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Short Communication

tert-Butylation of diphenylamine over zeolite catalysts comparison of different alkylation agents and catalysts

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ABSTRACT

tert-Butylation of diphenylamine (DPA) with different *tert*-butylation agents isobutylene (IB), *tert*-butanol (TBA), and C_4-fraction (C4-IB) in the liquid phase was studied over zeolite catalyst H-BEA (H-BEA CP 814E). This zeolite and acidic clay catalysts Nobelin and Fulcat 22B were compared in *tert*-butylation of diphenylamine with isobutylene and *tert*-butanol.

The study of the influence of *tert*-butylation agents in alkylation of DPA over H-BEA showed that isobutylene is the most suitable in *tert*-butylation of diphenylamine over the particular H-BEA zeolite catalyst in terms of conversion and selectivity to desired products.

Comparative study of catalyst type influence on *tert*-butylation of DPA with TBA and IB employed zeolite catalyst H-BEA and two clay ones Nobelin and Fulcat 22B. The study showed that all catalysts perform well in alkylation of DPA but H-BEA with the highest total acidity is the most active.

tert-Butylation of diphenylamine over H-BEA zeolite catalyst and acidic clays appears to be an environmental alternative to other catalysts (e.g. Friedel-Crafts) in industrial preparation of *tert*-butylated diphenylamines.

1. Introduction

Alkylation of aromatics is an acid catalyzed reaction and it is an important process in petrochemistry as well as in fine chemical syntheses [1,2].

Some alkylated diphenylamines are important additives for stabilizing organic products that are subjected to oxidative, thermal, and/or light-induced degradation. These organic products are widely used in engineering, for example as lubricants, hydraulic fluids, metal-working fluids, fuels, or polymers.

Alkylated diphenylamines are manufactured by alkylation of diphenylamine with monomers or oligomers of isobutylene (IB), propylene and with 1-nonene, styrene, α-methylstyrene (AMS) and others using different acid catalysts (mostly classical Friedel-Crafts) to produce *tert*-butylated, octylated, nonylated, styrenated and cumylated diphenylamines which are the most important chemicals used in antioxidant formulations [3] (Scheme 1).

Acidic clay catalysts reported in the patent literature are claimed to be excellent in the production of various alkylated diphenylamines [4–13]. Acid-treated and rare earth-modified clays have received considerable attention as catalysts for this industrially important reaction [14,15]. Acid-treated clays are especially active catalysts for the alkylation of DPA with α-methylstyrene as the alkylating agent [15].

Zeolite catalysts have been successfully used for the production of fine organic chemicals [16–18]. They have limited utilization for the transformations of large molecules due to diffusion limitations caused by their restricted pore size. The question remains whether these limitations can be considered as absolute or exceptions can be found.

In our previous work [22] we have studied various zeolite catalysts to evaluate their efficiency in *tert*-butylation of DPA with *tert*-butanol in the liquid phase. After preliminary screening we have concluded that H-BEA CP 814E showed the best results in conversion, selectivity and dialkylation. Subsequently we have optimized reaction conditions — temperature, TBA/DPA molar ratio and catalyst charge amount.

In the presented paper we have investigated the possibility of utilization of zeolite catalyst H-BEA (CP 814E) and clay catalysts Nobelin and Fulcat 22B in the alkylation of DPA with different *tert*-butylation agents as *tert*-butanol, isobutylene and C_4-fraction containing isobutylene. The influence of catalytic activity and selectivity of these catalysts on alkylation of DPA with different *tert*-butylation agents is evaluated, compared and discussed in this paper.

2. Experimental

2.1. Catalysts and chemicals

Commercially available zeolite catalyst H-BEA (CP 814E) from Zeolyst Int. and clay catalysts Nobelin (Rudex s.r.o., Bratislava, Slovakia) and Fulcat 22B (Rockwood Additives, UK) were used as alkylation

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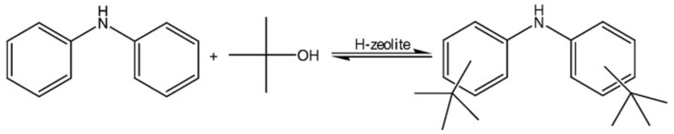

Scheme 1. *tert*-Butylation of diphenylamine.

catalysts. Characteristic properties of these catalysts are in Table 1. All clay catalysts were used as purchased. H-BEA was activated by calcination in a stream of dry air at 500 °C during 6 h. Clay catalysts without thermal activation were chosen for the DPA alkylation because it was proven during previous studies, that they are more active than activated ones. During thermal activation (500 °C), they lose residual mineral acid they were pretreated with, therefore losing part of their acidity. Also clays during their thermal procedure are losing water and thus changing their structure. All this leads to decreased acidity after thermal procedure and subsequently to decreased catalytic activity.

All chemicals except IB containing C_4-fraction (diphenylamine, *tert*-butanol, isobutylene and *n*-heptane) were of analytical grade purity purchased from Sigma-Aldrich GmbH, Germany. IB containing C_4-fraction was obtained from a local producer (Kaučuk Kralupy, Czech Republic). Composition of IB containing C_4-fraction is in Table 2. 1,3-butadiene was removed from this industrial C_4-fraction by extraction.

2.2. Apparatus, procedure and analysis

The alkylation of diphenylamine was carried out in the laboratory autoclave reactor (100 ml) equipped with magnetic stirring and electrical heating with temperature regulation. The weighted amount of liquid isobutylene or C_4-fraction was introduced to the reactor from the special steel sampler through two needle valves after heating the sampler to circa 90 °C. In a typical run, diphenylamine (20 mmol), 70 ml *n*-heptane as a solvent and 0.7 g of freshly calcined zeolite catalyst kept at 200 °C after calcination were used in alkylation reactions. The clay catalysts (Nobelin and Fulcat 22B), were used as received without activation procedure because higher temperature has negative influence on the clay structure and its catalytic activity decreases. For reusabitity test, used zeolite catalyst was filtered from reaction mixture, washed with *n*-heptane and methanol and calcined to remove any trapped organics. Clay catalyst was washed with *n*-heptane and methanol and dried at 120 °C. As to alkylating agents, *tert*-butanol, isobutylene or isobutylene containing C_4-fraction were introduced into autoclave reactor in amount of 40 mmol. The amount of isobutylene containing C_4-fraction was calculated to meet IB content of 40 mmol. The reactor was flashed thrice with nitrogen to replace air before adding the alkylating agent. Alkylation reactions were carried out at 180 °C and at the autogenous pressure at stirring 1000 $\min^{-1}$ (see Ref. [22]).

The samples of the reaction mixture were withdrawn periodically from the closed reactor and were analyzed on CHROMPACK 9002 gas chromatograph equipped with CP Sil 5 CB column (25 m × 0.53 mm) and FID detector. The temperature program of the chromatographic analysis was: 110 °C (5 min), from 110 °C to 275 °C with a slope of 3 °C/min.

The reaction products were identified on GC/MS QP5000 (Shimadzu) with EI and capillary column (HP-1, 50 m × 0.2 mm × 0.33 μm), carrier gas was helium (0.5 ml/min). Temperature program: from 110 °C with gradient 3 °C/min to 270 °C.

Table 1
Characteristic properties of catalysts.

Catalyst	S_{BET} (m^2/g)	$V_{micro,t}$ (cm^3/g)	$S_{meso,t}$ (m^2/g)	Acidity[a] (mmol/g)
H-BEA (12.5) CP 814 E	707	0.196	309	1.03
Fulcat 22B	240	0.015	205	0.242
Nobelin	164	0.007	148	0.183

[a] Total acidity was determined by standard TPDA method.

Table 2
Composition of the used industrial C_4-fraction (C4-IB).

Component	wt.%
Propane	0.1
Propene	0.3
i-Butane	4.3
n-Butane	7.3
trans-2-Butene	8.4
1-Butene	28.4
2-Methylpropene (isobutylene)	44.9
Cis-2-butene	5.9
1,3-Butadiene	Traces only
Unidentified	0.4

Reaction time 0 min is defined as the time when reaction temperature is reached (180 °C).

Calculations are based on following formulas: 4,4′-DTBDPA/4-TBDPA = moles of 4,4′-di-*tert*-butyldiphenylamine/moles of 4-*tert*-butyldiphenylamine, $S_{4\text{-TBDPA}} = (4\text{-TBDPA}/\Sigma\ \text{TBDPA}) \times 100$, $S_{4,4'\text{-DTBDPA}} = (4,4'\text{-DTBDPA}/\Sigma\ \text{DTBDPA}) \times 100$.

3. Results and discussion

3.1. Comparison of alkylation agents over H-BEA

The influence of different *tert*-butylation agents on *tert*-butylation of diphenylamine (DPA) was studied over commercially available zeolite catalyst H-BEA. The reaction conditions were as optimized in Ref. [22].

The main reaction products have been identified by GC–MS and ^{1}H-NMR as 4-*tert*-butyldiphenylamine and 4,4′-di-*tert*-butyldiphenylamine () in all cases. Other reaction products were identified as mono-octylated diphenylamines, isomers of mono- and di-*tert*-butylated diphenylamines and isomers of *tert*-butyl octyl diphenylamine. The main desired reaction products are 4-*tert*-butyldiphenylamine and 4,4′-di-*tert*-butyldiphenylamine (*para*- or *para*, *para*′-isomers).

2-*tert*-butyldiphenylamine or other *ortho*-alkylated diphenylamines (mono or dialkylated) were not present in the final reaction mixture (^{1}H-NMR). Free electron pair on N activates *ortho*- and *para*-positions of DPA aromatic ring. This fact influences *tert*-butylation to these positions. *tert*-Butyl group on aromatic ring of DPA activates *ortho*- and *para*-positions on the second aromatic ring. The formation of *ortho*- or *ortho*, *ortho*′-isomers is hindered by the position of –NH in Ph–NH–Ph and bulky *tert*-butyl group. As to theoretically possible N-alkylation of diphenylamine, there was not any presence of N-*tert*-butylated diphenylamine in the reaction mixture (^{1}H-NMR) probably due to sterical hindrance of –NH and given reaction conditions which, as we assume, prefer N-dealkylation and further shift of alkyl from N- to aromatic ring of DPA.

Fig. 1 shows the influence of alkylating agents on the conversion of DPA. The highest conversion of DPA was obtained using IB. After 120 min the conversion reached 99% and then slowly decreased. In the case of IB containing C_4-fraction, the conversion of DPA was continuously increasing throughout reaction time interval reaching its maximum at 95%. The lowest conversion of DPA was achieved using TBA as alkylating agent; the local maximum was 94% at 120 min and slowly decreasing to 91% at 480 min of reaction time. The small formal decrease of conversion can be probably ascribed to secondary reactions, namely dealkylation i.e. splitting of IB from *tert*-butyl DPA and formation of isobutylene dimer. The dimerisation of IB decreases its concentration and shifts alkylation equilibrium to a higher concentration of DPA. In all alkylations with IB, where formal decrease of conversions of alkylated compound was observed, an increased formation of diisobutylene was detected [19–22]. IB

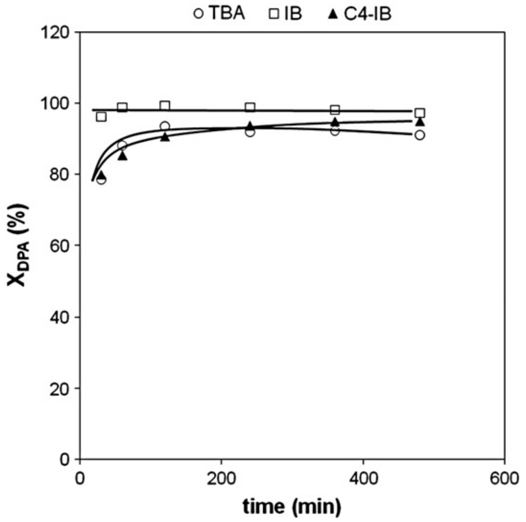

Fig. 1. The influence of the alkylation agent on conversion of DPA over H-BEA (for reaction conditions see Section 2.2).

in C_4-fraction is diluted other hydrocarbons and dimerisation of IB is depressed. In the case of TBA, water formed by dehydration of TBA can react with IB to form back TBA and part of IB can form dimer, so conversion of DPA formally decreases with time.

Fig. 2 shows the influence of alkylating agent on selectivity to 4-TBDPA and 4,4′-DTBDPA in *tert*-butylation of DPA over H-BEA. It can be clearly seen from Fig. 2 that all *tert*-butylation agents used in the DPA alkylation screening perform well. Selectivity to 4-TBDPA and also to 4,4′-DTBDPA is high and the obtained results do not differ much within studied range of *tert*-butylation agents. *Para*-selectivity (4-TBDPA and 4,4′-DTBDPA) is a result of activation of *ortho*- and *para*-positions of DPA molecule but due to steric reasons alkylation to the *ortho*-position is very problematic. So the differences in selectivities between alkylation agents are small.

Fig. 3 shows the influence of alkylating agent on 4,4′-DTBDPA/4-TBDPA ratio in the *tert*-butylation of DPA. It can be seen from Fig. 3 that alkylation agents used in the screening generate different, with reaction time increasing 4,4′-DTBDPA/4-TBDPA ratio. It shows how effective the combination of catalyst and particular alkylation agent is in the production of dialkylated DPA. The highest 4,4′-DTBDPA/4-TBDPA ratio (2.2) was achieved using IB, significantly lower ratio was observed with C4-IB (0.88) and the poorest result was obtained with TBA (0.62). We suppose that the achieved ratio of di/mono alkylated derivatives is a question of chemical equilibrium, which is shifted by the concentration of free IB. In C_4-fraction, IB is diluted by the other hydrocarbons. In TBA, it is chemically bonded. Moreover, water formed by alkylation with TBA depresses the evolution of IB from TBA and formation of reactive carbcation. Ratio of 4,4′-/4-isomers is a mirror of reactivity of different alkylation agents because of consecutive alkylation reactions. The decrease of this ratio with time for pure IB is connected to the partial dealkylation of *tert*-butylated DPA and di-*tert*-butylated DPA. H-BEA zeolites are the most acidic from the tested range of catalysts (Table 1), and dealkylation of 4,4′-di-*tert*-butyl DPA is preferred as a consequence of decreasing concentration of IB removed by dimerisation.

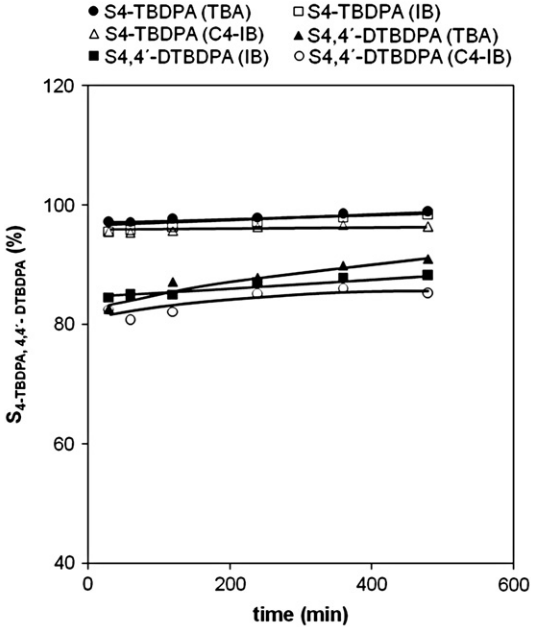

Fig. 2. The influence of alkylation agent on selectivity to 4-TBDPA and 4,4′-DTBDPA over H-BEA (for reaction conditions see Section 2.2).

The study of the influence of *tert*-butylation agents in the alkylation of DPA over H-BEA with TBA, IB and C4-IB revealed that all mentioned agents are good in *tert*-butylation of diphenylamine in terms of conversion and selectivity to desired products. Depending on specific demand for certain *tert*-butylated DPA product (mono- or di-*tert*-butylated DPA) and availability of *tert*-butylating feed one can decide which agent could be utilized. For example, in the case of high 4,4′-DTBDPA demand, IB can be beneficially used because with IB one can obtain 2.2 times higher 4,4′-DTBDPA yield at 97% conversion of DPA with 88% selectivity to 4,4′-DTBDPA.

3.2. Zeolite versus clay catalysts

3.2.1. Zeolite versus clay catalysts (TBA as alkylation agent)

Clay catalysts reported in the patents are claimed to be excellent and cheap catalysts in the production of various alkylated diphenylamines [4–12]. Acid treated and rare earth-modified clays have also received considerable attention as acid catalysts for this industrially important reaction [14,15].

The influence of two acidic clay catalysts — Nobelin and Fulcat 22B on *tert*-butylation of DPA with TBA is shown in this paragraph. The catalytic performance of these clay catalysts is compared to the zeolite H-BEA, which was considered as the very suitable one among a wider range of zeolite catalysts as concluded in Ref. [22].

Fig. 4 compares the influence of H-BEA and clay catalysts on conversion of DPA in *tert*-butylation of DPA with TBA. As seen in the picture, the highest, almost 97% conversion of DPA was observed over Fulcat 22B, comparable conversion (96%) was achieved over Nobelin but only after 480 min. H-BEA zeolite was more active (it is the most

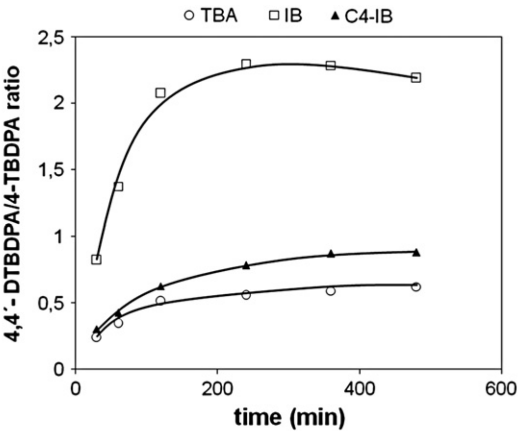

Fig. 3. The influence of alkylation agent on 4,4′-DTBDFA/4-TBDFA ratio over H-BEA (multiplied by 100, for reaction conditions see Section 2.2).

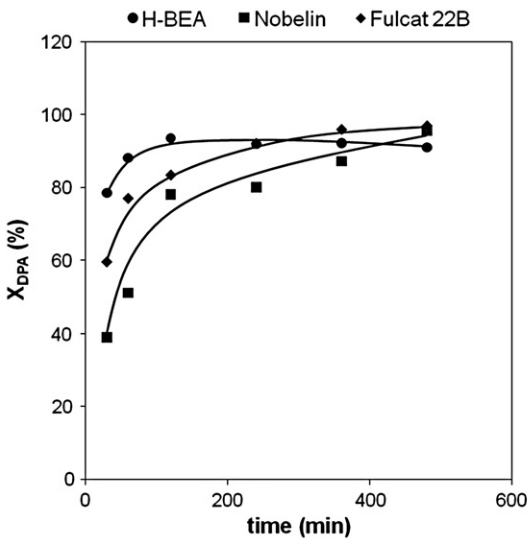

Fig. 4. The influence of H-BEA and clay catalysts on conversion of DPA with TBA as alkylating agent (for reaction conditions see Section 2.2).

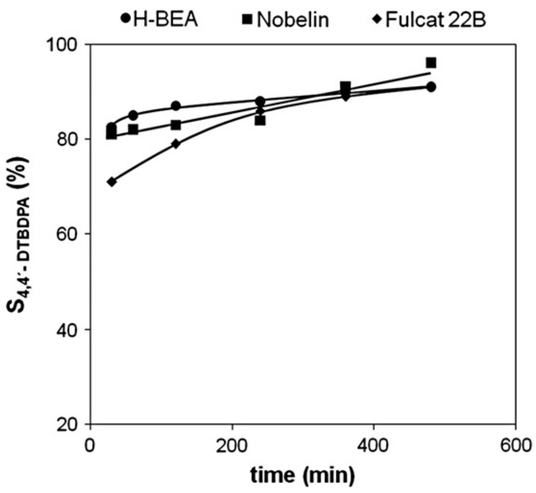

Fig. 6. The influence of H-BEA and clay catalysts on selectivity to 4,4′-DTBDPA with TBA as alkylating agent (for reaction conditions see Section 2.2).

acidic) because the highest conversion was obtained after 120 min and after that time we can see a conversion decrease because of dealkylation and DPA formation and diisobutylene formed from IB. Clays are not as active (they are not as acidic as H-BEA) and so their reactivity is lower also for back (dealkylation) reactions and so conversion of DPA is increasing (Fig. 4).

The most part of H-BEA acidity is inside pores, which are easily achievable for IB. However for DPA and its *tert*-butyl derivatives the transport inside narrow pores is hindered. Thus acidic sites inside narrow pores increase the rate of IB dimerisation and allow dealkylation of DPA after achieving the chemical equilibrium between DPA, IB and alkylderivatives of DPA. Nobelin and Fulcat 22B do not have a significant part in the acidic sites, which are differently achievable for IB and DPA. Also these clays are not as acidic as H-BEA zeolite.

Fig. 5 shows the influence of H-BEA and clay catalysts on selectivity to 4-TBDPA. The obtained selectivities over all catalysts are higher than 90%, especially in the case of Nobelin, almost 100% and Fulcat 22B, having 99% selectivity to 4-TBDPA after 480 min. The selectivity to 4-TBDPA over H-BEA (99%) is comparable to both clay catalysts. Nobelin is the least acidic and so dealkylation of 4-*tert*-butyl DPA is not significant as for more acidic catalysts (H-BEA and Fulcat 22B). From these results it is seen that “shape-selective” H-BEA and two non-shape-selective clays have very near selectivity to 4-TBDPA and 4,4′-DTBDPA and so such high selectivity to *para*- and *para*,*para*′-isomers is not a question of shape-selectivity but of thermodynamic stability of *tert*-butylated groups in the *para*- and *para*,*para*′-positions on the aromatic rings of DPA.

Fig. 6 shows the influence of H-BEA and clay catalysts on selectivity to 4,4′-DTBDPA in the *tert*-butylation of DPA with TBA. It is seen, that 4,4′-selectivity is after 6 h comparable for all studied catalysts. Probably it is also a matter of thermodynamic stability of 4,4′-isomer, not the matter of catalysts.

From Figs. 5 and 6 it is evident that mono- and di-alkylated DPA are transformed to the thermodynamically more stable isomers.

Fig. 7 shows the influence of H-BEA and clay catalysts on 4,4′-DTBDPA/4-TBDPA ratio in the *tert*-butylation of DPA with TBA indicating the catalyst efficiency in producing more valuable dialkylated DPA (4,4′-DTBDPA). It can be clearly seen from Fig. 7 that catalysts utilized have different with time increasing 4,4′-DTBDPA/4-TBDPA ratio. The highest 4,4′-DTBDPA/4-TBDPA ratio was achieved over H-BEA and Fulcat 22B (more reactive catalysts), significantly lower was observed over Nobelin, which is not as reactive — has lower total acidity. The most active catalyst (the highest acidity) has the highest ratio of 4,4′-/4-isomers, because of consecutive reactions from mono- to di-*tert*-butyl DPA. Fulcat 22B and Nobelin need longer time to achieve higher 4,4′-/4-isomers ratio.

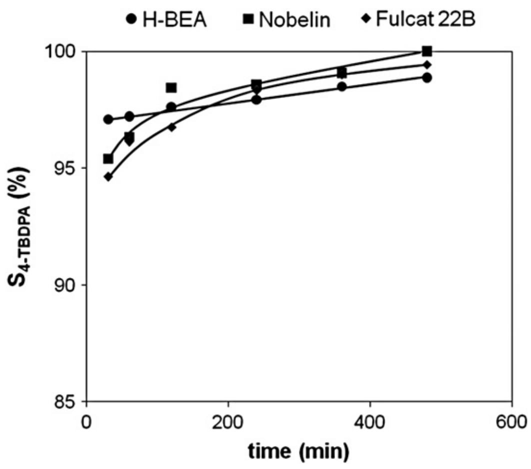

Fig. 5. The influence of H-BEA and clay catalysts on selectivity to 4-TBDPA with TBA as alkylating agent (for reaction conditions see Section 2.2).

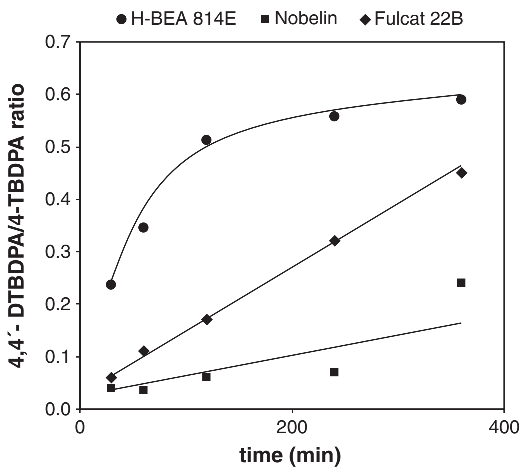

Fig. 7. The influence of H-BEA and clay catalysts on 4,4′-DTBDPA/4-TBDPA ratio with TBA as alkylating agent (for reaction conditions see Section 2.2, 4,4′-DTBDPA/4-TBDPA ratio multiplied by 100).

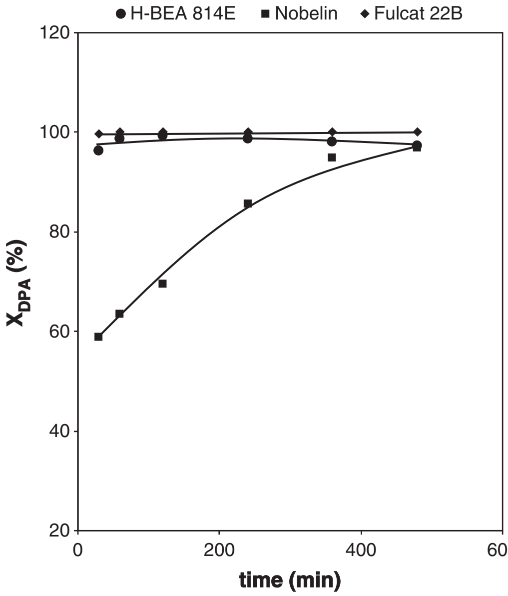

Fig. 8. The influence of H-BEA and clay catalysts on conversion of DPA with IB as alkylating agent (for reaction conditions see Section 2.2).

3.2.2. Zeolite versus clay catalysts (IB as alkylation agent)

Fig. 8 shows the influence of studied catalysts on conversion of DPA in *tert*-butylation of DPA with IB. As it is seen in the picture, the highest (almost 100%) maximal conversion of DPA was observed over H-BEA and Fulcat 22B (after 120 min), slightly lower (97%) was achieved over Nobelin (but after 480 min). Nobelin with the lowest acidity was the least active.

Fig. 9 shows the influence of H-BEA and clay catalysts on selectivity to 4-TBDPA. The obtained selectivities over all catalysts are higher than 90%, especially in the case of H-BEA and Fulcat 22B. The slightly lower selectivity to 4-TBDPA was achieved after 480 min over the least Nobelin (96%) which is also excellent. H-BEA started with selectivity to 4-TBDPA at 97% and even increased it during whole period of reaction time. Fulcat started at 91% and its selectivity increased to almost 100%. Acidities of Fulcat 22B and Nobelin are lower than H-BEA and the formation of 4-tert-butyl DPA is slower. In comparison with H-BEA, the dealkylation of alkylated DPA is also slower.

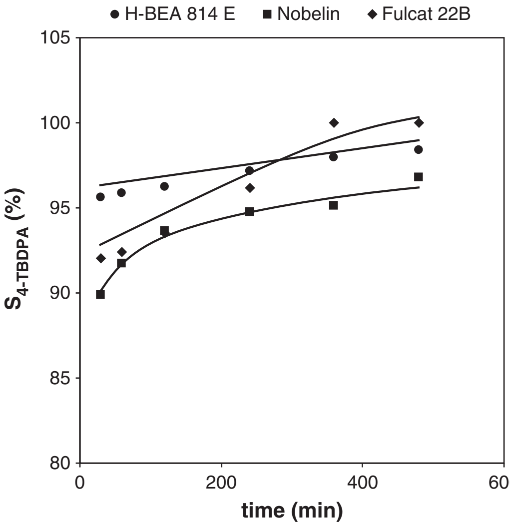

Fig. 9. The influence of H-BEA and clay catalysts on selectivity to 4-TBDPA with IB as alkylating agent (for reaction conditions see Section 2.2).

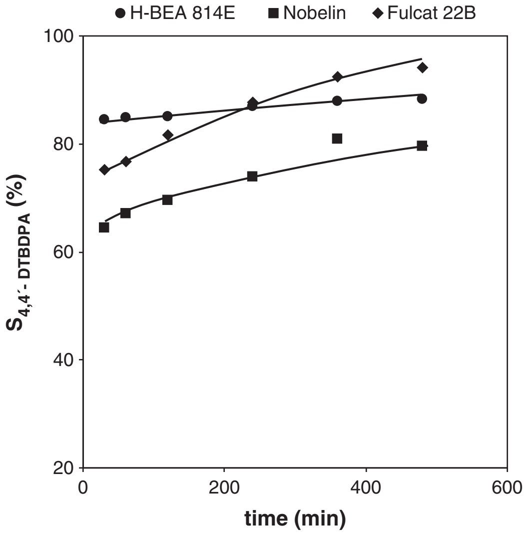

Fig. 10. The influence of H-BEA and clay catalysts on selectivity to 4,4′-DTBDPA with IB as alkylating agent (for reaction conditions see Section 2.2).

Fig. 10 shows the influence of H-BEA and clay catalysts on selectivity to 4,4′-DTBDPA in *tert*-butylation of DPA with IB. The highest, 94% selectivity to 4,4′-DTBDPA was achieved over Fulcat 22B but after 480 min. Lower selectivity to 4,4′-DTBDPA was obtained over both H-BEA and Nobelin (88 and 80%, respectively). DFA, as has been previously mentioned, is activated to *ortho*-, and *para*-position on aromatic ring for electrophilic substitution reaction, but due to sterical hindrance *para-/para,para′*-position is preferred for mono/disubstituted DFA.

Fig. 11 shows the influence of H-BEA and clay catalysts on 4,4′-DTBDPA/4-TBDPA ratio in the *tert*-butylation of DPA with IB indicating the catalyst efficiency in producing more valuable dialkylated DPA (4,4′-DTBDPA). It can be clearly seen from Fig. 11 that the used catalysts allow different 4,4′-DTBDPA/4-TBDPA ratio. The highest 4,4′-DTBDPA/4-TBDPA ratio was achieved over Fulcat, significantly lower was observed over H-BEA (more acidic and thus more active for dealkylation) and even worse result was obtained over Nobelin which acidity is the lowest.

Fulcat 22B catalyzes DPA alkylation slower than H-BEA due to its significantly lower acidity. Lower acidity also explains lowed contribution of secondary reactions, namely dealkylation, which is also significantly lower than in the case of H-BEA. Dealkylation reaction produces IB, which can form DIB, thus lowering IB concentration in

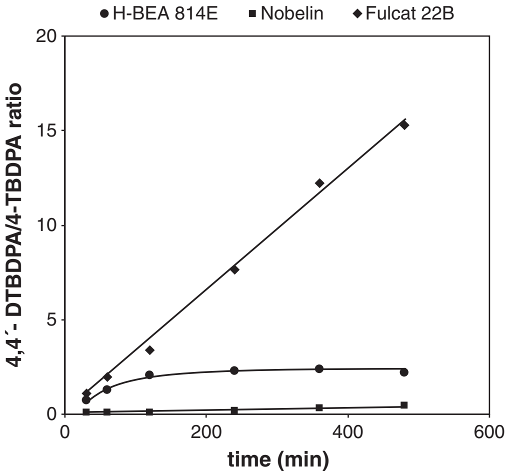

Fig. 11. The influence of H-BEA and clay catalysts on 4,4′-DTBDPA/4-TBDPA ratio with IB as alkylating agent (for reaction conditions see Section 2.2).

Table 3
Reusability of zeolite and clay catalysts.

Catalyst	X_{DPA} (%)	$S_{4\text{-TBDPA}}$ (%)	$S_{4,4'\text{-DTBDPA}}$ (%)
H-BEA	91	99	90
H-BEA 1x	89	99	89
H-BEA 2x	86	99	90
Nobelin	97	99	89
Nobelin 1x	94	98	87
Nobelin 2x	93	99	90

the reaction mixture. This is the reason why dealkylation of 4,4′-DTBDPA on Fulcat 22B is suppressed and 4,4′-DTBDPA/4-TBDPA ratio significantly increases.

The length of di-*tert*-butyl DPA molecule is circa 0.8 nm and its width circa 0.45 nm. Size of DPA, *tert*-butyl DPA and di-*tert*-butyl DPA allows these molecules to move in pores and channels of H-BEA zeolite. In the alkylation of DPA over H-BEA, external and internal acid sites are catalyzing the reactions. The acidic sites inside pores of H-BEA are more easily accessible for IB than for DPA, leading to more intense dimerisation of IB by H-BEA in comparison with Fulcat. In the case of clays, only accessible acid sites on the external surface are catalyzing the reaction, including residual mineral acids, clays were pretreated with (Fulcat 22B with sulphuric acid, Nobelin with hydrochloric acid). Here the accessibility of acid sites on the external surface is nearly the same for IB and DPA, thus dimerisation of IB is not preferred.

3.3. Zeolite reusability

The crucial issue concerning zeolite usage on the industrial scale is their reusability. The activity of zeolite catalysts tends to decrease sharply after few runs. Blocking of zeolites pores by coke formation is the culprit of drastic decrease of catalytic activity. Table 3 presents data on reusability of used zeolite and clay catalysts. Both catalysts activity decreased, but remained high after few runs.

4. Conclusion

tert-Butylation of diphenylamine over zeolite catalyst H-BEA and acid clays showed the possibility to utilize clay catalyst Fulcat 22B as an environmental alternative to the other classical catalysts in preparation of *tert*-butylated diphenylamines (Friedel-Crafts types or mineral acids). It also showed its potential to be a cheaper substitute for H-BEA.

tert-Butylation of diphenylamine was studied using three possible *tert*-butylation agents. It was proven that isobutylene is the most suitable *tert*-butylation agent. The highest conversion and selectivity to desired products — 4-*tert*-butyldiphenylamine and 4,4′-di-*tert*-butyldiphenylamine were achieved when isobutylene was used as *tert*-butylation agent, regardless on catalyst used.

Within the studied range of catalysts, the most active catalysts were H-BEA zeolite and acid clay Fulcat 22B, which is well known and utilized industrial acid catalyst. As it was proven, *tert*-butylation of DPA produces mainly *para*- and *para,para′*-*tert*-butylated DPA as final alkylation products what is the result of activation of *para*- and *para,para′*-positions in DPA.

Studied DPA alkylation reaction is important industrial process. 4-*tert*-butyldiphenylamine and 4,4′-di-*tert*-butyldiphenylamine are antioxidants with the utilization in lube oil formulations and polymer materials.

5. *Nomenclature*

DPA	diphenylamine
TBA	*tert*-butanol
IB	isobutylene
C4-IB	C_4-fraction isobutylene
X_{DPA}	conversion of DPA
DIB	diisobutylene

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