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Continuous flow toluene methylation over $AlPO_4$ and $AlPO_4$–Al_2O_3 catalysts

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Toluene methylation with methanol over $AlPO_4$ (AP) and $AlPO_4$–Al_2O_3 (APAl) catalysts, obtained through different methods, was carried out in a continuous down-flow fixed bed reactor. The main products were xylenes (XYL), although trimethylbenzenes (TMB) were also found over APAl catalysts. The benzene and ethylbenzene selectivities increased slightly with time on stream at the expense of XYL and TMB selectivities. Isomer distribution was approximately 50, 24 and 26 mol% for *o*-, *m*- and *p*-XYL, and 72, 27 and 0 mol% for 1,2,3-, 1,2,4- and 1,3,5-TMB. The initial reaction rate constants were higher on APAl catalysts and, furthermore, APAl catalysts exhibited similar catalytic activities, although those obtained in ethylene or propylene oxide are the most active ones. The same occurs on AP catalysts. Moreover, the changes in catalytic activity are similar to the changes in the acidic characteristics measured, in gas phase, versus pyridine. Furthermore, the activity decreased with time on stream due to coke deposition according to the expression $k = k_0 \exp(-\beta t)$. The rate of deactivation, evaluated from the deactivation coefficients (β), was greater for APAl than for AP catalysts.

Keywords: aluminum orthophosphate ($AlPO_4$); $AlPO_4$–Al_2O_3; toluene methylation; methanol; activity; selectivity

1. Introduction

The alkylation of aromatics, in particular benzene and toluene, has been the subject of several investigations [1–6] chiefly because of the importance of aromatic hydrocarbons in the petroleum industry. In this respect, it is now generally accepted that the alkylation process proceeds through a Rideal mechanism for alkylation with alcohols [4,5] where the Brønsted hydroxyl groups are the active sites and the reaction intermediates are carbenium ions.

In a previous paper we studied the methylation of toluene over $AlPO_4$ and

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$AlPO_4$–metal oxide (25 wt% metal oxide: Al_2O_3, TiO_2 and ZrO_2) catalysts by using a microcatalytic pulse reactor [7]. The results showed that $AlPO_4$–Al_2O_3 catalysts exhibited the highest catalytic activity. Moreover, the catalytic activity decreased in the order:

$$AlPO_4-Al_2O_3 \gg AlPO_4 > AlPO_4-TiO_2 > AlPO_4-ZrO_2 .$$

This order is well interpreted on basis of surface acid properties.

In this paper we will report on the results of continuous flow toluene alkylation with methanol over a series of $AlPO_4$ (AP) and $AlPO_4$–Al_2O_3 (25 wt% Al_2O_3, APAl) catalysts obtained by precipitation with aqueous ammonia (A), ethylene (E) or propylene (P) oxide. In particular, we will focus on the effects of the concentration of acid sites upon activity. The deactivation of the catalyst during reaction is also studied.

2. Experimental

2.1. MATERIALS

Methanol, toluene, *o*-, *m*- and *p*-xylene, 1,2,3-, 1,2,4- and 1,3,5-trimethylbenzene were high purity reagents (99+%) and were used without further purification.

Catalysts. Six different catalysts have been used. Three aluminum orthophosphates (AP) obtained by precipitation with aqueous ammonia (A), ethylene oxide (E), or propylene oxide (P). Three aluminum orthophosphate–alumina (25 wt% Al_2O_3) systems obtained by adding aluminum hydroxide to a reaction medium where the precipitation of $AlPO_4$ was initiated by the addition of aqueous ammonia, ethylene oxide or propylene oxide (A, E, or P samples). In all three cases, the total precipitation of $AlPO_4$ was then carried out by the addition of aqueous ammonia. Details on preparation, as well as on the characterization of all the catalysts, have been previously described [8,9]. The surface area (S_{BET}), pore volume (V_P), mean pore radius (r_P) and surface acidity versus pyridine (PY) are collected in table 1.

2.2. CATALYTIC ACTIVITY MEASUREMENTS

Alkylation reactions were conducted in a vapour phase continuous quartz down-flow fixed bed reactor (15 mm i.d.) surrounded by an electric heater. A Fe–Ko thermocouple was placed in the middle of the catalyst bed. The unit operated at atmospheric pressure. The substrate was delivered at a set flow rate using a liquid syringe pump (Harvard Md. 44) and was vaporized prior to passing it through the catalyst bed in the presence of a flow of nitrogen carrier gas (20 ml min^{-1}) regulated by flow controllers. The catalyst charges (W) were small, usually 0.1–0.5 g,

Table 1
Textural properties, surface acidity and initial rate constants (k) in toluene methylation on $AlPO_4$ (AP) and $AlPO_4$–Al_2O_3 (APAl) catalysts

Catalysts	S_{BET} ($m^2 g^{-1}$)	V_P ($ml g^{-1}$)	r_P (nm)	PY[a] ($\mu mol g^{-1}$)	PY[b] ($\mu mol g^{-1}$)	$k \times 10^6$[c] ($mol g^{-1} s^{-1}$)	$\beta \times 10^4$ (s^{-1})
AP-A	109	0.48	8.8	15	–[d]	1.78	0.86
AP-E	242	0.52	4.3	33		2.21	1.08
AP-P	228	0.75	6.6	23		1.95	0.95
APAl-A	244	0.37	3.1	41	12	3.48	1.40
APAl-E	242	0.54	4.5	67	35	3.71	1.22
APAl-P	319	0.67	4.2	70	30	3.59	1.24

[a] Adsorption at 573 K.
[b] Adsorption at 673 K.
[c] T: 873 K; F: 1.22×10^{-5} mol s^{-1}; W/F: 11.1 g h mol^{-1}; 4 molar toluene in methanol.
[d] There is no adsorption of the probe molecule.

retained by quartz wool at almost the center of the reactor. Pyrex glass beads (2 mm) were packed above and below the catalyst. Blank runs were carried out to ensure that the glass used to dilute the catalyst was inert. Standard catalyst pretreatment was carried out in situ at 823 K for 1 h under a stream of high purity nitrogen (99.998%, $H_2O < 3$ ppm). Liquid products were collected in an ice cooled trap over predetermined time intervals and then the reaction products were analyzed and characterized by GC-MS [7]. Reaction products were: *o*-, *m*- and *p*-xylene (XYL), 1,2,3-, 1,2,4- and 1,3,5-trimethylbezene (TMB) and minor amounts of benzene (BZ) and ethylbenzene (ETB).

3. Results and discussion

3.1. DIFFUSION CONTROL

Experiments were carried out in the region free of inter- and intraparticle diffusion effects. In order to estimate the external diffusional effects, runs were carried out with constant W/F but with varying feed rates (F) in each run. From the results, the liquid feed rate range, with which there is negligible mass transfer, was found (feed rates over 1.2×10^{-5} mol s^{-1}; i.e. W/F higher than 11 g h mol^{-1}). In all cases, feed rates in this range were used. To test the intraparticle diffusion limitation, experiments were conducted by varying the particle size and keeping the same W/F. The results were used to find the particle size range which shows no diffusion limitation. The particle size employed in this study (< 0.149 mm) falls within the intraparticle diffusion free range.

Furthermore, we have compared conversions at constant W/F by changing both the feed rate of reactant and the weight of the catalyst in the reactor. The attainment of the same conversion let us to strengthen negligible boundary layer diffusion effects.

3.2. RATE EQUATION AND CATALYTIC ACTIVITY

According to these results, the runs were performed at a fixed ratio of catalyst mass (0.4 g) and at least three feed rates in the range $(1.2–4.5)\times10^{-5}$ mol s^{-1} (4 molar toluene in methanol), and at a reaction temperature of 823 K. In these conditions, substrate conversion was kept well under 10 mol% in order to be able to apply the differential reactions for the treatment of the rate data. Calculations have been performed only in order to compare the reactivities of the different catalysts and were not aimed at finding the detailed rate equations.

The initial conversion data, X (<8 mol%), are fitted in a first order rate equation, at residence times over 10000 g_{cat} s mol_{tol}:

$$\ln[1/(1-X)] = kW/F\,.$$

The slope of straight lines yields the values of the initial reaction rate constants (k) in mol g^{-1} s^{-1}. The values obtained are collected in table 1 for the different catalysts. The position of the 98% confidence limit lines and the value of the coefficient of determination (always over 0.99) for the regressions are used to check the adequacy of the data. A Students' t-test of significance showed that these are significant at levels over 1%. At least three measurements were used to calculate each value of K. All values are reproducible to within about 7%.

The results in table 1 showed that APAl catalysts exhibited higher reaction rate constants than AP catalysts. Besides, APAl catalysts exhibited similar catalytic activities although those obtained in oxiranic medium are the most active ones.

Because toluene alkylation by methanol is a typical Brønsted acid-catalyzed reaction, the Brønsted acidity of the catalyst should affect the reaction. In this sense, the differences in initial activity can be explained by the differences in the number of acid sites measured through the adsorption of PY (573–673 K). Indeed, more PY was adsorbed on APAl catalysts than on AP catalysts. Besides, the acid strength may also affect the reaction. Table 1 suggests that the acidity is stronger on the APAl catalysts since they are able to retain more PY at higher adsorption temperatures (673 K). Thus, the differences in catalytic activity may be ascribed to the difference in number and strength of acid sites so that the more acidic catalysts are able to dialkylate toluene but, however, are unable to disproportionate toluene or isomerize xylenes, reactions that required stronger acid sites than the methylation of toluene [10–12]. Moreover, these results indicate that $AlPO_4$ Brønsted acidity increases with the incorporation of Al_2O_3.

Furthermore, the results obtained in flow experiments are similar to those obtained in a pulse reactor [7] as concerns catalytic reactivity order and reaction selectivities although the experimental conditions are very different. Besides, in flow experiments, coke formation occurs leading to the poisoning of part of the original acid sites. The coke formation in these experiments is, as expected, higher than that in pulse measurements.

Typical activity profiles of the toluene methylation as a function of time on

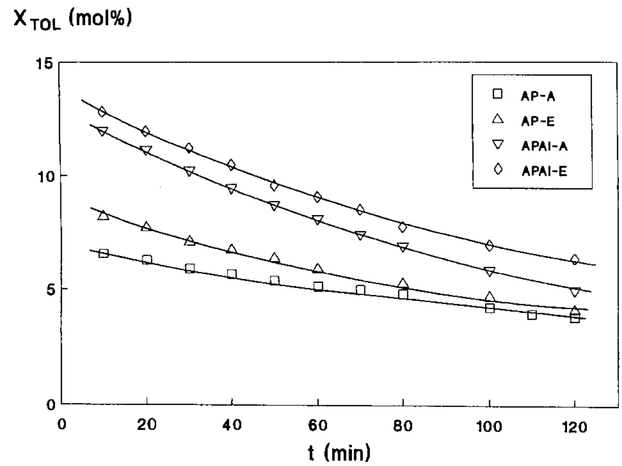

Fig. 1. Time-on-stream dependence of toluene conversion in toluene alkylation with methanol at 823 K and 11.1 g h mol^{-1} (4 molar toluene in methanol).

stream are presented in fig. 1 for APAl-E, APAl-A, AP-E and AP-A catalysts. Activity profiles for APAl-P and AP-P catalysts were essentially similar to respectively, APAl-E and AP-E catalysts, only showing a lower activity level than these catalysts. Fig. 1 showed that toluene conversion decreases with time on stream and the extent of the decrease differed from one catalyst to another.

The deactivation due to coke deposition was evaluated through the expression:

$$k = k_0 \exp(-\beta t), \tag{1}$$

where k_0 is the initial rate constant, k the rate constant at time t and β the deactivation coefficient, i.e. the deactivation rate. The ln k versus t plots, according to eq. (1), for the methylation of toluene on AP and APAl catalysts, are linear (fig. 2)

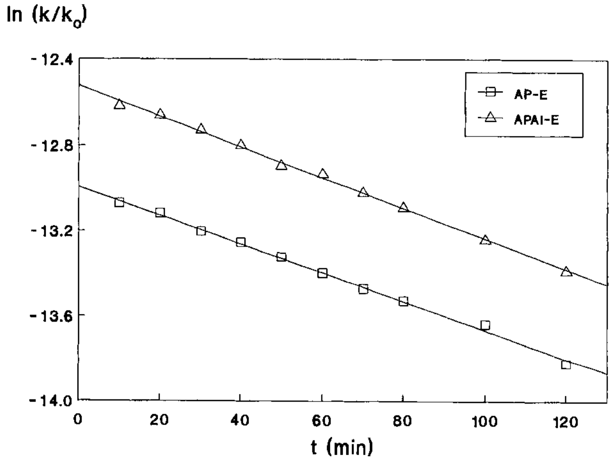

Fig. 2. ln k/k_0 versus t plots for the methylation of toluene.

indicating a good fit of the data to eq. (1). The slope of such linear plots, i.e. the deactivation coefficients β, are also collected in table 1. From table 1 it can be seen that APAl catalysts deactivate more quickly than AP catalysts as corresponds to their higher acidity and, hence, higher catalytic performance. The higher acidity of APAl catalysts favors deactivation, because of the formation of unsaturated polycyclic compounds over its more numerous and stronger acid sites.

3.3. REACTION SELECTIVITIES

Table 2 shows the reaction selectivities as well as the composition of the XYL and TMB isomers under comparable extents of conversion (7 mol%). As can be seen from table 2, AP catalysts exhibited higher S_{XYL} values than APAl catalysts since the latter are able to dialkylate toluene. However, the XYL compositions were essentially independent of the catalyst and varied between 49–52 mol% for *o*-XYL, 22–26 mol% for *m*-XYL and 25–27 mol% for *p*-XYL. The observed isomeric compositions are quite different from the equilibrium isomer compositions, namely 23.3, 50.0 and 23.7 mol% for, respectively, *o*-, *m*- and *p*-XYL. This is to be expected since AP and APAl catalysts are unable to catalyze XYL isomerization.

For all APAl catalysts the TMB composition was approximately 24, 76 and 0 mol% for 1,2,3-, 1,2,4- and 1,3,5-TMB, also far from thermodynamic equilibrium values (8.2, 67.5 and 24.3 mol% for, respectively, 1,2,3-, 1,2,4- and 1,3,5-TMB).

Kinetic control of alkylation, together with the absence of XYL isomerization, may explain the observed isomeric composition. The electrophilic methoxonium ion interacts preferentially with the carbon atoms of toluene that bear the highest negative partial charge, i.e. those at the ortho and para positions. *o*- and *p*-orientation leads to the abundance in *o*- and *p*-XYL. This *o*-rich composition was observed on non-shape-selective catalysts, such as SiO_2–Al_2O_3 and H-Y zeolites

Table 2
Reaction selectivities (S, mol%) and product distributions (mol%) in toluene methylation on $AlPO_4$ (AP) and $AlPO_4$–Al_2O_3 (APAl) catalysts

	AP-A	AP-E	AP-P	APAl-A	APAl-E	APAl-P
S_{BZ}	0.6	0.6	0.8	1.0	0.9	1.1
S_{ETB}	1.6	2.3	1.5	2.2	1.7	1.8
S_{XYL}	97.8	97.1	97.7	90.2	90.6	90.3
S_{TMB}	–	–	–	6.6	6.8	6.8
XYL composition						
para-	25.2	26.4	26.6	26.3	25.9	26.6
meta-	22.1	22.7	23.9	24.9	25.7	26.2
ortho-	52.6	50.7	49.6	48.8	48.3	47.2
TMB composition						
1,2,4-	–	–	–	76.2	75.6	76.9
1,2,3-	–	–	–	23.8	24.5	23.1

[5], as well as on the shape-selective ZSM-5 [10,12] or in liquid acidic media [13]. Also, the *o*-XYL/*p*-XYL product ratios on AP and APAl catalysts are equal to the SiO_2–Al_2O_3 and H-Y zeolite [14,15] catalysts.

OPE curves [16] also indicate that *o*-, *m*- and *p*-XYL are primary products while 1,2,3- and 1,2,4-TMB are secondary products (fig. 3). Thus, TMB are considered to be produced from the secondary alkylation of XYL by methanol. Among these compounds, 1,3,5-TMB is only obtained from *m*-XYL as long as the methyl shift is negligible. The small amount of *m*-XYL in XYL isomers and *o*-, *p*-orientation are responsible for the observed suppression in the production of 1,3,5-TMB.

On the other hand, S_{BZ} and S_{ETB} tended to increase while S_{TMB} tended to decrease with time on stream; S_{XYL} were fairly constant for APAl catalysts or tended to decrease for AP catalysts. Besides, in APAl catalysts S_{XYL} remained almost unchanged since the decrease in S_{XYL} with time on stream (due to the larger production of BZ and ETB) is compensated with an increase in S_{XYL} at the expense of the S_{TMB}.

Moreover, reaction selectivities also demonstrate that toluene methylation on AP and APAl catalysts proceeds via protonation of methanol, weak adsorption of toluene, interaction of weakly adsorbed toluene with the protonated methanol molecule and, in the final step, the transfer of the proton back to the strong Brønsted acid sites. Whatever the rate determining step in this sequence may be, the overall rate depends either on the concentration of protons or the concentration of the species protonated by Brønsted acid sites and, so, the different rates obtained accounted for the difference in Brønsted acidity in the catalysts tested. Besides Brønsted acid sites on AP and APAl catalysts ought to be moderately acidic since they are unable to catalyze XYL isomerization. In this sense Vinek et al. [12] indicate that in contrast to isomerization or disproportionation, alkylation can be effectively catalyzed by weak Brønsted acid sites.

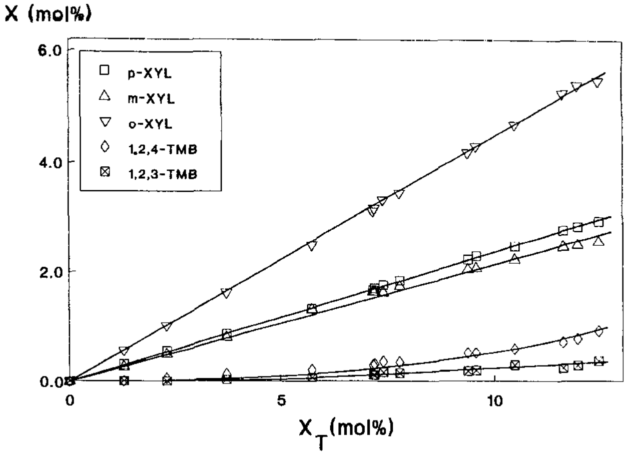

Fig. 3. OPE curves for toluene alkylation: fractional conversion at a particular reaction product (X) versus toluene conversion (X_T) for APAl-E catalyst.

Furthermore, the surface acid sites on AP and APAl catalysts ought to be *hard sites* since these favored "charge controlled" reactions, such as the ortho-substitution in toluene methylation. In this sense, Yashima et al. [14,15] indicate that the *o*-XYL/*p*-XYL product ratio changes with the *hard–soft* character of the catalyst surface sites on ion-exchanged Y zeolites. Thus, on aluminosilicates with *hard sites*, ortho-substitution predominates while over aluminosilicates with *soft sites* "orbital controlled" reactions predominate and so, para-substitution is favored.

4. Conclusions

The Brønsted acidity of $AlPO_4$ increases by the incorporation of Al_2O_3. This increase is reflected in the activity of the $AlPO_4$–Al_2O_3 catalysts in terms of toluene conversion and reaction selectivity. Moreover, the activity order is relatively well interpreted on the surface acid properties measured, in gas phase, versus pyridine (573–673 K). Brønsted surface acid sites on AP and APAl catalysts are *hard sites* since these favored ortho-substitution in toluene methylation. Furthermore, the rate of deactivation, evaluated from the deactivation coefficients (β), was greater for $AlPO_4$–Al_2O_3 than for $AlPO_4$ catalysts.

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