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Catalytic Studies with Dealuminated Y Zeolite

Part 2.—Disproportionation of Toluene

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Toluene disproportionation has been studied on a series of hydrothermally dealuminated Y zeolite catalysts, both in the 'as prepared', unextracted state and following extensive extraction of non-framework aluminium with aqueous Na_2H_2EDTA (H_4EDTA = ethylenediamine tetracetic acid). Extraction had negligible effect on the framework aluminium content, which ranged from 13–25 Al atoms per unit cell, but reduced the non-framework aluminium to an average of five Al atoms per unit cell. The initial activity at 673 K for both unextracted and extracted catalysts, using a microreactor in a continuous flow system, arose from a limited concentration of strong Brønsted-acid sites. These were generated by synergic interaction between framework hydroxy groups and non-framework aluminium species. After 4–20 h on stream a pronounced maximum in the activity was observed with all catalysts. Since considerable coke had formed at this stage, 'catalytically active coke' was considered to be the seat of reaction, with an active site concentration directly related to the total Brønsted acidity of the freshly activated zeolite. Two mechanisms, involving either proton addition to, or hydride ion abstraction from, the reactant toluene molecule, are suggested; the contribution these each make depends on the extent of reaction with respect to complete poisoning by coke.

Early studies of the disproportionation of toluene to benzene and dimethylbenzene on Y zeolites, made in pulse-flow microreactors at 623–673 K, established that Brønsted-acid centres were the seat of catalytic acitivity.[1–3] However, a maximum in the activity of HY generated from NH_4Y at a temperature above that for complete NH_3 evolution,[1] the high initial activity of AlHY compared with HY,[2] and the small fraction of the total acidity active with stabilised Y zeolites,[3] pointed to the need for superacid sites to effect reaction. Such superacidity can be achieved by synergic interaction between the framework hydroxy groups of Brønsted acidity with the extra-framework Lewis-acid centres associated with charge-balancing cations containing Al or with polymeric oxoaluminium species.[4,5] More recent studies of toluene disproportionation, using continuous-flow microreactors, include comparisons of the activity of unstabilised[6] and stabilised[7,8] Y zeolites with those of HZSM-5 and HZSM-11. Ultrastable Y was found[7] to be considerably more active than HZSM-5 of similar framework aluminium content under the same reaction conditions at 723 K. Further measurements[8] with ultrastable Y led to the conclusion that the concentration and acid strength of the active centres is regulated by the non-framework aluminium content.

The fall in activity for toluene disproportionation on Y zeolites with pulse number,[2,3] or time-on-stream,[6–9] is accompanied by the increasing retention of carbonaceous compounds, termed 'coke', within the zeolite pore system. At temperatures where the disproportionation reaction predominates, the coke consists of polyaromatic molecules of size approaching that of the zeolite supercages.[9] Albeit with HZSM-5, studies show that both benzene and toluene can form tricyclic aromatics in a reaction where biphenyl and diphenylmethane are the primary condensation products.[10]

The present paper reports an investigation of toluene disproportionation on the same series of hydrothermally dealuminated Y zeolites previously used in studies of ethylbenzene disproportionation.[11] Activity measurements at 673 K were made with 'as prepared' catalysts and again following extraction of non-framework aluminium with Na_2H_2EDTA. Since extraction had minimal effect on the framework structure, this permitted the catalytic effects of non-framework aluminium to be assessed for a reaction which demands very strong acid sites. Unlike previous studies,[2,3,6–9] the activity passed through a maximum after 4–20 h on stream; this is attributed to the formation of coke which is catalytically active.

Experimental

Catalysts

The catalysts were prepared by steaming samples from a single batch of highly exchanged NH_4Y zeolite at six temperatures between 823 and 1073 K.[11] Non-framework aluminium was extracted by treatment with aqueous Na_2H_2EDTA followed by aqueous NH_4Cl. The unextracted catalysts are designated HYSTx where x is the final steaming temperature, and extracted catalysts are designated HYSTxEX. Our earlier paper[11] gives details of the determination of the framework aluminium content per unit cell, Al_F, by infrared spectroscopy, and of the non-framework aluminium content per unit cell, Al_{NF}, from the difference between Al_F and the total aluminium content per unit cell, Al_T, derived from bulk Si : Al ratios. Values of Al_F, Al_{NF} and the acidity per gram are given in Table 1 for the twelve dealuminated catalysts, the starting material NH_4YLS and a highly exchanged sample NH_4Y. Further information on the properties of these catalysts, including specific micropore and mesopore volumes, has previously been given.[11]

Catalytic Activity Measurements

The majority of activity measurements of toluene disproportionation were made using a continuous-flow microreactor system operating at a total pressure of 1 atm†, where the catalyst was in the form of a thin layer of powder supported on a disc of sintered silica fused to the walls of a tubular reaction vessel. Accurately weighed catalyst samples corresponding to *ca.* 20 mg of dry zeolite were activated within the silica reaction vessel at 673 K, unless stated otherwise, for 16 h in a 40 cm^3 min^{-1} flow of helium. Disproportionation was followed as a function of time-on-stream with a 30 cm^3 min^{-1} flow of toluene (884 Pa) in helium passing through the catalyst bed. Samples of the product

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† 1 atm = 101 325 Pa.

Table 1 Catalysts and their activities for toluene disproportionation at 673 K

catalyst	Al_F/atom per unit cell	Al_{NF}/atom per unit cell	acidity /mmol g^{-1}	$r_{B+DMB}/10^{17}$ molecule g^{-1} s^{-1} initial	maximum	total conversion of toluene to B + DMB /10^{22} molecules g^{-1}	carbon on spent catalyst/wt.%	molecules of toluene to B + DMB/molecules of toluene to coke
NH_4Y	56	0	3.69	3.89	8.84	0.56	11.8	6
NH_4YLS	40	13	2.52	2.71	12.38	1.60	15.7	12
HYST823	24	41	1.29	8.02	10.59	1.99	15.1	16
HYST823(H_2)[a]	24	41	1.29	6.88	8.72	2.72	15.2	21
HYST823EX	25	5	1.74	3.06	12.78	3.27	17.9	21
HYST823EX(H_2)[a]	25	5	1.74	2.10	10.91	4.78	17.8	31
HYST873	22	44	1.06	5.41	7.24	1.54	15.0	12
HYST873EX	22	6	1.46	2.60	11.02	2.87	18.2	19
HYST923	18	49	0.67	2.04	4.44	1.10	15.2	9
HYST923EX	20	4	1.28	1.72	9.45	2.43	18.7	15
HYST973	16	52	0.58	1.54	3.25	1.03	15.6	8
HYST973EX	17	6	1.17	1.30	8.91	2.41	18.9	14
HYST1023	15	54	0.54	1.28	2.89	1.13	15.4	9
HYST1023EX	16	5	1.12	1.03	8.56	2.65	19.3	15
HYST1073	13	56	0.49	1.19	2.24	0.93	15.3	7
HYST1073EX	13	4	0.95	0.71	5.62	2.12	17.7	14

[a] Experiments with H_2 carrier gas.

stream were injected automatically at controlled intervals into a Pye Unicam GCD gas chromatograph, with flame ionisation detection, coupled to a Pye Unicam PU4811 computing integrator. The product mixture was separated in a 1.5 m column of 10% Apiezon L on diatomite C at 373 K. *p*- and *m*-dimethylbenzene isomers remained unresolved at this temperature, but frequent measurements of overall activity were considered to be of greater interest than individual rates for the three dimethylbenzene isomers. For all the catalysts studied, toluene disproportionation was accompanied by the formation of carbonaceous residues which eventually totally poisoned the catalysts. Following purging with helium for 30 min at 673 K all spent catalysts were allowed to cool to room temperature in the same gas and were subsequently analysed for carbon content using a Perkin-Elmer 204B elemental analyser.

To measure the effects of temperature on reaction rate, a constant surface cleanliness is required if meaningful results are to be obtained. To this end, activities were determined with the same mass of catalyst under pulse-flow conditions, such that the total passage of reactant necessary to construct a ten-point Arrhenius plot corresponded to less than 1 min of continuous reactant-mixture flow.

Results and Discussion

Time-on-stream Effects

The activity of the zeolite catalysts for toluene disproportionation at 673 K was determined as function of time-on-stream, with initial measurements after 0.15 h and then at intervals until total catalyst poisoning had taken place. Activities expressed as the sum of the rates of benzene (B) and dimethylbenzene (DMB) formation r_{B+DMB} against time-on-stream are presented for unextracted catalysts in Fig. 1 and for Na_2H_2EDTA-extracted catalysts in Fig. 2. The figures show that all samples exhibited a progressive increase in activity, although for some of the more active catalysts this was proceeded by an initial decay in activity over the first 2 h. The activity was found to reach a maximum at between 4 and 20 h on stream; the time at which this occurred increased with the initial steaming temperature. The following deactivation proceeded more rapidly than the activation. Values for r_{B+DMB} after 0.15 h on stream and at the maxima are given in Table 1. Ratios of the rate of formation of benzene to that of dimethylbenzene r_B/r_{DMB} were approximately unity throughout the reaction, which is consistent with 'clean' disproportionation. Further alkylation of dimethylbenzene to trimethylbenzene only occurred in trace amounts, probably due to a low partial pressure of dimethylbenzene, since the extent of toluene conversion rarely exceeded 10%. However, after catalytic runs, a very small quantity of relatively involatile material was found to have condensed within the reaction vessel in the cold zone beyond the furnace. Mass spectrometric detection of parent ions at *m*/*z* 178 and 192, together with appropriate UV–VIS spectra for solutions in hexane, showed the condensed material to be a mixture of anthracene and methylanthracene. Total numbers of toluene molecules converted to benzene and dimethylbenzene, determined by the graphical integration of Fig. 1 and 2, are given in Table 1. Consideration of Table 1 shows that extraction of non-framework aluminium from material steamed at any one temperature invariably decreased the initial value for r_{B+DMB}, but invariably increased the maximum value and the total conversion to benzene and dimethylbenzene.

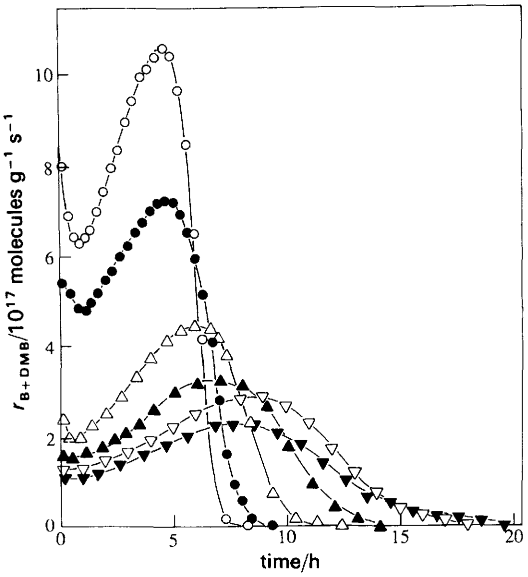

Fig. 1 The activity of unextracted, dealuminated Y zeolite for toluene disproportionation as a function of time-on-stream at 673 K: ○, HYST823; ●, HYST873; △, HYST923; ▲, HYST973; ▽, HYST1023; ▼, HYST1073

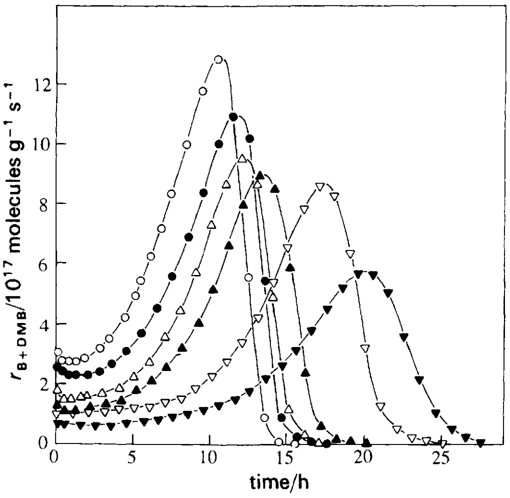

Fig. 2 The activity of Na_2H_2EDTA-extracted, dealuminated Y zeolite for toluene disproportionation as a function of time-on-stream at 673 K: ○, HYST823EX; ●, HYST873EX; △, HYST923EX; ▲, HYST973EX; ▽, HYST1023EX; ▼, HYST1073EX

Although separation of *o*-, *m*- and *p*-dimethylbenzene was incomplete in the present experiments, a $(m + p)/o$ composition ratio of *ca.* 3 was observed for all catalysts, but increased close to the full time-on-stream. Since the thermodynamic equilibrium distribution at 673 K gives a $(m + p)/o$ ratio of 3.2, there is no evidence for product-shape selectivity favouring *p*-dimethylbenzene, except when pore filling with carbonaceous residues was almost complete.

Carbonaceous Residue Formation

Total carbon contents of the spent catalysts following the time-on-stream experiments are given in Table 1. To assess the rate of carbonaceous residue or coke formation, a series of experiments were conducted with HYST823. The standard catalyst procedure was followed, but after a given time-on-stream at 673 K the reactant flow was stopped and the catalyst purged with helium at that temperature before cooling and determining the carbon content. In this way the progressive formation of carbonaceous residue was monitored at seven times before poisoning was complete; the results, together with r_{B+DMB} for HYST823, are given in Fig. 3. The sigmoid curve shows that the minimum activity occurs at *ca.* 10% of the carbon content associated with total poisoning, whilst the maximum activity occurs at *ca.* 55% of that carbon content. This suggests that reaction on catalytically active coke is responsible for the peak in activity occurring after a reaction time of *ca.* 4.8 h. From Table 1, the mean ratio of the carbon content of fully poisoned extracted catalysts to that of the corresponding unextracted catalysts is 1.21 ± 0.03. This is closer to the corresponding mean ratio of micropore volumes, 1.21 ± 0.05, than to that of mesopore volumes, 2.13 ± 0.27 (data from Table 2 of ref. 11) reinforcing the view[9,12] that carbon associated with poisoning resides within micropores. The final column of Table 1 presents ratios of the number of toluene molecules converted to benzene and dimethylbenzene to the calulated number converted to coke. In all cases, coke formation is suppressed by the extraction of non-framework aluminium.

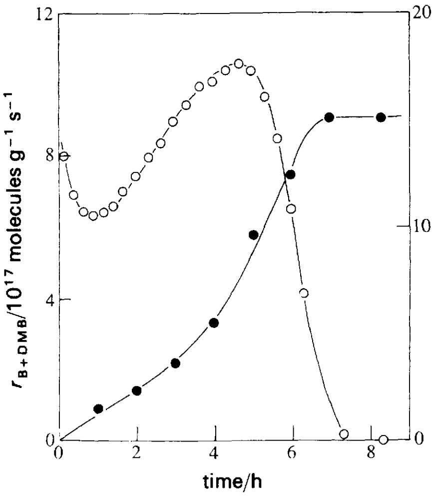

Fig. 3 Carbonaceous residue formation and catalytic activity of HYST823 as a function of time-on-stream at 673 K: ○, r_{B+DMB}; ●, carbon content following termination of reaction

The activity of HYST823 and HYST823EX for toluene disproportionation was determined as a function of time-on-stream at 673 K with either He or H_2 as the carrier gas in the reactant mixture. The results presented in Fig. 4 show that using H_2 almost doubles the time required to attain the maximum activity that was observed with He carrier. Although the maximum value for r_{B+DMB} is lower with H_2, Table 1 shows that the total toluene coversion and the ratio of toluene molecules converted to benzene and dimethylbenzene to those converted to coke are both appreciably higher with H_2.

Activation Temperature Effects

The results presented above follow activation at 673 K, which should largely avoid structural dehydroxylation[13] and so maximise the Brønsted-acid site concentration. Any Lewis-acid sites, which may be involved in synergic relationships with Brønsted-acid sites, should thus be associated with existing non-framework aluminium species. The framework Si : Al ratios of the present dealuminated Y zeolites lay between 7 and 14, giving the lattice greater thermal stability than the HY zeolites (Si : Al ≈ 2.5 : 1) where increases in activity followed activation above 673 K.[2,3] Nevertheless, measurements were made to assess the effect of activation temperatures above 673 K on toluene disproportionation activity. In Fig.

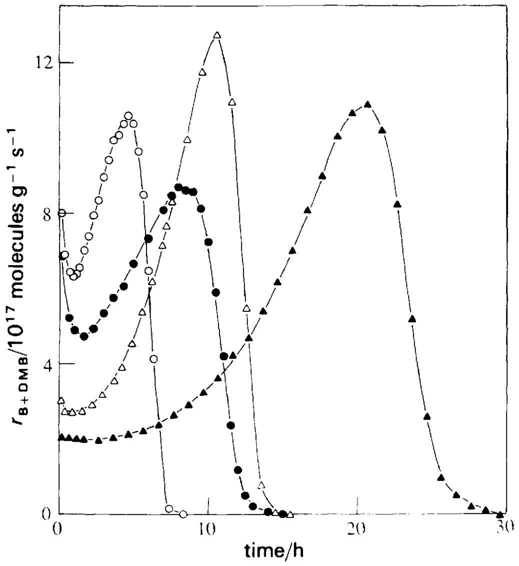

Fig. 4 The activity of HYST823 and HYST823EX for toluene disproportionation as a function of time-on-stream at 673 K, with either He or H_2 as the carrier gas: ○, HYST873 with He; ●, HYST823 with H_2; △, HYST923EX with He; ▲, HYST823EX with H_2

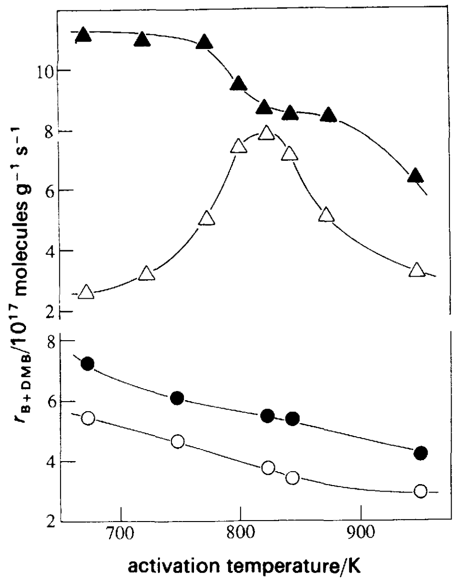

Fig. 5 The activity of HYST873 and HYST873EX for toluene disproportionation at 673 K as a function of activation temperature: ○, HYST873 initial activity; ●, HYST873 maximum activity; △, HYST873EX initial activity; ▲, HYST873EX maximum activity

5, a progressive decrease in both the initial and maximum activity of HYST873 is observed as the activation temperature is increased from 673 to 949 K. Any synergic increase in activity of framework hydroxy-group sites, through an inductive effect with Lewis sites generated during dehydroxylation, appears to be negated by an overall decrease in the concentration of Brønsted-acid sites. Table 1 shows that $Al_{NF} > Al_F$ for HYST873, suggesting that any further generation of Lewis acidity makes no appreciable increase to the acid strength of the framework hydroxy groups. However, when a similar series of measurements were made with HYST873EX, the initial activity increased with activation temperature, passed through a maximum at *ca.* 823 K before decreasing as the temperature approached 949 K. However, the maximum in activity fell with activation temperature, though not as smoothly as HYST873. Two factors may account for the different behaviour of the initial activity in HYST873 and HYST873EX. First, HYST873EX has been cation exchanged with NH_4^+, but only the strongest Brønsted-acid sites, which release NH_3 above 673 K, are catalytically active. This is in contradistinction to HYST873, which is totally in the hydrogen form after the hydrothermal method of preparation. Secondly, since $Al_{NF} = 6$ for HYST873EX, it is necessary to generate further non-framework aluminium, or the associated Lewis acidity, to enhance the catalytic activity.[5,14,15] Both catalysts show a fall in the maximum activity with increasing activiation temperature. This difference in behaviour from the initial activity, may reflect that the reaction proceeds on catalytically active coke at this stage. The mean values for the carbon content of the spent catalysts from these experiments, 15.1 ± 0.1 wt.% for HYST873 and 18.0 ± 0.2 wt.% for HYST873EX, are in excellent agreement with the corresponding values given in Table 1.

Temperature Dependence of Catalytic Activity

Experiments to determine the effect of temperature on toluene disproportionation were made under pulse-flow conditions using catalysts previously activated at 673 K. Activity measurements were made with each catalyst sample at ten temperatures in the range 553–723 K, selected such that the extent of reaction did not exceed 6% for any one pulse of reactant. Where this is so, the reactor is operating in the differential mode and the response of the gas chromatograph is directly proportional to the amount of each product. It follows that meaningful activation energies can be obtained from Arrhenius plots of the area of either the benzene or dimethylbenzene peaks given by the computing integrator. Activation energies obtained this way for all 12 dealuminated Y zeolites are given in Table 2; the probable error on each value does not exceed ±3 kJ mol^{-1}. No significant difference in the mean activation energy can be seen between that determined from benzene production ($E_a = 71.6 \pm 3.9$ kJ mol^{-1}) and that determined from dimethylbenzene production ($E_a = 72.3 \pm 5.5$ kJ mol^{-1}). More importantly, there is no significant difference between the mean value for unextracted catalysts ($E_a = 70.5 \pm 4.7$ kJ mol^{-1}) and that for extracted catalysts ($E_a = 72.8 \pm 4.7$ kJ mol^{-1}). It follows that differences in activity between catalysts probably arise from differences in the concentration of active centres rather than from differences in energetics.

Activity Dependence on Acid Site Concentration

The initial activity and maximum activity of both unextracted and extracted dealuminated Y zeolites at 673 K is given as a function of the Brønsted-acid site concentration in Fig. 6. These concentrations, given in Table 1, were previously determined[11] by the temperature-programmed desorption of NH_3; they decrease with increasing steaming temperature and are invariably greater following extraction of non-framework aluminium. Considering initial activities, it is evident from Fig. 6 that the fraction of Brønsted-acid sites that are effective in catalysis is greater for the unextracted zeolites than for the extracted zeolites. This we attribute to synergic interactions between the Brønsted sites and extrastructural hydroxoaluminium species; for unextracted zeolites $Al_{NF} > Al_F$, whilst for extracted zeolites $Al_{NF} < Al_F$ where the average value for Al_{NF} is 5. Considering the maximum in activity, a single linear plot incorporates points for both extracted and unextracted zeolites. Accepting that the reaction proceeds on catalytically active coke, it appears that all, or a constant fraction of, the acid sites originally available as hydroxy groups generate active sites.

Mechanistic Considerations

At this stage it is appropriate to consider possible mechanisms for toluene disproportionation on the present catalysts. A dealkylation–alkylation mechanism, as previously proposed for ethylbenzene disproportionation,[11] is inapplicable

Table 2 Activation energies for toluene disproportionation

	activation energy/kJ mol^{-1}	
catalyst	from benzene formation	from dimethylbenzene formation
HYST823	75	77
HYST823EX	70	71
HYST873	71	77
HYST873EX	73	76
HYST923	64	62
HYST923EX	76	77
HYST973	69	72
HYST973EX	67	61
HYST1023	66	68
HYST1023EX	76	77
HYST1073	71	74
HYST1073EX	75	75

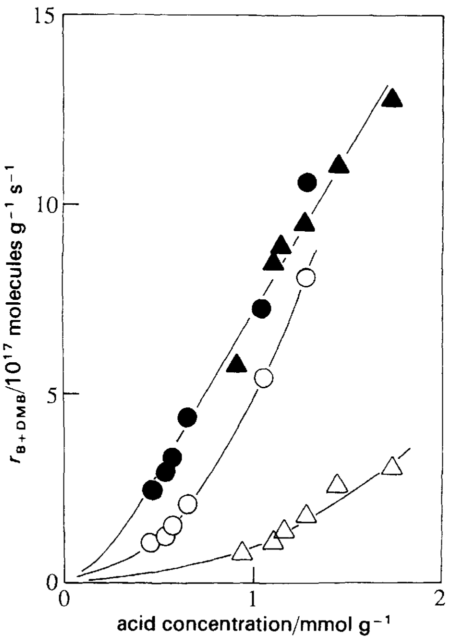

Fig. 6 The activity for toluene disproportionation at 673 K as a function of acid-site concentration: ○, initial activity and ●, maximum acitivity of unextracted HYST*x* catalysts; △, initial activity and ▲, maximum activity of extracted HYST*x*EX catalysts

due to the instability of the CH_3^+ carbocation.[16] Fig. 7 presents a possible mechanism, where protonation of a toluene molecule is followed by transfer of the methyl group *via* a bimolecular transition complex. The dimethylbenzene carbocation must then transfer a proton directly, or indirectly *via* the zeolite framework, to another toluene molecule to continue reaction. This mechanism explains the role of strong Brønsted-acid sites in protonating the aromatic ring, but does not account for the formation of fused-ring aromatics which act as both the precursors and components of coke.[9,10,17]

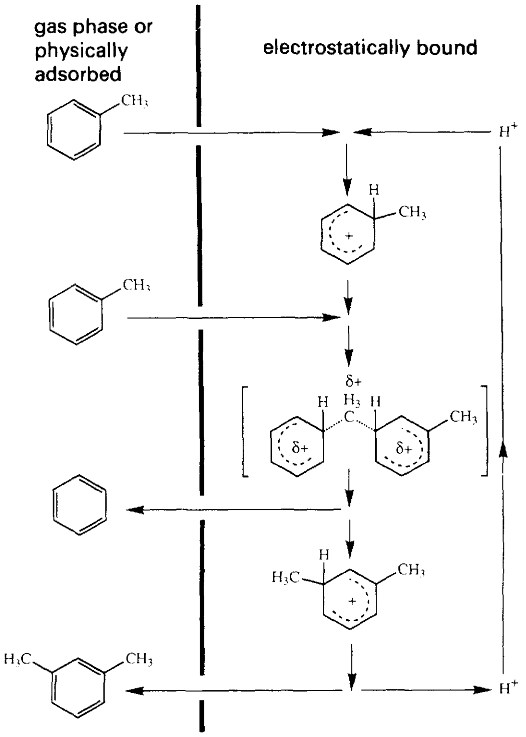

Fig. 7 Scheme for toluene disproportionation by protonation of toluene to form a toluene carbocation

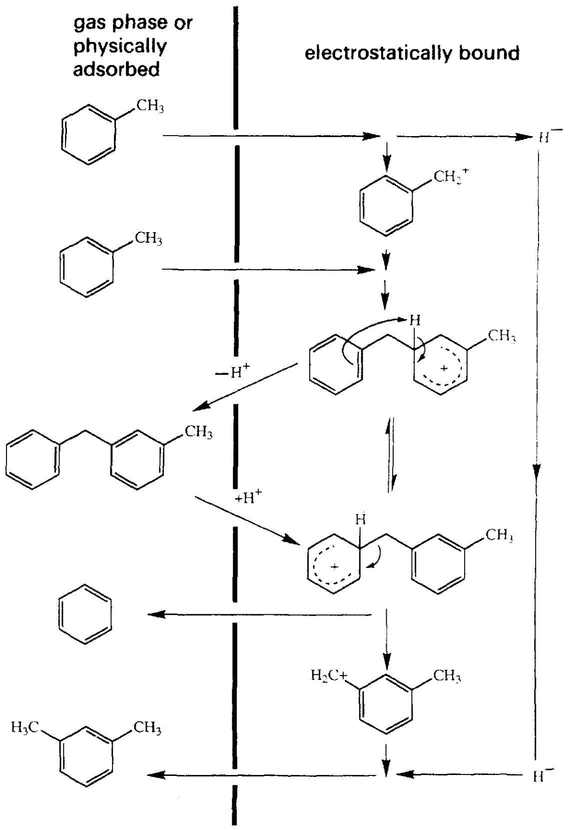

Fig. 8 Scheme for toluene disproportionation by hydride ion abstraction from toluene to form a benzyl cation

The second possible mechanism, presented in Fig. 8, requires the formation of a diarylmethane intermediate.[18] Initial generation of the benzyl cation requires hydride ion abstraction from the methyl group of the toluene molecule, which is most likely to occur by protonation of a C—H bond of the methyl group followed by loss of molecular hydrogen. The diarylmethane carbocation may then lose a proton to form a discrete intermediate, where subsequent protonation of the methyl–phenyl bond leads to benzene and the dimethylbenzene carbocation. Alternatively, rearrangement of the diarylmethane carbocation may yield the same products directly. This scheme also provides a route for coke formation starting from the diarylmethane intermediate. For example, aromatisation of the *ortho*-substituted isomer to anthracene, by facile proton and hydride ion-transfer steps,[9,10] followed by further addition steps to yield the complex polycyclic aromatics that constitute coke.

The coke formed within the zeolite participates in the mechanism associated with the peak in activity observed about 4–20 h on stream. The sensitivity of the timing of the peak to structural and extrastructural aluminium content and to the use of He or H_2 as the carrier gas, emphasises the importance of the chemical constitution of the coke. In the first mechanism, Fig. 7, the unsaturated coke may participate in the proton transfer from the protonated dimethylbenzene to a further toluene molecule, so that the proton is recycled without return to the zeolite lattice. The presence of coke is thus effectively promoting the acidity of the framework hydroxy groups, so that maximum activity is more indicative of the total number of Brønsted-acid sites than upon the number of superacid sites associated with the initial activity. Such an explanation would also account for the high maximum activities achieved by NH_4Y and NH_4YLS, which initially possess a high concentration of weak Brønsted-acid sites due to the low Si : Al ratio of the framework. In the second mechanism, Fig. 8, the dimethylbenzene carbocation may extract a hydride ion from a polyatomatic coke molecule, thus forming dimethylbenzene and a coke carbocation. Subsequent hydride abstraction from a toluene molecule by the coke carbocation forms the benzyl cation which continues the reaction. Chen *et al.*[19] have suggested that a radical mechanism may be involved in the formation of benzyl cations during the disproportionation of toluene over HY and other zeolites. Using spectroscopic techniques they detected the presence of both benzyl radicals and diarylmethane carbocations; a good corrlation between disproportionation activity and the ability of the zeolite to form diarylmethane carbocations was observed. It follows that coke may participate in a radical mechanism for benzyl cation formation in the present work, where abstraction of a hydrogen atom to form a benzyl radical is followed by electron transfer. Whatever the mechanism for benzyl cation formation on coke might be, it should result in a maximum disproportionation activity directly related to the total number of Brønsted-acid sites.

Conclusions

The initial activity for toluene disproportionation at 673 K, with both unextracted and extracted HY zeolites, is catalysed by a limited concentration of strong Brønsted-acid sites. These arise from synergic interaction between framework hydroxy groups and extrastructural aluminium species. Two mechanisms, involving either proton addition or hydride ion abstraction from the reactant toluene molecule, are proposed and it is probable that both contribute to the reaction.

The clear maximum in activity for toluene disproportionation presently observed after 4–20 h on stream is not known to have been previously reported. The time to achieve this maximum rate is sensitive to both the catalyst and carrier gas (He or H_2) used and occurs after considerable coke formation. Reaction is associated with 'catalytically active coke', where the concentration of active sites is directly related to the total Brønsted-acid site concentration of the freshly activated zeolite. Both mechanisms considered for the initial reaction are applicable, but, since the activity eventually falls to zero through complete coking, the second mechanism producing the diarylmethane intermediate must occur in part.

Considering the activity on a unit weight basis, the initial activities of unextracted catalysts are consistently greater than those of extracted catalysts. However, the maximum activities of the extracted catalysts are the greater, so that the total toluene conversion to useful products prior to complete poisoning by coking is greater with extracted catalysts. This points to possible catalytic advantages to be gained from the partial extraction of non-framework aluminium from hydrothermally treated Y zeolites.

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