Alkylation of toluene with 1-dodecene over HFAU zeolite. Deactivation and regeneration

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The alkylation of toluene with 1-dodecene was carried out over a HFAU zeolite (total and framework Si/Al ratio = 25) under the following conditions: fixed-bed reactor, 90 °C, molar toluene/dodecene ratio of 3, WHSV = 10 h^{-1}. Monododecyltoluenes are selectively formed, bidodecyltoluenes appearing only in low amounts at a complete conversion of dodecene. Tridodecyltoluenes are also formed inside the supercages but cannot desorb from the zeolite. These compounds, mainly located in the outer part of the crystallites are responsible for catalyst deactivation. However, tridodecyltoluenes can be completely removed by treatment under toluene flow, which allows a complete regeneration of the catalyst. This removal occurs by transalkylation between tridodecyltoluenes and toluene molecules with a final formation of monododecyltoluenes. At least, the first transalkylation steps occur between toluene in the liquid phase and tridodecyltoluenes in the zeolite pores (pore mouth catalysis).

Keywords: toluene alkylation, HFAU zeolite, coking, regeneration, pore mouth catalysis

1. Introduction

Linear monoalkylbenzenes (LAB), which are intermediates of the production of biodegradable surfactants, are prepared by benzene alkylation with linear C_{10}–C_{13} alkenes [1–3]. In the industrial processes, one of the main problems is the use of corrosive and polluting acid catalysts (HF, $AlCl_3$). That is why a great effort is now being made for their substitution by solid acids such as zeolites which do not present this inconveniency [4–11]. However, while these solid catalysts present a high initial activity and can be very selective for the production of 2-phenylalkanes which are the most biodegradable isomers, they are unfortunately not very stable.

The deactivation of zeolites is generally due to the formation and trapping in the zeolite pores of heavy secondary products (called coke for sake of simplification). Thus, in the liquid-phase alkylation of toluene with 1-heptene, i.e., a model reaction of the synthesis of LAB, carried out in a batch reactor, we have shown that the deactivation of various large-pore zeolites (HFAU, HMOR, HMAZ, HBEA) was due to heptyltoluenes blocked in the pores [10,12,13]. Mesopores created by dealumination which facilitate the desorption of alkylates improve significantly the zeolite stability. However, formation and trapping of heavy secondary products, hence deactivation, cannot be completely avoided and regeneration of the catalyst by coke removal is necessary.

Generally, coke removal is carried out through oxidative treatment under air or oxygen flow at high temperatures. This method, which can be easily applied to catalysts operating at high temperatures, is very costly for catalysts operating at low temperatures, especially in liquid phase. Fortunately, coke molecules formed at low temperatures result mainly from condensation reactions without practically no intervention of hydrogen transfer reactions. Therefore, it should be possible by simple treatment under nitrogen flow at the reaction temperature or at temperature slightly higher to retransform (to crack) the condensation products into the reactants. This possibility of coke removal has furthermore been demonstrated with HMFI and HFAU samples coked with propene at 120 °C [14]. In this paper, the deactivation and regeneration of a HFAU zeolite catalyst used for the continuous liquid-phase alkylation of toluene with dodecene was investigated. We show that a complete removal of coke and a complete regeneration of the catalyst can be obtained by simple treatment of the deactivated sample under toluene flow although the same treatment under nitrogen or decane flow has practically no effect.

2. Experimental

The HFAU zeolite sample, supplied by Beijing University, has total and framework Si/Al ratios of approximately 25 and practically no sodium atoms. This sample presents a micropore volume of 0.333 $cm^3\,g^{-1}$ and a mesopore volume of 0.136 $cm^3\,g^{-1}$. Its acidity was characterised by pyridine adsorption followed by IR spectroscopy. The concentration of protonic and Lewis sites retaining pyridine adsorbed at 150 °C were found to be equal to 0.185×10^{-3} and 0.07×10^{-3} $mol\,g^{-1}$, respectively.

The reaction was carried out in a fixed-bed reactor operating at 90 °C under a nitrogen flow of 30 $ml\,min^{-1}$, at atmospheric pressure, with 0.150 g of zeolite *in situ* pretreated at 500 °C for 16 h under dry air flow. After cooling at 90 °C, the reactant mixture, composed of toluene and 1-dodecene (molar ratio = 3), was introduced in the reactor at a flow rate of 4.8 ml h^{-1}, which corresponds to flow rates of 0.0267 and 0.0089 mol h^{-1} of toluene and 1-dodecene, respectively. Toluene and 1-dodecene from Aldrich (99.0% purity) were previously dried. The effluents were recovered and analyzed for different time on stream values by gas chromatography on a 25 m fused silica column (DB5).

The amount of non-desorbed products on the deactivated and regenerated samples was determined with a Thermoquest analyzer. The experimental method used to recover and to analyze the non-desorbed products (coke) has already been described [15].

The regeneration was carried out *in situ* after the reaction under the following conditions: nitrogen flow (30 ml min^{-1}) for 10 min at the reaction temperature, then toluene flow (20 ml h^{-1}) for 1 or 12 h. Retained material (coke) was analyzed before and after 1 h treatment as well as the toluene extract recuperated during this time.

3. Results and discussion

3.1. Activity, selectivity and deactivation

Under the operating conditions, 1-dodecene is totally converted during the first 40 min. Afterwards, 1-dodecene and double-bond shift isomers (2-, 3- and 4-dodecenes and traces of 5- and 6-dodecenes) appear in the effluents. Figure 1 shows that the conversion of the dodecene mixture into alkylation products decreases when time on stream increases, becoming close to zero after 210 min reaction.

The alkylation products consist mainly of monododecyltoluenes (MDT) and of a small amount of bidodecyltoluenes (BDT) at high dodecene conversion (table 1). 2-, 3-, 4-, 5- and 6-monododecyltoluenes can be separated by GC but not the corresponding *ortho, meta* and *para* isomers. 2-monododecyltoluenes (M_2) should result from toluene alkylation with 1- or 2-dodecenes, M_3, M_4, M_5 and M_6 from alkylation with 2- or 3-, 3- or 4-, 4- or 5- and 5- or 6-dodecenes, respectively. Table 1 shows that deactivation causes an increase in the percentage of M_2 in the MDT products at the expense of M_3–M_6 isomers. This increase can be related to an increase in the percentage of 1-dodecene in the dodecene mixture. These increases are most likely due to the decrease in conversion even if a direct effect of deactivation cannot be excluded.

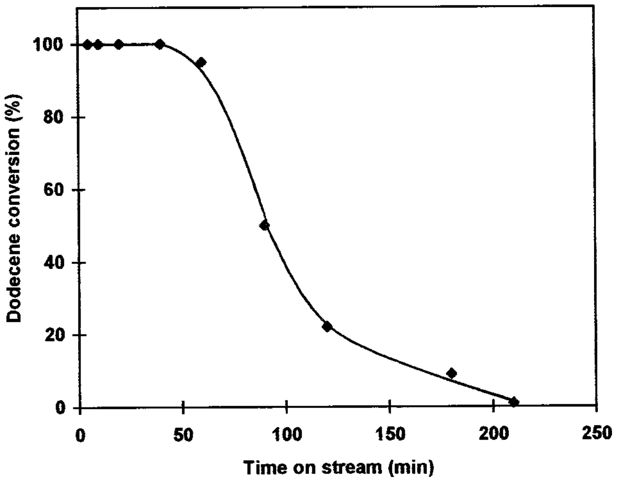


Figure 1. Dodecene conversion into alkylation products as a function of time on stream over a HFAU zeolite.

The deactivation is due to the retention of carbonaceous compounds (coke) on the zeolite: 10 wt% after 210 min, which corresponds to 0.2 wt% of dodecene converted into coke. Only a very small part of these compounds (<5%) can be dissolved in methylene chloride through a direct soxhlet treatment, whereas all of them are dissolved after dissolution of the zeolite in a hydrofluoric acid solution. Therefore, it can be concluded that all the coke molecules are located inside the zeolite pores.

GC analysis shows that coke is constituted by alkylation products: MDT (3 wt%), BDT (9 wt%) and tridodecyltoluenes TDT (88 wt%). TDT molecules, which are very bulky, can be formed and trapped inside the zeolite supercages but cannot escape out of them. Nitrogen adsorption on the totally deactivated sample confirms that deactivation is due to the coke deposit. Indeed, no adsorption is observed, which indicates a complete blockage of the access to the pores of HFAU. However, the volume really occupied by coke molecules, estimated from their amount and their liquid density ($\sim$0.90 $cm^3\,g^{-1}$), is only equal to 25% of the pore volume which is characteristic of deactivation by pore blockage: coke molecules (mainly TDT), preferentially located in the cages near the outer surface of the crystallites, block the access of adsorbates and of reactants towards the inner pores. If it is admitted that only one TDT molecule can lodge in a supercage, approximately 25% of the supercages would be occupied by coke molecules.

Table 1

Distribution of the products of the alkylation of toluene with 1-dodecene as a function of time on stream.[a]

Time (min)	10	20	60	90	120	180
Conversion (%)	100[b]	100[b]	90[b]	50	22	10
MDT (mol%)	96	98	98.5	99	100	100
BDT (mol%)	4	2	1.5	1	0	0
Distribution (%)						
Dodecenes						
1-dodecenes	[b]	[b]	38	40	45	50
2-dodecenes			25	25	30	34
3-dodecenes			20	20	15	10
4-dodecenes			17	15	10	6
MDT						
M_2	34.0	33.5	33.0	43.5	59.0	60.0
M_3	31.0	31.5	31.0	29.5	25.0	25.5
M_4	19.0	18.0	19.0	15.0	10.5	10.0
M_5	10.5	11.5	11.5	8.5	4.5	3.5
M_6	5.5	5.5	5.5	3.5	1.0	1.0

[a] Monododecyltoluenes (MDT), bidodecyltoluenes (BDT).

[b] No dodecene observed.

3.2. Coke removal and regeneration

The removal of coke by oxidative treatment requires generally high temperatures, which is very costly for reactions such as the synthesis of LAB carried out at low-temperatures. Furthermore, low-temperature coke is constituted of simple molecules which, in certain cases, can be removed by simple treatment under nitrogen flow [14]. This is not the case with the completely deactivated Y sample: only traces of coke can be eliminated by treatment of the sample under nitrogen flow (1.8 $\mathrm{l\,h^{-1}}$) for 6 h at 90 °C. A negative result is also obtained by treating the sample under n-decane flow (20 $\mathrm{ml\,h^{-1}}$) for 6 h. Whereas, very good results are obtained by treatment of the deactivated sample under toluene flow (20 $\mathrm{ml\,h^{-1}}$). After 1 h, the coke content is 6.5 wt% instead of 10 wt% on the deactivated sample and after 12 h, all the coke is removed. The activity of the catalyst is then completely restored and the change in conversion with time on stream is the same as with the fresh sample. On the other hand, the initial conversion is only 50% with the sample treated for 1 h (figure 2). For the same degree of conversion, the product distributions are identical on the fresh, totally and partially regenerated samples (figure 3).

In order to specify the mechanism of coke removal, the composition of coke remaining after the treatment of 1 h under toluene flow was established. This composition is completely different from that found on the deactivated sample. The regeneration treatment causes a large decrease in the amount of TDT blocked in the pores but a large increase in those of BDT and MDT (table 2). Furthermore, no TDT but mainly MDT (90% for 10% of BDT) are found in the toluene used for treating the deactivated sample. In the MDT fraction, M_2 and M_3 are largely predominant (77%).

These observations suggest that the removal of coke is due to transalkylation reactions between tridodecyltoluenes (TDT) trapped in the micropores and toluene (scheme 1).

Part of BDT may diffuse in the liquid phase, the other part reacting with toluene with formation of two MDT molecules, one in the liquid phase, the other one in the pores desorbing slowly from the zeolite (scheme 2).

It should, however, be remarked that BDT found in toluene can also result from transalkylation between MDT molecules of the liquid phase and BDT or TDT molecules in the pores (scheme 3).

As the access to the pores of the deactivated zeolite is completely blocked, at least the first alkylation steps occur at the pore mouth. This pore mouth catalysis between mol-

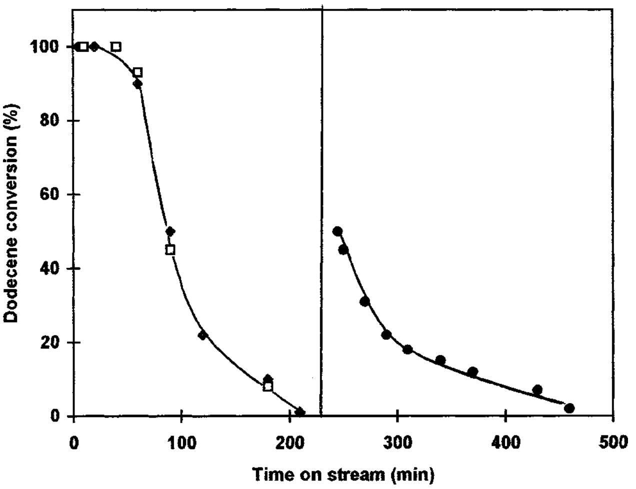


Figure 2. Dodecene conversion into alkylation products as a function of time on stream over fresh (◆), partially (●) and totally regenerated (■) HFAU samples.

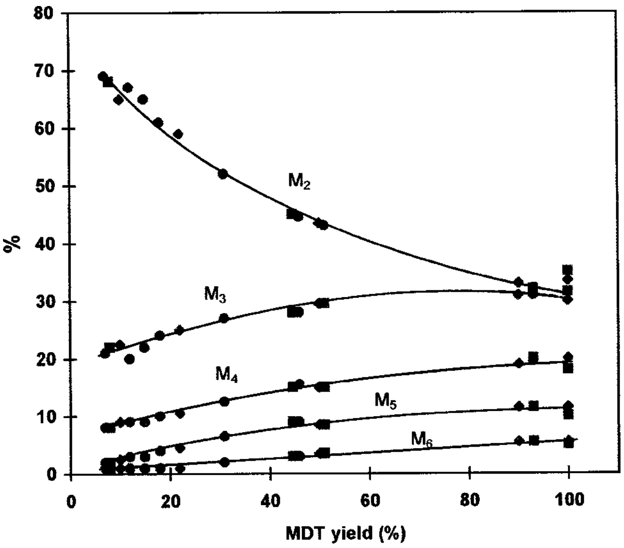
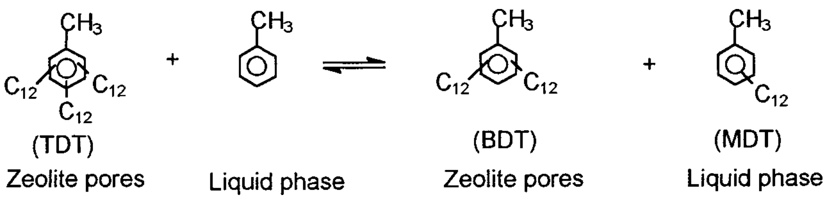


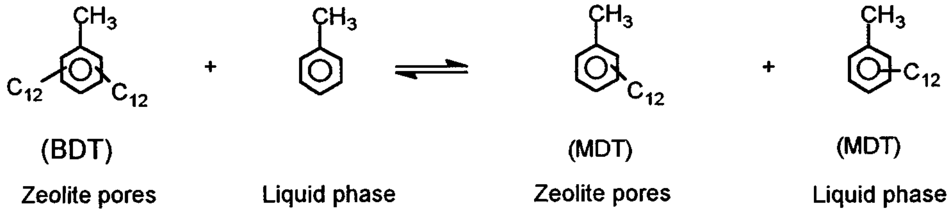
Figure 3. Distribution of monododecyltoluenes (MDT) as a function of the yield in alkylation products (mainly MDT) for fresh (◆), partially (●) and totally regenerated (■) HFAU samples.

Table 2
Coke composition (wt%) after 210 min reaction and after partial regeneration under toluene flow for 1 h.

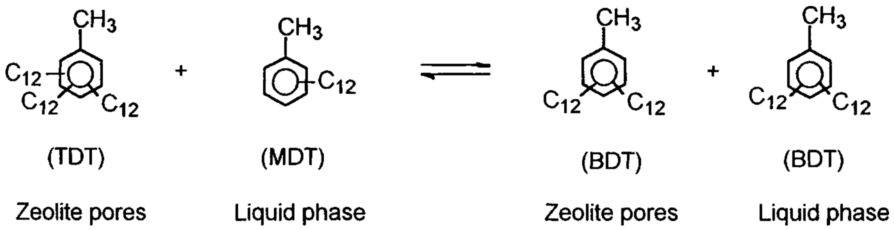
	Coke	Coke composition (wt%)		
	(wt%)	MDT	BDT	TDT
After reaction	10	0.3 (3%)	0.9 (9%)	8.8 (88%)
After partial regeneration	6.5	2.5 (38.5%)	2.5 (38.5%)	1.5 (23%)



Scheme 1.



Scheme 2.



Scheme 3.

ecules occluded in the zeolite pores and molecules in liquid or in gas phase has already been proposed for explaining isopropylation of naphthalene over various large-pore zeolites [16] and the skeletal isomerization of n-butene over a HFER zeolite [17]. This pore mouth catalysis could be responsible for the preferential formation of M_2 and M_3 in the toluene phase. However, it is most likely that, after the removal of a significant part of TDT, the access of toluene to the micropores becomes again possible, transalkylation occurring then inside the supercages.

It is thus possible to restore completely the activity and the selectivity of zeolites for toluene alkylation with dodecene by a simple treatment with toluene flow, one of the reactants under the operating conditions of alkylation. Moreover, monododecyltoluene, the desired product of alkylation, is produced during this treatment. This type of treatment can be adapted to the regeneration of zeolite catalysts used in alkylation of benzene with C_{10}–C_{13} alkenes, benzene being substituted for toluene in the regeneration step [9].

4. Conclusion

During the liquid-phase alkylation of toluene with 1-dodecene over a HFAU zeolite, there is formation of tridodecyltoluenes in the micropores. These compounds which cannot desorb from the zeolite are mainly located in the supercages of the outer part of the crystallites, causing deactivation by pore blockage. A simple treatment under toluene flow of the deactivated catalyst allows the elimination of tridodecyltoluenes, hence a complete regeneration of the catalyst. It is shown that transalkylation between tridodecyltoluene molecules located in the micropores and toluene molecules is responsible for this elimination. As, in the completely deactivated catalyst, the access of nitrogen, hence of toluene, to the pores is completely blocked, it can be proposed that at least the first transalkylation steps occur at the pore mouth.

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