8	2.79	7.6
	$H_2 + C_6H_6$	7.8	2.77	1.2
	$H_2 + C_6H_6 + C_4H_4S$	7.0	2.79	3.5
Pt/K-LTL	H_2	7.2	2.76	4.4
	$H_2 + C_6H_6$	6.6	2.74	6.0
	$H_2 + C_6\ H_6 + C_4H_4S$	5.3	2.76	4.4

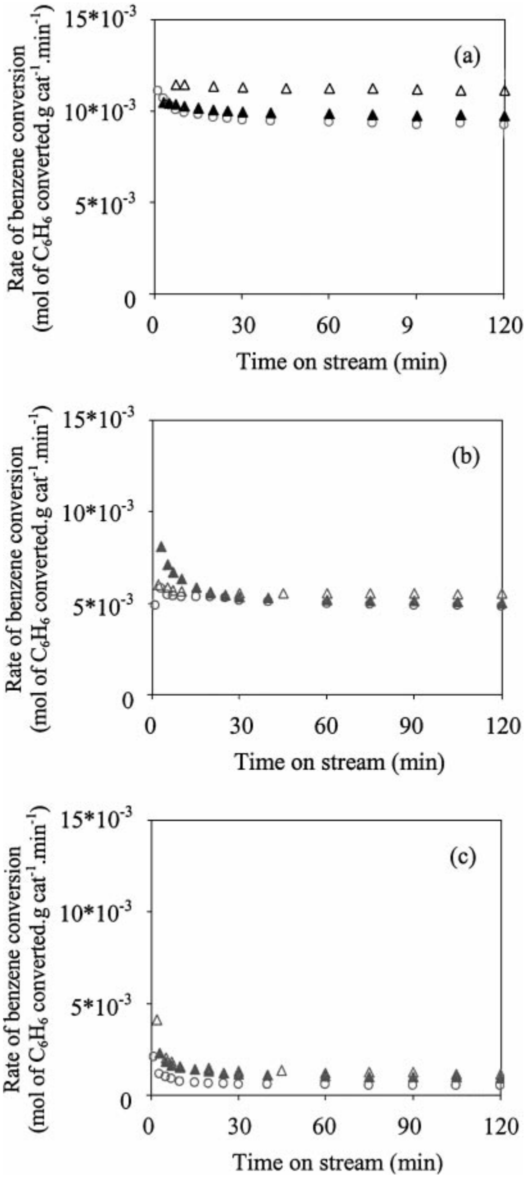

FIG. 2. Rates of benzene hydrogenation versus time on stream for (a) Pt/KH-LTL, (b) Pt/NaH-MOR, and (c) Pt/H-MOR in the absence (△) and the presence of 3.5 (▲) and 50 ppm (○) thiophene (25 bar, $H_2/C_6H_6 = 20.3$).

Pt/NaH-MOR, and Pt/H-MOR at 25 bar. For all catalysts a stable-state activity was observed after 30 min of time on stream. The presence of increasing thiophene concentrations decreased, in general, the benzene hydrogenation rates but stable rates were still observed after 30 min of time on stream. After an initial deactivation during the first 30 min of time on stream, changes in benzene hydrogenation rates in the presence of 50 ppm thiophene for Pt/NaH-MOR were not observed during 3 days TOS (not shown here). Pt supported on partially exchanged zeolite catalysts showed higher benzene conversion rates than the more acidic catalyst. Rates and TOF changed similarly upon changing the pressure from 1 to 25 bar as shown in Fig. 3. Increasing the pressure increased the rate of benzene conversion and the TOF for all catalysts.

Impact of Supports on Benzene Conversion

Selectivities and rates of benzene hydrogenation at 25 bar after 1 h time on stream are reported in Table 3. The rate of benzene hydrogenation for Pt/KH-LTL was higher

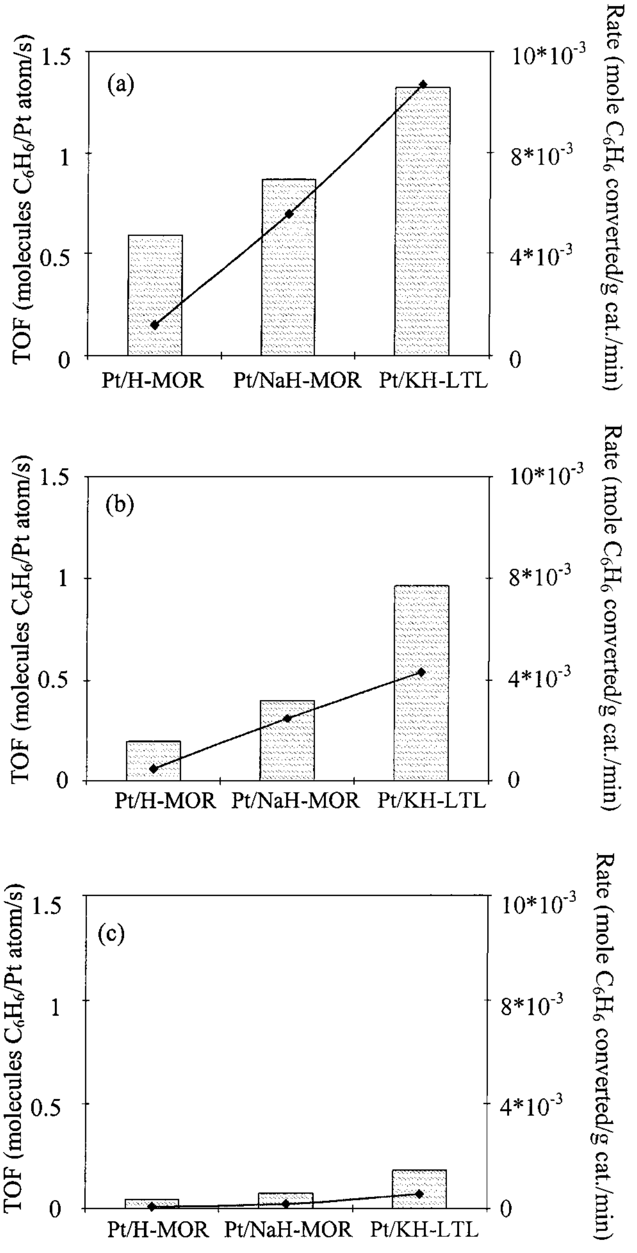

FIG. 3. Rates (—◆—) and TOF (▭) of Pt/H-MOR, Pt/NaH-MOR, and Pt/K-LTL after 1 h of benzene conversion at (a) 25 bar, (b) 10 bar, and (c) 1 bar (623 K).

TABLE 3

Effect of the Support on the Kinetic Behavior for Benzene Hydrogenation in the Absence and Presence of 50 ppm Thiophene (623 K, 25 bar, $H_2/C_6H_2 = 20.3$)

Samples	Status	Selectivities (%)				
		Cracking	Methylcyclopentane	Cyclohexane	Rate[a]	r/r_s[b]
Pt/H-MOR	No thiophene	10.6	52.5	36.9	1.2×10^{-3}	
	50 ppm thiophene	16.0	48.5	33.5	5.5×10^{-4}	2.2
Pt/NaH-MOR	No thiophene	0.2	11.6	87.9	5.6×10^{-3}	
	50 ppm thiophene	0.3	29.3	70.3	5.0×10^{-3}	1.1
Pt/Na-MOR	No thiophene	0.0	5.2	94.8	6.2×10^{-3}	
	50 ppm thiophene	0.1	19.1	80.5	3.1×10^{-4}	20.3
Pt/KH-LTL	No thiophene	5.1	14.5	80.5	1.0×10^{-2}	
	50 ppm thiophene	10.3	17.3	72.3	8.9×10^{-3}	1.2
Pt/K-LTL	No thiophene	2.6	1.3	96.0	3.7×10^{-3}	
	50 ppm thiophene	3.0	2.5	94.4	2.2×10^{-4}	17.3

[a] moles of benzene converted per gram catalysts per min.

[b] Ratio between the rates of benzene hydrogenation in the absence (r) and the presence (r_s) of 50 ppm thiophene.

compared to all other catalysts. In the presence of 50 ppm thiophene a decrease of activity was observed for all catalysts. The ratio between the rates of benzene hydrogenation in the absence and presence of 50 ppm thiophene (r/r_s) was the highest for the completely ion-exchanged samples, i.e., Pt/Na-MOR and Pt/K-LTL, with r/r_s of 20.3 and 17.3, respectively. For Pt/H-MOR a lower r/r_s of 2.2, and for Pt/NaH-MOR and Pt/KH-LTL the lowest r/r_s of 1.1 and 1.2, respectively, were observed. These results indicate that the activity of Pt supported on partially exchanged zeolites decreased to a lower extent in the presence of thiophene compared to fully ion-exchanged catalyst-based zeolites.

The selectivity to cyclohexane decreased with increasing acid site concentration. The formation of cracking products was, however, only observed with Pt/H-MOR and Pt/LTL catalysts. The presence of thiophene increased the selectivity to methylcyclopentane and the cracking products for all catalysts.

Temperature Effect on Benzene Conversion

The effects of temperature on benzene hydrogenation in the presence of 50 ppm thiophene are compiled in Fig. 4. For all catalysts an increase of the benzene hydrogenation rates with increasing temperature was observed. This highest benzene hydrogenation rates in the presence of thiophene were observed for the partially alkali-exchanged samples, namely Pt/KH-LTL and Pt/NaH-MOR, which indicates a higher activity and sulfur resistance during benzene hydrogenation for these catalysts with increasing temperature.

Similar selectivities were observed for Pt/Na-MOR and Pt/K-LTL, and for Pt/NaH-MOR and Pt/KH-LTL as shown in Fig. 5. The selectivity to cyclohexane formation increased with increasing alkali content of the zeolite. The increase of methylcyclopentane selectivity observed with increasing temperature was higher for more acidic samples (see Fig. 5). For Pt/H-MOR the decrease of methylcyclopentane selectivity and the lower decrease in cyclohexane selectivity at

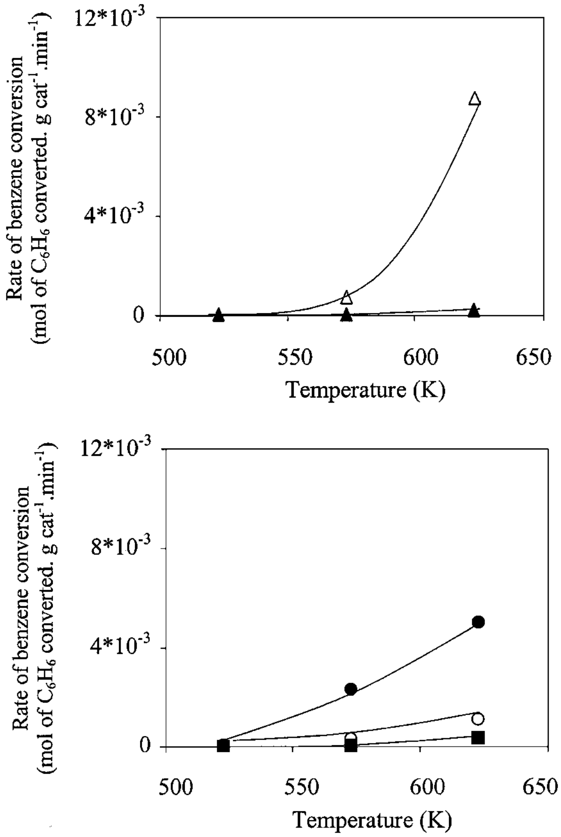

FIG. 4. Effect of temperature on the rate of benzene conversion after 1 h TOS in the presence of 50 ppm thiophene (25 bar, $H_2/C_6H_6 = 20.3$) for (▲) Pt/K-LTL, (△) Pt/KH-LTL, (■) Pt/Na-MOR, (●) Pt/NaH-MOR, and (○) Pt/H-MOR.

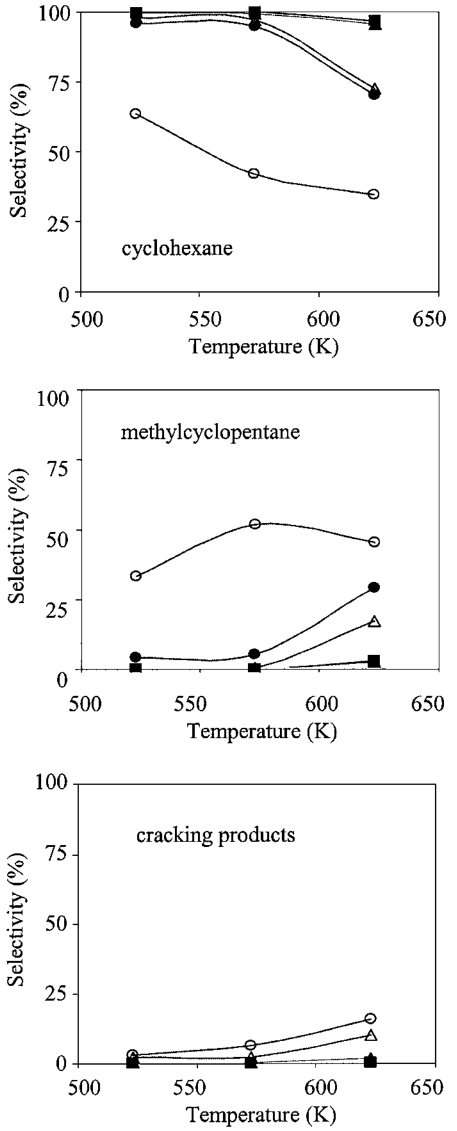

FIG. 5. Selectivities to cyclohexane, methylcyclopentane, and cracking products after 1 h of benzene hydrogenation in the presence of 50 ppm thiophene (25 bar, $H_2/C_6H_6 = 20.3$) for (▲) Pt/K-LTL, (△) Pt/KH-LTL, (■) Pt/Na-MOR, (●) Pt/NaH-MOR, and (○) Pt/H-MOR.

625 K were due to the increase of the cracking products formed.

Influence of Pressure on Benzene Conversion

The effects of pressure and sulfur poisoning for Pt/H-MOR, Pt/NaH-MOR, and Pt/KH-LTL are shown in Table 4. The rate of benzene hydrogenation increased with increasing the pressure to 10 bar (keeping the H_2/C_6H_6 ratio at 7.6) and to 25 bar by increasing the partial pressure of hydrogen (increasing the H_2/C_6H_6 ratio to 20.3). The rate of benzene hydrogenation decreased with increasing thiophene concentration. At 1 bar, higher $r/r_{\rm s}$ ratios were observed for Pt/H-MOR and Pt/KH-LTL compared to Pt/NaH-MOR, which indicates a lower deactivation of the latter. The $r/r_{\rm s}$ ratios were similar at 1 and 10 bar for Pt/KH-LTL, indicating a similar deactivation of this catalyst at both pressures. In general, $r/r_{\rm s}$ ratios decreased with increasing the hydrogen partial pressure to 25 bar for all catalysts. This increase of $r/r_{\rm s}$ ratios was higher for Pt/H-MOR than for Pt/NaH-MOR and Pt/KH-LTL.

At 1 bar the cyclohexane selectivity increased with increasing alkali content of the zeolite as shown in Fig. 6. The increase of the pressure to 10 bar increased the selectivity to cyclohexane for more basic supports, while it decreased for Pt/H-MOR. A very low concentration of cracking products was observed for Pt/NaH-MOR and Pt/KH-LTL at all pressures. The formation of cracking products decreased with increasing pressure for Pt/H-MOR.

In the absence and presence of thiophene at 1 bar total pressure cyclohexane selectivities did not change significantly for Pt/H-MOR and Pt/KH-LTL (Figs. 6 and 7). The increase of the pressure to 10 bar increased the cyclohexane selectivity in the presence of thiophene for more basic catalysts and decreased it for Pt/H-MOR. The cyclohexane selectivity decreased with increasing pressure to 25 bar for all catalysts. However, a decrease of the methylcyclopentane selectivity was observed for Pt/KH-LTL due to a higher formation of cracking products, while an increase was observed for Pt/H-MOR and Pt/NaH-MOR.

DISCUSSION

Pt Particle Size

A particle size of 2 nm for the fresh Pt/MOR catalysts was observed by HRTEM (Fig. 1), hydrogen chemisorption with H_2/Pt ratio between 0.5 and 0.6 (Table 1), and EXAFS analysis with Pt–Pt coordination numbers around 9 (Table 2) as already reported (24). The higher metal dispersion of Pt supported on LTL compared to Pt supported on MOR is attributed to the stabilization of small Pt particles by K^+ in the LTL lattice (20). After 1 h of benzene hydrogenation in the presence of 50 ppm thiophene significant changes in Pt–Pt coordination numbers were not observed by EXAFS for the more basic catalysts, while an increase was observed for Pt/H-MOR. This suggests a more severe effect of the presence of sulfur-containing compounds for Pt/H-MOR than for Pt supported on more basic supports, which results in sintering and growth of Pt particles. Note, however, that the change in the average particle sizes observed by EXAFS analysis for Pt/H-MOR could not be detected by HRTEM.

Benzene Hydrogenation

In a previous study (25), we showed that on Pt/MOR benzene hydrogenation occurs *via* two pathways (i) on the metal and (ii) on the acid sites close to the metal particles implying a spillover of hydrogen from the Pt surface or at

TABLE 4

Rate of Benzene Conversion at 1 ($H_2/C_6H_2 = 7.6$), 10 ($H_2/C_6H_6 = 7.6$), and 25 bar ($H_2/C_6H_6 = 20.3$) after 1 h of Benzene Hydrogenation in the Absence and Presence of 3.5 and 50 ppm Thiophene at 623 K

Catalysts	Thiophene in the feed (ppm)	1 bar		10 bar		25 bar	
		Rate[a]	r/r_s[b]	Rate[a]	r/r_s[b]	Rate[a]	r/r_s[b]
Pt/H-MOR	0	6.8×10^{-5}		4.9×10^{-4}		1.2×10^{-3}	
	3.5	—		3.4×10^{-4}	1.4	1.0×10^{-3}	1.2
	50	2.0×10^{-5}	3.3	7.5×10^{-5}	6.5	5.5×10^{-4}	2.2
Pt/NaH-MOR	0	1.6×10^{-4}		2.5×10^{-3}		5.6×10^{-3}	
	3.5	—		2.4×10^{-3}	1.1	5.2×10^{-3}	1.1
	50	9.9×10^{-5}	1.6	6.5×10^{-4}	3.9	5.0×10^{-3}	1.1
Pt/KH-LTL	0	5.4×10^{-4}		4.3×10^{-3}		1.0×10^{-2}	
	3.5	—		4.3×10^{-3}	1.0	9.7×10^{-3}	1.0
	50	1.6×10^{-4}	3.4	1.2×10^{-3}	3.5	8.9×10^{-3}	1.2

[a] Moles of benzene converted per gram catalysts per min.

[b] Ratio between the rates of benzene hydrogenation in the absence (r) and the presence (r_s) of 50 ppm thiophene.

the metal-support boundary (see Fig. 8). The highest benzene hydrogenation rates and sulfur tolerance during the conversion of benzene were observed for Pt/NaH-MOR, which indicates that the optimum balance between acidic and metallic sites was present on this catalyst (25). The deactivation of Pt supported on H-MOR was due to a higher thiophene decomposition rate on Brønsted acid sites, which resulted in (i) a higher coke formation decreasing the benzene hydrogenation rate on the acid sites and (ii) on a higher H_2S formation increasing the poisoning of the metal. For Pt supported on Na-MOR the low rate of benzene hydrogenation was explained by the absence of the acidic pathway for benzene hydrogenation (25). Consequently, the low rate of benzene hydrogenation observed for Pt/K-LTL (see Table 3 and Fig. 4) is also attributed to the absence of the acidic pathway for benzene hydrogenation, which lowers the overall rate of benzene hydrogenation.

The high activity observed for Pt/KH-LTL can be explained by two factors: (i) the high Pt dispersion increases the metal surface available for benzene conversion and the hydrogen dissociation on the metal, which increases hydrogen spillover; and (ii) the lower Si/Al ratio of LTL compared to MOR increases the Brønsted acid site concentration of the former. Both factors enhance the probability for acid sites to be in the vicinity of the metal surface and, thus, to participate to the conversion of benzene. Furthermore, for MOR two of the five available sites for ion exchange (site I and I′) are located in the 8-member ring channels of MOR (26), which has been shown not to be accessible for benzene and cyclohexane (27, 28). For LTL, four positions of cations have been reported (29). Three of the sites are outside of the main channels of LTL, which have been shown to be very difficult to be ion-exchanged and, thus, we speculate that the negative charges of the lattices are balanced by K^+ after ion-exchange treatment. The fourth one, easily exchangeable, is located in the middle of the main channel. Therefore, the acid site concentration determined by ammonia TPD (see Table 1) included acid sites located in the 8- and 12-member ring channels for MOR, while it included only those in the main channels for LTL. Thus, more acid sites are available in the main channels of Pt/KH-LTL to participate in the reaction compared to Pt/NaH-MOR. Consequently, the vicinity of the two types of sites, i.e., metal sites and acid sites, increases the rate of benzene hydrogenation for Pt supported on partially alkali-exchanged LTL.

In the absence of thiophene (Fig. 6), the selectivities for both Pt supported on partially alkali-exchanged zeolites were changing similarly. The higher methylcyclopentane selectivity for Pt/KH-LTL can be explained by the higher concentration of acid sites available for benzene to react compared to MOR.

Sulfur Poisoning of Fully Alkali-Exchanged Catalysts

A decrease in benzene hydrogenation rates with increasing thiophene concentrations was observed. Pt supported on LTL and, in general, Pt supported on basic supports has been shown to be very sensitive to sulfur (30). The highly dispersed Pt particles in LTL are poisoned by the presence of less than 2 ppm thiophene, which induces a sintering and growth of the metal particles (4). The high r/r_s ratios observed at 25 bar confirm that for Pt supported on K-LTL and Na-MOR, which do not convert benzene *via* the acidic pathway due to the absence of Brønsted acid sites, the sulfur tolerance is very low. On these completely alkali-exchanged catalysts, temperature-programmed studies showed that a very low concentration of thiophene was decomposed on the catalysts surface (31). Therefore, the sulfur poisoning is mainly attributed to the adsorption and decomposition of thiophene on the metal sites, which results in a loss of metal surface available for the reaction to take place. On these two supports the conversion of benzene only occurs on the Pt surface and is, therefore, strongly affected by the adsorption of thiophene.

Sulfur Poisoning of Partially Alkali-Exchanged Catalysts

At 1 bar the significantly higher r/r_s ratios observed for Pt/H-MOR and Pt/KH-LTL suggest a stronger deactivation of those catalysts compared to Pt/NaH-MOR (Table 4). From the results discussed above, the activity remaining in the presence of thiophene is mainly attributed to benzene conversion on Brønsted acid sites with hydrogen spilt over from the Pt surface. Consequently at 1 bar, benzene conversion on Brønsted acid sites is very low. For Pt/H-MOR the substantial deactivation compared to Pt/NaH-MOR is attributed to a higher sulfur poisoning of the metal surface and a higher coke formation reducing the fraction of acid sites available for benzene hydrogenation (25). In contrast to the poisoning of the fully exchanged catalysts, temperature-programmed studies showed that the thiophene decomposition increases with increasing the acid site concentration, thus increasing the formation of H_2S and the coke precursor species on those catalysts (31). Therefore, the deactivation of those catalysts was caused by three different mechanisms, i.e., a metal sulfur poisoning by thiophene adsorption, a metal sulfur poisoning by H_2S

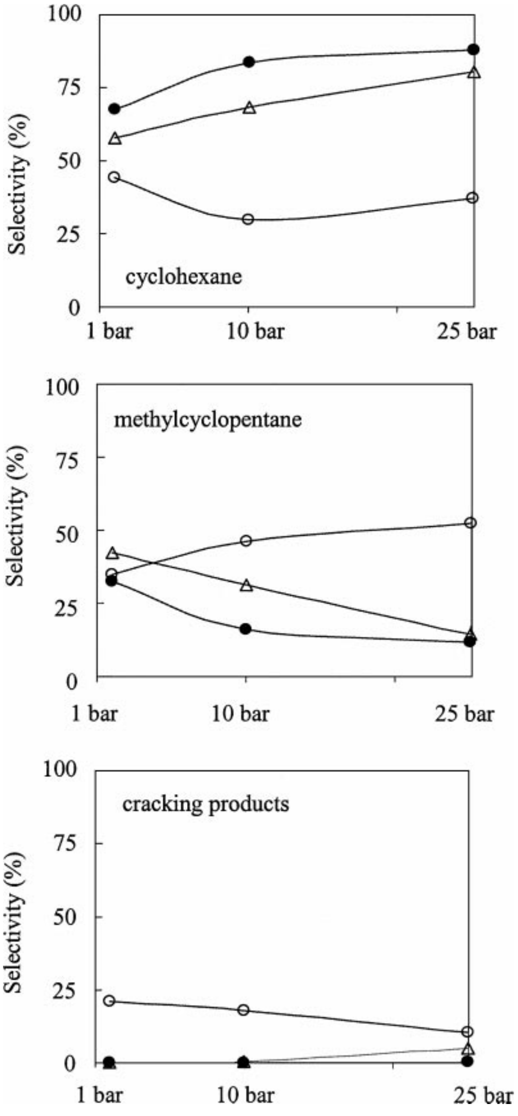

FIG. 6. Effect of the pressure on the selectivities to cyclohexane, methylcyclopentane, and cracking products after 1 h benzene hydrogenation in the absence of thiophene at 623 K for (△) Pt/KH-LTL, (●) Pt/NaH-MOR, and (○) Pt/H-MOR.

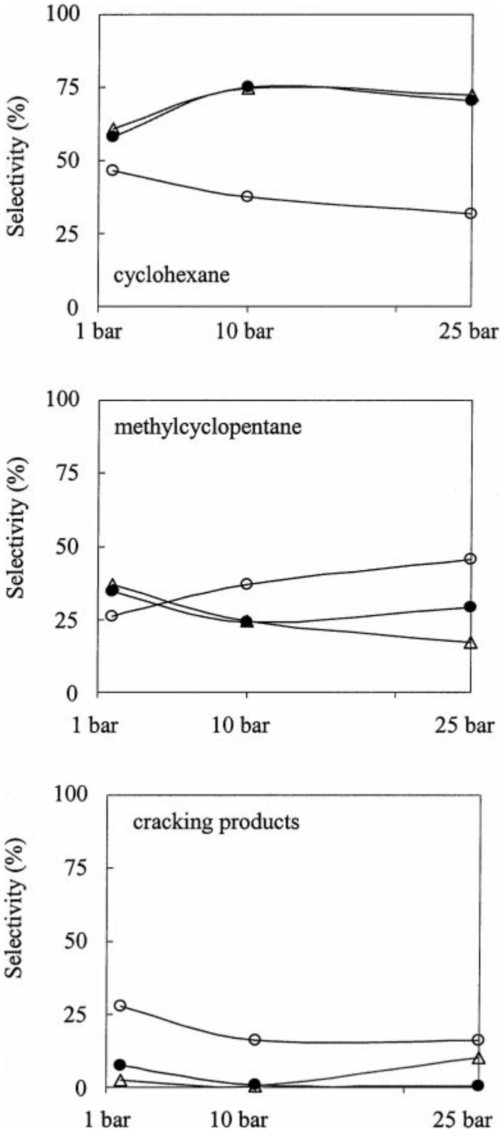

FIG. 7. Effect of the pressure on the selectivities to cyclohexane, methylcyclopentane, and cracking products after 1 h of benzene hydrogenation in the presence of 50 ppm thiophene at 623 K for (△) Pt/KH-LTL, (●) Pt/NaH-MOR, and (○) Pt/H-MOR.

adsorption, and an enhanced coke formation induced by the presence of the unsaturated hydrocarbon species, which were produced by decomposition of thiophene on the acid sites.

For Pt supported on MOR an increase of the r/r_s ratio was observed after increasing the pressure from 1 to 10 bar (keeping the ratio $H_2/C_6H_6/C_4H_4S$ constant). At 1 bar the Pt surface of both catalysts was not completely poisoned in the presence of 50 ppm thiophene (25). Consequently, the increase of the pressure increased the local concentration of thiophene on the support and on the metal surface, which resulted in a more pronounced metal sulfur poisoning and decomposition of thiophene on Brønsted acid sites. The poisoning of the metal surface is, thus, stronger for Pt supported on more acidic zeolites compared to more alkali-exchanged zeolites.

For Pt/KH-LTL the increase of the total pressure to 10 bar did not change the r/r_s ratio, which confirms that at 1 bar all the metal active sites for benzene hydrogenation were already blocked by sulfur. However, the remaining activity observed on this sample led us to conclude that the dissociation of hydrogen on the metal surface and the migration of hydrogen atoms to the Brønsted acid sites by spillover are still possible.

The increase of pressure to 25 bar (increasing the hydrogen partial pressure) decreased the r/r_s ratios, indicating a lower effect of sulfur poisoning. We speculate that the increase of the hydrogen partial pressure has two effects: (i) the decrease of the thiophene concentration on the metal surface and on the support reduces the H_2S formation by thiophene decomposition on Brønsted acid sites and, thus, decreases the poisoning of the metal surface, and (ii) the increase of hydrogen dissociation on the metal increasing the benzene hydrogenation rate on Brønsted acid sites. The faster dectivation observed for Pt/H-MOR is attributed to a higher rate of coke formation, which deactivates significantly the acidic pathway of benzene hydrogenation.

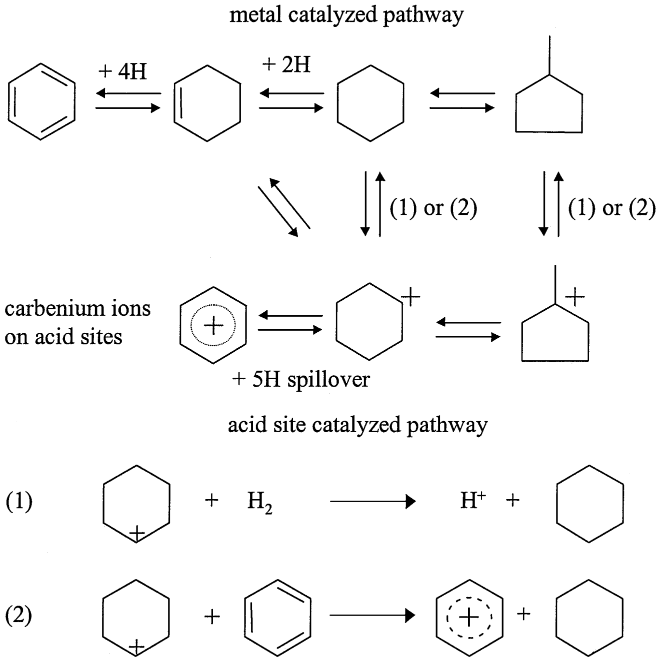

FIG. 8. Two routes of benzene hydrogenation over Pt-supported LTL and MOR.

Despite the fact that Pt supported on LTL zeolite has always been described to be very sensitive to sulfur, the high rate of benzene conversion in the presence of up to 50 ppm thiophene observed for Pt/KH-LTL (see Fig. 4 and Table 4) shows that Pt supported on partially alkali-exchanged LTL zeolite tolerates 50 ppm thiophene during benzene hydrogenation. This is attributed to the presence of two routes for benzene hydrogenation on Pt-supported zeolites as discussed above, i.e., one *via* hydrogenation on the metal surface and the other *via* hydrogenation of a carbenium ion sorbed on Brønsted acid sites in the vicinity of metal atoms by spillover of hydrogen (Fig. 8). Consequently, although the benzene conversion rate on the metal surface decreased due to blocking of Pt sites by sulfur, the benzene conversion remained high on Brønsted acid sites close to the metal surface.

CONCLUSIONS

The rate of benzene hydrogenation and the sulfur tolerance of Pt supported on partially exchanged LTL and MOR were higher compared to Pt supported on fully alkali ion-exchanged zeolites. Although the Pt sulfur poisoning was higher for Pt/KH-LTL, the remaining activity on Brønsted acid sites in the vicinity of the metal was higher for Pt supported on partially alkali-exchanged LTL zeolites compared to MOR. The higher activity of Pt/KH-LTL is attributed to smaller metal particles and the higher availability of protons in the main channels of LTL for benzene hydrogenation compared to MOR. Consequently, Pt/KH-LTL is active and stable for benzene hydrogenation in the presence of up to 50 ppm thiophene. The activity and sulfur tolerance of Pt supported on partially alkali-exchanged LTL and MOR were improved by increasing hydrogen partial pressure to 25 bar, which favors benzene hydrogenation *via* both reaction pathways.

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