EFFECT OF ACID ACTIVATION ON THE DE-TERT-BUTYLATION ACTIVITY OF SOME JORDANIAN CLAYS

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Abstract—Jordanian natural kaolin and bentonite show good catalytic activity towards debutylating 2-tert-butylphenol, and varying debutylation *vs.* isomerization selectivity after acid activation. The resulting catalytic activity of these samples is dependent on the acid employed for activation; the samples treated with acetic acid showed relatively low conversions, whereas those treated with hydrochloric or phosphoric acid were found to be very active. Treatments with strong acids such as HCl have various effects on the activity of the samples depending on the concentration of the acid. For example, treatment with 1 M HCl gives the highest activity, whereas a treatment using 12 M HCl produced the lowest activity. The debutylation selectivity of the acid-activated samples is affected by the acid type and/or concentration. This selectivity ranges from 20 to 60%, whereas that of water-treated samples is between 46–82%.

Key Words—Bentonite, Butylphenol, Catalyst, Clay, Debutylation, Kaolin, Kaolinite, Montmorillonite.

INTRODUCTION

Natural clays are increasingly used in industry as catalysts or catalyst supports in many organic reactions (Auer and Hofmann, 1993; Li and Jin, 1996; Ravichandran *et al.*, 1996, Upadhya *et al.*, 1996; Chitnis and Sharma, 1997; Clark *et al.*, 1997). For example, montmorillonite and kaolinite are two clays commonly used in these reactions. The catalytic properties of clays are affected by chemical composition, structure, and pretreatment conditions (Auer and Hofmann, 1993; Ravichandran *et al.*, 1996).

The catalytic properties can be improved by different acid treatment and/or pillaring methods (Auer and Hofmann, 1993; Ravichandran *et al.*, 1996; Upadhya *et al.*, 1996; Chitnis and Sharma, 1997; Clark *et al.*, 1997). For example, the alkylation of many organic compounds, including phenols, aromatics, and other hydrocarbons, is catalyzed by acid-treated clays (Chitnis and Sharma, 1997). Also, acid treatment with HCl has produced an overall increase in the surface acidity and acidic sites of clays, which increases their catalytic activity in the isomerization of *cis*- and *trans*-2-butenes, and in the cracking of cumenes (Ravichandran *et al.*, 1996).

The tert-butyl group is used as a protector in the synthesis of many organic products (Corma and Wojciechowski, 1985), because this group may be easily detached even at relatively low temperatures. Such a reaction usually involves an acid catalyst, such as pillared clay molecular sieves (Gao and Jiao, 1989) and natural clays (Tkac *et al.*, 1994; Al-No'aimei, 1997; Komadel *et al.*, 1997; Saleh and Mahmoud, 1998).

We investigated the stability and catalytic activity of some Jordanian clays in a variety of reactions, such as hydrogenation of acetylenes, hydrocracking of paraffins, and debutylation of some substituted arenes (Al-No'aimei, 1997; Saleh and Mahmoud, 1998), to determine the suitability of these clays to be catalysts or catalyst supports. These clays proved to be good debutylation catalysts and better than tested Bulgarian and Turkish samples (Saleh and Mahmoud, 1998).

Here, we report the effect of acid treatment with varying concentrations on the catalytic properties of Jordanian bentonite and kaolin in the de-tert-butylation of 2-tert-butylphenol. Such treatment includes the use of weak and strong acids of different concentrations. It is then possible to investigate the effect of acid type and/or concentration on the strength and density of the active acid sites on the clay surface. The debutylation of 2-tert-butylphenol was chosen as the model reaction because the tert-butyl group is ortho to the hydroxyl group that activates positions 2, 4, and 6. Therefore, in addition to catalytic activity, it is possible to study the selectivity of these clays in producing various mono- and di-substituted tert-butylated isomers as a result of transalkylation.

MATERIALS AND METHODS

Bentonite samples were collected from southeastern Al-Azraq area, east of Jordan, whereas kaolin samples were obtained from the northeastern region of Jordan. All chemicals used were of reagent grade and were not purified further before use. The chemical composition of the samples was determined by atomic absorption spectrometry (Pye Unicam SP9) after digestion with HNO_3, HCl, and HF (Table 1). All samples were soaked overnight in acid solutions of HCl, H_3PO_4, or CH_3COOH of proper concentrations (Table 1), then washed with distilled water, and dried at 100°C for 2 d. The clays were then calcined at 450°C in flowing air (100 cm^3 min^{-1}) in a fixed-bed flow reactor for 4 h.

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Table 1. Elemental analysis, BET surface area, surface acidity, and the concentration (ppm) of leached Al^{3+} of the activated Jordanian bentonite and kaolin clay samples.

| | Clay composition (wt. %)[1] | | | Bentonite[2] | | | Kaolin[3] |
	Bentonite[2]	Kaolin[3]	Activating acid	$[Al^{3+}]$	S.A.	$[H^+]$	$[Al^{3+}]$
SiO_2	52.9	60.6	Water	0	134	0.183	0
Al_2O_3	13.1	24.8	0.5 M HCl	5.9	229	0.823	5.7
Fe_2O_3	7.8	1.9	1.0 M HCl	6.4	242	0.800	6.2
MgO	5.3	0.2	2.0 M HCl	6.6	256	0.621	6.8
CaO	3.7	0.6	6.0 M HCl	9.1	269	0.415	8.2
Na_2O	0.8	0.4	12.0 M HCl	10.5	299	0.323	9.2
K_2O	1.8	1.6	1.0 M CH_3COOH	1.4	163	0.456	1.4
TiO_2	0.1	1.4	1.0 M H_3PO_4	8.7	233	0.738	7.1
L.O.I.[4]	13.1	8.5					

[1] Chemical composition of water-treated clay samples as determined by atomic absorption spectrometry.

[2] ~70% montmorillonite; S.A.: surface area in $m^2\ g^{-1}$; $[H^+]$: total surface acidity in mmol $H^+\ g^{-1}$, with $H_o \leq 4.8$; $[Al^{3+}]$: concentration of leached Al in ppm.

[3] ~90% kaolinite; S.A. ~ 15 $m^2\ g^{-1}$, $[H^+]$: total surface acidity in mmol $H^+\ g^{-1}$ ~0.10, with $H_o \leq 4.8$.

[4] Loss on ignition.

Catalytic reactions

Samples (5.0 cm^3 each) of 2-tert-butylphenol (Fluka) were added with a 1.0 g catalyst sample in a three-neck round bottom flask, equipped with a condenser, a thermometer, and a serum cap for sample removal. The flask was then immersed in a silicon oil bath and the reaction mixture was heated under reflux at 230°C. Samples for analysis (~0.05 cm^3) were taken from the reaction mixture at 15 min intervals, then diluted with methanol, and analyzed by gas chromatography.

BET analysis of each clay was measured by nitrogen adsorption using a glass apparatus built and modified for this purpose (Johne and Severin, 1965). Also, the Bronsted surface acidity of the samples was determined by the amine titration method using several indicators (Lucio, 1973).

Analysis

All reaction samples were analyzed by a Pye-Unicam gas chromatograph with a FID detector, and connected to an electronic integrator (Spectra-Physics, Ink-Jet) interfaced to a computer. Analysis was performed on a 1.5 m long × 6 mm O.D. stainless steel column, packed with 10% silicon E30 and supported on silanized acid-washed diatomite "C" with a mesh size of 100–120. Helium carrier gas was passed at a flow rate of 45 $cm^3\ min^{-1}$. The injector, detector, and oven temperatures were, 250, 300, and 150°C, respectively.

^{1}H-NMR (nuclear magnetic resonance) spectroscopy was used to identify the isomeric forms by using the chemical shifts of the tert-butyl group in different tert-butylated phenols.

RESULTS

Chemical analysis showed that Jordanian bentonite contains ~70% montmorillonite, which is the principal active component in this acid-catalyzed reaction. The remaining ~30% consists of non-clay minerals of quartz, feldspar, and carbonates. Montmorillonite possesses both Bronsted and Lewis acid sites, which are responsible for its dealkylation and transalkylation activities (Gonzalez et al., 1992). Jordanian kaolin contains ~90% kaolinite and ~10% quartz. Kaolinite is catalytically active due to strong Lewis acid sites (Benesi, 1956). These clays also contain some oxides of (periodic table) GIA, GIIA, and transition elements (Table 1) that influence their thermal stability and catalytic properties (Tanabe, 1983).

Clay properties such as surface area, surface acidity, and thermal stability vary with composition and/or structure. These properties are decisive in establishing the catalytic behavior of these clays. For instance, the BET surface area of the water-treated Jordanian bentonite is high (~134 $m^2\ g^{-1}$) and that treated with 1.0 M HCl is even higher (~240 $m^2\ g^{-1}$). BET surface area increases with the concentration of the activating acid. Such an increase in surface area upon acid treatment is due to an increase in porosity caused by leaching Al_2O_3 from the clay mineral (Tkac et al., 1994; Komadel et al., 1997). This surface area becomes very high at high acid concentrations (Newman and Brown, 1987) and provides a relatively suitable surface for acid-catalyzed reactions. Jordanian kaolin, similar to all kaolinitic clays, has a low BET surface area (~15 $m^2\ g^{-1}$), but possesses strong Lewis acid sites making it a suitable catalyst in acid-catalyzed reactions.

Table 1 shows surface acidity measurements using several indicators at $H_o \leq 4.8$ have total Bronsted-surface acidity values for bentonite samples (0.18–0.82) that are much higher than those of kaolin samples (~0.10). In the debutylation reaction of 2-tert-butylphenol, all samples gave the same products but at different rates (Tables 2 and 3).

DISCUSSION

The presence of constituent metal oxides in the clay mineral decreases the Bronsted surface acidity and

Table 2. De-tert-butylation activity of different activated Jordanian bentonite samples in the debutylation of 2-tert-butylphenol at 230°C where C = % conversion of 2-tert-butylphenol and S = debutylation selectivity.[1]

| Time (h) | HCl conc. (M) | | | | | | | | | | H_3PO_4 1.0 M | | CH_3COOH 1.0 M | | Dist. water | |
| | 0.50 | | 1.0 | | 2.0 | | 6.0 | | 12.0 | | | | | | | |
	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S
0.25	36	40	68	30	40	49	30	58	30	60	63	26	43	47	28	78
0.50	68	36	90	33	64	40	42	56	38	55	86	28	66	39	44	72
1.0	80	28	95	44	90	20	73	42	70	46	92	40	81	33	62	64
1.5	87	24	96	52	93	18	82	40	83	39	95	44	88	30	70	62
2.0	90	22	97	58	95	20	86	35	84	34	96	43	91	28	77	55
Butyl.[2]	~25%		~8%		~22%		~22%		~23%		~11%		~22%		~20%	

[1] Debutylation selectivity = (% phenol)/(% 4-tert-butylphenol) × 100%.
[2] Butyl. = average percentage of 2,4-di-tert-butylphenol at conversions ≥50%.

thus affects the catalytic debutylation activity and selectivity. Therefore, the studied clays were pretreated with acids of different strengths and various concentrations to improve their surface acidity. For example, strong acids such as H_2SO_4 or HCl may generate new surface acid sites quickly, but they may also cause extensive leaching of Al_2O_3 from the clay mineral, thereby leading to structure collapse (Newman and Brown, 1987; Rupert *et al.*, 1987; Lussier, 1991; Mokaya and Jones, 1995). Weak acids may preserve the clay structure, but are less effective in generating surface acid sites.

Tables 2 and 3 and Figures 1 and 2 show the percentage conversion of 2-tert-butylphenol by acid-treated bentonite and kaolin samples at different time intervals. High-percentage conversions indicate high catalytic activity of the sample, and thus greater acid activation. It appears that 1 M HCl is the best acid solution for the activation of both samples; after 30 min of reaction, 90 and 92% conversions were obtained for bentonite and kaolin, respectively. The effectiveness of HCl clay-activation may be because HCl is a strong acid, which completely dissociates in water to H^+ and Cl^- ions. Also, the produced metal chlorides due to this acid treatment are completely soluble in water, and removed by the pretreatment process. Although HCl is a strong acid, it has not caused significant deterioration of the clay structure as indicated by the BET surface area measurement data (Table 1). On the other hand, acetic acid is a weak acid (pH ~ 2.4 for 1 M) and hence is far less effective at activation of the clays compared to HCl of the same concentration. A conversion of ~66% after 30 min reaction was observed for both samples when treated with 1 M acetic acid. Moreover, phosphoric acid was more effective than acetic acid and was comparable to HCl. This may be attributed to the phosphoric acid being stronger (pH ~ 1 for 1 M) than acetic acid, but it is still weaker than HCl. Also, free phosphate ions (PO_4^{3-}) form insoluble complexes with the leached metal ions, and hence decrease the clay mineral activity (Lussier, 1991).

It was also found that the 1 M HCl is the best solution for this acid activation process, and as concentration increases above 1 M the activity of these samples decreases. Thus, the activity is directly related to surface acidity. For example, the 12 M HCl-treated bentonite sample has a low Bronsted surface acidity (0.323) and consequently, a low percentage conversion (38%) after 30 min of reaction. Whereas, as given in Tables 1 and 2, the bentonite sample treated with 1 M HCl has much greater surface acidity and percentage

Table 3. De-tert-butylation activity of different activated Jordanian kaolin samples in the debutylation of 2-tert-butylphenol at 230°C where C = % conversion of 2-tert-butylphenol and S = debutylation selectivity.[1]

| Time (h) | HCl conc. (M) | | | | | | | | | | H_3PO_4 1.0 M | | CH_3COOH 1.0 M | | Dist. water | |
| | 0.50 | | 1.0 | | 2.0 | | 6.0 | | 12.0 | | | | | | | |
	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S
0.25	78	22	80	20	52	38	32	60	22	64	80	27	24	52	20	82
0.50	90	15	92	25	70	31	51	47	43	52	89	30	65	37	35	71
1.0	95	15	95	40	88	23	82	26	76	29	94	45	83	29	50	56
1.5	96	19	96	48	93	23	89	22	84	24	96	48	89	32	58	51
2.0	96	28	97	50	94	25	91	20	87	24	97	50	92	31	67	46
Butyl.[2]	~15%		~8%		~20%		~24%		~26%		~8%		~20%		~22%	

[1] Debutylation selectivity = (% phenol)/(% 4-tert-butylphenol) × 100%.
[2] Butyl. = average percentage of 2,4-di-tert-butylphenol at conversions ≥50%.
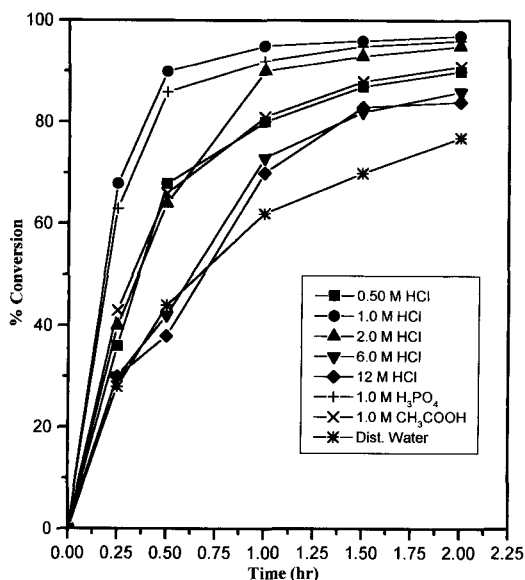
Figure 1. De-tert-butylation activity of Jordanian bentonite samples treated with different acid solutions.
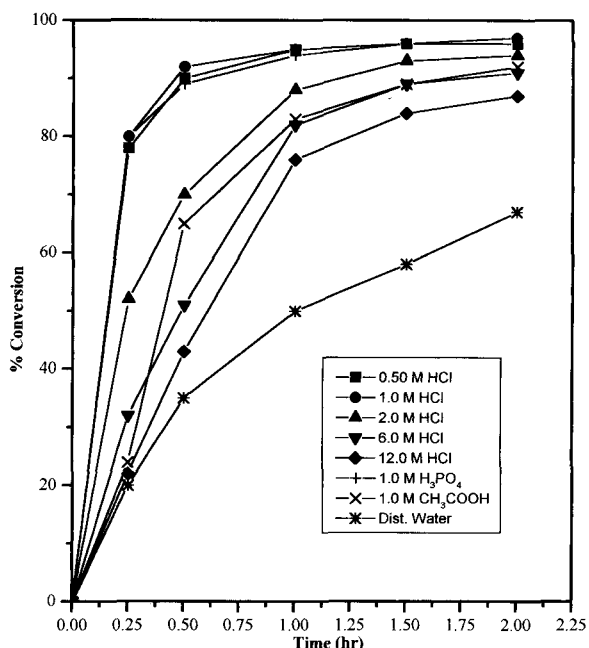

Figure 2. De-tert-butylation activity of Jordanian kaolin samples treated with different acid solutions.

conversion values (0.80 and 90%, respectively). Extensive leaching of the constituent oxides, especially Al_2O_3 and Fe_2O_3, may have caused this effect. Evidence of leached oxide minerals is found in the Al^{3+} data of the filtrate of the acid-treated bentonite and kaolin samples (Table 1). When the concentration of HCl was increased from 0.50 M to 12.0 M, Al^{3+} concentration increased from 5.9 and 5.7 ppm to 10.5 and 9.2 ppm, respectively. Moreover, the percentage conversion for the 12.0 M HCl-treated samples was comparatively low at short reaction times, but at longer times conversions for all samples become more similar. This suggests that the structures of these samples were greatly affected by the high concentration of the acid used. Such a change is consistent with changes observed in the physical properties of the clays. Color changed from light yellowish brown to dark brown, and the BET surface area of the bentonite increased from ~134 m^2 g^{-1} to ~300 m^2 g^{-1} upon treatment with 12.0 M HCl. Such an increase in BET surface area caused by extensive loss of aluminum was not associated with an increase, but with a decrease in catalytic activity (Table 1).

The acid-activated samples behaved similarly with respect to the products formed and with respect to selectivity in the conversion of 2-tert-butylphenol. Phenol and 4-tert-butylphenol were the major products, whereas 2,4-di-tert-butylphenol was obtained in minor quantities. These products are a result of a reaction that involves three possible pathways (Figure 3). First, the debutylation of the substrate 1 occurs to produce phenol 2 and isobutene, which partly becomes adsorbed on the clay acid sites, thereby forming tert-

carbocation (Greensfelder *et al.*, 1949). The partial release of isobutene was consistent with stoichiometric calculations based on the collected volumes of this gas over water, and is in agreement with other studies (Gill *et al.*, 1998). Second, the butylation of phenol 2 at the para position to produce 4-tert-butylphenol 3. Third, the butylation of 2-tert-butylphenol 1 to produce 2,4-di-tert-butylphenol 4.

The ability to produce compounds 2, 3, and 4 depends on the activity of the clay sample, as well as on the type and relative population of the acid sites (Shertukde *et al.*, 1993). More active clay samples are ex-
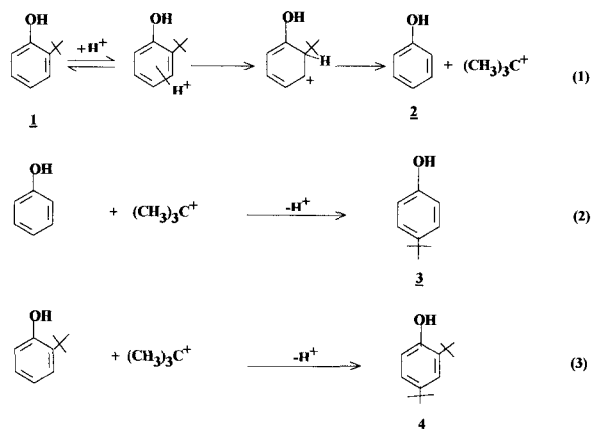

Figure 3. Mechanism of the de-tert-butylation of 2-tert-butylphenol by Jordanian bentonite and kaolin samples.
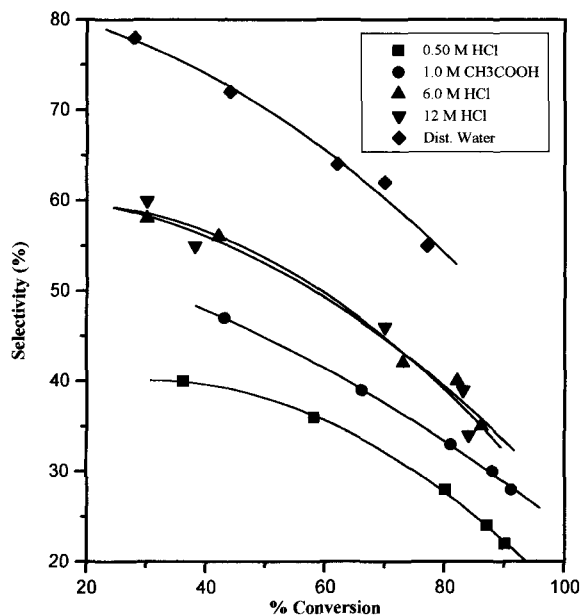
Figure 4.   The effect of conversion on selectivity of some Jordanian bentonite samples treated with different acid solutions. (Data points from left to right are, respectively, at 0.25, 0.50, 1.0, 1.5, and 2.0 h)

pected to involve all reaction pathways to yield initially all products at relatively high concentrations. However, as the percentage conversion increases, more debutylation products are obtained (*i.e.*, the debutylation of 3 and 4) thus showing a higher debutylation selectivity. For example, the 1 M HCl-activated bentonite sample shows initial and final debutylation selectivities of 30 and 58%, respectively, but only 8% butylation selectivity (Table 2). Consequently, this bentonite possessed initially low debutylation selectivity, but as the percentage conversion of 2-tert-butylphenol increases, the concentration of products 3 and 4 increases also. These products are then debutylated to produce 2, resulting in increasing the debutylation selectivity.

Contrary to the most active samples, the initially high debutylation selectivity of the less active samples, such as the water-treated samples and the samples treated with 1 M acetic acid or with high concentrations of HCl, decreases with both time and percentage conversion (Tables 2 and 3; Figure 4). Since the concentration of phenol and the concentration of the intermediate tert-carbocation increase with time, reactions (2) and (3) become highly competitive. This leads to a lower debutylation selectivity after 2 h of reaction. During this time, the clay sample may have become deactivated so that it cannot debutylate products 3 and 4. Thus, this variation in selectivity trend is believed to be generally caused by the variation in activity. The selectivity is a function of percentage conversion, where at low conversions high debutyla-

tion selectivities were observed, and *visa versa* (Figure 4). Such a decreasing debutylation selectivity, relatively high butylation, and high isomerization selectivities are possibly due to low activity.

CONCLUSIONS

Mild acid treatment is believed to increase the debutylation activity and selectivity of Jordanian bentonite and kaolin samples through the improvement of their surface acidity. In contrast, treatment with strong acids of high concentrations, even though the BET surface area of the clay increases, has an adverse effect on the catalytic properties of the clays. Such effect is caused by the extensive leaching of the metal oxides.

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