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N-Alkylation of Aniline with Methanol over $CrPO_4$ and $CrPO_4$–$AlPO_4$ (5–50 wt% $AlPO_4$) Catalysts

F. M. Bautista, J. M. Campelo,[1] A. Garcia, D. Luna, J. M. Marinas, A. A. Romero, and M. R. Urbano

Departamento Química Orgánica, Facultad de Ciencias, Universidad de Córdoba, Avenida San Alberto Magno, s/n, E-14004 Córdoba, Spain

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The vapor-phase alkylation of aniline with methanol was carried out at atmospheric pressure and different temperatures (573–673 K) and feed rates over $CrPO_4$ (CrP) and $CrPO_4$–$AlPO_4$ (CrAlP, 5–50 wt% $AlPO_4$) catalysts. Aniline methylation was a pseudo-first-order process with respect to aniline concentration. The effect of surface acidity on aniline alkylation, as measured by pyridine and 2,6-dimethylpyridine adsorption, is discussed. The influence of feed rate (WHSV), time-on-stream and temperature on both activity and product selectivity was also investigated. Alkylation is a sequential reaction process, in which methylation of aniline produces N-methylaniline (NMA), then N,N-dimethylaniline (NNDMA) and subsequently N,N-dimethyltoluidines (NNDMT, *p*- > *o*-). N-methylation products (NMA + NNDMA) are predominant with a selectivity over 90 mol% in the temperature range 573–673 K. Selectivity to N,N-dimethylaniline is enhanced as reaction temperature and/or contact time increases. N,N-dimethyltoluidines are only present in very small amounts at higher temperatures and/or contact times. © 1997 Academic Press

INTRODUCTION

Aniline alkylation is an industrially important reaction due to the fact that many valuable bulk, intermediate and fine chemicals can be prepared. Thus, alkylanilines form the basic raw materials for synthesis of organic chemicals and chemical intermediates or additives in dyes, synthetic rubbers, explosives, herbicides, and pharmaceuticals. Vapor-phase aniline alkylation over environmentally safe solid catalysts is an answer to the conventional method of producing alkylanilines using mineral acids and Friedel–Crafts type catalysts (1). The traditional route also presents the disadvantage of high capital cost, reactor corrosion, and formation of by-products that cannot be recycled. Several types of catalysts based on oxides and supported oxides (2–10), zeolites (11–23), and microporous aluminophosphates (23–25) have been tested for aniline methylation. The main factors influencing activity and selectivity (N- and/or C-alkylation) are acid-base properties (number and strength) and shape-selectivity in the solid acid catalyst as well as reaction conditions (temperature, composition and feed rate). Low reaction temperatures favor N-alkylation, whereas at high temperatures C-alkylation appears. There are examples in the literature which showed that the formation of N- and C-methylanilines depend on reaction conditions and catalysts. Zeolites with large pores and a three-dimensional channel structure (faujasite and beta) favor polyalkylated phenyl-rings even when no strong Brönsted acid sites are present, such as for Mg- or Zn-ion-exchanged Y zeolites (18). Moreover, the activity of acid catalysts for aniline alkylation might be suppressed by the adsorption of aniline since it is a strong base. It therefore seems that the use of a strong acid catalyst is not suitable for this reaction. In this sense, Woo *et al.* (16) using metallosilicates of the pentasil family, suggest that strong, medium, and weak acid sites are active sites to produce, respectively, C-alkylate and coke, N,N-dimethylaniline and N-methyltoluidine, and N-methylaniline.

As far as the aniline alkylation is concerned, in two previous papers (26, 27) we studied the N-methylation of aniline over $AlPO_4$, Al_2O_3, $AlPO_4$–Al_2O_3, $AlPO_4$–TiO_2, and $AlPO_4$–ZrO_2 catalysts. The results showed that $AlPO_4$–Al_2O_3 catalysts exhibited significantly higher activity (an order of magnitude) and, besides, there was a slight increase in activity on increasing Al_2O_3 loading up to 15 wt% (27), thereby showing that $AlPO_4$–Al_2O_3 catalysts are suitable for selectively obtaining N-alkylation products. Moreover, a comparison with SAPO-5 (28, 29) and a commercial SiO_2–Al_2O_3 (13 wt% Al_2O_3, Si-235 Harshaw Chemie) catalysts (26), which displayed a greater number of medium and strong acid sites than $AlPO_4$–Al_2O_3 catalysts, showed that the former catalysts exhibited a decrease in aniline methylation activity with respect to the latter ones. Nevertheless, selectivity to N-alkylation (N-methyl and N,N-dimethylanilines) attained 100 mol% in all cases.

On the other hand, in previous papers (30–35) we prepared and characterized different $CrPO_4$ (CrP, $Cr/P = 1$) and $CrPO_4$–$AlPO_4$ (CrAlP, 5–50 wt% $AlPO_4$) catalysts. Their texture, crystal structure, and surface acid–base character are affected by the preparative method (gellification

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[1] To whom correspondence should be addressed.

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agent), $AlPO_4$ loading and calcination temperature. Thus, with regard to $CrPO_4$ catalysts, those obtained in propylene oxide-aqueous ammonia mixed medium exhibited higher surface acidity and, hence, improved catalytic activity for acid catalyzed reactions like cyclohexene (30, 31, 33) and 3,3-dimethyl-1-butene (35) isomerizations, cumene conversion (30, 31, 33), and 2-propanol dehydration (34). Besides, this $CrPO_4$ catalyst exhibited an improved activity in relation to $AlPO_4$ and $AlPO_4$–Al_2O_3 catalysts, similarly prepared. Moreover, the modification of $CrPO_4$ with small amounts of $AlPO_4$ leads to $CrPO_4$–$AlPO_4$ catalysts exhibiting greater catalytic activity for the above-cited processes. In all cases, $AlPO_4$, $AlPO_4$–Al_2O_3, $CrPO_4$, and $CrPO_4$–$AlPO_4$ catalysts, the activities can be well interpreted to result from the differences in the number and strength of acid sites.

In the present work we have carried out the vapor-phase N-methylation of aniline over $CrPO_4$ and $CrPO_4$–$AlPO_4$ catalysts, prepared in different ways, under identical reaction conditions that are described elsewhere for $AlPO_4$, $AlPO_4$–Al_2O_3, SAPO-5, and SiO_2–Al_2O_3 catalysts (26, 27). We will focus on the effect of surface acidity upon activity and reaction selectivity. In addition, the influences of methanol/aniline molar ratio, time-on-stream, reaction temperature, and contact time are also studied.

EXPERIMENTAL

Materials

Methanol, aniline, N-methylaniline, N,N-dimethylaniline, and N,N-dimethyltoluidines (*ortho* and *para*) were of high purity (99+%) and used without further purification.

Catalysts

$CrPO_4$ (CrP, Cr/P = 1) catalysts (Table 1) were obtained by precipitation, from chromium nitrate and aqueous phosphoric acid solutions, with aqueous ammonia (CrP−A), propylene oxide (CrP−P), or propylene oxide-aqueous ammonia (CrP−PA). $CrPO_4$–$AlPO_4$ catalysts of varying composition (5–50 wt% $AlPO_4$) were obtained with aqueous ammonia (CrAlP−A) and $CrPO_4$–$AlPO_4$ catalysts with 5 and 10 wt% $AlPO_4$ were also obtained by precipitation with propylene oxide-aqueous ammonia (CrAlP−PA). Details on the preparation, as well as on the characterization of all catalysts, have been previously described (30–33). The catalysts are designated by CrP or CrAlP followed by the letters indicating the precipitation medium, a number that indicates the $AlPO_4$ loading (wt%) in CrAlP catalysts and by another number which refers to the calcination temperature in K (CrP−A-923, CrAlP−PA-10–773, and so on).

The surface area (S_{BET}), pore volume (V_{p}), and mean pore radius (r_{p}) are collected in Table 1.

Surface Acidity

The surface acidity was measured in a dynamic mode by means of the gas-phase adsorption of probe molecules by using a pulse-chromatographic technique (36, 37). As probe molecules we used pyridine (PY), which reacts with Brönsted acid sites and Lewis acid sites, and 2,6-dimethylpyridine (DMPY) which titrates only Brönsted acid sites. The results are in Table 1.

Catalytic Activity Measurements

The reactions were conducted in a vapor-phase continuous stainless-steel down-flow fixed-bed reactor (6 mm ID) surrounded by an electric heater. An iron–constantan thermocouple was placed in the middle of the catalyst bed and the unit operated at atmospheric pressure. The substrate was delivered at a set flow rate using a liquid syringe pump (Harward Md. 44) and was vaporized prior to passing it through the catalyst bed in the presence of a flow of nitrogen

TABLE 1

Textural Properties and Surface Acidity (vs PY and DMPY) of $CrPO_4$ and $CrPO_4$–$AlPO_4$ Catalysts

Catalysts	S_{BET} (m^2/g)	V_{p} (ml/g)	r_{p} (nm)	PY[a] (μmol/g)	PY[b] (μmol/g)	DMPY[a] (μmol/g)	DMPY[b] (μmol/g)
CrP−A-923	8	—	—	18	17	9	—[c]
CrP−P-923	6	—	—	24	17	7	—[c]
Cr−PA-923	23	0.18	15.5	70	52	58	58
CrAlP−PA-5–923	55	0.26	9.3	91	56	61	50
CrAlP−PA-10–773	58	0.29	9.9	86	63	60	54
CrAlP−PA-10–993	38	0.28	14.9	85	64	54	40
CrAlP−A-5–923	16	0.08	9.9	25	14	13	13
CrAlP−A-10–923	16	0.09	10.6	26	26	8	8
CrAlP−A-20–923	9	0.08	18.4	27	22	6	6
CrAlP−A-30–923	13	0.10	17.6	38	37	17	10
CrAlP−A-50–923	40	0.20	10.0	76	26	15	15

[a] Adsorption at 573 K.

[b] Adsorption at 673 K.

[c] There is no adsorption of the probe molecule.

carrier gas ($3\ \mathrm{L\ h^{-1}}$) regulated by mass-flow controllers. The catalyst charges (W) were small, usually 0.1–0.3 g, retained by quartz wool at almost the center of the reactor, and reaction temperature was 673 K, except where otherwise specified. Standard catalyst pretreatment was carried out *in situ* at 673 K for 1 h under a stream of high purity nitrogen (99.999%, $H_2O < 3$ ppm). In order to prevent any condensation of reactant and products all connections were heated by heating tapes at 490 K. Blank runs at 673 K showed that under the experimental conditions used in this work, the thermal effects could be neglected.

The reaction products were on-line sampled every 15 min and analyzed by GLC (Varian Md. 3400) by using a stainless-steel column (2 m × 3 mm) of 10% Carbowax 20 *M*/2% KOH on Chromosorb W-AW 80/100. Product characterization was performed by GC-MS (HP 5890 gas-chroatograph coupled with a VG AutoSpec high-resolution mass spectrometer) using products condensed in a cold trap. Reaction products were: N-methyl (NMA) and N,N-dimethylaniline (NNDMA) and minor amounts of N,N-dimethyltoluidines (NNDMT, *p*- > *o*-). Product such as diphenylamine was never found by high-resolution mass spectrometry. Response factors of the reaction products were determined with respect to aniline from GC analysis using known compounds in calibration mixtures of specified compositions. The conversions reported here are on a methanol-free aniline basis and the selectivities are expressed as the ratio of moles of a given product to the total number of moles produced (mol%). Deactivation by coke was negligible in all cases except for the CrP−PA-923 catalyst.

RESULTS AND DISCUSSION

The alkylation of aniline with methanol on $CrPO_4$ and $CrPO_4$–$AlPO_4$ (5–50 wt% $AlPO_4$, CrAlP) catalysts produces N-methyl (NMA) and N,N-dimethylaniline (NNDMA) with a selectivity over 90 mol% with respect to the sum of both products, thus indicating the selective formation of N-alkylated products. N,N-dimethyltoluidines (*p*- > *o*-) are only present in very small amounts at the highest reaction temperatures.

In the absence of boundary, inter- and intraparticle diffusion effects (feed rates over $3 \times 10^{-6}\ \mathrm{mol\ s^{-1}}$ and catalyst particle size lower than 0.149 mm) aniline conversion data (X_{AN}) are fitted in a first-order rate equation:

$$\ln[1/(1 - X_{AN})] = k(W/F), \qquad [1]$$

where W is the catalyst weight and F the feed rate. Runs were performed with at least three feed rates in the range $3.0–6.7 \times 10^{-6}\ \mathrm{mol\ s^{-1}}$ (5 *M* aniline in methanol), and at reaction temperatures in the range 573–673 K. Under these conditions, substrate conversion was easily kept well under 20 mol%. The $\ln[1/(1 - X_{AN})]$ versus (W/F) plots, according to Eq. [1], are linear and also pass through the origin, indicating a good fit of the data to Eq. [1] and, therefore, the methylation process is a first-order reaction with respect to aniline concentration. Moreover, calculations were used only to compare the reactivities of the different catalysts and not aimed at finding the detailed rate equations.

The slope of these straight lines yielded the values of the initial reaction rate constants (k) in $\mathrm{mol\ g^{-1}\ s^{-1}}$. The values obtained at 673 K for the different catalysts, after 2 h and 4 h on stream, are collected in Table 2. A Students' *t*-test of significance, using the position of the 98% confidence limit lines and the determination coefficient value (always over 0.99) of the regressions, showed that the activity data are significant at levels over 1%. At least three measurements were used to calculate each value of k and all values are reproducible to within about 8%. The conversion of aniline (X_{AN}) and the reaction selectivities to N-methylaniline

TABLE 2

Aniline Conversion (X_{AN}, mol%), Reaction Rate Constant (k, mol/g s) and Product Selectivities (S, mol%) in Aniline Alkylation with Methanol over $CrPO_4$ and $CrPO_4$–$AlPO_4$ (5–50 wt% $AlPO_4$) Catalysts[a]

	2 h on-stream				4 h on-stream			
Catalyst	X_{AN}	$k \times 10^6$	S_{NMA}	S_{NNDMA}	X_{AN}	$k \times 10^6$	S_{NMA}	S_{NNDMA}
CrP−A-923	1.0	0.3	100	—	1.0	0.3	100	—
CrP−P-923	1.3	0.4	100	—	1.3	0.4	100	—
CrP−PA-923	10.0	3.5	92.7	7.3	8.2	2.8	93.6	6.4
CrAlP−PA-5–923	5.9	2.0	94.6	5.4	5.9	2.0	94.9	5.1
CrAl−PA-10–923	6.1	2.1	94.3	5.6	6.0	2.1	94.3	5.6
CrAlP−A-5–923	2.4	0.8	97.7	2.3	2.1	0.7	98.4	1.6
CrAlP−A-10–923	1.5	0.5	98.6	1.4	1.5	0.5	98.5	1.5
CrAlP−A-20–923	1.6	0.6	98.3	1.7	1.6	0.5	98.4	1.6
CrAlP−A-30–923	1.8	0.6	98.1	1.9	1.8	0.6	98.0	2.0
CrAlP−A-50–923	3.4	1.2	96.1	3.9	3.3	1.1	96.1	3.9

[a] T, 673 K; $F = 3.36 \times 10^{-6}$ mol/s; WHSV = $9.53\ \mathrm{h^{-1}}$; 5 *M* aniline in methanol.

(S_{NMA}) and N,N-dimethylaniline (S_{NNDMA}) are also collected in Table 2.

On $CrPO_4$ catalysts the aniline conversions are in the range 1–10 mol% and increase in the order CrP–A < CrP–P < CrP–PA, i.e., as the surface acidity increases. The incorporation of $AlPO_4$ into $CrPO_4$ resulted in CrAlP catalysts in which the catalytic performance depends on the precipitation method. Thus, those CrAlP catalysts obtained in aqueous ammonia (CrAlP–A) exhibit, irrespective of the $AlPO_4$ loading, an increase in surface acidity and activity relative to the CrP–A catalysts; the increase in activity is more significant in the case of CrAlP–A-50 catalyst. Moreover, when the CrAlP catalyst is prepared in propylene oxide-aqueous ammonia (CrAlP–PA), aniline methylation activity decreases with respect to the CrP–PA catalyst. Notwithstanding, CrAlP–PA-5 and CrAlP–PA-10 catalysts exhibit higher aniline methylation activity than those obtained in ammonia (CrAlP–A-5 and CrAlP–A-10).

With respect to the surface acidity, the incorporation of $AlPO_4$ to the CrP–PA catalyst results in CrAlP–PA catalysts exhibiting higher thermal stability and surface acidity and, hence, greater catalyst activity in cyclohexene (30, 31, 33) and 3,3-dimethyl-1-butene (35) skeletal isomerizations, typical acid-catalyzed reactions. However, in aniline methylation this increased acidity not only did not result in increased activity, but also decreased X_{AN}. Thus, the increase in acidity is not reflected in the aniline methylation activity. This raises the basic question of the role of acidity in this aniline alkylation reaction. Comparing the acidity data in Table 1 and the corresponding aniline methylation in Table 2, one is tempted to believe that there is not a simple relationship between aniline alkylation activity and acidity as measured by pyridine and 2,6-dimethylpyridine adsorption at 673 K.

A similar decrease has been reported in aniline alkylation activity with an increase in acidity (16, 19, 38), so that it may be suggested that strong acid sites are not required for aniline N-alkylation. In this sense, when using zeolites as catalysts, the acidity increases as SiO_2/Al_2O_3 ratio while the catalytic activity showed a maximum at intermediate SiO_2/Al_2O_3 ratio (38). This behavior may be explained because that reaction proceeded to a great degree in the weak Brönsted acid sites because aniline and its derivatives, being basic, could be more strongly adsorbed at strong acid sites, thus deactivating the catalyst. Moreover, in the presence of strong Brönsted acid sites, the aniline molecule can be protonated, thus reducing its alkylation. Thus, Woo *et al.* (16) suggested that strong, medium, and weak acid sites are active sites to produce C-alkylate and coke, NNDMA, and NMA, respectively, so that strongly acidic catalysts ought to be modified by the incorporation of alkali metal species in order to increase the selectivity to NNDMA.

The present results using $CrPO_4$ and $CrPO_4$–$AlPO_4$ catalysts and those previously obtained on $AlPO_4$, $AlPO_4$-metal oxide (Al_2O_3, TiO_2, and ZrO_2), SAPO-5, and commercial SiO_2–Al_2O_3 catalysts (26, 27) provide enough data to corroborate that strong acid sites are not required for aniline N-methylation.

TABLE 3

Selectivities to N-Methylaniline and N,N-Dimethylaniline (mol%) at Various Aniline Conversions[a]

Catalyst	$X_{\mathrm{AN}} = 5$ mol%		$X_{\mathrm{AN}} = 10$ mol%		$X_{\mathrm{AN}} = 20$ mol%	
	S_{NMA}	S_{NNDMA}	S_{NMA}	S_{NNDMA}	S_{NMA}	S_{NNDMA}
CrP–PA-923	93.7	6.3	91.3	8.7	83.6	16.4
CrAlP–PA-5–923	93.6	6.4	89.1	10.9	87.0	13.0
CrAl–PA-10–923	94.5	5.5	88.3	11.7	79.9	20.1
CrAlP–A-5–923	94.6	5.4	88.4	11.6	—[b]	
CrAlP–A-10–923	92.5	7.5	—[b]		—[b]	
CrAlP–A-20–923	91.8	8.2	89.0	11.0	—[b]	
CrAlP–A-30–923	93.9	6.1	88.9	11.1	—[b]	
CrAlP–A-50–923	94.1	5.9	88.6	11.4	—[b]	

[a] WHSV = 9.53 h^{-1}; 5 *M* aniline in methanol.

[b] There is no result at this conversion.

As far as selectivity of aniline N-methylation is concerned. Table 3 compares product selectivities (S_{NMA} and S_{NNDMA}) at three similar conversion levels (5–20 mol%) and at a constant reaction temperature of 673 K. Under the conditions used, data in Table 3 show that the addition of $AlPO_4$ to $CrPO_4$ did not cause any significant change in the selectivity patterns exhibited by $CrPO_4$; thus similar adsorbed species must be formed on $CrPO_4$ and $CrPO_4$–$AlPO_4$ catalysts. Moreover, S_{NNDMA} increased with aniline conversion. As compared to previously studied $AlPO_4$, $AlPO_4$-metal oxide (Al_2O_3, TiO_2, and ZrO_2), SAPO-5, and commercial SiO_2–Al_2O_3 catalysts (26, 27), $CrPO_4$, and $CrPO_4$–$AlPO_4$ catalysts are less active but, however, they are more selective for the N-monomethylation process, yielding N-methylaniline, when similar conversion level are attained.

Effect of Feed Rate

Figure 1 shows the influence of weight hourly space velocity (WHSV = 1.5–9.5 h^{-1}) on aniline conversion and the product selectivities for CrAlP–PA-5–923 catalyst after 2 h on stream at 673 K. On increasing WHSV, aniline conversion decreases. This decrease is from 40 mol% (WHSV = 1.51 h^{-1}) to 6 mol% (WHSV = 9.53 h^{-1}). The product pattern with respect to WHSV reveals that selectivity to N-methylaniline continuously increases with the feed rate. Moreover, decreasing the WHSV enhances the alkylation rate, leading to the favorable formation of N,N-dimethylaniline and N,N-dimethyl-*p*-toluidine, although the latter appears at low selectivity. There is always more N-methylaniline produced than N,N-dimethylaniline, and the formation of N,N-dimethyltoluidines (*p*- > *o*-) is found only over the more acidic catalysts and at low WHSV.

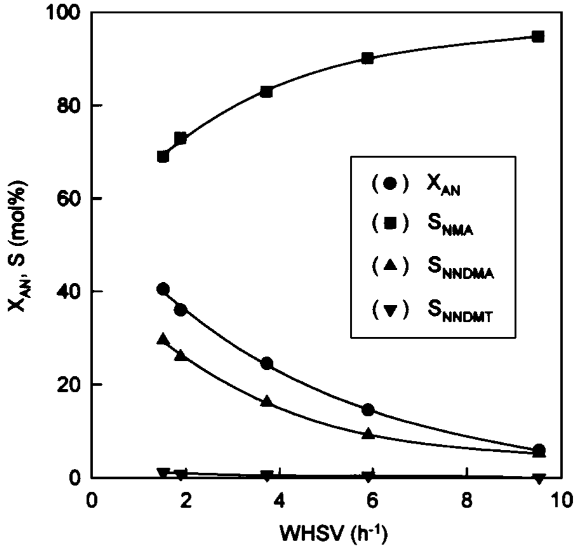

FIG. 1. Effect of feed rate (WHSV, h^{-1}) on aniline conversion and product selectivities over CrAlP–PA-5–923 catalyst (*T*, 673 K; time-on-stream, 2 h).

The selectivity to N,N-dimethyltoluidines decreases strongly as WHSV increases.

Effect of Time-on-Stream

A time-on-stream (t.o.s.) study was performed at 673 K with a WHSV of 9.53 h^{-1} and a 5 *M* solution of aniline in methanol. A typical activity profile of aniline methylation as a function of t.o.s. on CrP and CrAlP catalysts is presented in Fig. 2 for CrP–PA-923 catalyst. Here we can see that the aniline conversion decreased slightly initially but after 2 h on-stream remained almost unchanged with t.o.s. Moreover, the selectivities to N-methyl and N,N-dimethylaniline did not show any change within 10 h on-stream. All catalysts displayed almost the same behavior and so there was not much deactivation of catalysts at 673 K and the selectivity of N-alkylation remained at 100 mol% during this period of process time.

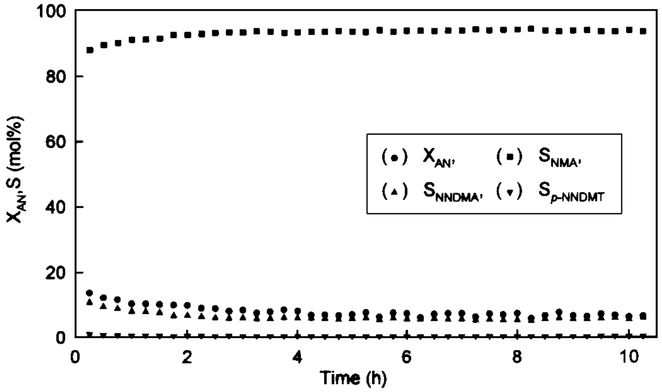

FIG. 2. Time-on-stream dependence of aniline conversion (X_{AN}) and product selectivities in aniline alkylation with methanol at 673 K and WHSV = 9.53 h^{-1} (5 *M* aniline in methanol) over CrP–PA-923 catalyst.

Effect of Reaction Temperature

Under the experimental conditions used here (WHSV = 3.73 h^{-1}), the aniline conversion increased continuously with reaction temperature (573–673 K), as Fig. 3 shows for CrAlP–PA-10–773 catalyst after 2 h on-stream. The other catalysts showed similar behavior.

Although at a given temperature the actual conversion was different for different catalysts, as the temperature increases from 573 to 673 K, the aniline conversion always increases. Figure 3 also includes the variation of selectivity with temperature and, thus, the selectivity for N-methylaniline decreases, whereas that for N,N-dimethylaniline increases, as the temperature rises. The selectivity of the former product decreases from 99 mol% (573 K) to 57 mol% (673 K), whereas that of the latter increases from 1 mol% to 36 mol%. A small increase in the amount of C-alkylated anilines, namely N,N-dimethyltoluidines (N,N-dimethyl-*p*-toluidine almost exclusively), was observed at temperatures above 573 K. N-alkylation was the predominant reaction with selectivity nearly 100 mol% up to 623 K, whereas the selectivity to N,N-dimethyltoluidines in any case attained a high value at the highest reaction temperature (673 K) even with the most active catalyst (never surpassing 12 mol% of the total selectivity).

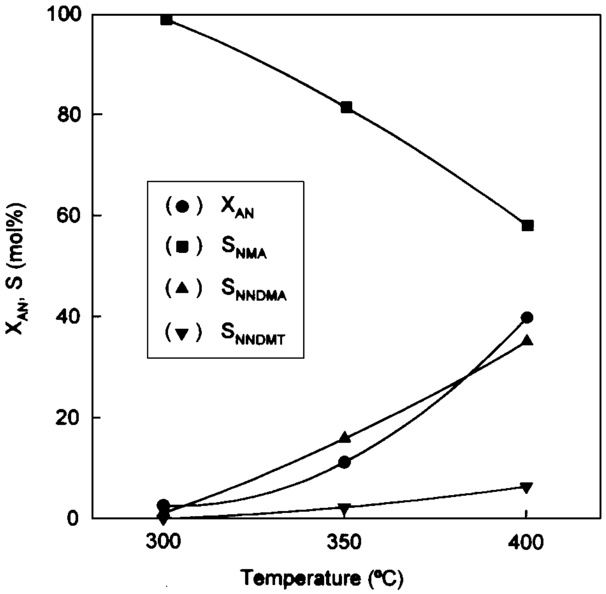

FIG. 3. Effect of reaction temperature on aniline conversion and product selectivities over CrAlP–PA-10–773 catalyst (WHSV, 3.73 h^{-1}; time-on-stream, 2 h).

Reaction Pathway

In order to better understand the reaction sequence, we have built the optimum performance envelope (OPE) curves by plotting fractional conversion to each reaction product against aniline conversion (X_{AN}) for different weight ratios of catalyst with respect to introduced aniline (Fig. 4), such as recently described by Best and Wojciechowski (39). In these curves we have included experimental data corresponding to different temperatures and feed rates on the same diagram. By using such a procedure, an insignificant scattering of the data is evident in the selectivity diagrams and clear tendencies can be observed from these curves. Thus, analysis of selectivity data for aniline methylation through OPE curves (as illustrated in Fig. 4 for CrAlP–PA-10–773 catalyst), indicated that, in all cases, N-methylaniline was a primary product coming from aniline by alkylation, although it is a reactive intermediate since a maximum on its OPE curve was found. Moreover, N,N-dimethylaniline is a secondary product since a zero slope at the origin, together with an upward deviation as X_{AN} increases, was found by plotting their fractional conversion (X_{NNDMA}) versus X_{AN}. At higher X_{AN} values, N,N-dimethyltoluidines *(p- > o-)* also appeared and so they seem to be secondary reaction products. These secondary products are formed at the expense of N-methylaniline.

From the data on feed rate, temperature, and OPE curves, it can be concluded that aniline methylation on $CrPO_4$ and $CrPO_4$–$AlPO_4$ catalysts follows a sequential reaction pathway in the formation of N-methylaniline, which is further converted to N,N-dimethylaniline and, then, this undergoes further C-methylation to give N,N-dimethyltoluidines (*p*- > *o*-) at higher temperatures,

$$\mathrm{AN} \xrightarrow{\mathrm{MeOH}} \mathrm{NMA} \xrightarrow{\mathrm{MeOH}} \mathrm{NNDMA} \xrightarrow{\mathrm{MeOH}} \mathrm{NNDMT}\ (p\text{-} > o\text{-}),$$

as occurs on $AlPO_4$, $AlPO_4$–Al_2O_3, and other acid catalysts (10, 16, 19, 23, 26, 27, 38). The driving force here is the greater nucleophylicity of the N atom over the C atom. Besides, N-methylaniline reacts faster than aniline due to its greater negative charge on the N-atom associated with the electron donating effect on the methyl group that facilitates its alkylation. Moreover, dimethyl substitution on N-atom makes easy ring alkylation at *o*- or *p*-position by electron donation to the benzene ring, while the steric hindrance in the *o*-isomer is responsible for the larger formation of *p*-isomer. Notwithstanding, N-methylation always predominates. The formation of N,N-dimethylaniline via disproportionation is less favorable than its formation via successive alkylation (16).

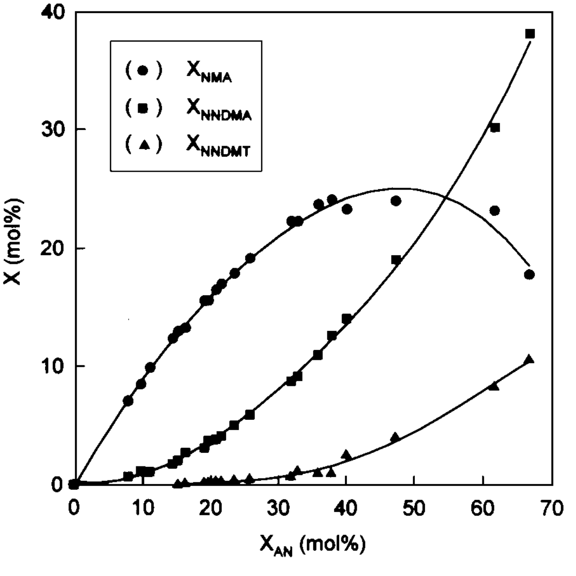

FIG. 4. OPE curves for aniline conversion over CrAlP–PA-10–773 catalyst. Fractional conversion at a particular reaction product (X) versus aniline conversion (X_{AN}).

CONCLUSIONS

In the present reaction conditions, alkylation to N-methyl and N,N-dimethylaniline is the major reaction path in the alkylation of aniline with methanol over $CrPO_4$ and $CrPO_4$–$AlPO_4$ catalysts prepared in different ways. Thus, N-alkylated products result in selectivity over 90 mol% throughout the 573–673 K temperature range. Varying the feed rates indicates that low contact time and low temperature promote the N-monomethylation reaction. Moreover, N,N-dimethyltoluidines (*p*- > *o*-) are only present in very small quantities at the highest temperatures and/or contact times. On the other hand, the additon of $AlPO_4$ to $CrPO_4$ did not cause any significant change in the selectivity pattern exhibited by the $CrPO_4$ catalyst. This behavior could indicate that similar adsorbed active species are formed on $CrPO_4$ and $CrPO_4$–$AlPO_4$ catalysts. Furthermore, there is no simple relationship between aniline alkylation activity and surface acidity measured by pyridine and 2,6-dimethylpyridine adsorption at 573–673 K. As compared to previously studied $AlPO_4$, $AlPO_4$-metal oxide (Al_2O_3, TiO_2, and ZrO_2), SAPO-5, and commercial SiO_2–Al_2O_3 catalysts (26, 27), $CrPO_4$ and $CrPO_4$–$AlPO_4$ catalysts are less active, but, however, they are more selective for the N-monomethylation process, yielding N-methylaniline, when similar conversion levels are attained.

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