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Influence of the surface acidity of ZSM-5 support on the catalytic activity of Rh/ZSM-5 for hydrodearomatization of toluene

Kalpesh B. Sidhpuria [a,b], Parimal A. Parikh [c], Pratap Bahadur [b], Beena Tyagi [a], Raksh Vir Jasra [d,*]

[a] Discipline of Inorganic Materials and Catalysis, Central Salt & Marine Chemicals Research Institute (CSMCRI), G.B. Marg, Bhavnagar 364002, Gujarat, India
[b] Department of Chemistry, Veer Narmad South Gujarat University, Surat 395007, Gujarat, India
[c] Chemical Engineering Department, Sardar Vallabhbhai National Institute of Technology, Surat 395007, Gujarat, India
[d] R & D Centre, Reliance Industries Limited, Vadodara Manufacturing Division, Vadodara, 391346, Gujarat, India

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ABSTRACT

Rh/ZSM-5 catalysts with varied SiO_2/Al_2O_3 ratio (24–900) were prepared and characterized by powder X-ray diffraction, N_2 adsorption–desorption, temperature-programmed desorption of NH_3 and cyclohexanol dehydration model reaction. The hydrodearomatization of toluene was studied at different reaction temperature, reduction temperature, hydrogen partial pressures and in the presence of dibenzothiophene (sulfur compound) in a continuous-down-flow catalytic fixed bed reactor. The hydrodearomatization activity and the sulfur tolerance were observed to be strongly dependent on the acidity of the zeolites particularly upon the proximity between metallic and Brønsted acid sites and the concentration of the Brønsted acid sites.

1. Introduction

Clean fuels research including desulfurization and dearomatization has become an important subject in environmental catalysis worldwide. The presence of aromatics imparts poor ignition quality and low cetane number to diesel, enhances smoke point of jet fuel and increase in emission of particulate matters. These particulate matters as well as aromatics emissions are environmental hazards and are known to be responsible for various health problems when inhaled. Therefore, stringent environmental regulations are being directed to lower these emissions from vehicle exhausts. Liquid fuels are essentially produced from petroleum except in South Africa where a coal-based gasification system produces the synthesis gas, which is then converted to liquid fuels [1]. Consequently, the growing demand for high quality diesel fuels has brought hydrotreating processes center stage in the modern refinery strategies [2]. The decreased amount of aromatic content results into an increase in the cetane number of the diesel. For example, typically, an aromatic reduction of 10 wt% results into cetane number increase by 3–3.5 [3]. Two approaches namely catalytic hydrogenation and selective extraction are commonly used for removing aromatic compounds from gasoline or diesel in industry [4].

Sulfided mixed oxides such as Ni–Mo, Ni–W, Co–Mo are the commonly used hydrotreating catalysts; however the drawbacks of these conventional catalysts include severe operating conditions such as high temperature, low space velocity, high pressure and hydrogen/feed mole ratio to achieve acceptable aromatic reduction. Furthermore, conventional hydrotreating catalysts can only accomplish moderate levels of aromatic saturation under typical hydrotreating conditions in a single-stage operation [5–7]. Using these catalytic systems, increasing severity of temperature and pressure does not result in higher levels of aromatics saturation because of thermodynamic limitations. Noble metal-based catalysts, which can work at lower temperatures, thus avoiding the thermodynamic constraints associated with the sulfided oxides, are preferred for aromatic saturation. However, noble metal hydrogenation catalysts get poisoned by small amounts of sulfur and nitrogen containing hetro organic compounds normally present in the feed [8]. Furthermore, sulfur tolerance of the hydrogenation catalysts may be enhanced by deposition of noble metal (Pt, Pd, etc.) on acidic supports, namely, zeolite beta, Y, mordenite, LTL and MCM-41 [2,6,9–11].

Noble metals deposited on acidic support show higher turnover frequencies (TOF) compared to those supported on non-acidic supports either due to the polarization of the metal particles by nearby cations or to a metal–support interaction, which induce a partial electron transfer between the metal and the support oxide ions [9], or between the metal and the zeolite support protons

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[*] Corresponding author. Tel.: +91 265 6693935; fax: +91 265 66693934.
E-mail address: rvjasra@gmail.com (R.V. Jasra).

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[10,11]. The positive effect of the acidity on sulfur resistance of noble metal was explained by the changes in the metal electron deficiency induced by metal/support interactions [12–14]. This interaction leads to the formation of electron-deficient metal sites, which lowers the strength of the sulfur–metal bond and thus resulting to higher catalytic activity [10,11,15].

Studies related to sulfur tolerance of Pt, Pd noble metal and bimetallic Pt–Pd catalyst supported on various supports, including alumina, titania and acidic zeolites for the hydrogenation of aromatics have been reported [16–20]. Koningsberger et al. [21] investigated the potential for developing non-acidic sulfur tolerant catalyst.

Toluene hydrogenation over Ni, Ru, Pt, Pd, and bimetallic Pt–Pd, Pt–Ir, Pt–Rh, Pt–Re supported on silica, alumina, silica–alumina, beta- and Y-zeolite have been studied extensively [22–27]. Rhodium supported on ZSM-5 has not been reported so far for toluene hydrogenation in the literature. In the present paper, we report hydrodearomatization of toluene in a fixed bed reactor using Rh supported on ZSM-5 having varied SiO_2/Al_2O_3 ratio. Rhodium is chosen as it is relatively easy to reduce compared to other transition metals like Fe, Co and Ni [28]. Toluene is used as a model compound to simulate the aromatics in diesel fuels, because the hydrogenation of toluene is known to be more difficult than that of benzene and naphthalene [29]. The effect of different reaction temperatures, pressures, reduction temperatures and the presence of sulfur compound, dibenzothiophene (DBT) were correlated with varied acidity of the ZSM-5 support.

2. Experimental

2.1. Materials

A commercial grade [Na] ZSM-5 zeolite samples having SiO_2/Al_2O_3 ratio of 24, 100 and 900 were obtained from Zeocat, Uetikon (Switzerland). Toluene (99.5%) and silver nitrate (99.8%) were purchased from Qualigens Fine Chemicals (India). *n*-Tridecane (95%) and ammonium chloride (99.8%) were purchased from S.D. Fine Chem Ltd. (India) and Ranbaxy Fine Chemicals Limited (India), respectively. Rhodium trichloride ($RhCl_3 \cdot 3H_2O$) and dibenzothiophene (98%) were procured from Merck (Germany). Hydrogen gas (99.8%) was purchased from Alchemie Gases and Chemicals Pvt. Ltd. (India).

2.2. Preparation of catalyst

A commercial grade [Na] ZSM-5 having SiO_2/Al_2O_3 ratio of 24 was treated with 1 M NH_4Cl solution (zeolite to NH_4Cl solution ratio 1:80) at 353 K for 4 h. The mixture was cooled and filtered after the treatment. Solid obtained was washed with deionized water till the filtrate was free from chloride ions (checked by $AgNO_3$ test). Thus washed solid was dried in an oven at 378 K. The above procedure was repeated to ensure complete exchange of Na by NH_4 ions. NH_4-exchanged zeolite was calcined in a furnace for 4 h at 823 K in air to obtain the protonic form (H-form) of ZSM-5 zeolite. Thus, prepared sample is designated as H-24, where 24 is SiO_2/Al_2O_3 ratio, while remaining catalysts of sodium form having SiO_2/Al_2O_3 ratio of 24, 100 and 900 were designated as Na-24, Na-100 and Na-900, respectively.

The Rh metal was supported on all the four zeolite supports, H-24, Na-24, Na-100 and Na-900 by impregnating 1 wt% aqueous $RhCl_3 \cdot 3H_2O$ solution on the surface of ZSM-5. The solution containing the $RhCl_3 \cdot 3H_2O$ was added dropwise to the slurry of zeolite and stirred for 6 h. The sample was then dried in an air oven overnight at 378 K and finally calcined in air at 723 K for 4 h. The samples prepared thus were designated as Rh-H-24, Rh-Na-24, Rh-Na-100 and Rh-Na-900, respectively.

2.3. Catalyst characterization

The relative crystallinity of the ZSM-5 samples was determined by X-ray diffraction (Phillips X'PERT MPD system, The Netherlands) using Cu Kα radiation (λ = 1.5405 Å) by comparing the summation of the peaks area between 2θ = 23.2 and 24.5 with that for the corresponding starting Na [ZSM]-5 zeolite. The textural properties of the catalysts were determined from N_2 adsorption–desorption isotherms at 77.4 K over the whole range of relative pressures, using ASAP-2010, Micromeritics (USA). The catalysts were degassed under vacuum (1×10^{-2} mm Hg) for 4 h at 623 K prior to N_2 adsorption measurements.

2.4. Surface acidity measurement

2.4.1. Temperature-programmed desorption (TPD) of NH_3

Acidity measurement by temperature-programmed desorption of NH_3 was carried out using Micromeritics Pulse Chemisorb 2720 instrument. Typically, sample (~0.1 g) was taken in the reactor and activated *in situ* in flow of helium at 673 K for 1 h, then cooled down to 393 K and mixture of 5% ammonia with helium is passed for 10 min to chemisorb ammonia. The excess physisorbed ammonia was flushed out with pure helium gas flow during 1 h at 393 K. Then the sample is heated at a rate of 10 K min^{-1} up to 973 K and volume of gas desorbed was measured by detector. The instrument calculates the volume of gas desorbed as per calibration.

2.4.2. Brønsted acidity measurement by cyclohexanol dehydration

Vapor phase cyclohexanol dehydration to cyclohexene in a fixed bed reactor was used as a model reaction to determine the Brønsted acidity of zeolite samples. The catalyst sample (0.2 g) was packed in a glass reactor bed and activated *in situ* at 723 K for 2 h under N_2 (15 ml min^{-1}). Catalyst bed temperature was brought down to reaction temperature of 448 K and cyclohexanol (2 ml) was delivered by syringe pump injector (Cole Parmer, 74900 series) with a flow rate of 0.0166 ml min^{-1} under N_2 (15 ml min^{-1}) flow. Product samples were collected after 1 h and analyzed with a Hewlett-Packard gas chromatogram (HP 6890) having HP50 capillary column (30 m), FID detector and programmed oven temperature from 323 to 473 K and 0.5 ml min^{-1} flow rate of N_2 as carrier gas. The conversion of cyclohexanol and selectivity for cyclohexene were calculated as follows:

$$\text{conversion (wt\%)} = 100 \times [\text{initial wt\%} - \text{final wt\%}]/\text{initial wt\%}$$

$$\text{Selectivity} = 100 \times [\text{GC peak area \% of cyclohexene}]/\sum \text{total peak area of all the products}$$

2.5. Catalyst activity for hydrodearomatization of toluene

Hydrodearomatization of toluene was performed in a microprocessor-based continuous-down-flow stainless steel catalytic fixed bed reactor (i.d. 15 mm and length 524 mm) system with PC-PLC supplied by M/S, Chemito Technologies Pvt. Ltd. (India). The catalyst 0.5–2.06 mm size was sieved and kept at the center of reactor. The remaining space of catalyst bed at the top and the bottom of reactor were filled with glass beads (2–4 mm) to avoid the entrance–exit and dispersion effects; as well as to obtain a homogeneous thermal distribution in the reactor [30,31].

Catalyst was reduced *in situ* by hydrogen at particular temperature (523 or 723 K) for 2 h. The reactor was brought to the desired temperature before the reactant was introduced. Catalytic activity test was carried out at different reaction temperatures (448–523 K), pressures (10–30 bar), reduction temperatures (523 and 723 K) and dibenzothiophene (100 and 200 ppm) concentration. Liquid sample was withdrawn from the sample-collecting vessel and analyzed by gas chromatograph (Shimadzu 17A, Japan) equipped with a flame ionization detector (FID), universal capillary column (60 m length and 0.25 mm diameter, made of 5% diphenyl and 95% dimethyl siloxane). The initial GC column temperature was increased from 313 to 473 K at the rate of 10 K min^{-1}. Nitrogen gas (3.4 ml min^{-1}) was used as a carrier gas. The temperature of injection port and FID were kept constant at 473 K during product analysis. The retention times for different compounds were determined by injecting pure compounds under identical GC conditions. *n*-Tridecane was used as an internal gas chromatography (GC) standard. Furthermore, products were also confirmed by the GC–MS (Shimadzu, GC–MS QP 2010, Japan).

3. Results and discussion

3.1. Catalyst characterization

The relative crystallinity and textural properties data for ZSM-5 and Rh metal loaded ZSM-5 samples with different SiO_2/Al_2O_3 ratio are presented in Table 1. Partial loss of crystallinity in zeolite structure upon Rh metal loading is observed. Nitrogen adsorption–desorption isotherms of all the samples are found of type I as per IUPAC classification which correspond to the adsorption in microporous materials [32]. BET surface area slightly decreased while total pore volume increased upon Rh metal loading on pure ZSM-5 samples. Similar kind of observations are also reported over mordenite and beta-zeolite samples [27,33].

3.2. Surface acidity measurement

3.2.1. Acidity by temperature-programmed desorption of NH_3

Table 1 shows the total acid site concentration (mmol NH_3/g) and acid site density (mmol/m^2) per unit area for different ZSM-5 samples as determined from ammonia TPD. The acidity of a zeolite is related to its aluminum content, and a linear increase in the overall acidity is expected with increasing aluminum content in the zeolite [34]. We have also observed similar kind of behaviour in which the acid site concentration (mmol NH_3/g) and acid site density (mmol/m^2) increases with decreasing SiO_2/Al_2O_3 ratio from 900 to 24 (i.e., increasing aluminum content). The sample H-24 showed maximum acid site concentration (0.6254 mmol NH_3/g), and density (1.64×10^{-3} mmol/m^2). The order of acid site concentration and density observed for ZSM-5 samples follows the order H-24 > Na-24 > Na-100 > Na-900. Acid site concentration and density of the Rh metal loaded samples also increased with decreasing SiO_2/Al_2O_3 ratio from 900 to 24, however, the total acid site concentration and density per unit area is comparatively lower than its corresponding support which suggested that significant numbers of acid sites are shielded by the metal particles after Rh loading on ZSM-5 samples. These results are in agreement with previous findings [33].

3.2.2. Brønsted acidity by cyclohexanol dehydration

Table 1 shows the conversion (wt%) of cyclohexanol to cyclohexene over different ZSM-5 samples. Cyclohexanol conversion increases with decreasing SiO_2/Al_2O_3 ratio (i.e., increasing aluminum content) and H-24 sample showed maximum conversion (87%) with ~100% selectivity to cyclohexene. The order of Brønsted acidity observed from cyclohexanol dehydration for pure ZSM-5 samples is H-24 > Na-24 > Na-100 > Na-900, and Rh-H-24 > Rh-Na-24 > Rh-Na-100 > Rh-Na-900 for rhodium metal loaded samples. Na-ZSM-5 samples showed higher conversion of cyclohexanol compared to rhodium-supported samples, which suggested the presence of lower acid site concentration in Rh-supported ZSM-5 samples compared to Na-ZSM-5 samples, which is in good agreement with NH_3-TPD data.

3.3. Catalytic activity

Hydrodearomatization of toluene was observed to occur readily within studied temperature range and the selectivity for methylcyclohexane was found to be between 95 and 98%. Other products namely, 1,2- and 1,3-dimethyl cyclopentane and ethylcyclopentane were also observed due to isomerization and cracking reactions that could occur due to the acidity of zeolite. The steady state operation was obtained after ca. 180 min and remained constant even after 420 min.

3.3.1. Effect of reaction temperature

The effect of temperature (448–523 K) on toluene hydrogenation are compiled in Fig. 1a. The maximum toluene conversion (99%) was achieved with Rh supported on ZSM having higher acidity, i.e., Rh-H-24, at lower reaction temperature 448 K, while less acidic-supported catalysts, i.e., Rh-Na-24, Rh-Na-100 and Rh-Na-900 showed maximum conversion at relatively high temperatures such as 473, 473 and 498 K, respectively.

The activity for toluene hydrogenation passes through a maximum near 498, 473, 473 and 448 K for Rh-Na-900, Rh-Na-100, Rh-Na-24 and Rh-H-24, respectively (Fig. 1b), which is considered as optimum reaction temperature for each respective catalyst. The maximum for toluene hydrogenation is reversible and can be traversed from either high or low temperature side, which implies that it is not due to catalyst deactivation. The occurrence of this maximum for toluene hydrogenation has been explained by the continued decrease in the aromatic hydrocarbon surface coverage as temperature increases, which at some point becomes small enough to noticeably decrease the conversion [35]. Also, at high temperature, poisoning of the catalyst surface by organic residue is possible [36].

Table 1

Structural–textural properties, acid site concentration (mmol NH_3/g), acid site density (mmol/m^2) as determined from ammonia TPD and cyclohexanol dehydration reaction data of different ZSM-5 and Rh-supported ZSM-5 samples

Sample	Crystallinity (%)	BET-SA (m^2/g)	Total V_p (cm^3/g)	Acid site concentration (mmol NH_3/g)	Acid site density[a] (mmol/m^2)	Cyclohexanol dehydration % conversion
Na-900	100	330	0.167	0.1359	4.11×10^{-4}	1
Rh-Na-900	87	319	0.176	0.0289	9.06×10^{-5}	1
Na-100	100	354	0.205	0.4387	1.24×10^{-3}	3
Rh-Na-100	95	343	0.234	0.1155	3.36×10^{-4}	1
Na-24	100	364	0.408	0.5876	1.61×10^{-3}	7
Rh-Na-24	99	359	0.413	0.2384	6.64×10^{-4}	3
H-24	–	380	0.445	0.6254	1.64×10^{-3}	87
Rh-H-24	97	370	0.456	nd	nd	77

nd = not determined.

[a] Acid site density = acid site concentration/BET surface area (mmol/m^2).

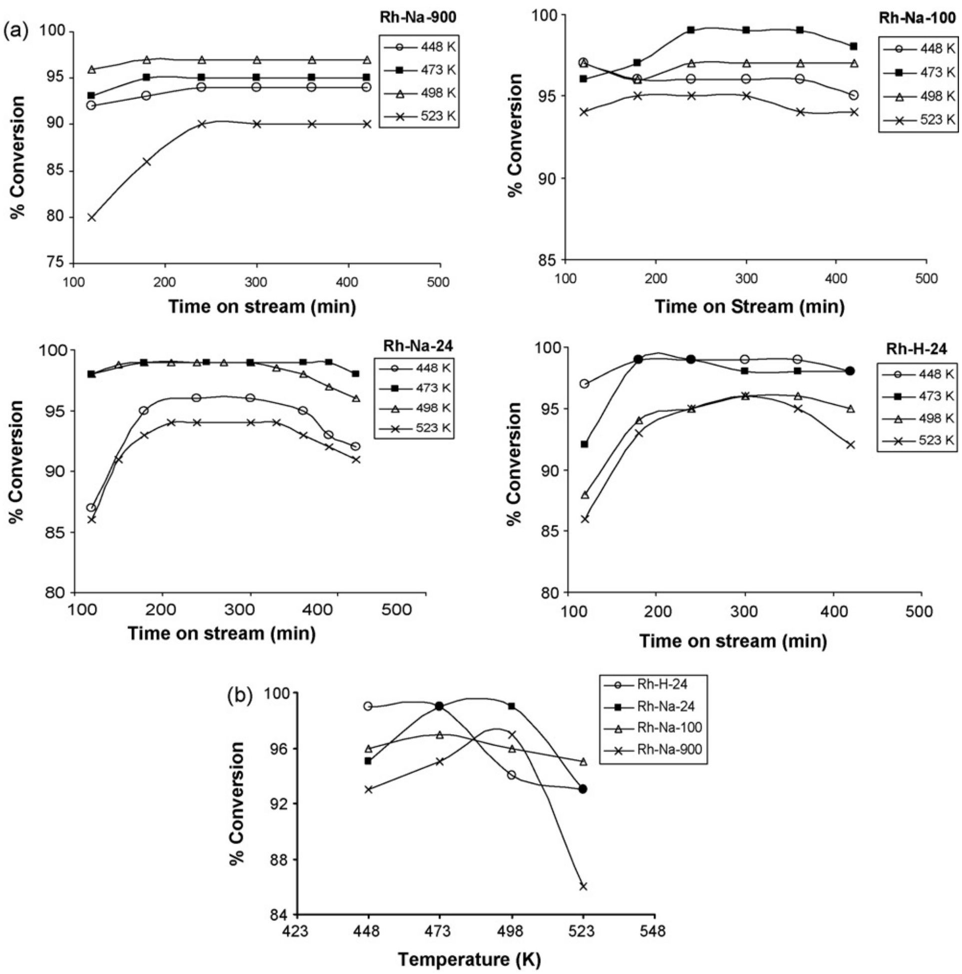

Fig. 1. (a) Effect of reaction temperature on toluene hydrodearomatization with time on stream at pressure = 20 bar, reduction temperature = 723 K, toluene feed rate = 0.123 mol h^{-1}, H_2 flow rate = 280 ml min^{-1} and H_2/feed mole ratio = 6. (b) Effect of reaction temperature on toluene hydrodearomatization at time = 180 min, pressure = 20 bar, reduction temperature = 723 K, toluene feed rate = 0.123 mol h^{-1}, H_2 flow rate = 280 ml min^{-1} and H_2/feed mole ratio = 6.

3.3.2. Effect of reduction temperature

Fig. 2 shows the effect of reduction temperature (523 and 723 K) on toluene hydrodearomatization at 20 bar pressure, and at optimized reaction temperature for each catalyst. Highly acidic Rh-H-24 sample showed almost same conversion at 523 and 723 K, while other samples (Rh-Na-24, Rh-Na-100 and Rh-Na-900) having lower acidity showed increase in the toluene hydrogenation activity when reduced at higher temperature of 723 K as compared to reduction at 523 K.

It is reported that benzene hydrogenation occurs via two pathways on Pt/MOR [37,38]. In the similar way, toluene hydrogenation is also expected to occur on two catalytically active sites (I) on the rhodium metal and (II) on the Brønsted acid sites close to the metal particles implying a spillover of hydrogen from the Rh surface or at the metal support interface. Furthermore, both, (i) higher reduction temperature to reduce all the Rh metal and (ii) higher acidity of support enhances the hydrogenation of toluene. However, higher acidity of support needs lower reduction temperature to obtain maximum conversion. The results also indicate that hydrogenation occurs on both catalytic sites, therefore, Rh metal supported on ZSM-5 having higher acidity showed higher conversion at a lower reduction temperature. It clearly shows the role of support acidity in toluene hydrodearomatization.

At lower reduction temperature of 523 K, all the Rh metal could not be reduced completely, hence lower acidic supports such as Rh-Na-24, Rh-Na-100 and Rh-Na-900 with low Brønsted acid sites showed lower conversion compared to the values obtained when these samples were reduced at higher temperature of 723 K, while in higher acidic support, i.e., in Rh-H-24, when reduced at lower temperature at 523 K, the hydrogenation reaction occurs via route I along with route II, hence maintaining the overall activity and showed similar toluene conversion. The optimized reduction temperature observed for 723 K for Rh-Na-900, Rh-Na-100, Rh-Na-24 and 523 K for Rh-H-24 (Fig. 2).

3.3.3. Effect of pressure

Fig. 3 depicts the effect of hydrogen partial pressure on toluene conversion at optimized reaction temperature of each Rh metal-supported catalysts. Toluene conversion linearly increased with increasing hydrogen partial pressure indicating that hydrogen partial pressure has significant effect on hydrogenation activity. Hydrogen and aromatic hydrocarbons adsorb on different types of sites and that the reaction occurs simultaneously on Rh surface (route I) and on acid sites in the interface region (route II) as mentioned above. The increase in hydrogen partial pressure increases hydrogen dissociation on the metal surface and, thus, increased the concentration of hydrogen available for toluene hydrogenation. It is seen that high pressure favors low equilibrium concentrations of aromatics, i.e., high conversions. This is particularly true for reactions where the number of moles of hydrogen, required for complete saturation is high. Toluene conversion is increased due to increase in the concentration of

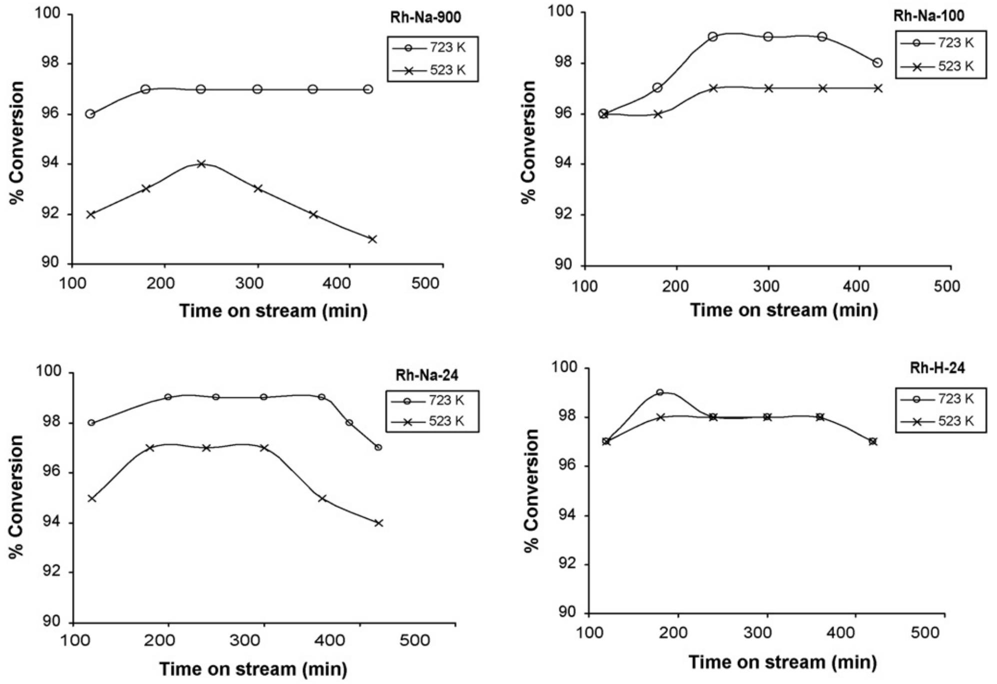

Fig. 2. Effect of reduction temperature on toluene hydrodearomatization at pressure = 20 bar, toluene feed rate = 0.123 mol h^{-1}, H_2 flow rate = 280 ml min^{-1}, H_2/feed mole ratio = 6 and reaction temperature = 498, 473, 473 and 448 K for Rh-Na-900, Rh-Na-100, Rh-Na-24 and Rh-H-24, respectively.

hydrogen on the support surface in the vicinity of the metal particles. Hence, the metal–support interface region could contribute to the overall activity of the toluene hydrodearomatization if the concentration of adsorption sites for toluene is high enough and the hydrogen transport rate is sufficiently rapid.

3.3.4. Sulfur tolerance on Brønsted acid sites

A solution of toluene and dibenzothiophene (DBT) (100 and 200 ppm), as a sulfur compound, was used to measure the sulfur tolerance of the catalyst at optimized reaction and reduction temperature of each catalyst. Toluene conversion was observed to decrease with increasing the DBT concentration (Fig. 4). Without DBT, steady state performance was observed even after 420 min for all the samples, while increasing the concentration of DBT from 0 ppm to 100 and 200 ppm the catalyst was found to deactivate rapidly. The decrease in the catalyst activity in the presence of DBT is mainly attributed to the adsorption and decomposition of DBT on the metal sites, which results in a loss of metal surface available for the reaction to take place. The lowest conversion and sulfur tolerance was achieved with Rh loaded on support having lower

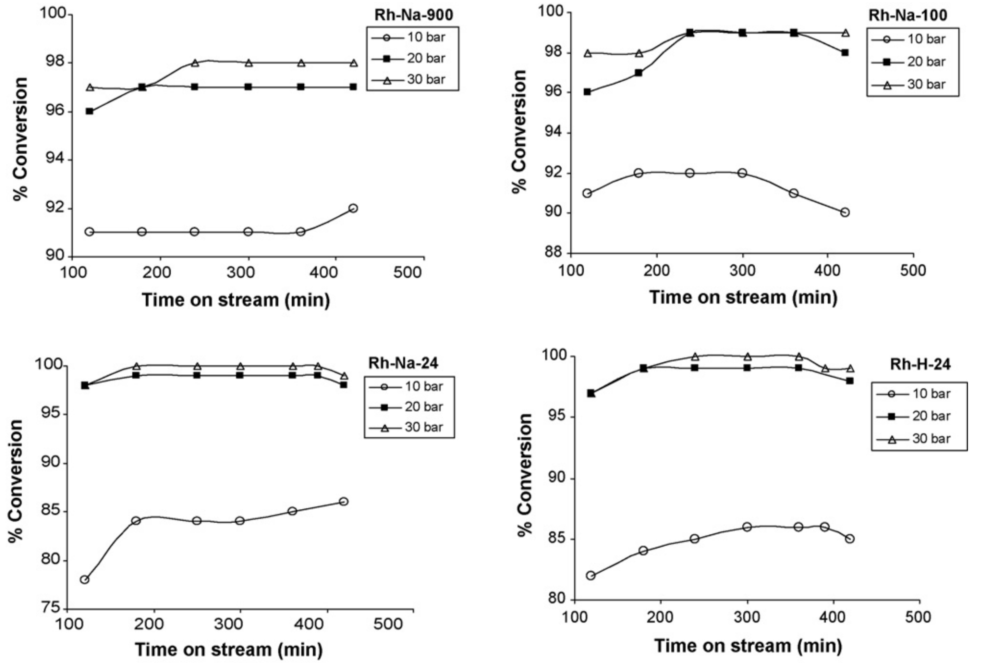

Fig. 3. Effect of hydrogen partial pressure on toluene hydrodearomatization at toluene feed rate = 0.123 mol h^{-1}, reduction temperature = 723 K for Rh-Na-900, Rh-Na-100, Rh-Na-24 and 523 K for Rh-H-24, H_2/feed mole ratio = 6 and reaction temperature = 498, 473, 473 and 448 K for Rh-Na-900, Rh-Na-100, Rh-Na-24 and Rh-H-24, respectively.

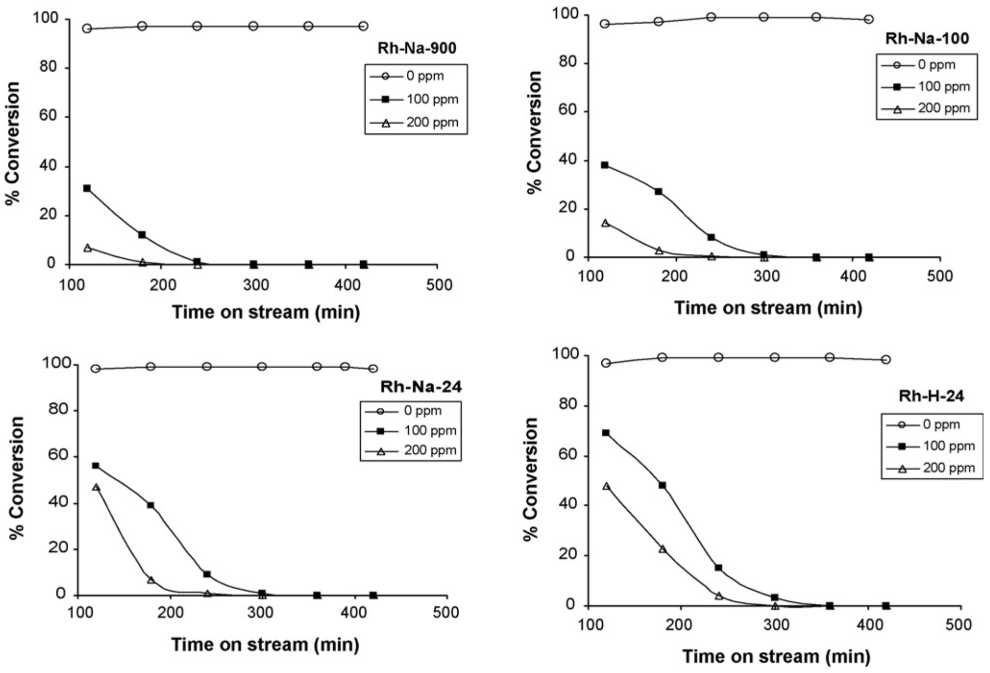

Fig. 4. Effect of dibenzothiophene (sulfur) on catalytic activity with time on stream at pressure = 20 bar, reduction temperature = 723 K for Rh-Na-900, Rh-Na-100, Rh-Na-24 and 523 K for Rh-H-24, toluene feed rate = 0.123 mol h^{-1}, H_2/toluene mole ratio = 6, reaction temperature = 498, 473, 473 and 448 K for Rh-Na-900, Rh-Na-100, Rh-Na-24 and Rh-H-24, respectively.

Table 2

Rate of toluene conversion at 20 bar pressure after 180 min of toluene hydrodearomatization in the absence and presence of 100 and 200 ppm dibenzothiophene at 498, 473, 473 and 448 K optimum reaction temperature for Rh-Na-900, Rh-Na-100, Rh-Na-24 and Rh-H-24, respectively

Catalyst	Temperature (K)	Sulfur concentration (ppm)	% Conversion	Rate[a]	r/r_{sx}[b]
Rh-Na-900	498	0	97	3.97×10^{-3}	–
		100	12	4.92×10^{-4}	8.07
		200	1	4.10×10^{-5}	96.83
Rh-Na-100	473	0	97	3.97×10^{-3}	–
		100	27	1.10×10^{-3}	3.59
		200	3	1.23×10^{-4}	32.27
Rh-Na-24	473	0	99	4.05×10^{-3}	–
		100	39	1.59×10^{-3}	2.54
		200	7	2.87×10^{-4}	14.11
Rh-H-24	448	0	99	4.05×10^{-3}	–
		100	48	1.96×10^{-3}	2.06
		200	23	9.43×10^{-4}	4.29

[a] Moles of toluene converted per gram catalyst per min.

[b] Ratio between the rates of toluene hydrodearomatization in the absence (r) and the presence (r_{sx}) of dibenzothiophene (where x = 100 and 200 ppm).

acidity (Rh-Na-900). This is attributed to the absence of the acidic pathway (route II) for toluene hydrogenation, which lowers the overall activity, while highest toluene conversion and sulfur tolerance was observed for Rh-H-24, which indicates that acidic, and metallic sites were present in the catalyst and reaction occurred via both the routes I and II. In very less acidic sample Rh-Na-900, the sulfur poisoning is mainly attributed to the adsorption and decomposition of DBT only on the metal sites, which results in a loss of metal surface available for the reaction to take place. Hence, we can conclude that the presence of acidic support plays a significant role towards the sulfur tolerance. The enhancement in sulfur tolerance can be explained as Brønsted acid sites of the support (electron acceptor) modified the electronic properties of the metal atom, resulting into the formation of electron-deficient metal sites, which in turns lowers the strength of the S–M bond between an electron-deficient metal and an electron-acceptor sulfur [10,11,27,39].

Table 2 shows the ratio between the rates of toluene hydrodearomatization in the absence and presence of 100 and 200 ppm DBT and the highest ratios were observed for less acidic Rh-Na-900 sample (8.07 and 96.83 for 100 and 200 ppm, respectively). At 20 bar, lowest r/r_{sx} (where x = 100 and 200 ppm DBT) ratios were observed for Rh-H-24 (r/r_{s100} = 2.06 and r/r_{s200} = 4.29) compared to other catalysts, which indicates a lower deactivation of the catalyst Rh-H-24 in the presence of dibenzothiophene.

4. Conclusions

Rh supported on ZSM-5 samples with varied SiO_2/Al_2O_3 ratio showed good catalytic activity for the hydrodearomatization of pure toluene. The total acid site concentration and acid site density per unit area is comparatively lower than its corresponding pure ZSM-5 sample, which suggested that significant numbers of acid sites are shielded by the metal particles after Rh loading on ZSM-5 samples.

Toluene hydrodearomatization is dependent on reaction temperature, pressure and also reduction temperature. Reduction temperature has been observed to significantly affect the toluene hydrodearomatization over less acidic support, while with highly acidic support toluene hydrodearomatization was not affected. Toluene hydrodearomatization on Rh-supported ZSM-5 occurs via two routes, i.e., hydrogenation (I) on the metal surface and (II) on the acid sites in the vicinity of Rh particles with hydrogen dissociated on the metal. The decrease of the catalyst activity in the presence of dibenzothiophene is mainly attributed to the adsorption and decomposition of DBT on the metal sites, which results in a loss of metal surface available for the reaction to take place. In the presence of DBT, a high toluene hydrodearomatization activity and sulfur tolerance on Brønsted acid sites of the support is maintained, while the activity on the metal sites is strongly reduced.

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