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ALKYLATION OF DIPHENYLAMINE WITH ALKENES CATALYZED BY ACIDIC CATALYSTS BASED ON BENTONITE

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Abstract

We examine the alkylation of diphenylamine with isobutylene, diisobutylene (DIB) and nonene in the liquid phase at 110–200°C. The liquid phase was catalyzed using commercially produced clay-based catalysts. The commercial catalysts consisted of different bentonite deposits and were activated via various mineral acids (e.g., sulfuric acid and hydrochloric acid). Following the alkylation analysis, we found that the conversion of diphenylamine decreased with increasing alkyl chain length. We also examined the dependence of conversion and selectivity on the surface properties of commercially produced catalysts. With increasing specific surface area catalyst (S_{BET}), there was also an increase in the conversion of diphenylamine; the selectivity of dialkylated diphenylamine decreased to the para position. An opposite correlation was found for the dependence of the total pore volume and particle size. With increasing micropore volume, the conversion of diphenylamine decreased while the selectivity for para dialkylated diphenylamine increased. In the case of the alkylation of DIB, the mixture was made up of 2,2,4-trimethyl-1-pentene (71.2 wt. %) and 2,2,4-trimethyl-2-pentene (20.6 wt. %). Higher temperatures cracked the mixture into isobutylene, thereby creating monobutyl difenylamine or dibutyl difenylamine that blocked the active centers of the catalyst and hindered the formation of the primary product of dioctyldiphenylamine.

Keywords: alkylation; diisobutylene; nonene; acidic heterogeneous catalysts.

1. Introduction

The alkylation of diphenylamine (DPA) with alkenes is of significant industrial importance because the products of the alkylation-dialkylated diphenylamines are used as additives in rubber, plastics, oils and lubricants that further serve as antioxidants and heat stabilizers [1]. These DPA derivatives have been commonly prepared via Friedel-Crafts alkylation of DPA with alkenes using mainly Lewis acid catalysts such as $AlCl_3$ and, to a lesser extent, Brönsted acids such as HF and H_2SO_4. When using $AlCl_3$, a very low selectivity of 1,4-dialkylated diphenylamine (DODPA, the desired product) was achieved, and difficulties also accompanied the separation of the catalyst from the reaction mixture. As evidenced by patents [2-5] at the end of the 20th century, there has been a gradual shift toward heterogeneous catalysts based on bentonite or zeolites. There is a requirement for a high content of 4,4-dialkyl diphenylamine due to its pronounced antioxidant capabilities.

Therefore, selecting a catalyst that is sufficiently active and selective is crucially important. From an economic point of view, it is necessary to use a catalyst that is heterogeneous, non-corrosive and safe for the environment [6-11]. Based on the available selection of heterogeneous acid catalysts, the most suitable catalyst should be based on bentonite due to its microporous and mesoporous surface area and sufficient number of acid centers.

In this article, we focus on comparing the performance of different commercial catalysts produced for DPA conversion and the selectivity of the desired products.

2. Experimental

We purchased commercial catalysts from different manufacturers in order to ensure that the bentonite consisted of different bentonite deposits. The catalysts included Fulcat 22B manufactured by Rockwood (England), K 5 Süd Chemie (Germany) and Nobelin MM Rudex s.r.o. (Slovakia). We measured the surface properties of all of the catalysts using nitrogen adsorption at −196°C using ASAP–2400 (Micromeritics, Norcross, USA). Prior to measuring the catalysts' surface properties, all of the catalysts were activated (each at an absolute pressure of 2 Pa at 150°C for 12 hours). We determined the total acidity via the Temperature-Programmed Desorption of Ammonia (TPDA) method, and we analyzed the Brönsted and Lewis acid centers at room temperature using infrared spectroscopy and pyridine adsorption with a Fourier transform infrared spectroscopy (FTIR) Genesis (Mattson-Unicam, Madison, USA) spectrophotometer. We divided the total acidity into Brönsted and Lewis acid centers on the basis of their extinction coefficients corresponding to the integral absorbance at 1550–1440 cm^{-1}. Prior to measuring the total acidity, we activated the catalysts in flowing helium at +500°C. Before measuring the FTIR spectra, we activated the self-supported catalyst tablets with a surface weight of approximately 8–10 mg/cm^2 at 480°C in a vacuum under 2 Pa.

We studied the size distribution of the individual catalysts using laser diffraction with a CILAS 930L/D analyzer (Orleans, France). We used Fraunhofer theory to evaluate the measured data. The DPA that we used was produced by Duslo a.s. (Šaľa, Slovakia), and the concentration of the active ingredients amounted to 99.76%. We analyzed the DPA using gas chromatography (Chrompack with a Flame ionization detector (FID), a 120-mm long metal column, a 2-mm internal diameter, filling: 10% OV 101 on Gas Chrom Q 100/120 mesh). The temperature programs ranged from 150–250°C with a temperature gradient of 20°C/min. Diisobutylene (DIB) was obtained from Basell ISO Cedex (France) and consisted of a mixture of 2,2,4-trimethyl-1-pentene (71.2%) and 2,2,4-timetyl-2-pentene (20.56%); the total amount of C_8 was 99.75%. We obtained nonene from Janex S.A. Lausanne (Switzerland); its concentration was 99.3%. We analyzed DIB and nonene using gas chromatography (Hewlett Packard with a FID detector and a CSW-PC integrator CP-Sil DB 15-meter long capillary column with a diameter of 0.32 mm). The temperature programs ranged from 60–300 °C, and the temperature gradient was 20°C/min.

We carried out alkylation in a semi-batch reactor at 110–200°C with a consistent dose of an alkene, as shown in 0, with 15 wt. % of catalyst per DPA dose.

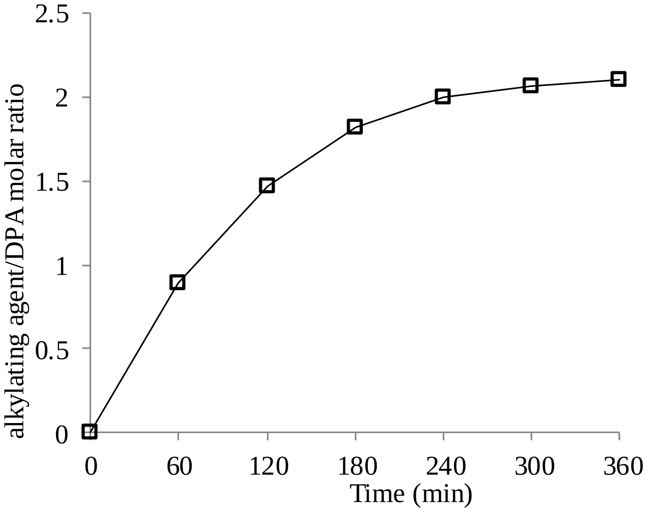


Figure 1. Alkylating agent dosing as a function of time

We analyzed the reaction mixture using gas chromatography (Chrompack CP 9002 with a FID detector and CSW-PC integrator. CP-Sil CB capillary column with a length of 15 m and an inside diameter of 0.32 mm). The temperature program ranged from 60–300°C and the temperature gradient was 5°C/min. Based on the composition of the alkylation mixture of the analyzed samples obtained 60 minutes after the beginning of the reaction, it was possible to calculate the degree of DPA conversion and the selectivity of each product.

3. Results and discussion

The primary characteristics of catalysts are listed in 0. Based on the measured values, one can see that the catalyst Fulcat 22B exhibited the largest measurable surface area (234 m^2/g) and that the catalyst K 5 had the smallest surface area (133 m^2/g). The catalyst Nobelin MM had a slightly larger surface area than that of K 5. Based on the analysis of the adsorption data using a t-line method, we found that a significant fraction of the surface of all three catalysts was located in the mesopores area. The micropore volume was relatively small (0.006–0.014 cm^3/g); catalysts accounted for only 2–3% (7%) of the total pore volume of Fulcat 22B and K 5 (Nobelin MM). The total acidity of the three catalysts was similar in the range of 0.19–0.23 mmol/g-and measurements of the Brönsted and Lewis acid centers revealed that the majority of acid centers were formed by Lewis acid centers.

Table 1. Physicochemical properties of the catalysts and their acid properties

Catalysts	S_{BET}	V_{micro}	V_a	V_{micro}/V_a	Mean diameter	Acidity determined by TPDA	Brönsted acid sites	Lewis acid sites
	($m^2\ g^{-1}$)	($cm^3\ g^{-1}$)	($cm^3\ g^{-1}$)	-	(μm)	(mmol g^{-1})	(mmol g^{-1})	(mmol g^{-1})
Fulcat 22B	234	0.006	0.301	0.020	71.72	0.23	0.03	0.20
K 5	133	0.014	0.201	0.031	42.42	0.22	0.05	0.17
Nobelin MM	158	0.009	0.295	0.070	43.12	0.19	0.02	0.17

3.1. The effect of the reaction temperature

The effect of the reaction temperature on the alkylation of DPA with a mixture of 2,2,4-trimethyl-1-pentene (71.2%) and 2,2,4-trimethyl-2-pentene (20.56%) is shown in 0 over the temperature range 110–200°C. Given an increase in temperature, we also found an increase in the conversion of DPA to alkylated DPA. At 110°C, the conversion of DPA reached 80.2% after 300 minutes; at 200°C, the conversation of DPA reached 98.1% (Table 2). The selectivity of DODPA was the largest at low alkylation temperatures; the selectivity of the cracking products (CP) was the lowest. Given increase in temperature, we also noted an increase in the amount of dimer in the product because the high temperature cracks 2,2,4-trimethyl-1-pentene to isobutylene (IB), which further reacts with another molecule of 2,2,4-trimethyl 1-pentene and forms 2,4,4,6,6-pentamethyl-2-heptene (C12) or 2,4,4,6,6,8,8-heptametyl-nonene-2 (C16). At 160°C and higher, IB alkylates with DPA, creating CP such as butyl-diphenylamine (BDPA) and dibutyldiphenylamine (DBDPA) or oktylbutyldiphenylamine (OBDPA), as shown in Figure 2B. The compositions of these reaction mixtures are listed in Table 2.

Table 2. The composition of the products of alkylation of diphenylamine with 2,2,4-trimethyl-1-pentene using Fulcat 22B at different reaction temperatures after 300 minutes

Temperature	MODPA selectivity	DODPA selectivity	Selectivity of dimmers	CP selectivity	DPA conversion
(°C)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)
110	58.08	39.03	0.66	2.23	80.22
160	31.85	14.12	2.51	51.52	94.16
200	20.95	3.08	3.57	72.41	98.11

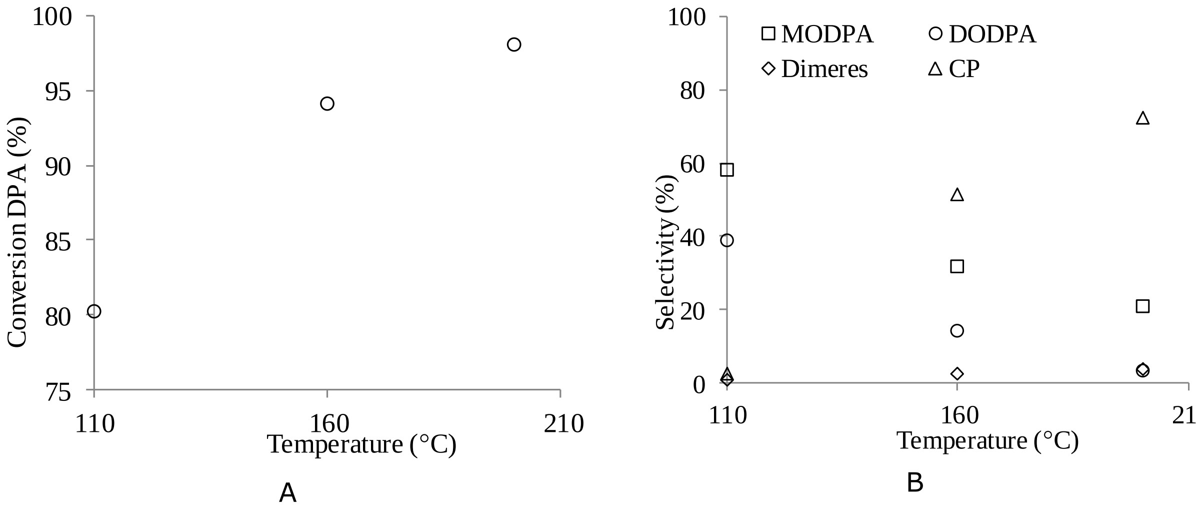


Figure 2. The effect of reaction temperature on the conversion of DPA (A) and the overall selectivity of isomers (B) using Fulcat 22B after 300 minutes of alkylation

MODPA monooctyldiphenylamine ;DODPA dioctyldiphenylamine, the desired product
CP cracking products; DIMERES triisobutylene 2,4,4,6,6-pentamethyl-2-heptene (C_{12}) or
tetraisobutylene (2,4,4,6,6,8,8-heptamethyl-2-nonene) (C_{16}); DPAdiphenylamine

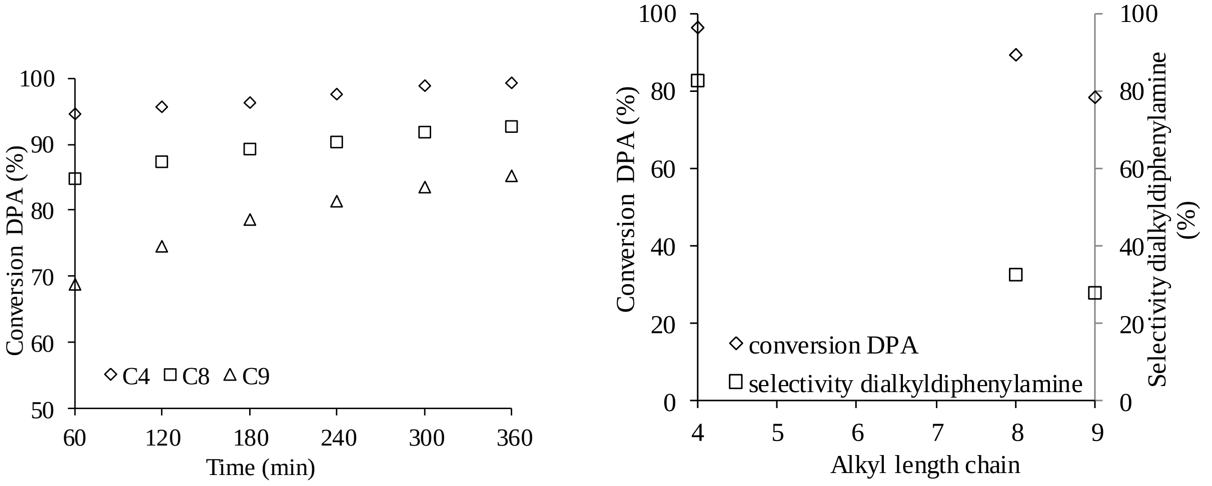
Increasing temperatures resulted in an increase in the concentration of CP and dimerization products. However, the degree of the DPA conversion was high. Conversely, at a lower temperature, e.g., 110°C, there was a greater proportion of alkylation products and a lower proportion of CP; the degree of DPA was lower. We accordingly carried out additional experiments at a temperature of 160°C; these experiments were chosen as a compromise between the conversion and selectivity of the alkylation products.

3.2.The effect of alkyl chain length on alkylation

Our analysis focused on DPA conversion during alkylation with various alkenes such as IB, a mixture of 2,2,4-trimethyl-1-pentene (71.2%) and 2,2,4-timetyl-2-pentene (20.56%) and 1-nonene using Fulcat 22B catalysts. The effect of reaction time on the DPA conversion during DPA alkylation with various alkylating agents is shown in 0A. Based on this monitoring, we found that the most reactive IB was the least reactive 1-nonene. Based on these results, we can conclude that the degree of DPA conversion decreases with increasing chain length (Figure 3). We compared the alkylation selectivity in the formation of DODPA at the 180th minute for all three alkenes using Fulcat 22B (Figure 3B). The degree of conversion decreased less significantly compared with the selectivity, and the selectivity decreased rapidly with increasing chain length of the alkylating agent (Table 3).

Table 3. The conversion of diphenylamine with 1-butene, DIB (a mixture of 2,2,4-trimethyl 1-pentene and 2,2,4-trimethyl-2-pentene) and 1-nonene using Fulcat 22B and the selectivity of dialkyldiphenylamines using Fulcat 22B at the 180th minute

Time	Conversion of DPA (wt. %)	Total selectivity (wt. %)
(min)	180	180
1-butene	96.32	82.65
a mixture of 2,2,4-trimethyl 1-pentene and 2,2,4-trimethyl-2-pentene	89.23	32.6
1-nonene	78.56	27.86



A B

Figure 3. The conversion of alkenes C4, C8 and C9 using Fulcat 22B at 160°C (A), the conversion of the particular alkenes at the 180th minute of the alkylation process, and the total selectivity of dialkyldiphenylamine using Fulcat 22 B (B)

C_4 isobutene;C_8 diisobutylene;C_9 nonene

3.3. The effect of the physical properties of the commercial catalyst in the alkylation process

We carried out a comparison of the various commercially produced catalysts for the alkylation of DPA using a mixture of 2,2,4-trimethyl-1-pentene (71.2%) and 2,2,4-trimethyl-2-pentene (20.6%). We focused on assessing the how the degree of conversion of DPA and differential selectivity to the para position of DODPA depended on S_{BET} parameters, V_{micro} and the average particle size at the 120th and 180th minutes of alkylation; the results are shown in Figures 4-6.

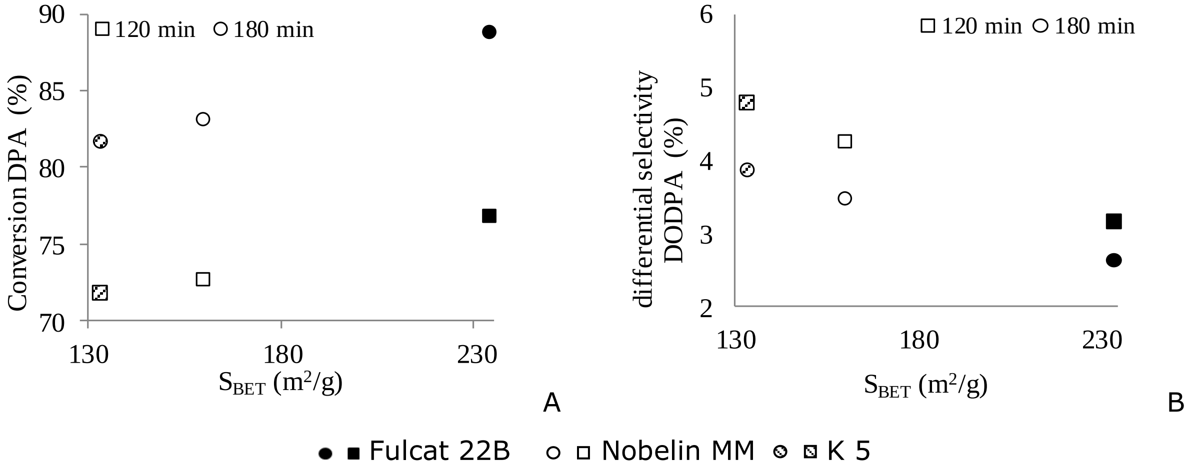


Figure 4. The conversion of DPA with DIB using heterogeneous acid catalysts based on bentonite for different S_{BET} surfaces (A), the selectivity in the formation of (DODPA) dioctyldiphenylamine at 160°C at the 120th and 180th minutes using heterogeneous acid catalysts based on bentonite (B)

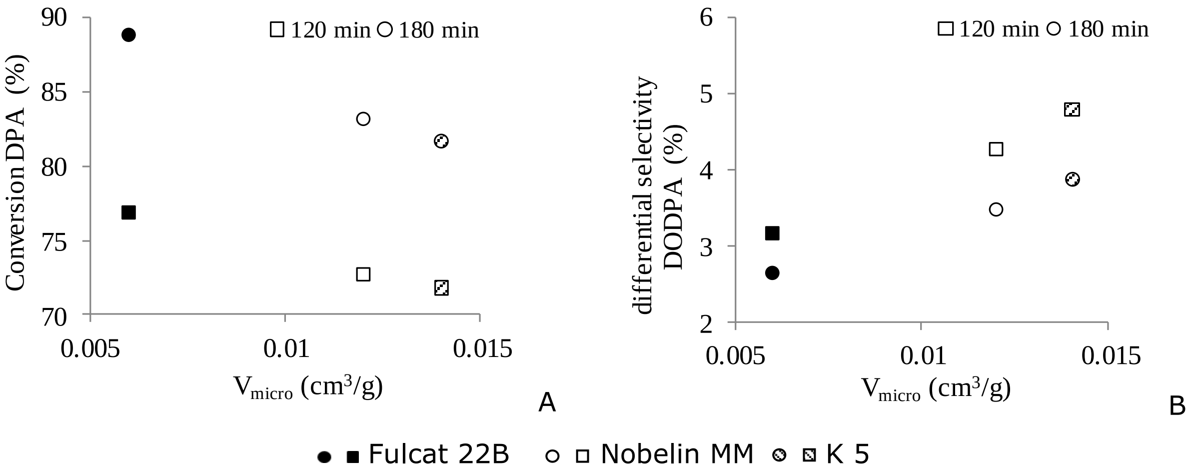


Table 5. The conversion of DPA with DIB using heterogeneous acid catalysts for V_{micro} micropores of different sizes (A); the selectivity of (DODPA) dioctyldiphenylamine at 160°C at the 120th and 180th minutes using heterogeneous acid catalysts based on bentonite as a function of the size of the V_{micro} micropores (B)

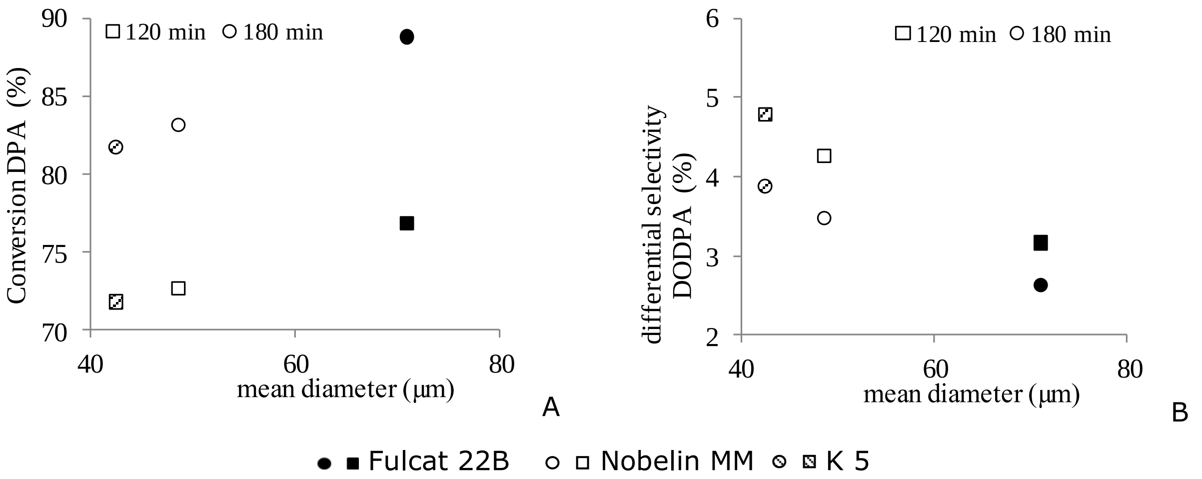


Figure 6. The conversion of DPA with DIB using heterogeneous acid catalysts based on bentonite for different average particle sizes (A); the selectivity in the formation of (DODPA) dioctyldiphenylamine at 160°C at the 120th and 180th minutes using heterogeneous acid catalysts based on bentonite as a function of the average particle size (B)

We compared the effect of the catalyst chosen from the monitored commercial catalysts using DPA conversion and the S_{BET} surface area of the relevant catalyst. With increasing surface area, we found a linear increase in the conversion of DPA, as seen in Figure 4A. Conversely, the differential selectivity to para dioctyldiphenylamine (DODPA) decreased with increasing surface area (0 4B). The DPA conversion increased with increasing average particle size (Figure 6A); while the differential selectivity of DODPA to the para position decreased (Figure 6B). The opposite trend can be observed for the volume of the micropores, i.e., the conversion of DPA decreases (Figure 5A), and the differential selectivity increases almost linearly (Figure 5B). The measured values are listed in 0Table 4. This phenomenon is caused by dimerization and the cracking reactions taking place on catalysts with larger surface areas. The products that are formed prevent alkylation in larger molecules, which is the reason why the conversion of this catalyst is higher but its selectivity is lower. The catalysts with smaller surface areas and a larger number of micropores do not allow dimerization and cracking reactions to such an extent; instead, they favor larger molecules. Therefore, catalysts with smaller surface areas and a larger number of micropores are more selective and have lower conversion rates.

Table 4. The composition of DPA alkylation with DIB at the 120th and 180th minutes and the physical properties of the heterogeneous catalysts

Catalysts	Conversion of DPA at the 120th min. (wt. %)	Conversion of DPA at the 180th min. (wt. %)	DODPA overall selectivity at the 120th min. (wt. %)	DODPA overall selectivity at the 180th min. (wt. %)	DODPA differential selectivity at the 60th and 120th min. (wt. %)	DODPA differential selectivity at the 120th and 180th min. (wt. %)
Fulcat 22B	76.84	88.81	5.74	7.60	3.16	2.63
Nobelin MM	72.69	83.13	8.36	10.79	4.26	3.48
K5	71.87	81.74	9.81	12.50	4.80	3.88

The optimum conditions for ensuring a high conversion of DPA and also a high selectivity of DODPA were achieved via alkylation in the following temperature regime (see also 0Figure 7). The alkylation process started at 200°C. Over time (360 minutes), the temperature of the reaction system decreased to 110°C. High temperatures forming CP also enable a high conversion of DPA. With a gradually decreasing alkylation process temperature, alkylation products with fresh DIB began to form.

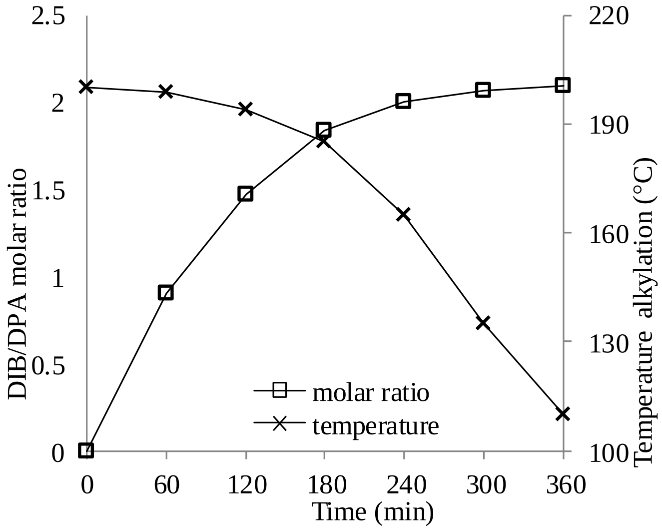


Figure 7. The temperature profile for the optimum conversion of DPA and the selectivity of (DODPA) and the dosing time f the DIB

4. Conclusions

We monitored the alkylation of DPA with alkenes-isobutylene, DIB, and nonene-in the liquid phase in a reactor using three different commercially produced catalysts with the alky-late dosages shown in 0 at 160°C in a nitrogen atmosphere. The maximum activity of the catalyst, i.e., the highest conversion of DPA during alkylation, was recorded for the catalyst with the largest S_{BET} surface area (Fulcat 22B). However, its differential selectivity to para dioctyl-diphenylamine was the lowest.

Increasing the alkylation temperature also increased the conversion of DPA. However, the resulting products were CP that blocked the active centers of the catalyst. The effect of the physical properties of the catalysts shows that the catalyst surface area, the total pore volume, and the particle size are all positively correlated with the conversion of DPA but negatively correlated with the differential selectivity. Conversely, increasing the volume of the micropores decreases the conversion of DPA and increases the differential selectivity in the formation of dialkyldiphenylamines in the para position. All in all, we achieved optimal alkylation conditions for a high conversion of DPA and simultaneously high selectivity of DODPA by regulating the temperature of alkylation from 200 to 110°C.

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