

Transalkylation of Toluene with 1, 2, 4-Trimethylbenzene over Large Pore Zeolites with Differing Si/Al Ratios

Faisal M. Almulla^a, Vladimir I. Zholobenko^b, John P. Waters^c and Arthur A. Garforth^{*a}

^aSchool of Chemical Engineering and Analytical science, The University of Manchester, M13 9PL, U.K.

^bSchool of Chemical and Physical Sciences, Keele University, UK

^cWilliamson Research Centre, School of Earth & Environmental Sciences, The University of Manchester, M13 9PL, UK

Arthur.garforth@manchester.ac.uk

The catalytic activity, selectivity to xylenes and time-on-stream stability were investigated in the transalkylation of toluene with 1, 2, 4-trimethylbenzene. The catalytic tests were carried out in a fixed bed reactor over zeolite Beta (Si/Al = 12.5, 75 and 150) and Y (Si/Al = 2.6, 6, 15 and 30). The operating parameters used were 400 °C, 1.0 Mpa, H₂/HC = 4 and WHSV of 5 h⁻¹. The length of each catalytic testing experiment was 50 hours, and for zeolite beta samples, the highest stability and selectivity to xylenes were achieved using the lowest Si/Al ratio with conversion of 41 wt. % and selectivity of 61 wt. %. In contrast, zeolites Y with Si/Al ratio of 2.6 showed the highest deactivation rate, whereas Y zeolites with Si/Al = 6 – 30 exhibited similar conversion (~ 27 wt. %) and selectivity to xylenes (~ 43 wt. %). The effects of Brønsted and Lewis acid sites on catalytic results are discussed.

1. Introduction

Xylene isomers are valuable raw materials for the production of many aromatic derivatives (e.g. polyesters, plastics, detergents, and others) with increasing market demand of about 6 % per year; it is expected to reach 70 MM tonnes in 2020 (Al-Khattaf, et al., 2014). As a result of recent environmental regulations which stipulate the reduction of aromatics in the gasoline pool from 36 % to less than 25% (Wang, et al., 2013), refineries are looking for alternative processes to shift the catalytic reformer product (C₉ aromatics) towards more valued xylenes. The process of transalkylation involves the reaction of heavy aromatics with toluene, e.g. 1,2,4-trimethylbenzene (40 wt.% of C₉ aromatics) is used as a representative model compound of C₉ in most transalkylation studies. The highest xylenes yield over various zeolites was obtained using a 1:1 mixture of toluene and C₉ (Aitani, et al., 2010 and Das, et al., 1994).

Catalyst lifetime is one of the key challenges in the transalkylation reaction (Tsai, et al., 1999), and the overall catalytic performance is influenced by the zeolite acidity, structure and pore dimensions. The acidity of catalyst plays a major role in manipulating the activity of the catalysts (Zaiku, et al., 2000; Lee, et al., 1998). In general, zeolites with higher acidity give a better catalyst performance. The medium pore zeolites such as ZSM-5 have been reported to undergo rapid deactivation due to the diffusivity restriction of bulky TMB molecules (Meshram, et al., 1984). However, large pore zeolites, such as Y, Beta and Mordenite, are better candidate catalysts with reduced diffusion restriction for alkyl aromatics and hence improved reaction rates.

In this work, the role of catalyst structure and acidity in the transalkylation of toluene with 1,2,4-TMB has been investigated for two large pore zeolites, namely Beta and Y with various Si/Al ratios, in terms of their activity and selectivity. The effect of time-on-stream on deactivation behaviour was also studied.

2. Materials and Methods

The main characteristics and sources of zeolite Beta and Y catalysts used are shown in Table 1. The feed was an equal-weight mixture of Toluene (Fluka > 99.7 %) and 1,2,4-TMB (Sigma-Aldrich > 98.0%), both chemicals were used as received. The catalyst powder (1 g) was pressed, crushed, sieved (250 - 425 µm) and then

placed in a stainless steel fixed bed reactor (530 mm × 10 mm ID). Zeolites were calcined in a three zone tubular furnace at 500 °C for 16 h under flowing air (30 ml/min), cooled to ambient temperature, and then heated to the reaction temperature at 1 °C/min in flowing hydrogen (70 ml/min). The liquid feed was introduced to the reactor using Jasco HPLC pump PU-980, while air and hydrogen flows were controlled using two gas flow controllers (Brooks 5880). The catalytic activity was carried out at 400 °C, 1.0 Mpa, H₂/HC = 4 and WHSV of 5 h⁻¹.

Table 1: Characteristics of tested catalysts

Sample	Catalyst	Si/Al	Form	Supplier
B1	Beta	12.5	Ammonium	Zeolyst International
B2	Beta	75	Hydrogen	ACS Material
B3	Beta	150	Hydrogen	Zeolyst International
Y1	Y	2.6	Ammonium	Zeolyst International
Y2	Y	6	Ammonium	Zeolyst International
Y3	Y	15	Hydrogen	Zeolyst International
Y4	Y	30	Hydrogen	Zeolyst International

The overall conversion (1,2,4-TMB + Toluene) and selectivity to xylenes were calculated using the following equations where m_{Tol} and m_{TMB} are the weight of toluene and 1,2,4-TMB, respectively.

$$X_{wt.\%} = \frac{(m_{Tol} + m_{TMB})_{in} - (m_{Tol} + m_{TMB})_{out}}{(m_{Tol} + m_{TMB})_{in}} * 100 \quad (1)$$

$$S_{wt.\%} = \frac{Xylenes\ Yield\ (wt.\%)}{X_{wt.\%}} * 100 \quad (2)$$

The feed and product liquid samples were analysed using a Varian 3400 Gas Chromatograph fitted with a Stabilwax Capillary Column (30 m, 0.32 mm ID, with film thickness of 1.00 µm) and a flame ionization detector (FID).

BET surface area was determined using a Micromeritics Gemini 2365 surface area analyser. The measurements were carried out by nitrogen adsorption at -196 °C using ~ 0.2 g of sample, purged for 18 h at 100 °C under a constant flow of He using a Micromeritics Flowprep 060. The Si/Al value for all tested catalysts was measured using HF digestion followed by inductively coupled plasma optical emission spectroscopy ICP-OES analysis. Approximately 7 mg of the sample was accurately weighed and 1 ml of HF acid added to digest the sample. The catalysts acidity was measured using pyridine adsorption monitored by FTIR. The catalyst activation temperature was 450 °C with the temperature ramp of 1 °C/min. Pyridine adsorption was carried out using a vacuum in situ cell and FTIR spectra were collected using a Nicolet Protege 460 and Thermo iS10 spectrometers. Following pyridine adsorption, the sample was evacuated for 20 min at 150 °C to remove physically adsorbed pyridine. The IR peaks at ~ 1455 and 1545 cm⁻¹ were used to determine the concentration of Brønsted (B) and Lewis (L) acid sites. The characterization results are listed in Table 2.

Table 2: Catalyst characterization Results

Catalyst	Mesopore area (m ² /g)	Micropore area (m ² /g)	Pore volume (m ³ /g)	Si/Al
B1	225	309	0.18	12.6
B2	261	216	0.15	82.8
B3	314	161	0.18	113
Y1	62	429	0.24	3
Y2	143	429	0.25	6.8
Y3	226	434	0.25	16.8
Y4	260	461	0.27	28.7

3. Results and Discussion

3.1 Characterization Results

Both the strength and concentration of acid sites in zeolites are affected by their aluminum content. Figure 1 presents a comparison of the acidity profiles for all tested samples. Zeolites B1 showed the total acidity with an equal concentration of Brønsted to Lewis acid sites. Dealuminated zeolites B2 and B3 showed a decrease in total acidity (~ 80 %) while the ratio of B/L increased. Over zeolite Y samples, the total acid site concentration decreases with increasing Si/Al ratio; the fraction of Lewis acid sites is decreasing whereas the number of Brønsted acid sites are very similar over Si/Al = 6 – 30.

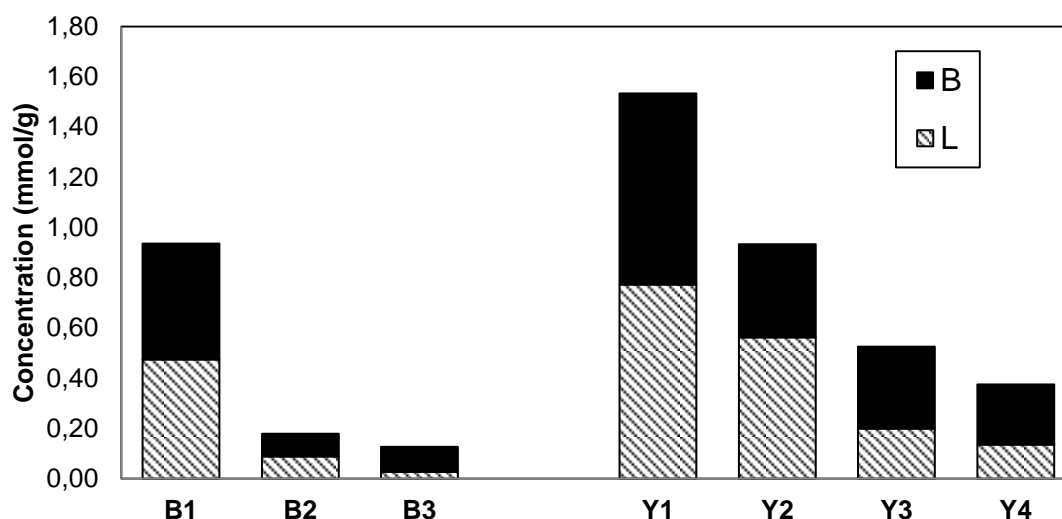


Figure 1: The concentration of Brønsted acid sites (B) and Lewis acid sites (L) over zeolites Beta and Y

3.2 Catalytic Performance

3.2.1 Effect of Time on Stream

The main reaction mechanism of transalkylation involves xylenes as primary products with other possible reactions including disproportionation (Toluene and 1,2,4-TMB), isomerization (1,2,4-TMB), and dealkylation (Waziri, et al., 2010).

The effect of time-on-stream stability among the three Beta zeolites (B1, B2 and B3) has been studied at 50 hours on stream (Figure 2a). Conversion decreases sharply in the first 6 hours, and then plateaus reaching 41 wt. % for B1 compared to 33 wt. % for B2 and B3. Selectivity towards xylenes is much higher typically between 60 – 70 % over B1, however it drops to 42 % over B2 and B3 (Figure 2b).

Zeolites Y exhibit similar but slightly lower initial activities (around 48 wt. % of conversion) but greater deactivation. Dealuminating zeolite Y from Si/Al = 2.6 to Si/Al = 6 improves the overall conversion while further dealumination makes little difference to the conversion. Selectivity for zeolites Y with Si/Al = 6 – 30 is similar to that for zeolites B2 and B3 (Figure 2d). Total acidity decreases with increasing Si/Al ratio, and Lewis acidity significantly decreases (B/L increases). The decreased acidity appears to limit secondary reaction leading to reduced coking and hence improved catalyst lifetime.

The results can be explained in terms of acidity and pore geometry. Both zeolites Beta and Y are 12 T-rings pore mouths typically of diameter 6.7 nm and 7.4 nm, respectively (Ernst, 2009), and 1,2,4-TMB is similar at 7.4 nm (Röger, et al., 1997). However, the presence of large super-cages (α -cages) in zeolite Y mean that reactant molecules can be converted to bulkier coke precursors. The pore structure of zeolite Beta prevents the formation of large molecule due to the restricted space for the relevant transition state. Hence, zeolite Y deactivates more rapidly than Beta. In addition, zeolites with a greater fraction of lewis acid site deactivate more rapidly.

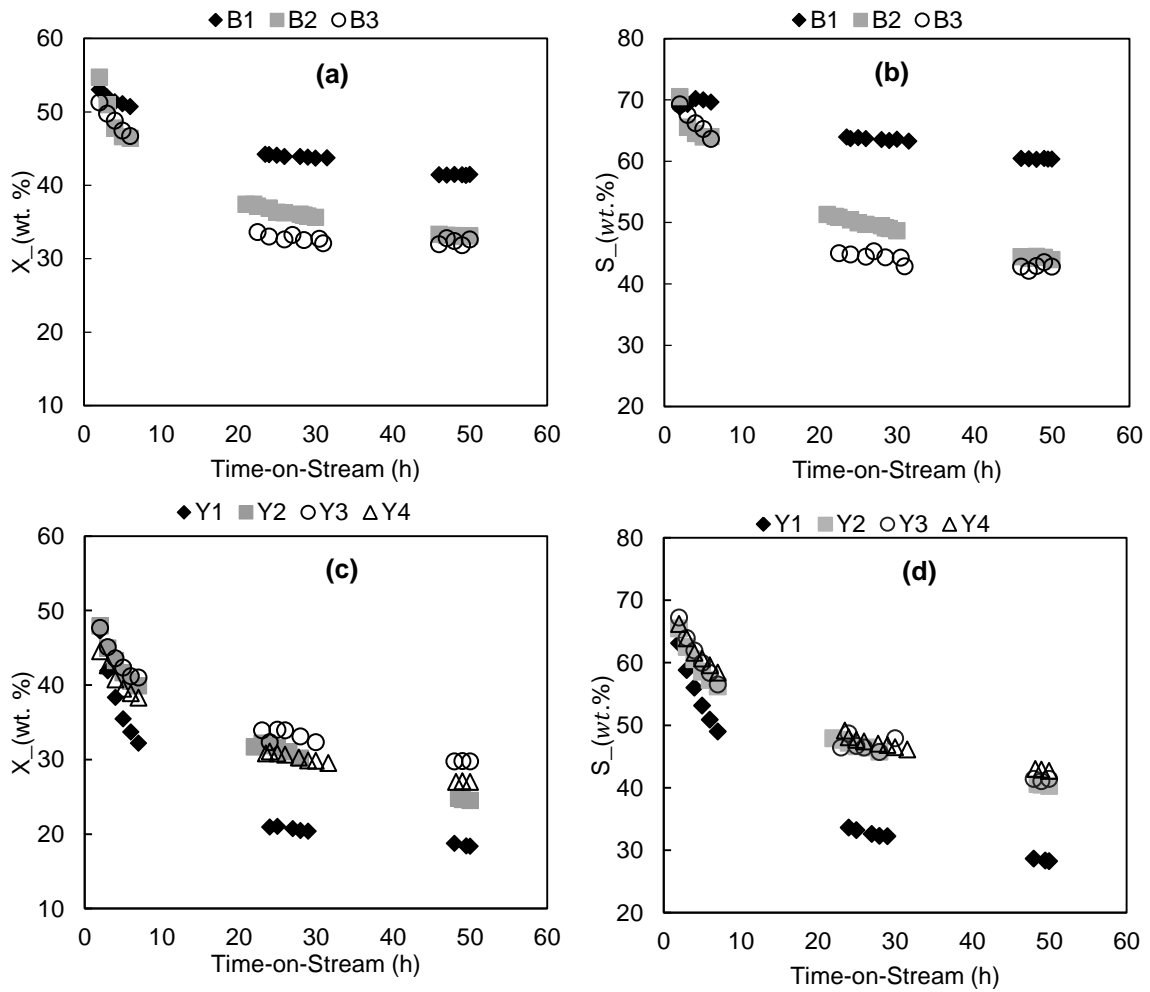


Figure 2: Catalytic conversion (a & c) and selectivity (b & d), $T = 400\text{ }^\circ\text{C}$, $P = 1.0\text{ Mpa}$, $H_2/HC = 4$, and $WHSV = 5\text{ h}^{-1}$

3.2.2 Para-xylene (p-xylene) Selectivity

Within the xylenes product fraction, the value of para xylene in thermodynamic equilibrium is 24 % (Dumitriu et al., 2002). The experimental p-xylene selectivity falls within the range of thermodynamics equilibrium (Figure 3). These results indicate that the tested large pore zeolites possessing 12-ring pores show virtually no shape-selectivity effects with regards to the distribution of xylene isomers.

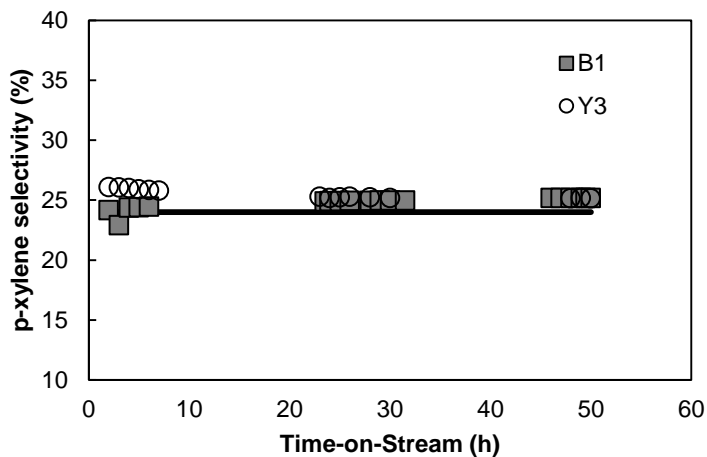


Figure 3: Selectivity to p-xylene over B1 and Y4

3.2.3 Product Selectivity

In the transalkylation reaction of toluene with 1,2,4-TMB, the major products are benzene, xylenes (p-, m-, and o-), TMBs (1,2,3-, 1,2,4-, and 1,3,5-) and TeMBs (1,2,3,4-, 1,2,3,5-, and 1,2,4,5-). At time = 50 hours, the samples of each of the tested zeolites were shown to have different product selectivity (Figure 4). The product selectivity has been calculated using the following equation:

$$S_a = \frac{Y_a}{Y_{\text{benzene}} + Y_{\text{xylenes}} + Y_{\text{TMBs}} + Y_{\text{TeMBs}}} * 100 \quad (3)$$

Considering the Beta zeolites, B1 had a relatively higher benzene selectivity (2.0 wt. %) compared to B2 and B3 (0.94 wt. %) which can be attributed to the higher concentration of Brønsted acid sites (Figure 1). The high xylene production over B1 clearly indicates the influence of acidity of catalytic stability resulting in ~ 28 % higher selectivity than that for B2 and B3 with higher Si/Al. It has been stated that higher Si/Al enhances the isomerization reaction of TMBs (Cejka, et al., 2004). Indeed, B1 zeolite has the lowest selectivity of ~ 28 wt. % compared to ~ 45 and ~ 47 wt. % over B2 and B3. The TeMBs (C10s) produced from the disproportionation of 1,2,4-TMB show approximately an equal selectivity of 8 – 9 wt. %.

In contrast, the selectivity to benzene over all Y zeolites was equal to 1.0 – 1.2 wt. %. The xylene selectivity is varied with Y1 showing the lowest value of 28.7 wt. %, whereas the dealuminated samples produce 40 – 43 wt. %. Moreover, isomerization from 1,2,4-TMB to 1,3,5- and 1,2,3-TMB is the highest over Y1 at 60 wt. %, followed by 46 wt. % for Y2. The selectivity values for C10s were increase from 10 to 14 wt. % with increased Si/Al.

The low benzene content (≤ 2 wt. %) over all tested samples indicates that disproportionation of toluene in this reaction is negligible.

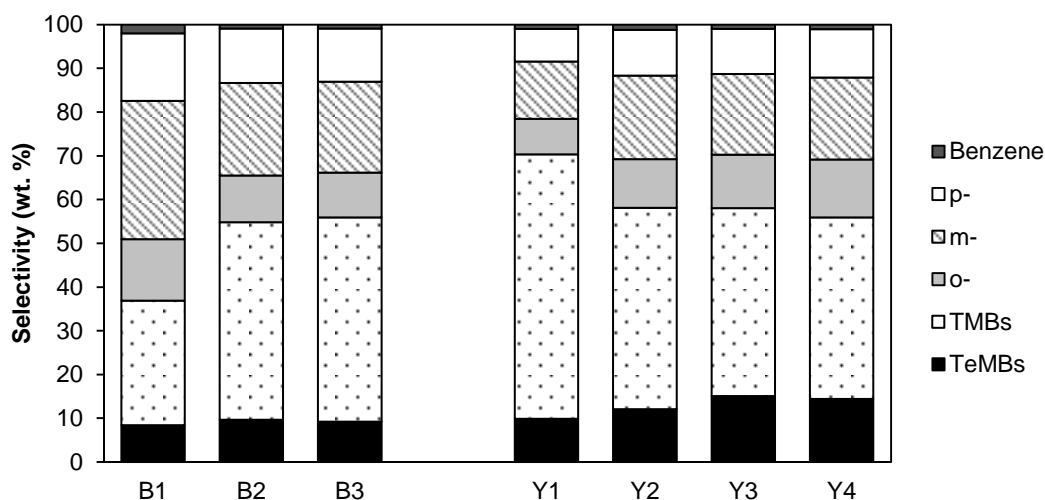


Figure 4: Product selectivity for all tested catalysts at time = 50 hours, $T = 400$ °C, $P = 1.0$ Mpa, $H_2/HC = 4$, and $WHSV = 5$ h^{-1}

4. Conclusions

This study shows the effect of zeolite structure and acidity on the catalytic activity and selectivity in the transalkylation reactions over two large pore zeolites, Beta and Y with various Si/Al ratios. The key catalytic properties such as time-on-stream stability, the total feed conversion and xylene's selectivity have been explored for a series of dealuminated zeolites with a range of Si/Al ratios and concentrations of Brønsted and Lewis acid sites. Zeolite Beta with the lowest Si/Al ratio shows the slowest rate of deactivation, while the dealuminated zeolite Y samples ($Si/Al = 6 - 30$) demonstrate an increasing conversion with the order of Si/Al ratios $15 \geq 30 > 6$ with little effect on selectivity. Further research is underway investigating the modification of zeolite Beta as a potential catalyst for transalkylation of aromatics.

Acknowledgements

The authors would like to acknowledge the financial support from Saudi Aramco and the contributions of Mr. Loris Doyle, Mrs. Shahla.Khan and Mrs. Gemma.Chapman.

References

- Aitani, A., Ali, A., Waziri, S. and Al-Khattaf, S. 2010. Production of Xylenes from Toluene and 1,2,4-Trimethylbenzene over ZSM-5 and Mordenite Catalysts in a Fluidized-Bed Reactor. *Chemical Engineering & Technology*, 33(7), 1193-1202.
- Al-Khattaf, S., Ali, S., Aitani, A., Žilková, N., Kubička, D. and Čejka, J. 2014. Recent Advances in Reactions of Alkylbenzenes Over Novel Zeolites: The Effects of Zeolite Structure and Morphology. *Catalysis Reviews*, 56(4), 333-402.
- Čejka, J., Kotrla, J. and Krejčí, A. 2004. Disproportionation of trimethyl benzenes over large pore zeolites: catalytic and adsorption study. *Applied Catalysis A: General*, 277(1-2), 191-199.
- Das, J., Bhat, Y. and Halgeri, A. 1994. Transalkylation and disproportionation of toluene and C9 aromatics over zeolite beta. *Catalysis Letters*, 23(1-2), 161-168.
- Dumitriu, E., Guimon, C., Hulea, V., Lutic, D. and Fechete, I. 2002. Transalkylation of toluene with trimethylbenzenes catalyzed by various AFI catalysts. *Applied Catalysis A: General*, 237(1-2), 211-221.
- Ernst, S. 2009. *Advances in nanoporous materials*. 1st ed. Amsterdam: Elsevier Science, 97-149.
- Röger, H., Möller, K. and O'Connor, C. 1997. The transformation of 1,2,4-trimethylbenzene A probe reaction to monitor external surface modifications of HZSM-5?. *Microporous Materials*, 8(3-4), 151-157.
- Lee, Y., Park, S. and Rhee, H. 1998. Transalkylation of toluene and 1,2,4-trimethylbenzene over large pore zeolites. *Catalysis Today*, 44(1-4), 223-233.
- Meshram, N., Kulkarni, S. and Ratnasamy, P. 1984. Transalkylation of toluene with C9 aromatic hydrocarbons over ZSM5 zeolites. *Journal of Chemical Technology and Biotechnology. Chemical Technology*, 34(3), 119-126.
- Tsai, T. 1999. Disproportionation and transalkylation of alkylbenzenes over zeolite catalysts. *Applied Catalysis A: General*, 181(2), 355-398.
- Wang, Y. and Ercan, C., 2013. Process for the Production of Xylenes and Light Olefins from Heavy Aromatics. US20130261365 A1.
- Waziri, S., Aitani, A. and Al-Khattaf, S. 2010. Transformation of Toluene and 1,2,4-Trimethylbenzene over ZSM-5 and Mordenite Catalysts: A Comprehensive Kinetic Model with Reversibility. *Industrial & Engineering Chemistry Research*, 49(14), 6376-6387.
- Zaiku, X., Qingling, C., Chengfang, Z., Jiaqing, B. and Yuhua, C. 2000. Influence of Citric Acid Treatment on the Surface Acid Properties of Zeolite Beta. *The Journal of Physical Chemistry B*, 104(13), 2853-2859.