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Selective O-Alkylation of Phenol with Methanol over Sulphates Supported on γ-Al_2O_3

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The reaction of phenol with methanol was studied in a fixed-bed reactor system as a potential source for the production of methyl aryl ethers. For this reason, the performance of alumina-supported catalysts impregnated with sulphate salts of metals of the groups VIIB and IIB was studied. The effects of reaction temperature, reaction time, type of metal, metal content, and potassium content on the selectivity of methyl aryl ethers (MAE), as well as the phenol conversion and the yield of MAE, were established. The reaction temperature and the potassium content were found mainly to affect the selectivity of the catalyst, the phenol conversion, and the yield of MAE. Empirical equations were derived which proved to be useful for predicting the performance of a catalyst over a broad range of reaction conditions. A catalyst (K_3^S) containing only potassium (3 wt%) in the form of potassium sulphate supported on γ-alumina was found to have the most promising performance compared to those reported in the literature in terms of MAE selectivity and phenol conversion at atmospheric pressure (selectivity of MAE = 98%, phenol conversion = 65 wt%). The catalyst remains stable over a broad range of temperatures (290–330°C). K_3^S is an inexpensive catalyst, showing major selectivity advantages and product composition (anisole, 92 wt%; *o*-cresol, 8 wt%) and a low coke production (7 wt%). The presence of potassium sulphate in the catalyst proved to be the controlling factor for the production of MAE and it was found to be the active phase of the catalyst. The MAE selectivity of potassium sulphate catalysts is determined by the potassium content of the catalyst, while its optimum value is achieved, when acid sites of medium strength ($+ 1.5 < H_0 \leq + 4.8$) with low acidity values (22×10^{-4} mmol/m^2) exist on their surface.

INTRODUCTION

Phenols constitute a significant source of oxygen and are mainly responsible for many undesirable properties of biomass pyrolysis liquids. Particularly, the continuous polymerisation of phenols is responsible for the detected increase of the molecular weight and the viscosity of these liquids (1, 2). Phenols can be either purified and used as pure chemicals or they can be used as a raw material for the production of methyl aryl ethers (MAE) (3).

The positive effect of the addition of methyl aryl ethers into the gasoline pool has been studied (4, 5) and the measured RON and MON values of gasoline were found to be substantially improved when a mixture of MAE was used instead of only anisole (6). It should be noted here that only the methyl aryl ethers of phenol, cresols, and xylenols, namely anisole, methyl and dimethyl anisoles, can be effectively utilized in this application, because these compounds are characterised by boiling points within the gasoline boiling range. A technoeconomic analysis for the use of methyl aryl ethers as gasoline octane improvers produced from lignin wastes is quite promising (7) and it was found that a mixture of MAE can effectively substitute for the currently used nonmetallic additives such as the methyl tertiary butyl ether (MTBE).

The alkylation of phenols with methanol proceeds via O-alkylation producing MAE and ring alkylation producing mainly methylated phenols (8). These ring methylated phenols possess all the above-mentioned undesirable properties of phenol; therefore, their yield should be minimized in the etherification process. Since the alkylation of phenols is essentially an "acid–base" reaction, the product selectivity is expected to depend strongly on the catalyst acidity. Thus, several scientists have attempted to relate the performance of the phenol alkylation catalysts with either acidity and/or the strength of the acid or basic sites present on the catalyst surface.

In the recent literature, a quite wide variety of catalysts have been tested for the alkylation of phenol with methanol, such as metal oxides (9–12), sulphates (13–15), phosphates (16), and zeolites (8, 17). It has been found that catalysts with strong acid sites favor the O-alkylation of phenol leading to the production of MAE, while catalysts with weak acid and/or strong basic sites promote the production of methylated phenols (11, 12, 16, 18). On the other hand, Marczewski and his co-workers (19) claimed that weak acid sites favor the O-alkylation of phenol and by increasing the strength of the acid sites of the catalyst (USHY zeolite), the formation of anisole, *o*-, *p*-cresol and other secondary methylated products is gradually favored. The acidic form of zeolites (e.g., H–ZSM5) was

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found also to be selective towards O-alkylation, while their basic form (e.g., Na–ZSM5) was found to favor the ring methylation (20). So far, the Lewis acid sites of the catalysts have been mainly considered, while Brønsted acid sites present on the catalysts surface were considered responsible for coke formation and subsequent catalyst deactivation (10).

Alumina has been widely used both as a carrier (10, 21, 22) and as a catalyst (21, 22) for the methylation of phenol with methanol. Its increased acidity compared to other oxides such as TiO_2 (18) and its lack of radioactivity, a real problem when other supports are used (e.g., ThO_2) (23), are the main reasons for its wide use in this area of catalysis. The presence of strong Lewis acid sites on γ-alumina surface was found to promote the parallel formation of alkylated phenols, thereby decreasing the selectivity of anisole (15). However, it has been found that alumina is more active in O-methylation compared to H–ZSM5 (23), while its impregnation with sulphate salts increases its selectivity in MAE production and the number of by-products as well (23).

Sulphates form a major class of low acidic compounds, which have been used as catalysts in the reaction of phenol with methanol either in unsupported form (15) or supported on a high surface area material (14, 24–27). Even though they are characterised by an especially high anisole selectivity the achieved phenol conversion, in the case of the pure sulphate compound, is considerably lower than that obtained with γ-alumina alone. Therefore, the impregnation of sulphates on a high-surface-area carrier appears to be a promising process. However, the employment of special conditions, such as high operating pressures (even 600 psi), were necessary for the improvement of the achieved phenol conversion (15, 26). It has been found that the use of compression during the preparation of certain sulphate compounds has a great influence on the number of the acid sites on the catalyst surface (24). In this case, the products selectivity is also affected. Moreover, the addition of potassium to the sulphate catalysts supported on γ-alumina, is claimed to improve their performance in terms of O-alkylation selectivity (27).

Consequently, a good etherification catalyst should not only promote a high selectivity to oxygen methylation but also provide an acceptable value of phenol conversion. It is known that sulphates supported on a high surface carrier such as γ-alumina, are especially selective to O-alkylation of phenol with methanol (26, 27). The effect of the composition of the catalyst in terms of the supported metal sulphate, the metal content and the potassium content, has not been explored as yet on its performance in the alkylation reaction of phenol with methanol. However, it is obvious that if the high operating pressures, as reported by Mossman (26), and Pierantozzi and Nordquist (15), could be avoided, the process would become economically more attractive.

In this study, a series of sulphate catalysts was prepared and tested at atmospheric pressure in a fixed-bed reactor system equipped with on-line analysis of the reaction products. The effect of the reaction temperature on the catalysts performance was also investigated. The reaction of phenol with methanol was used as a probe reaction. Finally, a novel, simple, and especially active catalyst for the production of MAE under favorable conditions was prepared in our laboratory and its performance was studied and is reported here for the first time. The acidic character and the nature of the new catalyst were studied in order to relate them to the catalytic activity.

METHODS

The alkylation experiments were carried out in a catalytic fixed bed reactor at atmospheric pressure. The reactor consisted of the following parts: (a) a feeding system, (b) a fixed bed reactor, and (c) the liquid products collection and analysis section.

a. Feeding System

The liquid mixture of the reactants (phenol and methanol) was fed into the reactor at the top of the catalyst bed by means of a microsyringe pump, capable of achieving an accurate, constant, and small feed rate (0.3 cc/min). The reactants were introduced on the top of the catalytic bed passing through a narrow stainless steel tube. The reaction mixture consisted of a methanol/phenol molar ratio of 4/1, which was selected as optimum based on our earlier experiments (28).

b. The Fixed Bed Reactor

The fixed-bed reactor (height, 0.5 m; i.d., 12.7 mm) was made of stainless steel 316 with two entrances at its upper end: the first for introducing the liquid mixture of the reactants into the catalytic bed and the second for the carrier gas introduction. The liquid mixture was vaporized by flowing downwards through a heated stainless steel tube (30 cm × $\frac{1}{8}$ in. i.d.) before being passed through the catalytic bed. The inert carrier gas (N_2) was preheated and used for the continuous removal of the reaction products from the reaction zone. The reactor was heated to the desired temperature by a three-zone radiant furnace. The temperature of each zone and the inert gas introduction line were maintained using standard temperature controllers. The temperature of the reactor exit was kept at 320°C by two temperature controllers to avoid the condensation of the reaction products. This temperature value is quite low, thus preventing the thermal decomposition of products and reactants alike.

A fixed amount of catalyst (2 g) was introduced into the reactor and the GHSV was 6041.5h^{-1}. Continuous monitoring of the bed temperature was achieved by a thermocouple placed inside the catalyst bed. The carrier gas flow was controlled by a pressure regulator and a needle valve. The gas flow was set so the mean gas phase residence time was 125.4 ms.

c. Collection and Analysis of Products

A heated six-port gas sampling valve was installed at the reactor outlet connected with a gas chromatograph HP 5710 (detector, FID; column, SP 1000 on Carbopack C; 6 ft. × $\frac{1}{8}$ in. i.d.; flow rate, 30 ml/min; temperature program, 170°C for 16 min; rate, 2°C/min up to 220°C) for the on-line analysis of the reaction products. The main advantages of this procedure are summarised as follows: (a) on-line analysis of the reactor outlet at any time during the reaction course and (b) minimization of the products degradation due to the small elapsed time between production and analysis. Furthermore, the products not analyzed can be condensed and collected in a small vessel placed inside a cold liquid bath (0°C). The data collected from the on line GC analysis were used for the determination of the catalysts performance for phenol conversion, selectivity, and yield of MAE. The material balance of our experimental system was in the range of 95–96 wt %, while the reproducibility of the experimental system was better than ±10%.

Description of the design and selection of parameters. Two techniques are commonly used for the identification of the effects of the operating parameters to an experimental system response: (a) by varying one parameter at a time while keeping the others constant; (b) by using a factorial design. In our case, a two-level factorial design was applied first. When the significant parameters were established their effect was thoroughly studied by employing the classical approach of varying one parameter at a time.

The reaction temperature was found to be the most important operational variable for the etherification process in a preliminary experimental unpublished work of the authors (30). The reaction time on the other hand, proved to be a rather insignificant factor in the range of 3–30 min, due to the low deactivation rate of the catalyst. Consequently, the experiments of the present study were carried out at a constant reaction time of 3 min. In the same work (30), it was observed that the use of sulphates render a positive effect on the performance of pure γ-alumina in terms of MAE production as it has been reported elsewhere (15, 26, 27). In this study, metal sulphates of the group VIIB (e.g., Mn) and IIB (e.g., Cd) supported on γ-alumina were used as catalysts. Thus, an experimental design consisting of 16 experiments was planned by applying a conventional procedure (29) in order to probe the effect of the reaction temperature and the catalyst composition. The term catalyst composition implies the potassium content, the type of the precursor supported metal salt (VIIB group-Mn or IIB group-Cd), and its content.

TABLE 1

The Factors of the Statistical Experimental Design

Factor	Tested range
Bad temperature (X_1)	260–330°C
Metal content (X_2)	2.4–7.8 wt%
Metal kind (X_3)	Cd or Mn
Promoter content (X_4)	0.7–1.3 wt%

The parameters used for the experimental design, along with their range of variation, are listed in Table 1. The phenol conversion (C, wt%), the yield of MAE (Y, wt%) and the MAE selectivity (S, %), were considered as the responses of the experimental system.

The term MAE (methyl aryl ethers) used in this study includes anisole as well as *o*- and *p*-methyl anisole, while alkylated phenols include *o*-, *p*-cresol and 2,6-xylenol. Other phenols such as 2,4-xylenol and some trimethylphenols were also identified in trace amounts, only at high reaction temperatures (>320°C) and considered negligible in this study.

Preparation of catalysts. The catalysts used were prepared by applying the incipient wetness method along the lines reported by Mossman (26, 27). Moreover, a major modification was introduced concerning the independent impregnation of potassium, called a promoter, and the primary metal (Mn or Cd). In the method proposed by Mossman (26), the simultaneous impregnation of the two metals in the form of a single compound ($KMnO_4$) posed restrictions in the independent variation of the metal loadings.

γ-Alumina (Amocat 1A; 425–600 μm), a porous and of relatively high surface area support (BET, 191.5 m^2/g), was impregnated first with an aqueous solution of KOH followed by drying. Then, the desired metal salt, $MnSO_4 \cdot H_2O$ or $3CdSO_4 \cdot 8H_2O$, was dissolved in an aqueous solution of H_2SO_4 (10 wt%), sufficient to fill the internal volume of the catalyst support at least once, determined by the pore volume of the support (Hg, 1.1 cm^3/g). The metal sulphates were impregnated on alumina by drying and reimpregnation until the total solution had been deposited on the support. The catalysts were then calcined in air under programmed conditions (at 540°C for 4 h). A series of catalysts KCd_1, KCd_2, KCd_3, KCd_4,

TABLE 2

Catalysts Characterisation

Catalyst	Crystal Phases[a]	Pore Volume (cm^3/g)	BET surface area (m^2/g)	Acid amount[b] (mmol/g)
KCd_1(2.6 wt% Cd, 0.7 wt% K)	γ-Al_2O_3, $Al_2(SO_4)_3$, $CdSO_4$, K_2SO_4	1.17	180.0	0.44
KCd_2(2.6 wt% Cd, 1.3 wt% K)	γ-Al_2O_3, $CdSO_4$, K_2SO_4, $K_2Cd_2(SO_4)_3$, $Al_2(SO_4)_3$	1.18	167.8	0.45
KCd_3(7.8 wt% Cd, 0.7 wt% K)	γ-Al_2O_3, $Al_2(SO_4)_3$, $CdSO_4$, K_2SO_4	1.16	135.6	0.40
KCd_4(7.8 wt% Cd, 1.3 wt%K)	γ-Al_2O_3, $CdSO_4$, K_2SO_4	1.05	161.2	0.48
KMn_1(2.6 wt% Mn, 0.7 wt% K)	γ-Al_2O_3, $Al_2(SO_4)_3$, $MnSO_4$, K_2SO_4	1.02	178.6	0.38
KMn_2(2.6 wt% Mn, 1.3 wt% K)	γ-Al_2O_3, $Al_2(SO_4)_3$, $MnSO_4$, K_2SO_4	0.96	160.7	0.46
KMn_3(7.8 wt% Mn, 0.7 wt% K)	γ-Al_2O_3, $KAl(SO_4)_2$, $Al_2(SO_4)_3$, $MnSO_4$, K_2SO_4	1.04	112.5	0.57
KMn_4(7.8 wt% Mn, 1.3 wt% K)	γ-Al_2O_3, $MnSO_4$, K_2SO_4, $KAl(SO_4)_2$	1.13	128.7	0.56
K_1^s (1.3 wt% K)	γ-Al_2O_3, K_2SO_4, $KAl(SO_4)_2$	1.38	180.6	0.45
K_2^s (0.7 wt% K)	γ-Al_2O_3	1.15	183.9	0.38
K_3^s (3.0 wt% K)	γ-Al_2O_3, K_2SO_4, $KAl(SO_4)_2$	1.19	175.4	0.40
K_4 (0.7 wt% K)	γ-Al_2O_3	1.13	184.4	0.00
Al_2O_3	γ-Al_2O_3	1.11	191.5	0.00
$Al_2O_3^s$	γ-Al_2O_3, $Al_2(SO_4)$	1.15	182.7	0.65

Note. [s]Indicates the existence of sulphates.

[a] Identified by XRD analysis.

[b] Refers to acid sites of medium strength ($+1.5 < H_0 \leq 4.8$).

KMn_1, KMn_2, KMn_3, and KMn_4 was prepared (Table 2) by varying the metal and the potassium content based on the factorial design, according to the above described method. The name of each catalyst reflects the metal salts deposited on the alumina.

Another series of catalysts (K_1^s, K_2^s, and K_3^s) containing only potassium as sulphate at different loadings was also prepared following the same methodology. Finally, a sulphate-free potassium catalyst, K_4, was prepared by impregnating the desired amount of an aqueous solution of KOH on the alumina carrier, while sulphate alumina ($Al_2O_3^s$) was prepared by simply using a sufficient volume of 10% H_2SO_4.

The prepared catalysts were analyzed and their structure studied by X-ray diffraction analysis (XRD), using a Siemens D500 diffractometer (Table 2). The BET surface area and the pore volume were determined using the Micromeritics Accusorb 2100E and the Micromeritics AutoPore II 9220 Porosimeter respectively (Table 2). The acidity was measured (Table 2) by the conventional method of *n*-butylamine titration using Hammett indicators with different pK_a values (31).

RESULTS AND DISCUSSION

Controlling Factors of Phenol Alkylation

The factorial design was repeated and the mean experimental values were used for the calculation of the effects of each factor of the experimental responses considered. The calculated effects are listed in Table 3. According to the statistical design procedure, the effect of a factor is considered to be significant when the value of that effect is higher than the response error estimate, STD. For more details concerning the equations employed for the calculation of these figures the reader is referred to the Appendix. Comparing the effect of each factor (Table 3) with its respective STD value ($STD_C = 3.7$, $STD_Y = 2.3$, $STD_S = 3.5$), where C is phenol conversion, Y is the MAE yield, and S is the MAE selectivity, it appears that the bed temperature and the potassium content of the catalyst are the only significant factors. The active metal content of the catalyst as well as the type of the impregnated metal appear to be less important factors for the production of MAE.

The negative effect of temperature on the MAE selectivity (Table 3) indicates that the use of low bed temperatures results in high values of the MAE selectivity. This trend has been reported in the literature (10), though our values for MAE selectivity were remarkably lower at the considered temperature range, due to the nature of the catalyst used and the experimental setup. Phenol conversion is expected to decrease at these conditions due to the positive effect of temperature on phenol conversion (Table 3). Moreover, the sign of the effect of potassium indicates that the use of a catalyst containing an increased potassium content should give higher values for MAE selectivity and lower values of phenol conversion (Table 3).

Based on the quantitative results drawn from the application of the statistical experimental design, empirical equations were derived for the prediction of the system output at a given set of experimental conditions (Fig. 1).

TABLE 3

Results of the Experimental Design

	X_1	X_2	X_3	X_4	X_1X_2	X_1X_3	X_1X_4	X_2X_3	X_2X_4	X_3X_4
Effect_1	30.2	2.68	0.52	−10.6	1.85	−2.15	−1.15	3.12	−2.82	−1.92
Effect_2	1.88	−1.22	0.62	1.15	−0.05	−1.75	7.88	−0.9	−3.12	0.28
Effect_3	−33.8	−4.8	0.58	13.2	−1.2	0.68	9.2	−5.3	−0.92	1.4

Note. Effect_1, Effect_2, and Effect_3, are the respective factor effects on the responses C (phenol conversion), Y (yield of MAE), and S (MAE selectivity).

These equations are listed in their dimensionless form in the Appendix (Eqs. A3–A5). These models can be effectively applied within the range of the considered experimental conditions (Fig. 1). Otherwise, only qualitative predictions for the catalysts performance will be obtained.

The effect of the bed temperature on the selectivity of MAE, the phenol conversion, and the yield of MAE is shown in Figs. 1a and 1b at the two boundary levels of potassium tested. The effect of potassium on the MAE selectivity is especially significant at high reaction temperatures (>290°C). At the lower temperatures tested (260–290°C), this effect is considered negligible. The maximum values of MAE selectivity measured at the two boundary levels of potassium were equal, most probably due to the narrow concentration range. Finally, based on the detected effect of potassium, a catalyst containing 1.3 wt% potassium will be more favorable towards MAE production at a temperature ~300°C.

Performance of Potassium-Containing Catalysts

The potassium content of the catalyst was a decisive factor greatly affecting catalyst selectivity even though a primary supported metal (Mn or Cd) was also present. Catalysts containing solely potassium were chosen for the detailed study of the effect of potassium loading. Thus, the catalyst K_1^s (potassium content; 1.3 wt%) expected to have the optimum performance in the alkylation process was prepared. Catalyst K_2^s (potassium content: 0.7 wt%) was also prepared. These two potassium loadings were selected for the sake of comparison with the potassium content of the Mn- and Cd-tested catalysts (Table 2).

The performance of catalysts K_1^s and K_2^s was studied at various operating temperatures in terms of phenol conversion (C), yield of MAE (Y), and MAE selectivity (S). Their performance was satisfactorily predicted by applying our empirical equations, derived from the testing of the Mn- and Cd-contained catalysts. The good correlation between empirical prediction and experimental is shown in Figs. 2 and 3. Therefore, our equations, although empirical in character, proved to be appropriate for making reliable predictions of catalyst performance in spite of odd catalyst composition and structure compared to the metal contained catalysts (Table 2). It should be noted here that catalysts containing only potassium, which has been called a promoter (26, 27), at considerably low content (0.7, 1.3 wt%), exhibit similar performance with the

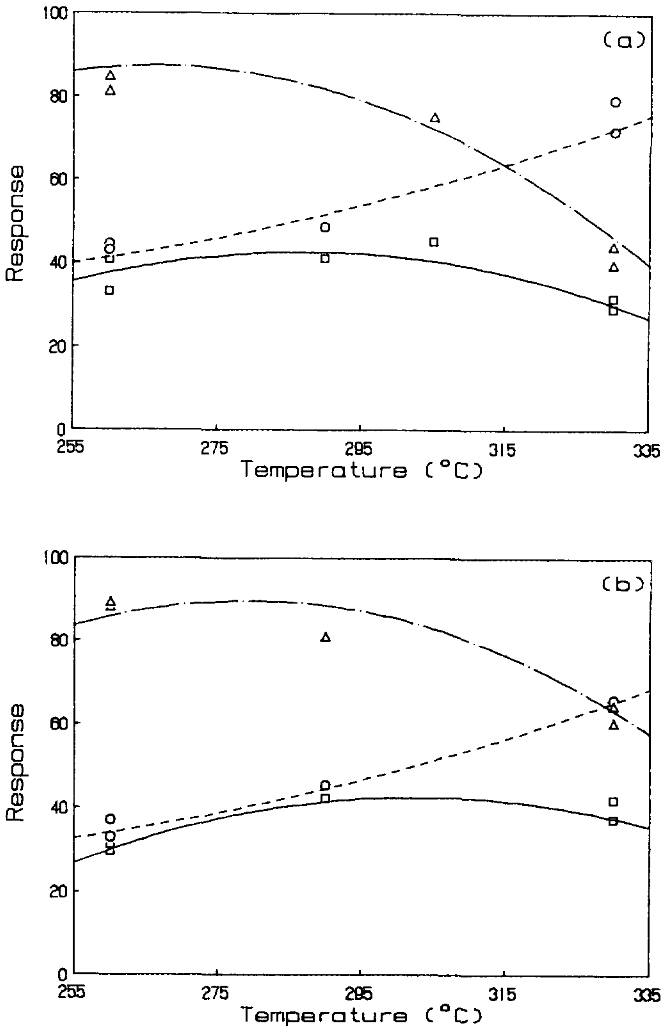

FIG. 1. Effect of the bed temperature on the performance of the supported metal sulphate catalysts (△, —·—) S (MAE selectivity, %); (○, – – –) C (phenol conversion, wt%); (□, —) Y (MAE yield, wt%); lines refer to the design predictions); (a) 0.7 wt% K; (b) 1.3 wt% K.

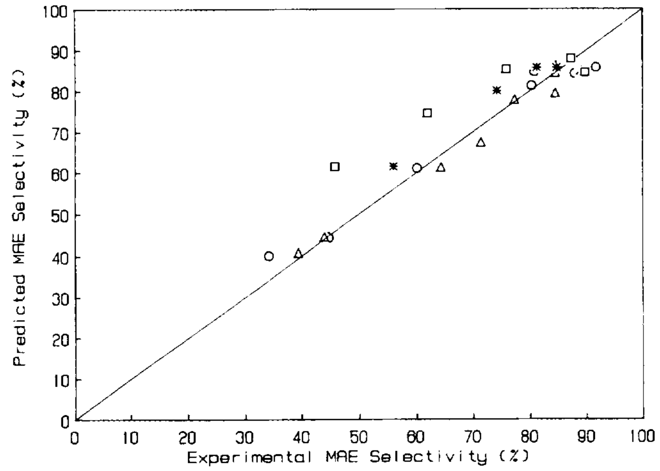

FIG. 2. Design predictions for MAE selectivity (S) (△) KCd_{1-4}; (○) KMn_{1-4}; (□) K_1^s; (*) K_2^s.

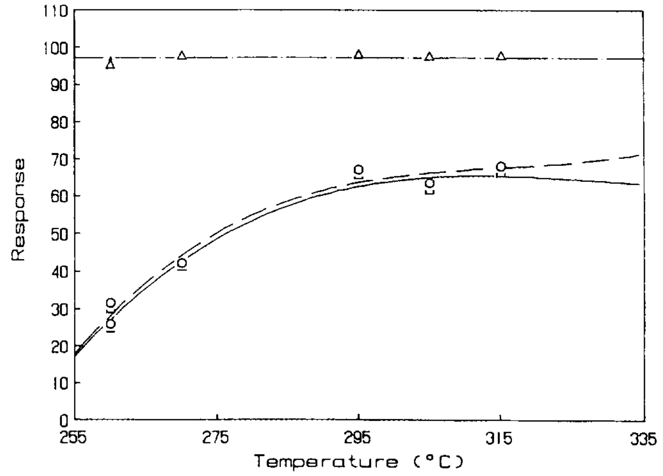

FIG. 4. Performance of K_3^s (sulphate catalyst, 3 wt% K) at various reaction temperatures ((△, —·—) MAE selectivity (%); (○, — —) phenol conversion (wt%); (□, —) yield of MAE (wt%); the lines reflect experimental trends).

composite catalysts Mn–K and Cd–K, previously described (Figs. 2, 3). This conclusion is of great importance, because it can be used as a guide for an easily available and prepared catalyst with a high selectivity for the production of MAE at atmospheric pressure.

The observed improvement in the MAE selectivity, achieved by increasing the potassium content (0.7–1.3 wt%) was modest, probably due to the narrow range of variation. Then, a catalyst (K_3^s) containing a higher potassium content (3 wt%) was prepared to clearly demonstrate the loading effect. The improved performance of K_3^s is shown in Fig. 4. The superiority of K_3^s is evident. Figure 4 demonstrates that the MAE selectivity remains constant (98%) over a wide range of operating temperatures (260–330°C). Phenol conversion and yield of MAE show a similar dependence on temperature, because the MAE selectivity has a value of almost 100% (Fig. 4). The optimum phenol conversion has a value of 65 wt% and remains constant for reaction temperatures in the range of 290–330°C (Fig. 4). The yield of MAE also remains constant in the same temperature range. Another major advantage of K_3^s catalyst over the previous catalysts (KMn_{1-4}, KCd_{1-4}, K_1^s, K_2^s) is its consistent performance. By further increasing the reaction temperature (>330°C) a decreased MAE selectivity (80%) and an increased phenol conversion (72 wt%) were observed. The overall performance of K_3^s is well predicted as the qualitative results drawn from the experimental design indicate.

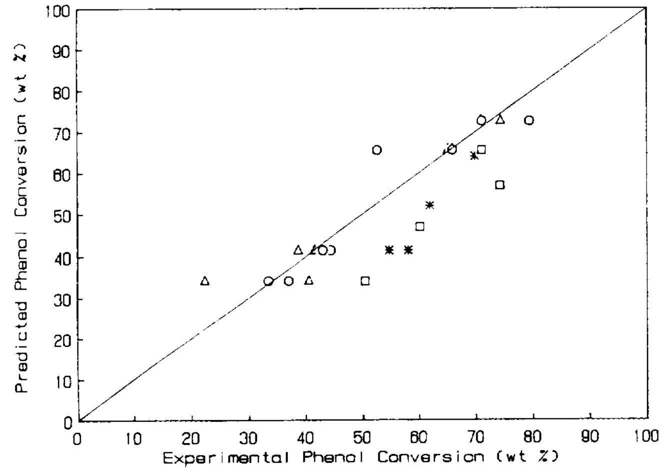

FIG. 3. Design predictions for phenol conversion (C) (△) KCd_{1-4}; (○) KMn_{1-4}; (□) K_1^s; (*) K_2^s.

As far as, the reaction products composition is concerned, catalyst K_3^s shows another advantage over the rest of the catalysts. More specifically, the alkylation products consist mainly of O-methylated compounds: anisole: 91 wt% and *o*-methyl anisole: 1 wt% (Table 4). The Mn or Cd containing catalysts, K_1^s and K_2^s, yield a more complicated alkylation product mixture (Table 4). Therefore, K_3^s catalyst is the favorable choice for the economical production of the desired product (MAE).

A comparison of the optimum performance of K_3^s with the best results reported in the recent literature is illustrated in Table 5. It can be seen that K_3^s shows the most promising selectivity value and reaction rate, expressed as r_s (mmol/h/m^2), under mild operating conditions (atmospheric pressure) using the highest GHSV value. This supports the evidence that the use of K_3^s improves to a great degree the process economics, considering the small amounts of catalyst required for the desired phenol conversion. The optimum value of phenol conversion accomplished with the proposed catalyst is comparable to that

TABLE 4

Products Composition (wt%) and Coke Yield (wt%) over Supported Sulphate Catalysts at Their Maximum Selectivity Point

Catalyst	Anisole	*o*-MA[a]	*p*-MA[a]	*o*-Cresol	*p*-Cresol	2,6-Xylenol	Coke[b]
Al_2O_3	68.5	2.9	—	24.3	—	4.3	23.6
$Al_2O_3^s$	83.4	3.0	1.2	11.7	1.4	—	8.3
K_1^s	82.0	5.4	1.4	9.1	0.8	1.3	7.8
K_2^s	78.6	4.8	1.0	13.4	1.0	1.2	9.7
K_3^s	90.8	1.1	—	8.1	—	—	7.1
K_4	81.8	—	—	18.2	—	—	24.3
$KMn_{1,3}$	76.3	4.4	1.2	14.4	1.4	1.5	7.6
$KMn_{2,4}$	78.9	3.0	0.9	14.8	1.3	1.1	6.2
$KCd_{1,3}$	75.7	3.6	0.9	17.1	1.2	1.5	9.8
$KCd_{2,4}$	78.4	3.6	0.9	14.6	1.4	1.1	8.5

Note. (Temperature: 260°C).

[a] Methylanisole.

[b] Percent conversion of feed carbon to coke.

achieved by Mossman (26) though our catalyst is much simpler to prepare (Table 5). Furthermore, the optimum K_3^s phenol conversion value of 67 wt% is two to six times greater than those reported at atmospheric pressure but with different alkylation catalysts (Table 5).

Finally, K_3^s catalyst was superior to the other composite catalysts in terms of MAE production and its higher activity even at mild reaction conditions (atmospheric pressure, 295°C), yielding a reaction product of almost pure anisole (91 wt%). This catalyst therefore, seems to have the most promising behaviour compared not only to those tested in this work (Table 4), but also to those reported in the known literature (Table 5).

Factors Affecting Catalyst Activity

The promoting action of SO_4^{2-} ions on alumina was studied in order to relate their presence with the special performance exhibited by K_3^s catalyst. This was accomplished by comparing the performance of alumina and potassium contained catalysts in their sulphate and sulphate-free forms. To this end, catalyst K_4 (0.7 wt% K) and sulphate alumina ($Al_2O_3^s$) were synthesized as previously described.

The performance of these catalysts was studied at different reaction temperatures. The optimum results are listed in Table 6, along with the results obtained using

TABLE 5

Comparison of Catalysts Tested for the O-Alkylation of Phenol with Methanol

Catalyst	Temperature (°C)	*P* (psig)	GHSV (h^{-1})	Phenol conversion (wt%)	Anisole selectivity (%)	MAE selectivity (%)	$r_s^e \times 10^3$ (mmol/h/m^2)	Reference
Sulphates on γ-Al_2O_3 (5.5% Mn, 3.9% K)	300	100	553.5[a]	64.6	92.9	99.0	9.1[a]	(26)
	300	0	553.5[a]	33.2	92.5	97.3	57.4[a]	(26)
Sulphates on γ-Al_2O_3 (2.76% Cd, 0.8% K)	300	55	276.8[a]	35.3	96.4	99.0	32.7[a]	(27)
$BaSO_4$	300	0	550[b]	7.4	90.9	90.9	51.0	(15)
APTi-31-770	250	0	[c]	10.6	100.0	100.0	[c]	(18)
HZSM5	200	0	[d]	10	90	90	20.0	(8)
K_3^s	280–315	0	6041.5	67.0	92.1	97.8	86.0[a]	This study

[a] Estimate based on the available experimental data.

[b] Mean value.

[c] Batch reactor.

[d] Impossible to be estimated.

[e] Surface specific rate of MAE production.

TABLE 6

Effect of Potassium and H_2SO_4 Addition on the Performance of Alumina and the Potassium-Containing Catalysts

Catalyst	T(°C)	C(wt%)[a]	Y(wt%)[b]	S(%)[c]
γ-Al_2O_3	260	41.2	30.4	73.9
$Al_2O_3^s$	260	35.2	31.3	89.0
K_1^s	280	60.1	52.4	87.2
K_2^s	260	56.0	46.5	82.7
K_3^s	295	67.0	65.5	97.8
K_4	260	3.5	2.9	82.8

[a] Phenol conversion.
[b] Yield of MAE.
[c] Selectivity of MAE.

K_{1-3}^s catalysts and pure γ-alumina. The presence of sulphate ions on K_3^s surface results in higher values for phenol conversion and yield of MAE, compared to K_4 (Table 6). These factors are not greatly affected by the sulphation process, when catalysts without potassium are used, such as $Al_2O_3^s$ (Table 6).

The sulphate modified alumina shows a considerable increase in the values of MAE selectivity (S), while the effect on the C and Y factors is rather unimportant. When the potassium contained catalysts, K_2^s–K_4, are used the S factor remains stable (Table 6). By further increasing the catalyst potassium content ($K_2^s < K_1^s < K_3^s$) higher values of the C, Y, and S factors are obtained (Table 6). The coke yield decreased when sulphate catalysts are used. γ-Alumina and K_4 give high yields of coke of almost 24 wt%, while all other sulphate catalysts tested gave much lower yields of coke (Table 4). Catalysts with high potassium loading produced less coke, as well (Table 4). Thus, the presence of a high potassium content combined with the presence of sulphate ions were found to be the controlling elements of the promising catalyst.

Based on the XRD results a possible explanation for the optimum performance of K_3^s catalyst appears to be the formation of the K_2SO_4 crystal phase above a certain concentration. This compound has been also identified in all the tested sulphate catalysts (Table 2), but at much lower concentrations, since lower potassium loadings were used. The existence of $MnSO_4$ or $CdSO_4$ on the catalyst surface was found to have no major effect on the performance of the alkylation catalyst.

The acidity of the tested catalysts was measured according to the methodology previously described (Table 2). The acid strength of the catalysts, H_0, lies between +1.5 and +4.8 ($+1.5 < H_0 \leq +4.8$), which proves the existence of medium strength acid sites, selective towards O-alkylation (19). Generally, γ-alumina is characterised by strong acid sites with a H_0 value of −5.5 to +1.5 (32). The impregnation of alumina with sulphate salts, which are compounds of low acidity, results in the appearance of acid sites with medium acid strength on its surface and thus in the increase of the MAE selectivity. K_2SO_4 is the less acidic sulphate compound among those identified on the surface of the tested catalysts, due to the lower electronegativity of potassium (24), which explains the role of the active phase of the catalyst towards O-alkylation. Moreover, the zero effect of compression on the concentration of the acid sites of K_2SO_4 (24) explains the optimum performance of K_3^s at atmospheric pressure (Table 5). On the other hand,the higher acidity of $Al_2O_3^s$ (Table 2) is due to the presence of $Al_2(SO_4)_3$ on the surface of the catalyst, which results in lower values of MAE selectivity and phenol conversion as compared to K_3^s catalyst (Table 6). The impregnation of γ-alumina with KOH (K_4 catalyst) does not alter the surface acidity of the medium strength acid sites (Table 2), but it contributes to the appearance of additional basic sites on the γ-alumina surface, thus favoring the production of ring alkylated phenols and coke (Table 4).

According to fundamental studies concerning the acidity of γ-alumina (33), a Lewis acid site exists adjacent to a basic one. This type of acidity is generated after dehydration. The concentration of the Lewis acid sites increases when SO_4^{2-} is introduced to the plain alumina structure (Table 2) thus improving the O-alkylation selectivity of the catalyst (Table 6). Moreover, the presence of a low acidity compound (K_2SO_4) on the surface of catalysts K_{1-3}^s may explain their decreased acid amount (Table 2) compared to $Al_2O_3^s$. This effect could be attributed to the exchange with alkali cations (K^+) of the acid sites on the surface of the carrier (34).

An attempt has been made to relate the acidity value of each catalyst (mmol/m^2) with its optimum MAE selectivity. This acidity value was used so that the variation of the catalyst surface would also be considered. The Cd- and Mn-containing catalysts were classified into two groups according to their potassium content, so that the amount of the K_2SO_4 present was taken into account. A linear relationship between the catalyst acidity and the selectivity of MAE was observed with an intercept proportional to the potassium content of the catalyst (Fig. 5). The selectivity of anisoles was affected by both the acidity and the potassium content of the catalyst, with an increasing tendency when catalysts of low acidity were used. The optimum MAE selectivity value of K_1^s and K_2^s is well predicted by the lines drawn considering the trends of the metal sulphate catalysts (Cd–K and Mn–K) with the same potassium content (Fig. 5). The nature of the existing sulphates on the catalyst surface affects the amount of the medium strength acid sites. Consequently, K_1^s and K_2^s are characterised by the lower acidity values, due to the presence of K_2SO_4 alone (Fig. 5). With increased potassium content, an increase of the active phase

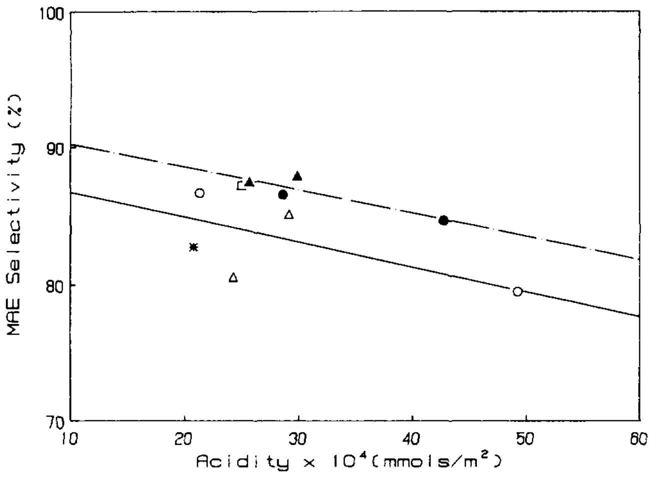

FIG. 5. Effect of catalysts acidity on MAE selectivity; (△, ○, —): the low potassium content catalysts (0.7 wt%); (▲, ●, —·—) the high potassium content catalysts (1.3 wt%); (△, ▲) KCd_{1-4}, (○, ●) KMn_{1-4}, (□) K_1^s, (*) K_2^s.

(K_2SO_4) concentration is expected and a concomitant increase in the MAE selectivity was observed (Table 6).

The proposed scheme for the reaction of phenol with methanol over the K_3^s catalyst is depicted in Fig. 6. Since K_3^s is an especially selective catalyst in MAE synthesis, it promotes the production of anisole via an O-alkylation reaction (reaction I), while *o*-cresol is produced via ring-alkylation of phenol with methanol in a side reaction (II). Since *o*-cresol is the main byproduct of anisole formation, its methylation also occurs through two successive reactions (III, IV). Thus, *o*-methyl anisole is formed through the O-alkylation reaction of *o*-cresol with methanol (reaction III), rather than through the ring methylation of anisole. The fact that initial alkylation leads favorably towards anisole formation verifies the foregoing statement. Moreover, it is expected that the activation of *o*-cresol through the OH^- group is more favorable than anisole activation. 2,6-xylenol is also formed through the ring alkylation of *o*-cresol (reaction IV). Even though this phenol constitutes a minor byproduct (Table 4) the inclusion of reaction IV to the proposed reaction scheme is important only in reactions at high temperatures (>300°C). The complicate reaction scheme proposed by Marchewski and his co-workers (8) for the alkylation of phenol with methanol over zeolites is greatly simplified in our case. The proposed reaction scheme is similar to that proposed for the alkylation of phenol with methanol over pure sulphates (15). The main difference is the inclusion of the isomerization reaction of *o*-cresol and the formation of *m*- and *p*-cresol found to occur in preference of its further ring alkylation (reaction IV, Fig. 6).

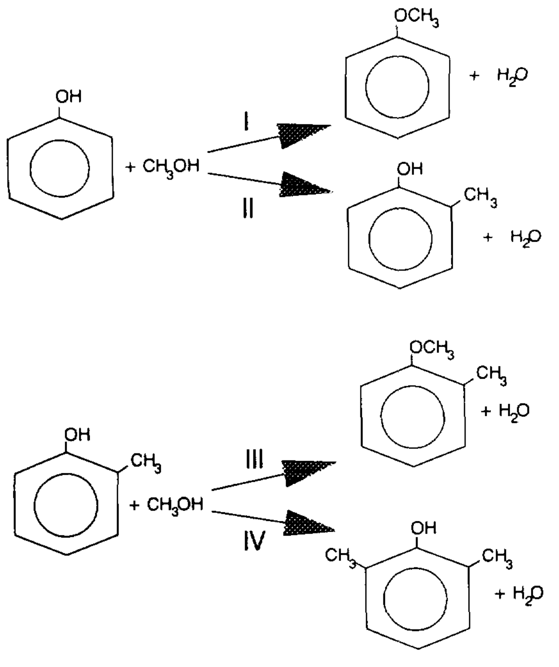

FIG. 6. Proposed reaction scheme for phenol alkylation with methanol over K_3^s (sulphate catalyst, 3 wt% K).

CONCLUSIONS

The main conclusions drawn from this work are summarized below.

(a) the reaction temperature and the potassium content of the catalyst were found to be the most important factors affecting the selectivity towards the O-alkylation of phenol.

(b) Empirical equations are proposed for the effective prediction of the reactor output as a function of the reaction temperature and the potassium content of the catalyst within the range of the parameters considered.

(c) K_3^s catalyst with a potassium content of 3 wt% in the form of potassium sulphate and characterised by a low acidity (22×10^{-4} mmol/m^2) is proposed to be suitable for the successful production of MAE. Its optimum performance is marked by a MAE selectivity of 98% and a phenol conversion of 65 wt%, remaining constant at a wide temperature range (290–330°C) and under mild conditions (atmospheric pressure).

(d) K_3^s is characterised by a low production cost, and a low yield of coke (7 wt%), while it is capable of providing an excellent reaction product composition (MAE: 92 wt% and *o*-cresol: 8 wt%).

(e) The impregnation of γ-alumina with potassium sulphate results in the appearance of acid sites of medium strength ($+1.5 < H_0 \leq +4.8$), the presence of which is essential for the O-alkylation of phenols.

APPENDIX

1. Calculation of Experimental Design Figures

When the two-level factorial designs are used each factor appears with a high (+1) and a low (−1) value. The number of experiments required for this kind of experimental designs depends on the number of parameters, p, and is equal to 2^p (29, 35).

The calculation of the effect of each factor along with the considered interactions is performed based on

$$\text{Effect}_i = \frac{\sum_{j=1}^{N} Y_j X_{ij}}{0.5N}, \qquad \text{[A1]}$$

where

Y is the value of the response;
X is the value of the factor;
i refers to the factor;
j refers to the experimental run; and
N is number of the experiments of the experimental design.

The effect of each factor is regarded as significant if it is greater compared to the error estimate of the considered response given from (35)

$$\text{STD} = \frac{ts}{\sqrt{N/4}}, \qquad \text{[A2]}$$

where

STD is the response error estimate;
s is the mean standard deviation of groups of replicated runs in order to estimate the system's reproducibility;
N is the number of experimental runs in the design;
t is the student's probability function with ν (N-p) degrees of freedom at the selected confidence level; and
p is the number of factors considered in the design.

A confidence level of 95% has been selected to be adequate for our experimental system, thus the appropriate value of the t function has been taken from statistical tables (29).

2. Prediction Equations

The following equations were obtained for the prediction of the MAE selectivity S, phenol conversion C, and yield of MAE as a function of the reaction temperature and the potassium content of the catalyst,

$$S(\%) = 81.3 - 16.2X_1 + 3.9X_4 - 12.5X_1^2 + 4.55X_1X_4 \qquad \text{[A3]}$$

$$C(\text{wt}\%) = 50.4 + 15.7X_1 + 2.9X_1^2 - 3.6X_4 \qquad \text{[A4]}$$

$$Y(\text{wt}\%) = 42.2 + 3.7X_1X_4 - 8.4(X_1X_4)^2, \qquad \text{[A5]}$$

where

X_1 is the dimensionless bed temperature, (T-295)/35;
X_4 is the dimensionless potassium content, (K-1)/0.3;
T is the reaction temperature (°C);
K is the potassium content of the catalyst (wt%).

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