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PHENOL METHYLATION OVER $CrPO_4$ AND $CrPO_4$-$AlPO_4$ CATALYSTS

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Abstract

The vapor-phase catalytic alkylation of phenol with methanol and dimethyl carbonate on a series of differently prepared $CrPO_4$ (Cr/P=1) and $CrPO_4$-$AlPO_4$ (CrAlP) catalysts, has been studied at different temperatures (473-673 K). The reaction is first order in phenol, giving a mixture of O- and C-alkylated products (C-alkylation taking place preferentially at the *ortho*-position). Moreover, dimethyl carbonate is a better methylating agent than methanol.

Keywords: chromium orthophosphate ($CrPO_4$), chromium aluminium orthophosphates ($CrPO_4$-$AlPO_4$), surface acidity, phenol/methanol and phenol/dimethyl carbonate alkylation, activity, selectivity

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INTRODUCTION

In previous papers [1-4] we showed that the surface acidities of $CrPO_4$ (CrP-, Cr/P=1) and $CrPO_4$-$AlPO_4$ (CrAlP) catalysts are affected by the preparation method. Thus, $CrPO_4$ and $CrPO_4$-$AlPO_4$ catalysts obtained in a propylene oxide-aqueous ammonia mixed medium exhibited better textural properties, a higher number and strength of acid sites as well as an improved catalytic activity for cyclohexene skeletal isomerization and cumene conversion [2,3,5], as compared to catalysts obtained in aqueous ammonia or propylene oxide.

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Moreover, the alkylation of phenol with methanol results in a range of phenolic compounds some of them are extensively employed in industry [6, 7]. The competition between n- and π-type nucleophilic centers in phenol leads to variable ratios of O-/C-alkylation. These appear to be dependent on the nature of the catalyst employed, which is related to the surface acid-base site ratio [8-14]. In this reaction, carbocation formation is suggested to proceed by the adsorption of the alkylating agent on the catalyst acid site, while phenol is supposed to form a π-complex on a Brönsted acid site. Dissociative adsorption of phenol is possible on Lewis acid sites and adjacent basic sites that retain the proton of the hydroxy group [11]. So, the acid-base character of the catalyst is very important in the alkylation of phenol.

In this work, we study the effect of the precipitation agent on the methylation of phenol on $CrPO_4$ and $CrPO_4$-$AlPO_4$ catalysts and compare the influence on activity and selectivity of the alkylating agent (methanol or dimethyl carbonate).

EXPERIMENTAL

Catalysts. Three $CrPO_4$ (Cr/P=1) catalysts obtained by precipitation with aqueous ammonia (CrP-A), propylene oxide (CrP-P) or propylene oxide-aqueous ammonia (CrP-PA) were used [1]. $CrPO_4$-$AlPO_4$ (CrAlP) samples of varying composition (5-50 wt.% $AlPO_4$) were obtained by precipitation with aqueous ammonia (CrAlP-A) and samples of 5-10 wt.% $AlPO_4$ were also obtained by precipitation with propylene oxide-aqueous ammonia (CrAlP-PA). Details of the method of preparation as well as of the characterization of all catalysts have been described previously [1-5]. Sample designation includes a number that indicates the amount of $AlPO_4$ (wt.%) in CrAlP catalysts as well as another number that indicates the calcination temperature (CrP-A-773, CrAlP-A-5-773, etc.). Surface areas are shown for $CrPO_4$ and $CrPO_4$-$AlPO_4$ in Table 1.

Methods. Acid-base properties measured in a dynamic mode through the gas-phase adsorption (573 and 673 K) of PY (B+L), DMPY (B) and phenol (PH) using a pulse chromatographic technique [2,3,5] are also shown in Table 1.

The catalytic properties of CrP and CrAlP catalysts in the alkylation of phenol/methanol and phenol/dimethyl carbonate were studied by using a pulsed microcatalytic fixed bed reactor inserted between the sample inlet and the analytical column of a HP-5890 II GC. The methanol to phenol molar ratio was 4 and the dimethyl carbonate to the phenol molar ratio was 2. Initially a series of pulses of varying sizes was injected onto the catalyst in order to optimize the pulse size within the linear range of adsorption isotherm. Thus, catalytic measurements were performed under the following conditions: volume/pulse

Table 1

Surface area (m^2/g) and Acid-Base properties (μmol/g) of $CrPO_4$ and $CrPO_4$-$AlPO_4$ catalysts

Catalyst	S_{BET}	Acidity *vs.*				Basicity *vs.*	
		PY [a]		DMPY [b]		PH [c]	
		573 K	673 K	573 K	673 K	573 K	673 K
CrP-A-773	9	36	24	9	9	104	86
CrP-PA-773	28	99	91	57	52	114	89
CrP-P-773	8	43	22	13	13	129	119
CrAlP-PA-5-773	62	93	51	77	55	140	85
CrAlP-PA-10-773	58	86	63	60	54	133	84
CrAlP-A-5-773	28	40	35	21	21	66	49
CrAlP-A-10-773	19	37	27	20	20	52	52
CrAlP-A-20-773	18	42	43	14	14	65	65
CrAlP-A-30-773	22	41	38	34	29	63	62
CrAlP-A-50-773	44	67	59	25	25	71	71

[a] PY: pyridine (B+L); [b] DMPY: 2,6-dimethylpyridine (B); [c] PH: phenol

size-1μL; catalyst weight, 10-70 mg; reaction temperature, 473-673 K (at 50 K intervals); flow rate of nitrogen carrier gas, 30 mL min^{-1}. A fresh catalyst was used in each run, and before use, the catalyst was pretreated by *in situ* heating under nitrogen (30 mL min^{-1}) for 2 h at 573 K. The reaction products, analyzed by gas chromatography, were anisole (A), methylanisoles (MA), dimethylanisoles (DMA), cresols (C, mainly *o*-isomer), xylenols (XY) and trimethylphenols (T). A blank test showed that an insignificant thermal reaction occurred in the absence of the catalyst.

RESULTS AND DISCUSSION

In the absence of diffusional influences and with pulse size always within the linear range of the adsorption isotherm, the alkylation of phenol/methanol and phenol/dimethyl carbonate (below 20%, where the equilibrium reaction can be neglected) satisfies the requirements of Bassett-Habgood kinetic treatment [15] for first order reactions, in which the reactant partial pressure is low and the adsorption rate is faster than the rate of surface reaction, the latter being the rate-determining step. The Bassett-Habgood equation is in the form:

$$\ln [1/(1-X_T)] = RT\, k_a\, (W/F) \tag{1}$$

where X_T is the conversion of phenol, k_a the apparent rate constant of the surface alkylation process, W the catalyst weight and F the flow rate of carrier gas.

The effect of the reaction temperature on the conversion of phenol alkylation was examined in the 523-673 K temperature range. Tables 2 and 3 give the apparent rate constants (k_a) and selectivity for all CrP and CrAlP catalysts.

Table 2

Apparent rate constants at different temperatures and product selectivities (mol %) over $CrPO_4$ and $CrPO_4$-$AlPO_4$ catalysts

Catalyst	T (K)	Phenol/methanol			Phenol/DMC		
		k_ax$10^{6,a}$	S_A	$S_{o\text{-}C}$	k_ax$10^{6,a}$	S_A	$S_{o\text{-}C}$
CrP-A-773	673	1.5	63.6	36.4	8.3	100.0	-
	523	0.7	100.0	-	4.5	100.0	-
CrP-PA-773	573	3.4	62.4	37.6	16.5	100.0	-
	623	12.3	40.3	49.1	49.6	78.5	19.5
	673	37.7	27.2	54.3	127.6	69.3	24.7
CrP-P-773	673	0.6	100.0	-	5.4	100.0	-
	523	2.0	100.0	-	8.9	100.0	-
CrAlP-PA-5-773	573	7.0	79.5	20.5	33.5	86.3	12.9
	623	19.9	75.8	22.5	102.9	76.7	20.2
	673	48.6	40.0	40.8	269.3	65.8	25.7
	523	2.5	100.0	-	10.6	100.0	-
CrAlP-PA-10-773	573	8.5	79.1	20.9	35.9	89.5	9.8
	623	24.2	55.0	36.6	100.2	75.1	21.8
	673	59.0	30.2	36.8	241.4	65.5	21.9

[a] k_a is expressed in mol/atm g s

As can be seen, alkylation activity increases with increasing temperature and the precipitation agent also affects the catalytic performance of $CrPO_4$ and $CrPO_4$-$AlPO_4$ catalysts. Thus, the catalysts obtained in a propylene oxide-aqueous ammonia mixed medium are always more active than $CrPO_4$ and $CrPO_4$-$AlPO_4$ obtained in an aqueous ammonia medium exclusively.

Moreover, the incorporation of $AlPO_4$ in $CrPO_4$ developed catalysts that exhibited increased activities (at all $CrPO_4$/$AlPO_4$ weight ratios) in alkylation as compared to $CrPO_4$ catalysts. Furthermore, the catalytic activity of the CrAlP catalyst also varied with $AlPO_4$ loading.

On the other hand, with regard to the selectivity of the alkylation reaction, we have constructed the OPE curves (Fig. 1) by plotting fractional conversion to a

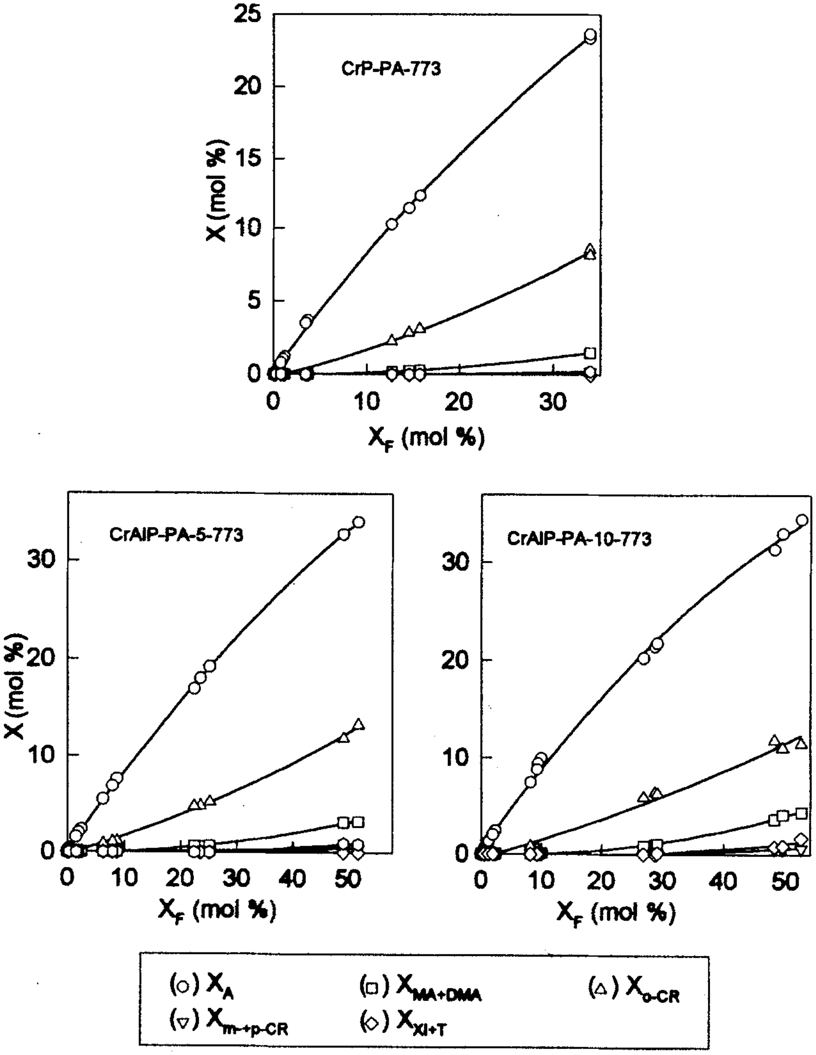

Fig. 1. OPE Curves for the methylation of phenol with dimethyl carbonate

particular product (X) against the phenol conversion (X_T), such as described by Ko and Wojciechowski [16].

Table 3

Apparent rate constants at different temperatures and product selectivities (mol %) over $CrPO_4$-$AlPO_4$ catalysts

	T (K)	Phenol/methanol			Phenol/DMC		
Catalyst		$k_a \times 10^{6,a}$	S_A	$S_{o\text{-}C}$	$k_a \times 10^{6,a}$	S_A	$S_{o\text{-}C}$
	523	0.4	100.0	-	2.4	100.0	-
CrAlP-A-5-773	573	0.9	100.0	-	6.1	100.0	-
	623	1.9	79.0	21.0	13.2	87.9	11.3
	673	3.5	53.4	44.3	25.8	79.2	18.1
	523	0.4	100.0	-	4.3	100.0	-
CrAlP-A-10-773	573	1.0	100.0	-	9.3	100.0	-
	623	2.0	79.8	20.2	17.7	89.5	9.7
	673	3.6	58.8	39.0	30.9	86.0	12.3
	523	0.2	100.0	-	3.6	100.0	-
CrAlP-A-20-773	573	0.5	100.0	-	7.9	94.2	5.8
	623	1.2	92.1	7.9	15.1	91.1	8.2
	673	2.5	67.3	30.4	26.3	88.0	11.0
	523	0.2	100.0	-	2.4	100.0	-
CrAlP-A-30-773	573	0.7	100.0	-	6.6	94.1	5.9
	623	2.0	81.5	15.6	15.4	87.5	11.3
	673	5.3	56.4	39.0	32.1	78.7	19.9
	523	0.8	100.0	-	11.8	100.0	-
CrAlP-A-50-773	573	3.0	100.0	-	30.2	94.3	5.7
	623	8.9	77.0	19.2	66.8	85.7	11.8
	673	22.9	48.8	40.3	132.0	76.3	17.8

[a] k_a is expressed in mol/atm g s

The results show that, in the range of the conversions studied, anisole was the primary reaction product. *o*-Cresol was a primary plus secondary stable reaction product coming from anisole by isomerization and by phenol alkylation at high reaction temperatures. So, O- and C-alkylation are two parallel processes. The other reaction products are secondary stable or unstable ones. Besides, selectivity is also affected by the precipitation agent and reaction temperature. Selectivity for anisol drops and cresols as well as di- and trimethylphenol selectivities increase with a rise in temperature.

Alkylation of phenol with dimethyl carbonate is similar to alkylation of phenol with methanol. CrP-PA and CrAlP-PA are more active than CrP-A and CrAlP-A and they show higher selectivity to *o*-cresol. A comparison of the two alkylations gives more catalytic activity in phenol/dimethyl carbonate alkylation than that in phenol/methanol, increasing anisol selectivity against *o*-cresol selectivity, mainly at 673 K.

CONCLUSIONS

CrAlP catalysts exhibited higher activity than CrP catalysts in the alkylation of phenol with methanol or dimethyl carbonate. Catalytic activity and selectivity are highly influenced by the catalyst, alkylating agent and reaction temperature. Catalysts obtained in propylene oxide-aqueous ammonia are the more active ones and, moreover, dimethyl carbonate is a better methylating agent than methanol. Furthermore, *o*-cresol selectivity increases with the reaction temperature, remaining higher when methanol is used as alkylating agent.

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