JOURNAL OF CATALYSIS **116**, 480–487 (1989)

The Alkylation of Toluene with Methanol on Microporous Heteropoly Oxometalates

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Received March 1, 1988; revised November 11, 1988

The alkylation of toluene with methanol has been studied on two microporous heteropoly oxometalates, the ammonium salts of 12-tungstophosphoric and 12-tungstosilicic acids. Alkylation of the benzene ring to produce xylenes and the trimethyl- and tetramethylbenzenes was found to be the predominant process. Evidence is presented for an alkylation mechanism involving the methylation of the anions of the catalysts. Compositions of the xylene isomers in the product suggest the presence of a shape-selective factor.

INTRODUCTION

The catalytic alkylation of aromatic hydrocarbons, in particular toluene, is a process of both fundamental and practical importance which has been studied for a number of years (*1*). Much of the current activity is related to the elucidation of various mechanistic aspects of the process as it occurs on heterogeneous catalysts and to the use of the reaction as a probe of the existence of shape selectivity. Although much of the published work has been concerned with the mechanism of the process on zeolites (*2–19*), the details are not yet understood even on these catalysts. While it appears to be generally recognized that acidic sites are important in the alkylation process (*3*), the participation of basic sites appears to be more in doubt (*4–8*). On the one hand Brønsted acidic sites have been suggested as responsible for the alkylation of the benzene ring (*1, 4–6*) and the side-chain alkylation has been attributed to basic sites (*1, 4–6*), others have considered that a dual site of acid and base is necessary for side-chain alkylation (*7, 8*).

Kaeding and co-workers (*9–11*) and Olson and Haag (*12*) have studied the alkylation of toluene on ZSM zeolites and have demonstrated that a selectivity to *p*-xylene approaching 100% can be attained under suitable conditions. However, Bhat (*13*) has shown that adsorption of reactant molecules on the cations and acid sites in the zeolite cavities may produce a steric modification of reaction rates (*14*). A number of recent studies (*15–21*) have also been concerned with the shape-selective aspects of the alkylation process. King and Garces (*20*) have very recently carried out IR spectroscopic studies to determine the structures formed on CsX, RbX, and KX zeolites during the alkylation of toluene with methanol. Ashton and co-workers have compared the alkylation of toluene on zeolites theta-1 and ZSM-5 (*21*).

The present work is concerned with the alkylation of toluene with methanol on certain microporous heteropoly oxometalates, a new class of microporous solids. Heteropoly oxometalates are ionic solids, with large cage-like anions which in the present work are of Keggin structure. While the catalytic functionalities of these substances can be altered by changing the elemental

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0021-9517/89 $3.00

composition of the anions the results reported here are concerned with those containing either phosphorus or silicon as the central atom and tungsten as the peripheral metal atoms. It has previously been shown (*22–25*) that with the proton as cation either of these solids is active in the conversion of methanol to hydrocarbons. Photoacoustic (PAS) FTIR spectroscopy (*26–32*) has also been employed to demonstrate that polar substances may enter the bulk structure of the solid acids although the BET surface areas are generally low (10 m^2 g^{-1}).

Recent work in this laboratory has shown that certain salts of the heteropoly oxometalates, with monovalent cations, can be prepared with microporous structures (*28, 30, 33–35*). Hard sphere models of the heteropoly oxometalates indicate that interstitial spaces, apparently separated from each other by the anionic terminal oxygen atoms, are present in the nonporous compounds. Substitution of cations of a particular size evidently produces a sufficient translation and/or rotation of the anions to remove the barriers separating the interstitial spaces and generate continuous pores (*33*). Recent studies of the sorption and diffusion of different organic species with the microporous heteropoly oxometalates have shown, not unexpectedly, significantly altered sorption and diffusivity of these compounds compared with their nonporous relations (*36*).

A study of the alkylation of toluene with methanol on the microporous heteropoly oxometalates should provide additional information on these catalytic solids, the mechanistic aspects of the process and the influence of the microporous structure on the reaction.

EXPERIMENTAL

The ammonium salts of 12-tungstophosphoric ($H_3PW_{12}O_{40}$) and of 12-tungstosilicic acids ($H_4SiW_{12}O_{40}$) were prepared as described previously (*24, 25*). For convenience these two salts will be denoted as NH_4PW and NH_4SiW, respectively. All organic reagents employed were of high purity and were used as received. The xylenes (99%), toluene (99+%), and benzene (99+%) were purchased from Baker and trimethylbenzenes (99+%) and tetramethylbenzenes (95%) were obtained from Aldrich.

Catalytic reactions were performed in a micropulse reactor constructed from stainless steel and Pyrex glass.

Various quantities and concentrations of two-component solutions of toluene and methanol were injected into a helium carrier gas at various controlled flow rates. Products were trapped at 78 K and subsequently flashed to an HP 5880 gas chromatograph equipped with a 2-m column of diisodecyl phthalate and Bentone-34 on Chromosorb WHP for liquid products and a 5-m Porapak Q column for gaseous products. The powdered catalyst was pretreated in a helium stream in the reactor for 2 h at various temperatures (350–550°C) before use at reaction temperatures from 100 to 400°C.

In some experiments quantities of methanol were first added to the catalyst followed by toluene after various periods of time. Selective poisoning experiments were carried out by the introduction of aliquots of gaseous NH_3. Estimates of the acidic strength distributions were obtained by the use of *n*-butylamine and Hammett indicators (*37*).

RESULTS

On the present catalysts, the major products from the alkylation of toluene were xylenes and the trimethyl- and tetramethylbenzenes.

With NH_4PW, a reactant MeOH/toluene ratio of 1/1 and a helium flow rate of 35 ml/min, the conversion and selectivities of the major products show extrema at temperatures between 200 and 250°C (Fig. 1). Below 200°C, increasing temperature reduces the selectivity of xylenes while that to trimethylbenzenes and tetramethylbenzenes increases, the former passing through a rather sharp minimum and the latter two a

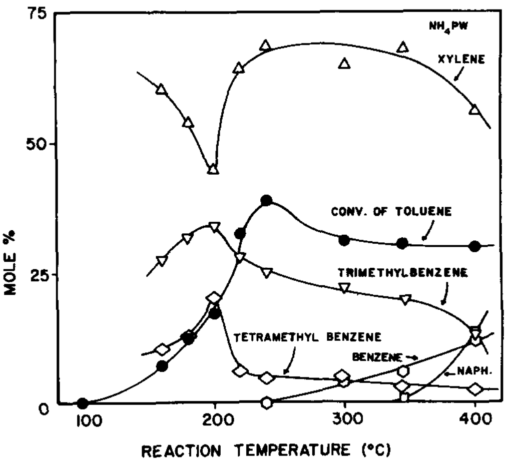

FIG. 1. Conversion and selectivity of methanol–toluene mixture over NH_4PW. Catalysts, 50 mg; pretreatment; 450°C, 2 h in He; reactant, MeOH/toluene = 1/1, 2 μl; carrier gas; He, 35 ml/min. ●, Conversion of toluene; △, selectivity of xylene; ▽, selectivity of trimethylbenzene; ◇, selectivity of tetramethylbenzene; ○, selectivity of benzene; □, selectivity of naphthalene.

maximum at approximately 200°C. Below 250°C, the conversion of toluene increases with increasing temperature and reaches a maximum of 40 mol% at approximately 250°C. The production of benzene and naphthalene increases continuously with temperature from 200 to 400°C.

With NH_4SiW and similar reaction parameters as above the conversion again passes through a maximum, in this case of 15 mol%, a considerably lower one than with NH_4PW, at approximately 250°C (Fig. 2). As with NH_4PW the selectivity to xylene on NH_4SiW shows a minimum and that to tri- and tetramethylbenzene passes through a maximum. However, in contrast to NH_4PW, no naphthalene is observed with NH_4SiW, although small quantities of pentamethylbenzene are produced. It is to be noted that the alkylation on both catalysts primarily occurs on the benzene ring. The only evidence for side-chain alkylation is found at a temperature greater than 350°C on NH_4PW, under which conditions small quantities of naphthalene are produced.

The addition of gaseous NH_3 to the NH_4PW catalyst prior to the reaction produced decreases in the conversion and the selectivity to tri- and tetramethylbenzenes while that to xylenes increased (Fig. 3). Addition of 300 μl NH_3 reduced the conversion to less than 1%.

The ratio of methanol/toluene added to the reaction had considerable influence on the selectivity while the toluene conversion changed only slightly for methanol/toluene from 1/1 to 1/5 (Fig. 4). On NH_4PW at 200°C the conversion to toluene and the selectivity to tetramethylbenzenes passed through a maximum at MeOH/toluene ratios greater than 1/1, while the selectivity to xylenes decreased with increasing MeOH/toluene. The selectivity to trimethylbenzene achieved a maximum at approximately 1/1 MeOH/toluene while that to penta- and hexamethylbenzene increased continuously, the latter remaining at relatively small values.

With NH_4SiW and increasing MeOH/

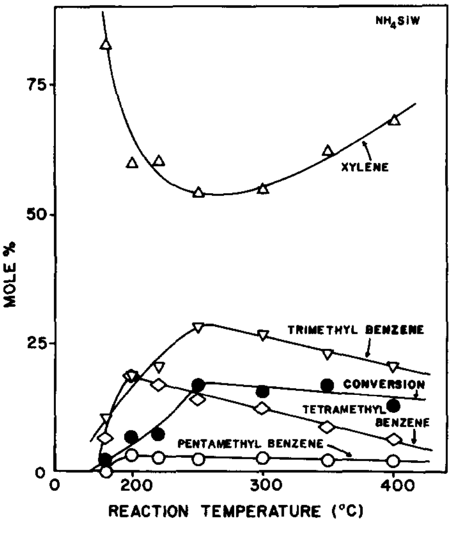

FIG. 2. Conversion and selectivity of methanol–toluene mixture over NH_4SiW. Catalysts, 50.4 mg; pretreatment, 450°C, 2 h in He; reactant, MeOH/toluene = 1/1, 2 μl; carrier gas, He, 35 ml/min. ●, Conversion of toluene; △, selectivity of xylene; ▽, selectivity of trimethylbenzene; ◇, selectivity of tetramethylbenzene; ○, selectivity of pentamethylbenzene.

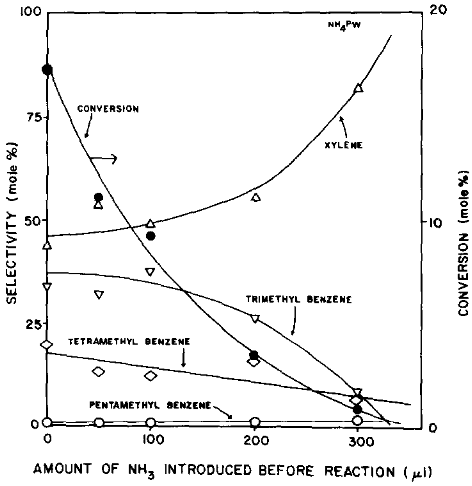

FIG. 3. Effect of NH_3 introduced to catalysts before reaction. Catalysts, NH_4PW, 50 mg; pretreatment, 450°C, 2 h in He; reactant, MeOH/toluene = 1/1, 2 μl; carrier gas, He, 35 ml/min; reaction temperature, 200°C. Symbols are the same as Fig. 2.

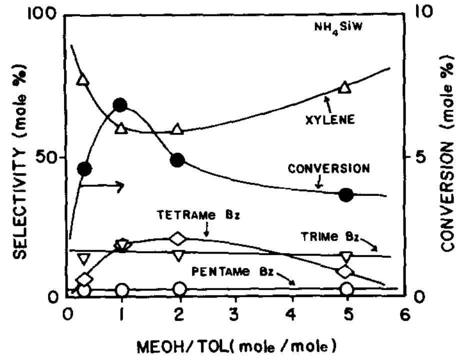

FIG. 5. Effect of methanol/toluene ratio over NH_4SiW. Conditions are the same as Fig. 4 and symbols are the same as Fig. 2.

toluene the selectivities to xylenes and tetramethylbenzenes passed through a minimum and maximum, respectively, but in contrast to the observations with NH_4PW, little change was observed with the trimethyl- and pentamethylbenzenes. The conversion as with NH_4PW displayed a maximum, but with NH_4SiW a considerably sharper peak is evident although conversions are small (Fig. 5).

With increase of the pretreatment temperature from 350 to 550°C and a reaction temperature of 200°C, the conversion of toluene on NH_4PW increases to a maximum between 450 and 500°C and decreases to a negligible value at 550°C (Fig. 6). Similar

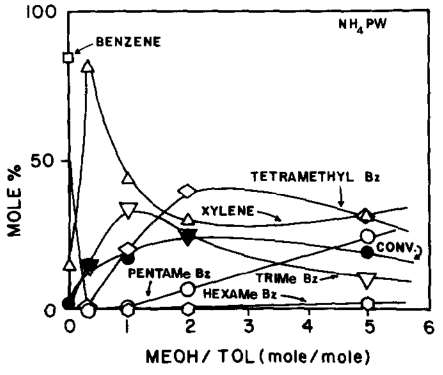

FIG. 4. Effect of methanol/toluene ratio over NH_4PW. Catalysts, 50 mg; pretreatment, 450°C, 2 h in He; reactant, 2 μl of mixture; reaction temperature, 200°C; carrier gas, He, 35 ml/min. ●, Conversion of toluene; △, selectivity of xylene; ▽, selectivity of trimethylbenzene; ◇, selectivity of tetramethylbenzene; ○, selectivity of pentamethylbenzene; ○, selectivity of hexamethylbenzene; □, selectivity of benzene.

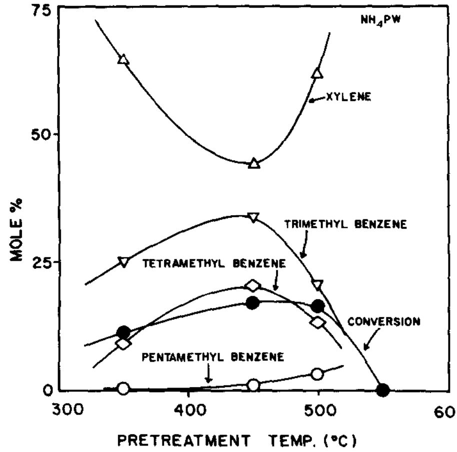

FIG. 6. Effect of pretreatment temperature on conversion and selectivity of methanol–toluene mixture over NH_4PW catalyst. Catalysts, 50 mg; pretreatment, 450°C, 2 h in He; reactant, MeOH/toluene = 1/1, 2 μl; reaction temperature, 200°C; carrier gas, He, 35 ml/min. Symbols are the same as Fig. 2.

trends are observed for the selectivities to trimethyl- and tetramethylbenzene while that to xylene passes through a minimum. In contrast with NH_4SiW the conversion has decreased to a negligible value by a reaction temperature of 500°C (not shown).

DISCUSSION

The major products formed with NH_4PW and NH_4SiW from the reaction of toluene and methanol are the xylenes and the trimethyl- and tetramethylbenzenes. In some cases relatively small quantities of benzene, naphthalene, and pentamethylbenzenes are formed. Evidently with the present catalysts the process is primarily one involving benzene ring alkylation. In addition the present observations suggest that the formation of the xylenes, trimethylbenzenes, and tetramethylbenzenes are consecutive reactions, the formation of the latter two being rapid processes.

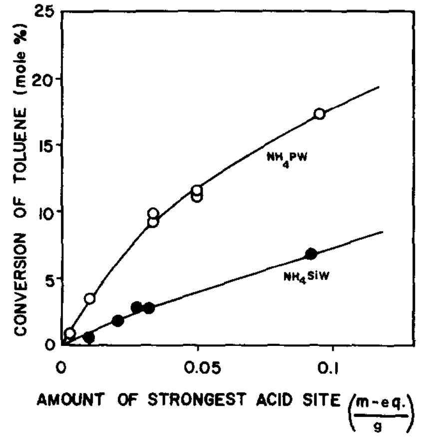

FIG. 7. The correlation between the amount of strongest acid site and the conversion of toluene. Conditions are the same as Fig. 4. ○, NH_4PW catalysts; ●, NH_4SiW catalysts.

Since the addition of ammonia in sufficient amounts reduces the conversion to negligible quantities it is evident that the alkylation process depends on the presence of acidic sites. Plots of the conversion of toluene versus the numbers of strongest acidic sites ($H_0 < -5.6$) (Fig. 7) show that such sites play an important role in the alkylation process on NH_4PW and NH_4SiW. It has previously been shown by PAS FTIR that many of the salts of the heteropoly oxometalates, although prepared to be stoichiometric, contain residual quantities of protons (*26–27*). These protons evidently serve as the Brønsted sites in the ammonium salts under present discussion. It should also be noted that temperature-programmed desorption studies (*38*) have shown that ammonia, water, and nitrogen are evolved beginning at about 600°C, similar to the pretreatment temperature subsequent to which the conversion of toluene becomes negligible. However, protons begin to be lost from the parent acids at somewhat lower temperatures. Consequently at the temperatures employed in the present work, the NH_4^+ cation is apparently largely intact. Earlier work from this laboratory has shown that methanol may be converted to hydrocarbons on various heteropoly oxometalates, including NH_4PW and NH_4SiW (*22–25*). More recent work employing PAS STIR has demonstrated that the methanol is first protonated at the Brønsted acidic sites of the heteropoly oxometalate, leading to a perturbation of the electron density distribution in the protonated species and a weakening and ultimate scission of the C–O bond (*29–32*). The resulting carbocation CH_3^+ is found to be associated with the (presumably terminal) oxygen atoms of the heteropoly oxometalate anions. Since the present process is seen to be dependent on acidic sites and to result primarily in benzene ring alkylation it appears reasonable to assume that the first step in the mechanism involves the methylation of the anionic terminal oxygen atoms or at least a portion thereof. As a test of this hypothesis several experiments were performed in which methanol was first injected on the catalyst followed at times of 30 min and 2 h by equal molar amounts of toluene. Although the conversions measured were less than those observed when methanol and toluene were added, nevertheless the natures and quantities of products were sufficiently similar to those found in the latter case to provide support for the aforementioned hypothesis. However, when this experiment was carried out at higher temperatures (e.g., 350°C) additional hydrocarbons were observed, presumably from the preliminary conversion of methanol (*31*, *32*).

The mechanism for the methylation of toluene on the heteropoly oxometalate catalyst can be summarized as

$$H^+A^- + CH_3OH \rightleftarrows A^- + CH_3OH_2^+$$

$$CH_3OH_2^+ + A^- \rightleftarrows CH_3^+A^- + H_2O$$

$$CH_3^+A^- + \text{toluene} \rightleftarrows (\text{toluene})CH_3$$

where A^- refers to the heteropolyanion.

It is of interest to comment on the extrema observed in both conversion and selectivities and with both catalysts as the temperature is increased from 100 through 400°C. These fall between 200 and 250°C. While such observations may suggest a change in the dominant mechanism, it should be noted that earlier temperature-programmed desorption studies on the parent acids HPW and HSiW showed, among others, peaks due to the evolution of water, believed to exist as hydrogen-bonded molecular water in these solid acids, in the temperature range 200–250°C. While such an observation may be coincidental, it should be recalled that Brown *et al.* (*39*) have shown by X-ray and neutron diffraction techniques that the proton in HPW · nH$_2$O exists in a web-like structure surrounded by four water molecules, although as a result of twofold thermal disorder hydrogen bonded to only two of such molecules. Consequently, below approximately 200°C it is conceivable that a portion of the protons in NH_4PW and NH_4SiW is guarded by water molecules and consequently less accessible to reactant molecules.

It is also of interest to compare the present results with those reported by other workers on various catalysts. Table 1 compares observations of Ashton *et al.* (*21*) with those from the present work yielding the largest *p*-xylene compositions. Ashton and co-workers compared the product compositions from the alkylation of toluene with methanol on H–theta-1 and H–ZSM-5. These are shown in Table 1 along with selected results from the present work. Although the temperatures employed in the present work are considerably lower than those employed by Ashton *et al.* (*21*) the conversions of toluene for NH_4PW and NH_4SiW at 200 and 250°C, respectively, are similar. The *p*-xylene compositions from the present work show high values of 45.1 and 49.9% for NH_4SiW and NH_4PW, respectively, the latter for 160°C and after NH_3 addition. Ashton *et al.* (*21*) note that H–theta-1 is a highly selective catalyst for the production of *p*-xylene. It is of interest to note that the present catalysts are capable of achieving values for percentage *p*-xylene in the xylene isomers as high as those obtained by Ashton *et al.* (*21*) for H–theta-1.

From X-ray diffraction studies the ratio of the reflection intensities associated with the [110] and [222] planes was found to be approximately inversely related to the total micropore volumes of a series of salts from monovalent cations and a particular heteropoly oxometalate anion. It has been concluded that the microporous structure in certain salts results from the interconnection of interstitial voids present even in the nonporous heteropoly oxometalates. Since the terminal oxygen atoms of the anions are found in the [110] planes the low values for the aforementioned reflection ratio which are observed with the microporous salts are attributed to the translation and/or rotation of the anions in such salts so that these terminal oxygen atoms are removed from their positions separating the interstitial voids from each other in the nonporous salts. It is important to note that the sizes of the micropores in these structures are not uniform since pore size distributions have been shown to range from approximately 6 to 13 Å, depending on the

TABLE 1

Product Compositions from the Alkylation of Toluene with Methanol on NH_4PW, NH_4SiW, Theta-1,[a] and ZSM-5[a] Catalyst

	NH_4PW	NH_4SiW	NH_4PW	NH_4PW[b]	Theta-1	ZSM-5
Conditions						
Temperature (°C)	200	250	200	160	550	600
Tol/MeOH molar	1/1	1/1	2/1	1/1	2/1	2/1
W/F [mg cat.min/ml He]	1.43	1.43	1.43	1.43	$1(h^{-1})$	$4.8(h^{-1})$
Conversion (%)						
Toluene	17.3	17.0	20.5	0.9	23.9	31.8
Liquid product (wt%)						
Benzene	0.0	0.0	0.0	0.0	0.7	3.4
Toluene	79.0	79.7	79.5	98.9	70.8	67.0
p-xy	3.0	4.6	4.3	0.40	10.2	11.1
m-xy	2.8	3.7	6.1	0.25	6.5	11.1
o-xy	2.5	1.9	3.9	0.15	6.0	4.6
1.3.5-TriMe	2.1	1.1	1.1	0.05	0.4	0.2
1.2.4-TriMe	4.4	4.0	3.3	0.09	4.3	2.4
1.2.3-TriMe	0.9	0.8	0.9	0.01	N/D	N/D
Xylene composition (%)						
p-xy	36.2	45.1	30.1	49.9	44.9	41.4
m-xy	33.7	36.0	42.6	31.3	28.6	41.4
o-xy	30.1	18.9	27.3	18.8	26.5	18.2

[a] Reference (*21*).

[b] 200 μl NH_3/50 mg cat. added to catalyst at 160°C prior to reaction.

cation and anion (*33–35*). In addition, there is little information as yet on the pore lengths, their wall regularities, and the intersections within the structure. Consequently, comparisons of the present results with those observed with other microporous solids are difficult. However, the data given here provide some insight into the mechanism of the alkylation process on microporous heteropoly oxometalates as well as demonstrating that shape selectivity may be occurring with such solids.

ACKNOWLEDGMENT

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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