

# Alkylation of Diphenylamine with $\alpha$ -Methylstyrene and Diisobutylene Using Acid-Treated Clay Catalysts

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Alkylation of diphenylamine was carried out with  $\alpha$ -methylstyrene and diisobutylene using acid-treated clay catalyst Engelhard F-24 to produce mono- and dialkylated diphenylamines. Dialkylated diphenylamines are industrially useful as antioxidants and heat stabilizers. Mono and dialkylated diphenylamines were separated in pure form from the reaction mixture and characterized by FTIR and <sup>1</sup>H NMR. Reaction conditions for obtaining high selectivity of each of the alkylated products were studied. A comparative study of the reaction rates, with various other grades of acid-treated clay catalysts, was done for the reaction between diphenylamine and  $\alpha$ -methylstyrene. The reaction between diphenylamine and  $\alpha$ -methylstyrene was also studied in a continuous mode of operation in a fixed bed reactor. Deactivation of the catalyst occurred during the course of these reactions and reuse of the catalyst posed problems; alternative schemes were considered to regenerate the deactivated catalyst. The basic reasons for the deactivation of the catalyst were investigated in the case of reaction between diphenylamine and  $\alpha$ -methylstyrene. The fresh and used catalysts were characterized using various spectroscopic and other techniques such as X-ray diffraction, X-ray photoelectron spectroscopy, UV-visible and nuclear magnetic resonance spectroscopy, surface area (BET) and surface acidity (TPD), pore size distribution, and pore volume. These studies indicated that the deactivation of the catalyst was due to irreversible adsorption on the surface, loss of microporous structure and loss of surface acidity. The adsorbed species appeared to be diphenylamine and/or alkylated product(s), coordinated to the surface oxygen of the catalyst through nitrogen, forming a nitro kind of species.

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## INTRODUCTION

The use of acid-treated clays, as heterogeneous catalysts, offers many advantages over homogeneous acid catalysts such as ease of separation, mild reaction conditions, better selectivity of the desired product, and elimination of waste disposal problems. In a large number of organic reactions acid-treated clays have been used as catalysts on laboratory/industrial scales (1, 2). Alkylation of diphenylamine is an academically and industrially important

process. Alkylated diphenylamines are manufactured by reacting diphenylamine (DPA) with alkenes such as  $\alpha$ -methylstyrene (AMS) and diisobutylene (DIB) over acid catalysts. The products of these reactions are mono and dialkylated diphenylamines, e.g., alkylation of DPA with AMS produces a mixture of 4-( $\alpha,\alpha$ -dimethylbenzyl)-diphenylamine, i.e., monocumyldiphenylamine (MCDPA), and 4,4'-bis( $\alpha,\alpha$ -dimethylbenzyl)diphenylamine, i.e., dicumyldiphenylamine (DCDPA). Alkylation of DPA with DIB produces a mixture of 4-(1,1,3,3-tetramethylbutyl)diphenylamine, i.e., monoocetyldiphenylamine (MODPA), and 4,4'-bis(1,1,3,3-tetramethylbutyl)diphenylamine, i.e., dioctyldiphenylamine (DODPA). The reaction scheme for alkylation of DPA with AMS is shown in Fig. 1 and for alkylation of DPA with DIB is shown in Fig. 2.

The dialkylated diphenylamines are industrially important as antioxidants and heat stabilizers. Due to its high antioxidant activity and reduced tendency to discolor during heat aging, DCDPA is reported to be an ideal antioxidant for many materials, e.g., hot melt adhesives, polyacetals, nylon 6, polypropylene, polyethylene, ethylene-propylene copolymer and terpolymers, ABS, synthetic lubricants, polyether polyols, etc. (3). DCDPA, in combination with some of the phenolic antioxidants, also serves as an effective antioxidant and stabilizer system for polyolefins, e.g., polypropylene and polyether polyols, etc. DODPA is reported to be a high-temperature antioxidant in petroleum and synthetic lubricants (4). It is also used in hydraulic fluids, various industrial oils, automatic transmission fluids, and synthetic and petroleum-based engine oils. It is effective as an antioxidant and corrosion inhibitor in silane and siloxane synthetic lubricants, both in fluids and greases. In addition, MCDPA is useful as a rubber vulcanization stabilizer, which stabilizes rubber against thermal oxidation, dynamic fatigue, and discoloration.

The literature available on alkylation of DPA with AMS and DIB is in the form of patents. Wheeler (5) and Sundholm (6) have reported formation of DCDPA with a montmorillonite clay catalyst at 303–308 K. Goegh *et al.* (7) have reported formation of MCDPA in the presence of clay catalyst at 353–393 K. Goegh *et al.* (8) have reported

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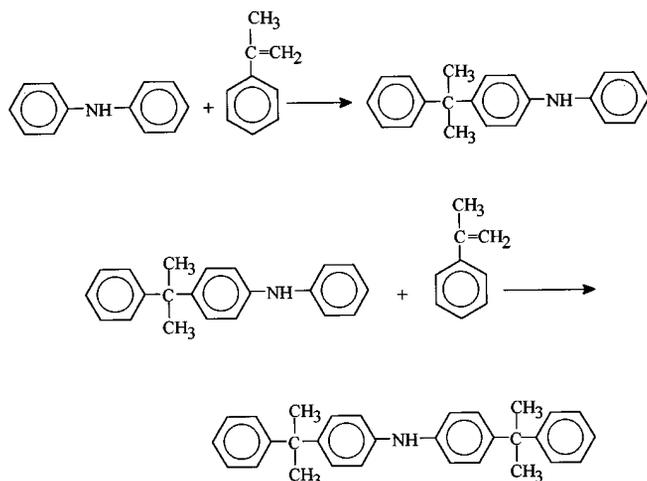


FIG. 1. Reaction scheme for alkylation of DPA with AMS.

formation of mixture of MCDPA and DCDPA at 363–413 K in the presence of montmorillonite or aluminosilicate catalysts. A semibatch addition of AMS for 3 h, at an overall mole ratio of DPA : AMS of 1 : 2 and 378 K produced a mixture of MCDPA and DCDPA in the ratio 9 : 91. Holcik *et al.* (9) have reported formation of mixture of MCDPA and DCDPA over  $H_3PO_4$ /bleaching earth catalyst at 453 K in an autoclave. Randell (10) has reported formation of mixture of MODPA and DODPA at 381–419 K over anhydrous aluminum chloride catalyst at 55% conversion of DPA. Mifune *et al.* (11) have reported formation of DODPA at 90% selectivity at 393–403 K with active china clay catalyst. Bayha *et al.* (12) have reported formation of DODPA at 373–473 K over  $AlCl_3$  catalyst in an atmosphere of  $N_2$  at 3.4–13.6 bar.

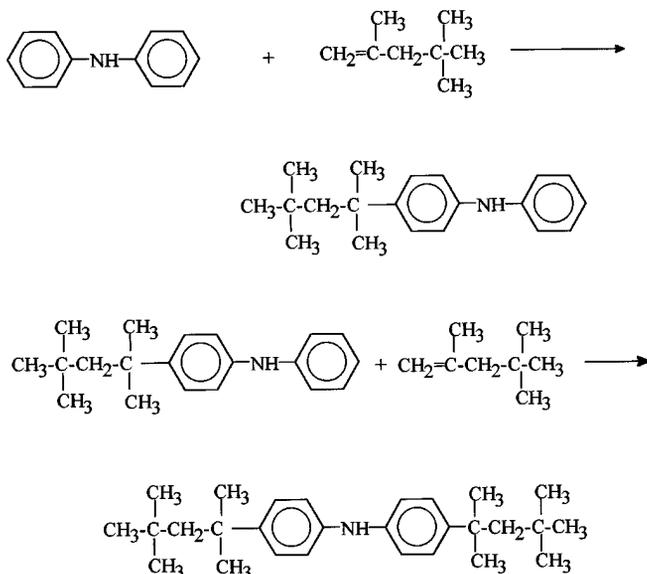


FIG. 2. Reaction scheme for alkylation of DPA with DIB.

Kurek *et al.* (13) have reported the reaction with high conversion of DPA and minimal cracking of DIB using a rare earth pillared clay, especially Ce and La Al chlorohydrate pillared clay catalyst. They have reported that the catalyst could be regenerated by heating in air at 823–873 K. DPA and DIB were alkylated at 453 K and 67 bar  $H_2$  gas pressure using a Ce Al chlorohydrate pillared clay catalyst and this produced 26% MODPA and 65% DODPA, at 98% conversion of DPA. Franklin (14) has reported formation of DODPA at 438 K over activated  $Al_2O_3$  catalyst.

Thus no systematic study appears to have been reported in the published literature. Therefore it was decided to study the alkylation of DPA with AMS and DIB systematically, where the selectivity for monoalkylated vs dialkylated product was explored. It was also proposed to study the life of the catalyst and reasons for deactivation.

### ALKYLATION OF DPA WITH AMS

#### Experimental

DPA was obtained from S. d. fine chemicals Ltd. (India). AMS was obtained from Herdillia Chemicals Ltd. (India). The acid-treated clay catalysts Engelhard F-24, F-25, F-34, F-44, F-54, F-124, F-224, and G-62 were obtained from Engelhard Corporation (USA); Tonsil K-306 and Tonsil KA3 catalysts were obtained from Sud Chemie (Germany). The properties of various grades of acid-treated clay catalysts used in this work are listed in Table 1 (15). All the experiments were carried out in a 0.05 m. i.d. 100 ml ( $1 \text{ ml} = 1 \times 10^{-6} \text{ m}^3$ ) fully baffled mechanically agitated glass reactor equipped with a stuffing box and a reflux condenser. A six-bladed glass disc turbine impeller was used for agitation. The reaction was carried out at the desired temperature by placing the reactor in a constant temperature bath. The reaction was studied in the temperature range of 363–423 K. All the catalysts used in this work were dried under vacuum (0.008 bar) at 373 K for 6 h before use.

The analysis was done on a gas chromatograph (Chemito 8510) equipped with a flame ionization detector. A 2-m-long ss column packed with 5% OV-17 on Chromosorb-WHP was used for the analysis. The injector and detector were kept at 613 K. The oven temperature was increased from 423 to 613 K at a ramp rate of 0.16 K/s. Nitrogen was used as a carrier gas and its flow rate was  $4 \times 10^{-7} \text{ m}^3/\text{s}$ .

X-ray diffraction patterns (XRD) were recorded on a Jeol JDX 8030 diffractometer (with a monochromator) using  $Cu K\alpha$  radiation at 35 KV and 25 mA. Diffractograms were recorded between  $2\theta$  value of  $2^\circ$  to  $70^\circ$  with a step angle of  $0.02^\circ$ .

X-ray photoelectron spectra (XPS) were recorded on VG ESCA-3 M K II spectrometer using  $Mg K\alpha$  radiation (1253.6 eV) as the exciting source. All the BEs were referred to the  $C_{1s}$  peak at 285 eV.

TABLE 1  
Physical Properties of Various Grades of Acid-Treated Clay Catalysts

Property	F-24	F-25	F-34	F-44	F-54	F-124	F-224
Shape	Granular	Granular	Granular	Spherical beads	Spherical beads	Granular	Granular
Size (mm)	0.6	1.05	<i>a</i>	<i>a</i>	<i>a</i>	0.48	0.48
Internal surface area (m <sup>2</sup> /g)	350	350	380	300	225	350	350
Weight capacity (meq/g)	0.3	NA	NA	NA	NA	NA	NA
Void fraction (packed)	0.32	0.26	0.36	0.36	0.36	0.32	0.32
Temperature stability	NA	NA	NA	NA	NA	NA	NA

Note. NA: data not available. Engelhard G-62, Tonsil K-306, Tonsil KA3, alumina pillared clay catalyst: properties are not available.

<sup>a</sup> Tyler standard sieve, passing 20 mesh% > 85.

UV-visible solid-state reflectance spectra were recorded on a Shimadzu UV-160 spectrometer.

The Fourier transform infrared (FTIR) spectra were recorded in the region between 4000 and 400 cm<sup>-1</sup> at 4 cm<sup>-1</sup> resolution on a Bruker IFS 88 spectrometer with a DTG detector.

Solid-state, magic angle spinning, nuclear magnetic resonance (MAS-NMR) spectra were recorded on a Varian VXR-300 S spectrometer. <sup>29</sup>Si spectra were obtained at 59.591 MHz with a spinning rate of 4.3–4.5 k at 45° pulse; 10 s delay was used between the scans. Tetramethylsilane was used as the standard.

Surface area of the samples were determined by the nitrogen adsorption isotherms at 77 K after outgassing the samples at 383 K. The BET method was used for surface area calculation. Pore size distribution and total pore volume was measured using Amico's porosimeter (4135 bar).

Total acidity of the samples were determined by temperature programmed desorption (TPD) of ammonia using nitrogen carrier gas. Samples were heated from 393 to 823 K with nitrogen flow rate of 5 × 10<sup>-7</sup> m<sup>3</sup>/s, at rate of 0.16 K/s and held at 823 K for 1.3 h. Samples were then cooled to 393 K and ammonia adsorption was carried out. After flushing the sample with nitrogen for 2 h, temperature-programmed desorption of ammonia was carried out.

### Results and Discussions

**Product separation and characterization.** MCDPA was obtained in pure form by fractional distillation of the reaction mixture on a Perkin-Elmer spinning band distillation column. DCDPA was obtained in pure form by crystallization from a solvent by the following procedure. The reaction mixture was dissolved in 96% aqueous methanol solution under reflux. DCDPA was crystallized out from the mother liquor and further purified by recrystallization from methanol. Both MCDPA and DCDPA were characterized

by FTIR and <sup>1</sup>H NMR spectra, which confirmed the purity of these compounds.

**Effect of speed of agitation.** The variation in stirring speed from 1000 to 1500 rpm had no effect on the rate of reaction, clearly indicating that external mass transfer resistance was absent. Hence all the further experiments were carried out at 1000 rpm.

**Effect of particle size of the catalyst.** The effect of particle size of the catalyst on the rate of conversion of DPA was studied in the range of particle size from 0.6 to 0.18 mm (1 mm = 1 × 10<sup>-3</sup> m). The effect of particle size of the catalyst on the rate of conversion of DPA is shown in Fig. 3. It was observed that when the particle size was reduced, the

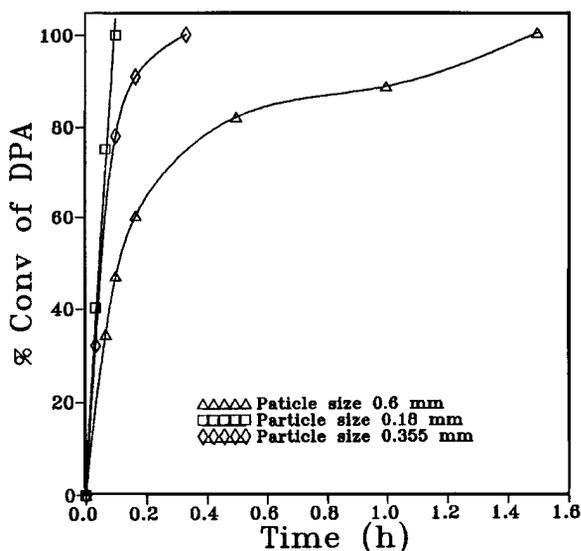


FIG. 3. Effect of particle size of the catalyst on rate of conversion of DPA. Reaction conditions: DPA : AMS mole ratio, 1 : 2; temperature, 363 K; catalyst loading, 10% Engelhard F-24.

rate of conversion of DPA increased but the selectivity of DCDPA decreased, e.g., in the reaction with DPA : AMS mole ratio of 1 : 2, 363 K, and 10% loading of Engelhard F-24 catalyst, when the particle size was reduced from 0.6 to 0.18 mm, the rate of conversion of DPA increased, as indicated in Fig. 3, but the selectivity of DCDPA decreased from 65.2 to 50.8%, at 100% conversion of DPA. Since an increase in the rate of conversion of DPA was obtained with a decrease in the particle size of the catalyst, it can be concluded that the intraparticle diffusion limitations are present for the reaction between DPA and AMS. The effect of intraparticle diffusion can be correlated to the Thiele modulus of the reaction system, which depends on radius of the catalyst particle, the reaction rate constant, and the effective diffusivity of the reactants.

**Effect of various catalysts.** It was observed that the reaction was unsuccessful with a macroporous ion exchange resin catalyst Amberlyst-15 upto 393 K, even in the presence of a solvent, e.g., cumene. The reaction was also unsuccessful with an alumina pillared clay catalyst which was calcinated upto 773 K. The reaction occurred with other grades of acid-treated clay catalysts such as F-25, F-34, F-44, F-54, F-124, F-224, G-62, and Tonsil K-306. However, the reaction did not occur with Tonsil KA3 catalyst. The Engelhard G-62 catalyst was in the pelleted form, whereas Tonsil K-306 and Tonsil KA3 catalysts were in the form of spherical beads. The Engelhard G-62, Tonsil K-306, and Tonsil KA3 catalysts were crushed to 0.6 mm size before using in the reaction. All the experiments were done with the fresh catalysts. The results of this study are reported in Table 2. Thus the reaction did not occur with some of the catalysts, whereas it occurred with the other catalysts at different rates of conversion of DPA and different selectivity of DCDPA with each of the catalyst. This difference can be attributed to the difference in the physical properties of the catalysts, e.g., acidity and surface area of these catalysts.

**Catalyst reusability.** The effect of repeated use of the catalyst on the rate of conversion of DPA and selectivity of DCDPA was studied. All the reactions for the catalyst reusability and regeneration study, in the further discussion, are carried out with DPA : AMS mole ratio of 1 : 2, 10% (w/w) loading of Engelhard F-24 catalyst, and at 363 K and the results of percentage conversion of DPA and selectivity of DCDPA after 1.5 h of reaction are reported. The effect of repeated use of the catalyst on the rate of conversion of DPA is shown in Fig. 4. The percentage conversion of DPA with the fresh catalyst was 100% and the selectivity of DCDPA was 65.2%. The percentage conversion of DPA decreased to 74.7, 62.2, and 58.2% and the selectivity of DCDPA decreased to 38.8, 34.7, and 32.5% for the first, second, and third reuse of the catalyst, respectively. Thus, this study revealed that deactivation of the catalyst occurred during the course of the reaction.

TABLE 2  
Comparison of Performance of Various Grades  
of Acid-Treated Clay Catalysts

Type of catalyst	% Conversion of DPA	% Selectivity of DCDPA	% Conversion of DPA per unit area of the catalyst
F-24	100	65.2	0.285
F-25	85.6	50.9	0.244
F-34	78	24.8	0.205
F-44	100	55	0.333
F-54	74.9	32	0.332
F-124	93.2	55.3	0.266
F-224	95.2	61.6	0.272
G-62	71.2	28	—
Tonsil K-306	74.5	45.6	—

Note. Reaction conditions: DPA : AMS mole ratio, 1 : 2; temperature, 363 K; catalyst loading, 10%; period of reaction, 1.5 h.

**Catalyst regeneration.** Various alternative schemes were tried for the regeneration of the deactivated catalyst.

**Effect of reflux methanol wash on catalyst regeneration.** It is known that methanol has a great affinity for the clay surface (16). Therefore, it was thought that the deactivated catalyst could be regenerated by refluxing with methanol. The deactivated catalyst was refluxed with methanol for 2 h, dried at 373 K under vacuum for 6 h, and then reused in the next reaction. The extent of catalyst regeneration was studied for three consecutive batches by refluxing the catalyst with methanol each time followed by drying. The percentage conversion of DPA was 100, 100, and 93.2% and the selectivity of DCDPA was 56.2, 48.5, and 42.7%

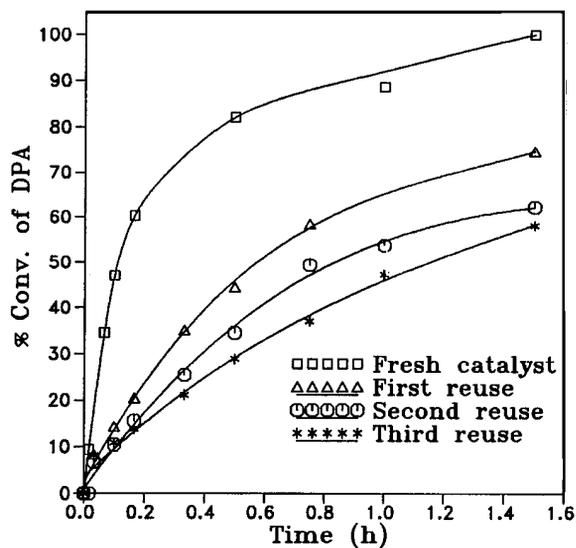


FIG. 4. Effect of repeated use of catalyst on rate of conversion of DPA. Reaction conditions: DPA : AMS mole ratio, 1 : 2; temperature, 363 K; catalyst loading, 10% Engelhard F-24.

for the first reuse after methanol wash, second reuse after methanol wash, and third reuse after methanol wash, respectively. Thus, for first two batches of the regenerated catalyst, the rate of conversion of DPA was the same as the rate with the fresh catalyst, whereas for the third batch it dropped marginally. The selectivity for DCDPA, even with the first batch of the regenerated catalyst, was lower than that with the fresh catalyst and it dropped significantly with every batch of the regenerated catalyst. This kind of regeneration of the catalyst, where the rate of conversion of DPA and/or the selectivity of DCDPA with the regenerated catalyst are lower than that with the fresh catalyst will be termed hereafter as partial regeneration of the deactivated catalyst.

**Effect of use of a solvent in the reaction on catalyst regeneration.** The extent of catalyst regeneration by the use of a solvent in the reaction was studied separately for two solvents, i.e., *ortho*-xylene and 1,2-dichlorobenzene. In the reaction with *ortho*-xylene solvent, the rate of conversion of DPA with fresh catalyst was lower than the rate without any solvent. In the reaction with 1,2-dichlorobenzene solvent, the rate of conversion of DPA with fresh catalyst was higher than the rate without any solvent. However, when these catalysts were reused in the respective reactions, the rates of conversion of DPA were drastically lower as compared to the rates with the fresh catalysts. Thus, the use of a solvent in the reaction produced an adverse effect on the extent of regeneration of the catalyst. The rates of conversion of DPA with *ortho*-xylene and 1,2-dichlorobenzene solvents for the fresh and used catalysts are shown in Fig. 5.

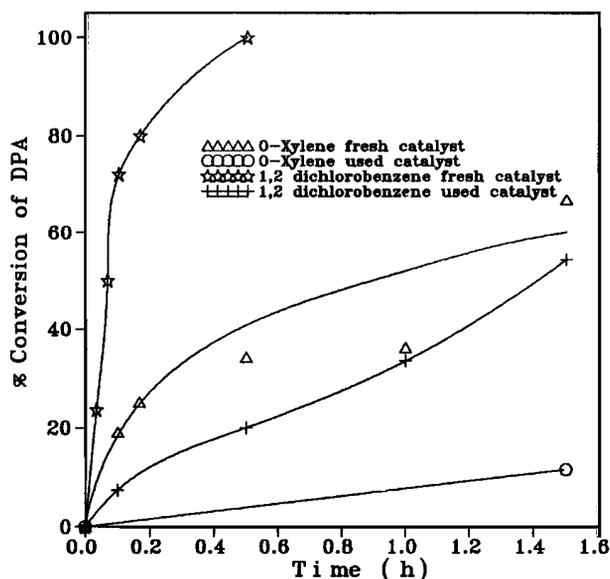


FIG. 5. Effect of use of a solvent in the reaction on catalyst regeneration. Reaction conditions: DPA : AMS mole ratio, 1 : 2; temperature, 363 K; catalyst loading, 10% Engelhard F-24.

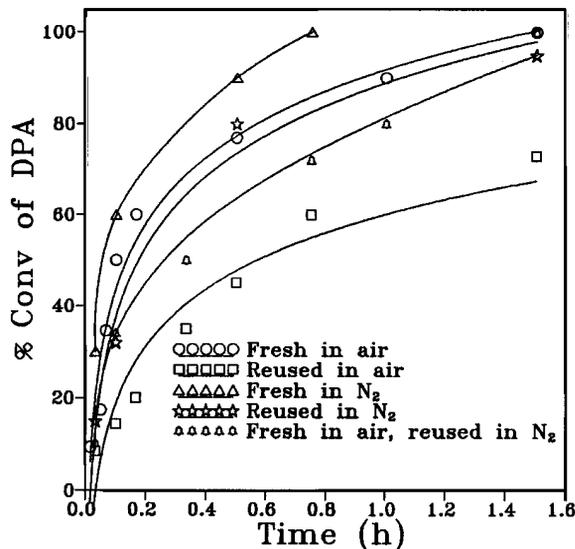


FIG. 6. Effect of nitrogen atmosphere on catalyst regeneration. Reaction conditions: DPA : AMS mole ratio, 1 : 2; temperature, 363 K; catalyst loading, 10% Engelhard F-24.

**Effect of nitrogen atmosphere on catalyst regeneration.** The effect of nitrogen atmosphere on the rate of conversion of DPA for both fresh and used catalyst was studied. The rates of conversion of DPA, for both the fresh and the used catalyst, were higher in nitrogen atmosphere than the rates of corresponding reactions in air. From the comparative study of reaction rates, it was thought that nitrogen atmosphere suppressed the formation of product(s) of either of the reactants, which deactivated the catalyst. The rates of conversion of DPA for reactions in nitrogen atmosphere and air with the fresh and used catalysts are shown in Fig. 6.

**Effect of ultrasonic irradiation on catalyst regeneration.** Ultrasonic irradiation is used for a wide variety of applications such as cleaning of surfaces, erosion, and sterilization. The formation and collapse of microbubbles, i.e., cavitation, is responsible for the chemical effects of ultrasonic irradiation. Cavitation causes the local temperatures at the center of the bubble to rise up to  $10^4$ – $10^6$  K and pressures to several thousands of bars, which promotes the cleaning process. Therefore, the effect of ultrasonic irradiation on the extent of catalyst regeneration was studied. Ultrasonic irradiation of the deactivated catalyst was carried out by suspending it in methanol solvent. The irradiated catalyst was then dried at 373 K under vacuum for 6 h and then reused. The time of ultrasonic irradiation was increased from 0.16 to 0.5 h. The percentage conversions of DPA were 100 and 100%, respectively, and the selectivities of DCDPA were 18.2 and 52.7%, respectively, for the catalysts which were reused after ultrasonic irradiation for 0.16 and 0.5 h. Thus, the catalyst could be partially regenerated with the help of

ultrasonic irradiation. Also, there was no further increase in the extent of regeneration, when the time of ultrasonic irradiation was increased beyond 0.5 h.

**Reaction in a fixed bed reactor (FBR).** As the reaction was found to be appreciably fast, it was studied in a continuous mode of operation in a shell and tube type of fixed bed reactor (FBR), having a tube diameter of 0.017 m and a length of 0.3 m. The tube side of the reactor was packed with Engelhard F-25 catalyst, in which the length of the catalyst bed was 0.25 m and a top portion of the bed (0.02 m) was filled with a layer of inert packings to ensure uniform distribution of the reactants in the bed. Hot water was circulated on the shell side of the reactor, as a heat transfer medium. A controlled feeding of the mixture of DPA and AMS (mole ratio 1:2; preheated to 393 K) was done from the top of the reactor and the reaction products were withdrawn at the bottom; i.e., the reactor was operated in a downflow manner. The percentage conversions of DPA and selectivity of DCDPA at residence times (RT) of 0.015, 0.066, and 0.17 h were measured. The percentage conversions of DPA at these RTs were 47, 70, and 100%, respectively, and the corresponding selectivities of DCDPA were 38, 44.3, and 58.2%, respectively. Thus, it was possible to obtain appreciably good conversion of DPA and selectivity of DCDPA at short residence times of reactants in the reactor.

The extent of deactivation of the catalyst in the FBR was studied by carrying out a reaction continuously for a period of 12 h, with Engelhard F-25 catalyst. During this reaction, there was no deactivation of the catalyst for a period of first 5 h. Beyond this period, the catalyst deactivated at a very slow rate and a marginal decrease in the percentage conversion of DPA and selectivity of DCDPA was observed. The results of this study are reported in Table 3.

The reactions with the pelleted catalyst Engelhard G-62 and the spherical bead-like catalyst Tonsil K-306, were carried out in a FBR having a tube diameter of 0.034 m and a length of 0.3 m. The length of the catalyst bed was

TABLE 3

Extent of Deactivation of Engelhard F-25 Catalyst in FBR for the 12-h Reaction

Period of reaction (h)	% Conversion of DPA	% Selectivity of DCDPA
0 to 5	100	58.2
6	92.3	57.6
7	91.6	57.2
8	90.3	57.2
9	90.3	57.2
10	86.6	53.5
11	86.6	53.5
12	86.1	53.3

Note. Reaction conditions: Residence time of reactants in the reactor, 0.17 h.

TABLE 4

## Physical Characterization of Fresh and Used Catalyst

Status of catalyst	BET surface area (m <sup>2</sup> /g)	Pore volume (m <sup>3</sup> /g)
Fresh catalyst (size, 0.6 mm)	277	0.207 × 10 <sup>-6</sup>
Used catalyst (size, 0.6 mm)	27.1	0.164 × 10 <sup>-6</sup>
Regenerated catalyst by reflux methanol wash (size, 0.6 mm)	254.8	—
Fresh catalyst (size, 0.18 mm)	225	0.857 × 10 <sup>-6</sup>

0.25 m for both the catalysts. When the FBR was operated in a downflow manner, insufficient wetting of the catalyst bed was observed for both these catalysts. Therefore, the FBR was operated in an upflow manner; i.e., addition of the mixture of DPA and AMS (mole ratio, 1:2; preheated to 393 K) was done from the bottom of the FBR through a tube of diameter 0.015 m, under the hydrostatic head of the reactants and the reaction samples were collected from an overflow point at the top of the reactor. With the Engelhard G-62 catalyst, 33% conversion of DPA and 51% selectivity of DCDPA was obtained at a RT of 0.9 h, whereas with the Tonsil K-306 catalyst, 25% conversion of DPA and 63% selectivity of DCDPA was obtained at a RT of 1.16 h. Thus, appreciably low conversion of DPA and moderate selectivity of DCDPA were obtained at high residence time of reactants in the FBR, with these catalysts.

Catalyst Characterization<sup>2</sup>

## Measurement of surface area, pore volume, and pore size.

The results of surface area and pore volume of fresh and used catalysts are reported in Table 4. The results of pore size distribution of the fresh and used catalyst of 0.6 mm size and 0.18 mm size are shown in Fig. 7. From these results, for the 0.6 mm size catalyst surface area is 277 m<sup>2</sup>/g, with pore size in the range of 0.003–0.5 μ (1 μ = 1 × 10<sup>-6</sup> m) and the total pore volume is 0.207 × 10<sup>-6</sup> m<sup>3</sup>/g. Maximum pores are in the range of 0.003 to 0.01 μ, which contributes to a total volume of 0.129 × 10<sup>-6</sup> m<sup>3</sup>/g. This suggests a microporous structure for the catalyst. After the reaction, the surface area of the catalyst reduced to 27.1 m<sup>2</sup>/g (9.78% of the original), but the loss of pore volume was marginal (0.164 × 10<sup>-6</sup> m<sup>3</sup>/g), 79% of the original pore volume being retained. However, this is due to the creation of larger pores of 0.01 to 60 μ, as evident from the pore size distribution curve. It would therefore seem that the deactivation of the catalyst is due to loss of micropores and subsequent reduction in surface area. The surface area of the regenerated catalyst, by reflux methanol wash, is 254.8 m<sup>2</sup>/g, indicating

<sup>2</sup> The catalyst characterization study has been carried out for Engelhard F-24 catalyst.

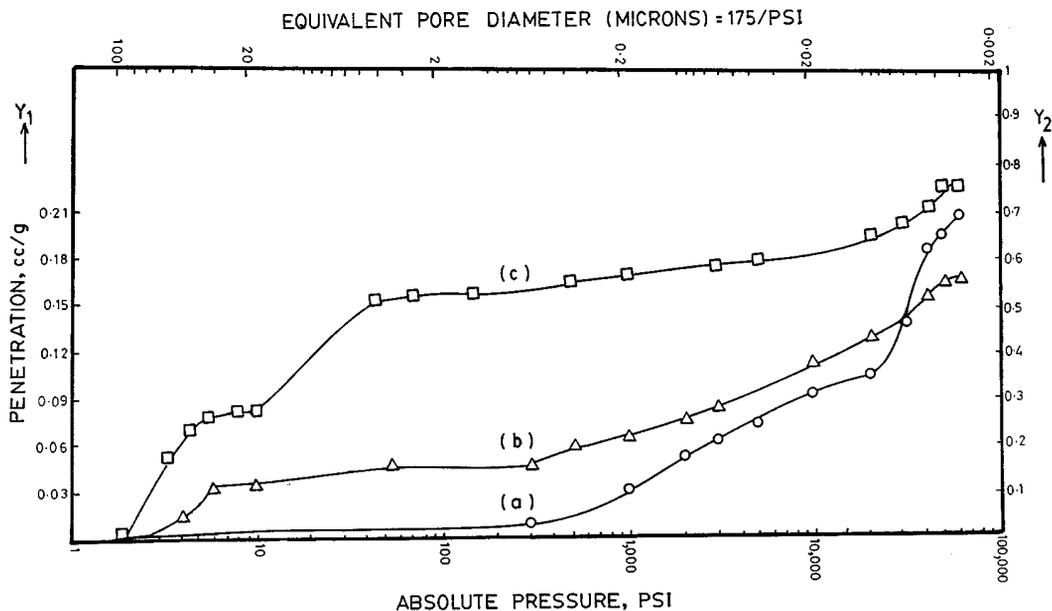


FIG. 7. Results of pore size distribution. (a) Fresh catalyst, (b) used catalyst, both of 0.6 mm size, (c) fresh catalyst of 0.18 mm size.  $Y_1$ , axis for (a) and (b);  $Y_2$ , axis for (c).

that there is a large recovery in the surface area after the reflux methanol wash of the catalyst.

**Measurement of surface acidity.** Total acidity of the fresh and used catalysts was determined by temperature programmed desorption (TPD) of ammonia. The chromatograms of ammonia TPD are shown in Fig. 8. There were two major peaks centered around 483 and 703 K representing weak and strong acidic sites, respectively, with the high temperature peak being more intense in the deactivated catalyst. The low temperature peak is due to desorption of ammonia from Brønsted acid sites and the high temperature peak is due to desorption of ammonia from Lewis acid sites. The total acidity, in terms millimoles of ammonia/g, for the fresh catalyst was 2.48 (100%) and for the used catalyst was 2.25 (90.7%). Although the reduction in the total acidity of the deactivated catalyst is only 9%, the loss of Brønsted acid sites is quite significant. This should be responsible for the deactivation of the catalyst.

**X-ray diffraction of fresh and used catalysts.** From the small angle X-ray powder diffraction patterns of the fresh and used catalysts, basal spacing in the both the catalyst samples, i.e., fresh and used, was found to be the same, i.e., 16.6 Å ( $1 \text{ Å} = 1 \times 10^{-10} \text{ m}$ ) at  $2\theta = 5.3^\circ$ . This suggested that there is no expansion in the interlayer spacing; hence there was no evidence of intercalation of the reactant and/or product into the clay lattice.

**$^{29}\text{Si}$  MAS-NMR.**  $^{29}\text{Si}$  MAS-NMR spectra of the fresh and used catalyst is shown in Fig. 9. The large peak at  $-95 \text{ ppm}$  and relatively smaller peak at  $-111.9 \text{ ppm}$  were assigned to  $Q^3$  (O Al) and  $Q^4$  (O Al) units, respectively. The

peak at  $-101.6 \text{ ppm}$  was assigned to OH containing silicon unit, i.e.,  $(\text{SiO}_3)_2 \text{Si OH}$  (17). Relative peak height, linewidths, and peak areas of the three peaks for fresh and deactivated catalysts are reported in Table 5. Although there is line broadening in case of deactivated catalyst, it is clear from individual component plots that the peak at  $-101.6 \text{ ppm}$  loses intensity after reaction. This could be due to possible interaction of the OH group with reactant and/or product species.

**UV-visible spectra.** From the UV-visible solid-state spectra of the fresh and the deactivated catalyst, the deactivated catalyst (which had an intense green colour) has an absorption band at 678 nm ( $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$ ), in contrast to 800 nm in the case of the fresh catalyst. The intense dark green coloration of the deactivated catalyst is thought to be due to the formation of a charge transfer complex by the interaction of adsorbed species with the surface functional groups of the catalyst.

**XPS studies.** Results of XPS studies are shown in Fig. 10. The XPS of the deactivated catalyst shows two peaks at binding energies (BE) of 401 and 406 eV in the  $N_{1s}$  region. The peak at 401 eV can probably be assigned to adsorbed DPA, since DPA has a  $N_{1s}$  BE of 400 eV, and the positive shift of 1 eV could be due to the drain of electrons away from the nitrogen of DPA due to adsorption on the catalyst. This was confirmed by recording XPS spectra of only DPA adsorbed on the catalyst. The higher binding energy peak at 406 eV is in the region of nitro compounds, suggesting therefore the formation of an adsorbed species with the nitrogen bound to the surface oxygen.

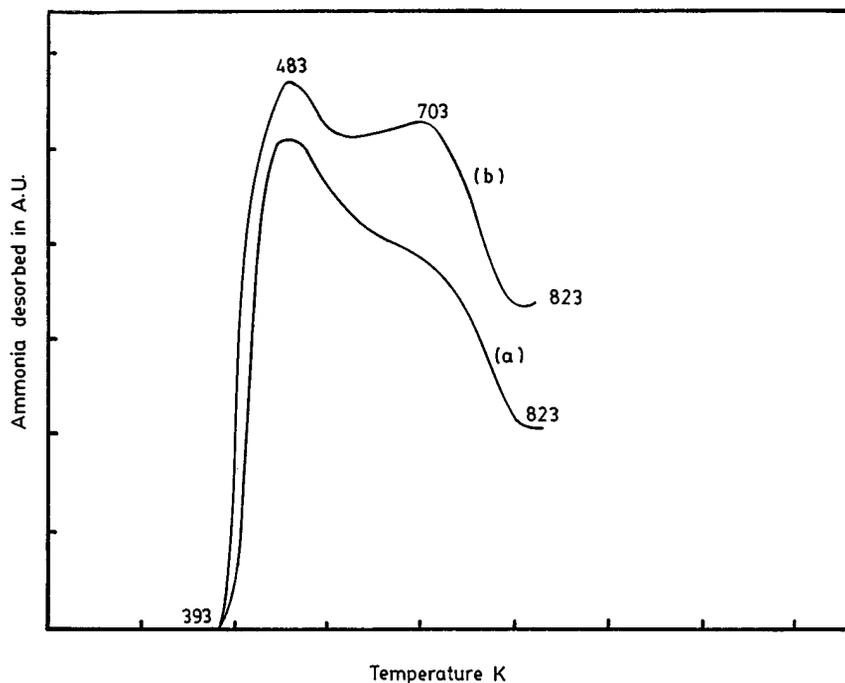


FIG. 8. Chromatograms of ammonia TPD. (a) Fresh catalyst—weight of the catalyst taken for analysis: 0.0819 g. (b) Used catalyst—weight of the catalyst taken for analysis: 0.1115 g.

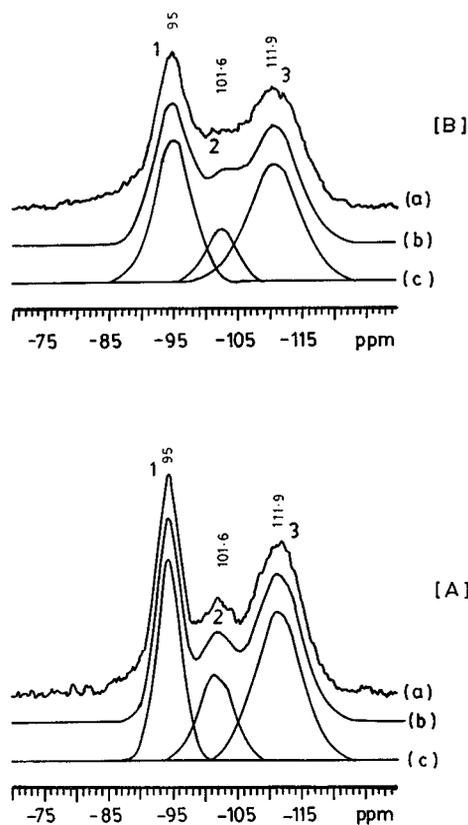


FIG. 9.  $^{29}\text{Si}$  MAS-NMR. [A] Fresh catalyst, [B] used catalyst. (a) Actual spectrum, (b) full-fit, and (c) individual component plots.

## ALKYLATION OF DPA WITH DIB

### Experimental

DIB was obtained from Maruzen Petrochemicals (Japan), through the courtesy of Herdillia Chemicals Ltd. The experiments at 373 K were carried out in a 0.05-m-i.d., 100-ml fully baffled mechanically agitated glass reactor equipped with a stuffing box and a condenser. All the experiments above 373 K were carried out in a 0.051-m-i.d., 100-ml Parr autoclave fitted with a stirrer, a sampling port, a pressure gauge, and a gas vent. The temperature was controlled by temperature controlling device. The reaction was studied in the temperature range of 373 to 453 K.

Analysis was done on a gas chromatograph (Chemito 8510) equipped with the flame ionization detector. A 3-m-long ss column packed with 5% SE-30 supported on

TABLE 5

Relative Linewidths and Peak Areas of  $^{29}\text{Si}$  MAS-NMR

Peak	Peak height		Linewidth (Hz)		Peak area	
	Fresh	Deactivated	Fresh	Deactivated	Fresh	Deactivated
1	53.9	38.1	170	251.9	9162.4	9588.2
2	22.9	14.2	229	206.4	5233.5	2930
3	39.5	31.6	310.6	373.3	12270.6	10855.7

Note. Weight of fresh catalyst sample: 0.2911 g. Weight of deactivated catalyst sample: 0.2803 g.

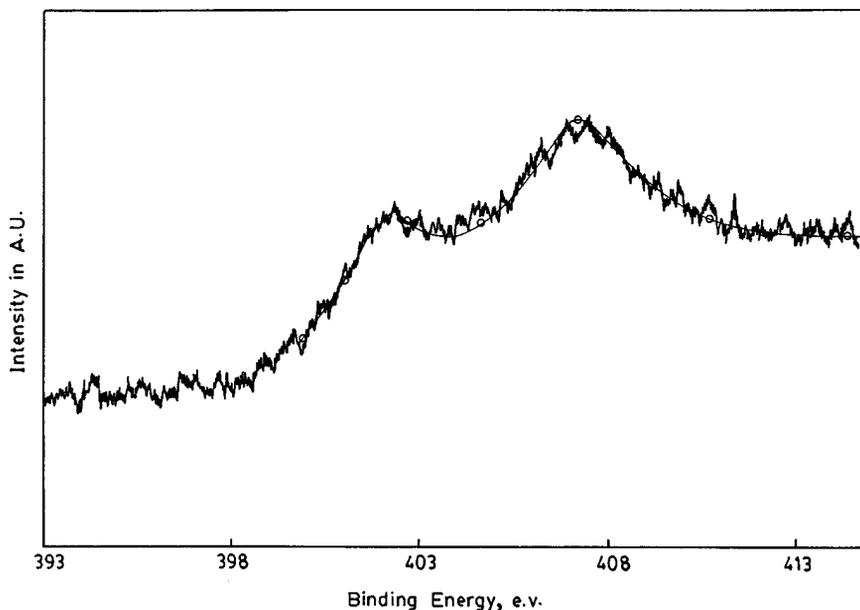


FIG. 10. X-ray photoelectron spectra of used catalyst.

Chromosorb-WHP was used for analysis. The injector and detector were kept at 573 K. The oven temperature was kept at 573 K isothermal. Nitrogen was used as a carrier gas and its flow rate was  $5 \times 10^{-7} \text{ m}^3/\text{s}$ .

### Results and Discussions

**Product separation and characterization.** MODPA and DODPA were obtained in pure form by fractional distillation of the reaction mixture on a Perkin Elmer spinning band distillation column. Both MODPA and DODPA were characterized by FTIR and  $^1\text{H}$  NMR spectra, which confirmed the purity of these compounds. In the range of mole ratios of DPA:DIB studied in this work, a part of DIB cracked into isobutylene gas (IB) at temperatures of 423 K and above. IB reacted with a part of DPA to form 4-*tert*-butyl diphenylamine and with a part of MODPA to form 4-(1,1,3,3-tetramethylbutyl), 4'-*tert*-butyl diphenylamine. The formation of 4-*tert*-butyl diphenylamine was confirmed by reacting DPA with IB in the presence of Engelhard F-24 catalyst in an autoclave at 383 K under 3.4 bar pressure of IB; whereas the formation of 4-(1,1,3,3-tetramethylbutyl), 4'-*tert*-butyl diphenylamine, was confirmed by reacting MODPA with IB in the presence of Engelhard F-24 catalyst in an autoclave under same conditions of temperature and pressure. *n*-heptane was used as a solvent for both these reactions.

**Effect of speed of agitation.** The variation in stirring speed from 1000 to 1500 rpm had no effect on the rate of reaction, indicating that the external mass transfer resistance was absent. Hence, all the further experiments were carried out at 1000 rpm.

**Effect of particle size of catalyst.** The effect of particle size of the catalyst on the rate of reaction was studied in the range of particle size from 0.6 to 0.18 mm. It was observed that there was no effect of particle size of the catalyst on the rate of conversion of DPA and selectivity of DODPA.

**Catalyst reusability.** The effect of repeated use of the catalyst on the rate of conversion of DPA and selectivity of DODPA revealed that deactivation of the catalyst occurred during the course of the reaction. All the reactions for the catalyst reusability and regeneration study, in the further discussion, are carried out, with DPA:DIB mole ratio of 1:4, 10% (w/w) loading of Engelhard F-24 catalyst, and at 423 K and the results of percentage conversion of DPA and selectivity of DODPA after 6 h of reaction are reported. The effect of repeated use of the catalyst on the rate of conversion of DPA is shown in Fig. 11. The percentage conversion of DPA with the fresh catalyst was 100% and the selectivity of DODPA was 45.7%. The percentage conversion of DPA decreased to 79, 73.8, and 71.1% and the selectivity of DODPA decreased to 25.5, 22.7% and 21.3% for the first, second, and third reuse of the catalyst, respectively.

**Effect of reflux methanol wash on catalyst regeneration.** The deactivated catalyst could be partially regenerated by refluxing with methanol for 2 h followed by drying at 373 K under vacuum for 6 h. The extent of catalyst regeneration was studied for three consecutive batches by refluxing the catalyst with methanol each time followed by drying. The percentage conversion of DPA was 100, 100, and 100% and the selectivity of DODPA was 37.8, 36.6, and 34% for the first reuse after methanol wash, second reuse after methanol wash, and third reuse after methanol wash, respectively.

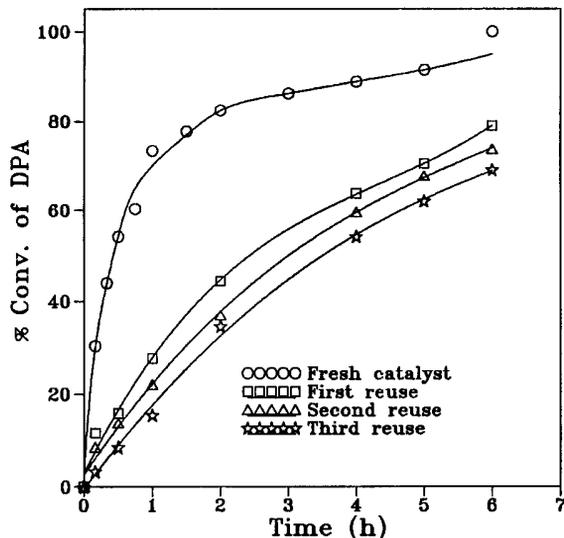


FIG. 11. Effect of repeated use of catalyst on rate of conversion of DPA. Reaction conditions: DPA : DIB mole ratio, 1 : 4; temperature, 423 K; catalyst loading, 10% Engelhard F-24.

*Comparison of the alkylation data for AMS and DIB.* The similar features of alkylation of DPA with AMS and DIB, were that the alkylation occurred at both the *para* positions of DPA for both the olefins and there was no *ortho*, *meta*, or N alkylation in either case. Deactivation of the acid-treated clay catalyst occurred during the course of both the alkylations. Also both these reactions were unsuccessful with the macroporous ion exchange resin catalyst.

The rate of alkylation of DPA with AMS, was much higher than that of DPA with DIB, e.g., in a reaction between DPA and AMS, with a mole ratio of DPA : AMS of 1 : 2, 10% (w/w) loading of Engelhard F-24 catalyst, 100% conversion of DPA was obtained, at 363 K after 1.5 h of reaction; whereas in a reaction between DPA and DIB, even with a mole ratio of DPA : DIB of 1 : 3, 10% loading of Engelhard F-24 catalyst, only 55.1% conversion of DPA was obtained, at 373 K even after 6 h of reaction. A comparison of the selectivities of dialkylated products of both the reactions, i.e., DCDPA and DODPA, indicated that high selectivity (~65%) of DCDPA was obtained even at low temperature like 363 K, whereas the selectivity of DODPA was very low (~12%) at a temperature of 373 K under otherwise identical conditions. At high temperatures, e.g., 423 K, the selectivity of DODPA reached a maximum (~62%), at a mole ratio of DPA : DIB of 1 : 5 and then decreased due to cracking of DIB into IB. In the case of reaction between DPA and AMS, as there was no question of cracking of AMS, very high selectivity (~95%) could be realized at a mole ratio of DPA : AMS of 1 : 4 and 423 K. Dimerization of AMS occurred in the presence of acid-treated clay catalyst even at low temperatures like 333 K. The extent of undesired AMS dimerization could be suppressed by carrying

out the reaction in semibatch mode of addition. In the case of reaction of DPA with DIB, the extent of dimerization of DIB was negligible.

To summarize, under otherwise identical conditions, AMS is a more reactive olefin than DIB for the alkylation of DPA. Also in the case of reaction between DPA and AMS, high selectivity of DCDPA could be realized at low temperature, e.g., 363 K, and atmospheric pressure; whereas in the case of reaction of DPA and DIB, to obtain the same selectivity of DODPA, the reaction had to be carried out at a higher temperature, i.e., 423 K, in an autoclave.

## CONCLUSIONS

Acid-treated clay, Engelhard F-24, was found to be a very effective catalyst for the alkylation of DPA with AMS and DIB, to produce mono- and dialkylated diphenylamines. It was possible to obtain high selectivity of each of the alkylated products by a proper selection of the reaction conditions. The various other grades of acid-treated clays were also found to be useful catalysts for the reaction between DPA and AMS. The reaction was unsuccessful with the macroporous ion exchange resin catalyst, Amberlyst 15. A comparison of the alkylation data for the two olefins indicated that, for the alkylation of DPA, AMS is more reactive as compared to DIB.

The reaction between DPA and AMS can be conducted in a continuous mode of operation in a FBR, where high conversion of DPA and selectivity of DCDPA could be realized.

Deactivation of the catalyst occurred during the course of these reactions. The characterization of the fresh and used catalysts, of the reaction between DPA and AMS, by various techniques indicated that the fresh catalyst had a microporous structure with a high surface area. The deactivation of the catalyst was due to adsorption of DPA and/or the alkylated product(s) on the surface of the catalyst, which led to a decrease in the surface area of the catalyst. The deactivation was also due to loss of microporous structure of the catalyst and due to a decrease in the number of Brønsted acid sites, which were responsible for the reaction, since the reaction is acid catalyzed.

It was possible to regenerate the deactivated catalyst partially, by washing it with methanol under reflux and also by the use of ultrasonic irradiation. Use of a solvent in the reaction produced an adverse effect on the catalyst regeneration.

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