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Kinetics of toluene disproportionation over fresh and coked H-mordenite

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Abstract

A TDP kinetics model was derived as the reversible second order kinetics on toluene with activation energy of 25 ± 1 kcal/mol. The kinetics model is applicable for coked mordenite with coke content up to ca. 24.6% and for the estimation of relative activity of the coked at various TOS and thus cycle length. Two stages of deactivation mechanism were devised. Pore plugging and deactivation by coke predominates the initial coking period at ca. 7% coke content, during that period the strong Brønsted acid site diminishes and also the pore voidage shrinks. Upon extending TOS, coke laydown on the external surface of zeolite with pore voidage unaffected and the deactivation is caused by the acid site coverage. Soft coke content was found remaining fairly constant ca. 1.7 wt.% and hard coke increases with extending TOS. As a result, total coke builds up to 24.6 wt.% at TOS of 340 days.

Keywords: Kinetics model; Coking; Deactivation; Mordenite

1. Introduction

Disproportionation and transalkylation of toluene are useful reactions for converting surplus toluene into the more valuable benzene and xylene as key raw materials for many intermediates of petrochemicals and fine chemicals [1]. Reaction kinetics study has shown to be a crucial research subject for process development, which provides valuable data for reactor design, process optimization, and cycle length prediction. Various kinetic models were proposed for toluene disproportionation (TDP) over several zeolites [2–8]. Most of the published reports studied mainly on the initial kinetics at low conversion levels and in short on-stream time (TOS) with very low coke formation. Since zeolite is inevitably deposited by coke with extending operation period, the effect of coke formation in industrial reactors on the catalyst deactivation and the applicability of kinetics model appear to be a key issue. It is indispensable to develop industrially applicable kinetics under catalyst deactivation.

Deactivation of zeolite from coke formation is due to either the mechanism of pore plugging or the mechanism of acid site coverage, which reduces diffusivity of reactants or available acid site number, respectively [9]. Deactivation mechanism varies with zeolite structure, reaction type, and also operating conditions. It is possible to elucidate the type of deactivation mechanism by means of kinetics study, such as determination of the reaction orders and activation energy, and systematic characterization of coked catalyst samples obtained at various TOS. Chen et al. reported from analyzing a series of coked mordenite catalyst in TDP by using ^{31}P-MAS-NMR that during initial coking at a total coke content of ca. 7 wt.%, strong Brønsted acid sites of mordenite diminish rapidly corresponding to ca. 80% decrease in total acidity [10].

The purpose of this study is to identify the deactivation mechanism of TDP over a commercial H-mordenite zeolite

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catalyst, and to develop a practical kinetics model for industrial application under representative industrial operation regimes, namely at high reaction pressure and wide conversion range.

2. Experimental

A mordenite based commercial catalyst was used in the present study. Its SiO_2/Al_2O_3 ratio is 20. Toluene transalkylation reaction test was conducted in a continuous flow fixed-bed pilot plant in the typical industrial operating conditions for long term aging study over 340 days. The pilot plant was operated at the material balance of 100 ± 1%. Various coked samples were taken from the pilot plant aging test and denoted as MOR/C-*x*, where *x* represents the total coke content of the sample. They were used to conduct kinetics study of TDP in a continuous flow fixed-bed microreactor. Reactor bed was packed with coked mordenite sample of 4 g in 12–25 mesh and with sand of 3 g in 80–120 mesh. The reactor was heated in air for 8 h at 813 K and then cooled down to reactor temperature under nitrogen at 45 cm^3/min flow rate. After reaching reactor temperature, reactor was purged with hydrogen and then pressurized to 2859 kPa. Reaction conditions were H_2/toluene of 4.4 molar ratio; WHSV: 0.2–4.4 h^{-1}; pressure: 2859 kPa; reaction temperature: 645–725 K. The reaction mixtures were analyzed by a gas chromatography using the ASTM D5134 DHA (detailed hydrocarbon analysis) procedure.

The total coke content of each spent samples was determined by thermogravimetric analysis (TGA, Netzsch TG209) measurement. Typically, ca. 10 mg of catalyst was heated from 298 to 573 K in nitrogen and from 573 to 1073 K in air. The weight loss between 423 and 573 K is ascribed due to soft cokes, whereas the weight loss between 573 and 1073 K is attribute to hard cokes (Table 1). The acidity of coked samples at various TOS was determined with ^{31}P NMR for the changes of acid site distribution. Solid-state ^{31}P-MAS-NMR spectra were acquired at a Larmor frequency of 202.46 MHz on Bruker MSL-500P instrument using a single-pulse sequence under the following conditions: pulse width 2 μs, recycle delay 5 s, spinning rate 12 kHz. An aqueous 85% H_3PO_4 solution was used as the chemical shift reference. Prior to the experiment, each sample was subjected to dehydration treatment at 623 K (473 K for coked samples) for 48 h under vacuum (ca. 1.3 kPa, 10^{-5} Torr). Detailed experimental setups and procedures involved in preparing samples loaded with various P-containing probe molecules can be found elsewhere [11].

3. Results and discussion

An aging curve of transalkylation of toluene and A_9 aromatics over a commercial mordenite catalyst was generated by maintaining the conversion in the vicinity of 45 wt.% at the following fixed operating conditions, 2859 kPa, 1.7 h^{-1}, 4.4 H_2/HC, but varying reaction temperature for over TOS of 340 days, as shown in Fig. 1. The conversion was 44.5% at 653 K at the beginning of the test and was 42.9% at 749 K in the end of the test. The aging curve data is then transformed into "normalized reaction temperature" curve at a conversion of 45%, by using the kinetic model to be discussed later, which can be used for the prediction of cycle length in a commercial reactor.

Several coked mordenite catalyst samples at various TOS were obtained. They were analyzed by TGA to determine coke composition and used in the tests of kinetics model. The types of coke are characterized as "soft coke" and "hard coke" for the constituent desorbed from catalyst

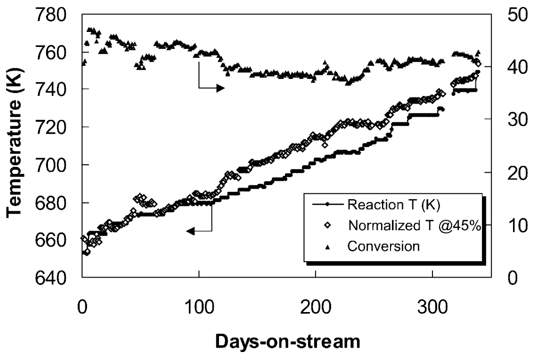


Fig. 1. Aging curve of toluene transalkylation over mordenite catalyst (temperature: 653–749 K; WHSV: 1.7 h^{-1}; pressure: 2859 kPa; H_2/toluene: 4.4 mol/mol).

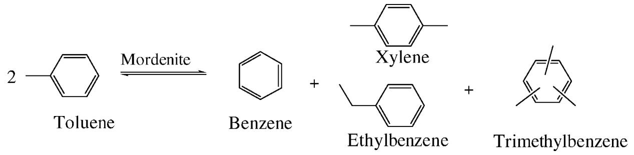
Table 1
Coke content and kinetic data of commercial H-mordenite samples obtained at various time-stream during TDP

Sample ID	TOS[a] (day)	Coke content[b] (wt.%)			Kinetics data	
		Soft coke (423–573 K)	Hard coke (573–1073 K)	Total coke (423–1073 K)	*k* at 653 K[c] (h^{-1} mol^{-1})	E_a (kcal/mol)
MOR/C-7	0.5	1.70	3.93	7.06	1.537	24.5
MOR/C-12[a]	20	1.68	8.95	12.46	1.137	25.4
MOR/C-25[a]	340	1.78	21.40	24.58	0.131	25.7

[a] Time-on-stream.
[b] Determined from TGA.
[c] Reversible second-order rate constant.

sample as measured by TGA at 423–573 K and 573–1073 K, respectively. As shown in Table 1, soft coke content remains fairly constant ca. 1.7 wt.% and hard coke increases with extending TOS.

The kinetic data over various coked samples with coke content of 7.1, 12.5 and 24.6 wt.%, obtained at TOS at 0.5, 20 and 340 days, respectively, were fitted by using various kinetic orders. Assuming a homogeneous kinetics model can derive a corresponding kinetics model. For toluene disproportionation (TDP).



$$2A \rightleftharpoons 2R \tag{1}$$

By using the first-order kinetics:

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A] \tag{2}$$

$$\ln[1-X] = -kt \tag{3}$$

By using the second reversible kinetics [12]:

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k_1[A]^2 - k_2[R]^2 \tag{4}$$

$$2k_1\left(\frac{1}{X_e}-1\right)tC_0 = \ln\frac{X_e-(2X_e-1)X}{X_e-X} \tag{5}$$

where X and X_e is the conversion and equilibrium conversion of TDP, respectively, and t represents the contact time and is the reciprocal of WHSV. The validity of a kinetic model is verified by the appearance of linear lines with intercepting at origin in the plot between the conversion term and contact time term. In applying the first-order kinetics model, the plot of $-\ln(1-X)$ versus 1/WHSV, as shown in Fig. 2(a), cannot be fitted as linear lines. On the other hand, in applying the reversible second-order reaction model, liner lines passing through the origin can correlate $\ln[(X_e-(2X_e-1)X)/(X_e-X)]$ term and $(1/X_e-1)(1/\mathrm{WHSV})C_0$ term (Fig. 2(b)), as shown in Fig. 2(b). Therefore, the reversible second-order model can well represent the reaction system, and the rate constant (k) is the slop of the line.

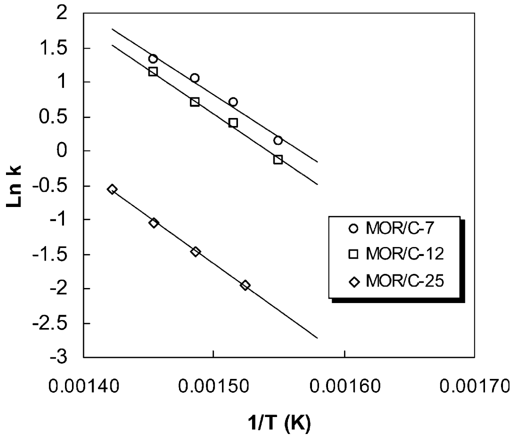


Fig. 3. Dependence of rate constant on reaction temperature in TDP over commercial H-mordenite catalyst (temperature: 645–725 K; pressure: 2859 kPa; H_2/toluene: 4.4 mol/mol).

The k values of several reaction temperatures were determined. Activation energy (E_a) is the slope of the Arrhenius plot between k and the reciprocal of temperature:

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \tag{6}$$

where R is the gas constant. It was found that the kinetic data of all the coked samples with coke content in between 7.1 and 24.6 wt.% can be fitted well with reversible second-order reaction model. As a result, the k value of various coked samples was determined from the slopes in the ln k versus $1/T$ relationship, as shown in Table 1. Interestingly, all those correlation lines parallel each other, as shown in Fig. 3. As a result, their activation energies are practically constant, ca. 25 ± 1 kcal/mol.

For a long term aging study under deactivation condition, the E_a is the sum of intrinsic activation energy, $E_{a_{\text{intrinsic}}}$ and the deactivation activation energy, $E_{a_{\text{deactivation}}}$:

$$E_a = E_{a_{\text{intrinsic}}} + E_{a_{\text{deactivation}}} \tag{7}$$

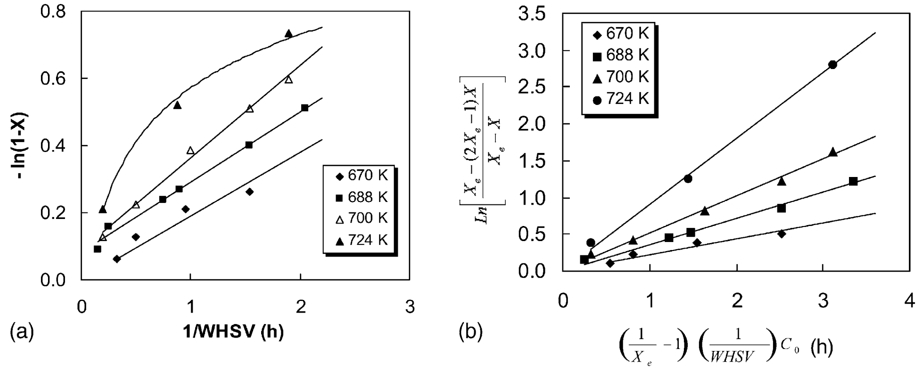


Fig. 2. Kinetics plot: (a) first-order kinetics fitting; (b) reversible second-order kinetics fitting (temperature: 645–725 K; WHSV: 0.2–4.4 h^{-1}; pressure: 2859 kPa; H_2/toluene: 4.4 mol/mol).

As all the coked samples used in the present study were generated from the same fresh mordenite sample and also the same kinetics model was used, the $E_{a_{\mathrm{intrinsic}}}$ should be all the same. The invariance of Ea and also $E_{a_{\mathrm{deactivation}}}$ among various coked samples along with ^{31}P NMR and ^{129}Xe NMR characterization, to be discussed below, indicate that the deactivation mechanism for the coke level in the range of ca. 7.1 and 24.6% is acid site coverage, rather than pore plugging.

The kinetics models in earlier literatures were in great discrepancy. Bhavikatti and Patwardhan observed a reversible second-order reaction model over Ni/mordenite with an activation energy of 14.5 kcal/mol [2]. Bharati and Bhatia observed a single-site adsorption over H-mordenite catalyst [5]. Dooley et al. reported a second-order rate Langmuir–Hinshelwood kinetics with toluene inhibition over Ni/Y zeolite [3]. On contrast, Aneke et al. reported a first-order kinetics with toluene inhibition over Cu/AlF$_3$/Y zeolites [6]. Bhaskar and Do observed a first-order dependence on the toluene partial pressure over H-ZSM-5 [7]. The discrepancy in kinetics models can be ascribed mainly due to variations in catalyst types, operating conditions, conversion levels and coking behaviors. The reaction kinetics is a form determining by reaction mechanism. Tsai and Wang [13] reported that disproportionation mechanism is monomolecular reaction over ZSM-5 and is bimolecular reaction over most 12-membered oxygen ring zeolites. The disproportionation mechanism over mordenite varies with conversion level; it is monomolecular reaction at low conversion level and is bimolecular reaction at high conversion level. Interestingly, Gnep and Guisnet found that kinetics depends strongly on the catalyst and on its treatment [4]. They found that the reaction order follows in the decreasing order as fluorinated alumina, wet-air treated and dry-air treated mordenite, and all the kinetics models involve a two adsorbed toluene molecules as the rate determining step.

The kinetics model is useful in estimation of the remaining activity of deactivated catalysts. Krishnaswamy and Kittrell reported a generalized formula of temperature-trajectory equation for *n*th-order decay [14]. In this context, the activity of the fresh catalyst sample at an arbitrary condition, namely 653 K, 2859 kPa, 1.7 h^{-1}, 4.4 H$_2$/HC, was used as the base condition. The activity of coked mordenite catalysts at various operating conditions can be transformed by using Eq. (8) with the activation energy measured above (25 ± 1 kcal/mol) to the base operating condition:

$$T_{\mathrm{norm}} = \left\{ \ln \left\{ \frac{\ln[X_e - (2X_e - 1)X/(X_e - X)]}{(1/X_e - 1)(1/\mathrm{WHSV})} \right\} - \ln k_0 \right\} \times \left(\frac{R}{E_a} \right) + \frac{1}{T_0} \qquad (8)$$

where T_0 is the initial reaction temperature, i.e., 653 K, T is the normalized reaction temperature, and k_0 is the initial rate constant of the fresh catalyst at the standard operating conditions at T_0, i.e., 1.588 h^{-1} mol^{-1}. The normalized temperature curve corrects the variation in the operating conditions and conversion. The temperature trajectory of normalized reaction temperature plot of the aging study mentioned above is presented in Fig. 1. It can be used for the prediction of cycle length, showing that rising reaction temperature by 95 °C, rising from 653 to 748 K, can compensate the catalyst deactivation within TOS of 340 days.

The coked samples were characterized by using ^{31}P NMR technique for acidity measurement and ^{129}Xe NMR for pore structures of coked mordenite samples. The newly developed ^{31}P NMR technique [11,15–19] can probe simultaneously the types and strengths of acid sites in zeolites and related catalysts and is very powerful for the determination of distribution of acid site type. In this context, trimethylphosphine (TMP) adsorption [15–17] was used to characterize coked samples, as shown in Fig. 4. The basicity of TMP (pK_b= 5.35) is in between pyridine (pK_b= 8.82) and ammonia (pK_b= 4.74). The characteristic peak of TMP adsorption at −4.8 ppm represents Brønsted acid sites and usually in doublet. The $J_{\mathrm{H-P}}$ value symbolizes the dipole–dipole interaction between hydrogen and phosphorous atom; the stronger the interaction, the higher the $J_{\mathrm{H-P}}$ value. The peak of Lewis acid site and physisorption of TMP appears at −49 and −65 ppm, respectively, and the site exchange between Lewis site and TMP appears at −60 ppm. The $J_{\mathrm{H-P}}$ is 457 Hz for fresh catalyst sample. With increasing coke content, the $J_{\mathrm{H-P}}$ value decreases down to 315 Hz at 7 wt.% coke content and the dipole–dipole interaction disappears

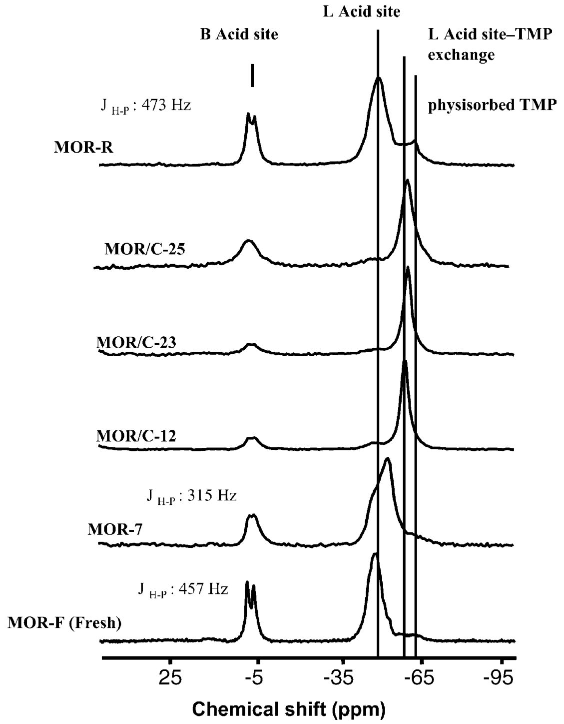


Fig. 4. ^{31}P MAS NMR spectra of TMP adsorbed on various coked mordenite samples.

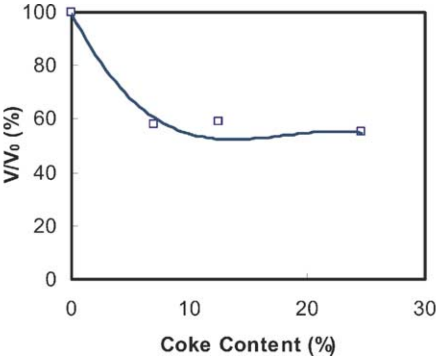


Fig. 5. Variations of relative voidage of various coked mordenite samples in against coke content.

upon higher coke content, the same as the Lewis acid site and its physisorption peak. On the other hand, the exchange peak of Lewis acid site–TMP interaction becomes more pronounced with coke formation on catalyst. The regenerated catalyst sample is also shown for reference, most of the strong acid site can be recovered from regeneration with the appearance of J_{H-P} value of 473 Hz. The results indicate that strong acid site is coked first. It was observed in our earlier study by using trimethylphosphine oxide (TMPO) and tributylphosphine oxide (TBPO) probe that as the sample coke content exceeding ca. 7 wt.%, the concentration of the strong Brønsted acid sites reduces by about 80% [10]. It was also found that in commercial H-mordenite zeolite sample, only mordenite possesses Brønsted acidity and the γ-Al_2O_3 binder exhibits only Lewis acidity. As the Brønsted acidity is responsible for the observed catalytic activity of disproportionation, therefore mordenite plays a predominant role in the catalytic reaction.

The characteristics of pore voidage of coked samples were characterized by using the ^{129}Xe NMR technique [19,21]. As shown in Fig. 5, the free-pore voidage remains only ca. 55% within the initial coking period at coke content of 7.1 wt.%. All the ^{129}Xe NMR along with TMP and TMPO probe study indicate that small amount coke, ca. 7.1%, forms inside mordenite pore and quickly covers Brønsted acid site, leading to dramatically reduction of pore volume. All the coked samples contain almost the same ‘‘soft coke’’ of 1.7%, as shown in Table 1.

With extending TOS with coke content goes beyond 7.1%, the pore voidage remains essentially the same, representing that reaction takes place on the external surface. Similar observation was also found in earlier study on ethylbenzene disproportionation over H-ZSM-5 zeolite using ^{129}Xe NMR spectroscopy [19,20]. It was found that during initial EB conversion, cokes tend to deposit on the strongest Brønsted acid sites locate in the intracrystalline channels of H-ZSM-5 and resulted in a notable decrease in catalytic activity. The invariance of activation energy of coked samples with various coke contents and the ^{31}P NMR technique as well as Xe NMR study indicates that for severe coke, such as coke content in between 7.1 and 24.6 wt.%, deactivation is mainly due to the acid site coverage, rather than pore plugging mechanism.

4. Conclusion

A TDP kinetics model was derived as the reversible second-order kinetics on toluene with activation energy of 25 ± 1 kcal/mol. It was found that with extending TOS, soft coke remains the same ca. 1.7 wt.% but hard coke content increases dramatically. Total coke rises up to 24.6 wt.% at day-on-stream of 340 days.

During initial coking period at ca. 7.1% coke content, the strong Brønsted acid site diminishes and also the pore voidage shrinks quickly, leading to the deactivation of catalyst by pore plugging. Upon extending TOS, coke laydown on the external surface of zeolite with pore voidage unaffected and the deactivation is caused by the acid site coverage. The same reversible second kinetics model is applicable for coked mordenite with coke content up to ca. 24.6%. The kinetics can be applied to estimate the relative activity of the coked at various TOS and thus is useful for cycle length estimation.

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