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Short Communication

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

Gabriel Kostrab [a,*], Martin Lovič [a], Andrej Turan [a], Pavol Hudec [a], Alexander Kaszonyi [a], Martin Bajus [a], Ján Uhlár [b], Peter Lehocký [b], Dušan Mravec [a]

[a] Institute of Organic Chemistry, Catalysis and Petrochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic
[b] VUCHT, a.s., Nobelova 34, 836 03 Bratislava, Slovak Republic

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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

* Corresponding author at: SLOVNAFT, a.s., Member of MOL Group, Slovak Republic.
E-mail address: gabriel.kostrab@slovnaft.sk (G. Kostrab).

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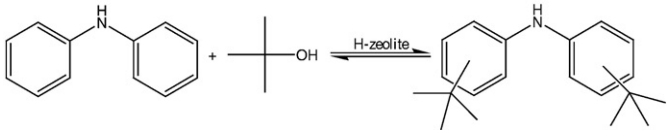

Scheme 1. *tert*-Butylation of diphenylamine.

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.

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, $S_{4\text{-TBDPA}} = (4\text{-TBDPA}/\Sigma\ \text{TBDPA}) \times 100$, $S_{4,4'\text{-DTBDPA}} = (4,4'\text{-DTBDPA}/\Sigma\ \text{DTBDPA}) \times 100$.

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

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