

PRETREATMENT EFFECTS ON THE CATALYTIC ACTIVITY OF JORDANIAN BENTONITE

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Abstract—De-tert-butylation of 2-tert-butylphenol was carried out over thermally-treated and acid-treated Jordanian bentonite clay samples. This reaction was found to follow first-order kinetics for all clay samples with different pretreatment procedures. The apparent rate constant, k , was also determined, and found to depend on the pretreatment. Thermal pretreatment at temperatures up to 250°C has an enhancing effect on surface acid sites. The total surface acidity ($H_o < 4.8$) and the concentration of strong acid sites peaked at 250°C. Also, as a result, the maximum catalytic activity was obtained with samples treated at this temperature. Acid pretreatment with 0.10 M HCl, 1.0 M H₂SO₄ or 1.0 M H₃PO₄, followed by thermal treatment at 250°C produced the best enhancement effect on the surface acidity and catalytic activity.

Key Words—Acid, Bentonite, Butylphenol, Catalyst, Clay, Debutylation, Montmorillonite, Thermal.

INTRODUCTION

In the last decade, the amount of research for improving the catalytic properties of clays by different pretreatment procedures or modification methods has increased significantly. Much work has been done to produce active and efficient industrial catalysts or catalyst supports of low-cost clays, *e.g.* the debutylation of tert-butylphenols (Saleh and Mahmoud, 1998; Mahmoud and Saleh, 1999) and the alkylation of many organic compounds (Chitnis and Sharma, 1997) are two of the reactions studied on acid-treated clays. For instance, treatments of Jordanian bentonite and kaolin samples with different acids of different concentrations have significantly enhanced their catalytic activity towards the conversion of 2-tert-butylphenol, with 1 M HCl treatment being the most effective in this respect (Mahmoud and Saleh, 1999). Moreover, Jordanian bentonite and kaolin were found to have higher activity in the conversion of tert-butylphenols than Bulgarian and Turkish bentonite samples (Saleh and Mahmoud, 1998). The HCl pretreatment of bentonitic clay samples has shown variations in the clays' overall surface acidity and density of both Lewis and Brønsted surface acid sites (Ravichandran and Sivasankar, 1997). Heat, acid and/or cation-exchange pretreatments have also shown significant changes in the catalytic activity and/or selectivity of bentonitic clay samples (Chitnis and Sharma, 1997; Ravichandran and Sivasankar, 1997; Haffad *et al.*, 1998; Saleh and Mahmoud, 1998; Mahmoud and Saleh, 1999; Breen and Moronta, 2000; Narayanan and Deshpande, 2000; Shaikh *et al.*, 2000). Platinum supported on K10 clay was reported to have caused the selectivity of the hydrogenation of cinnam-

aldehyde to be exclusive for the production of cinnamyl alcohol (Szollosi *et al.*, 1999).

Here, we present the results of our study on the effect of thermal and acid pretreatment on the surface acidity and catalytic activity of Jordanian bentonite in the de-tert-butylation of 2-tert-butylphenol (a reaction that needs acidic catalysts). A wide temperature range was chosen for the purpose of determining the best pretreatment temperature. Also, different acids with different concentrations were used in this study to provide a means of studying their effect on the type and density of surface acid sites, and thus on the catalytic activity of this clay in the probe reaction.

MATERIALS AND METHODS

Jordanian bentonite collected by the National Resource Authority from The southeastern Al-Azraq area, east Jordan was purified and separated from non-clay materials in a Mozely hydrocyclone (Noufal, 1990). The clay was dried in an oven at 100°C before crushing using a steel-ball mill. Only clay particles $\leq 63 \mu\text{m}$ in size were used. The elemental analysis of the purified, untreated clay samples is presented in Table 1.

Clay pretreatment

Acid treatment. 0.500 g samples of Jordanian bentonite were boiled separately with 50 cm³ of HCl, H₂SO₄ or H₃PO₄ with concentrations of 0.1, 1.0, 6.0 or 12 M for 30 min. The clay samples were then filtered under vacuum, washed with distilled water and dried overnight at 80°C.

Thermal treatment (calcination). The calcination of clay samples was accomplished by heating the samples for 1 h under flowing air in a fixed-bed flow reactor at

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Table 1. Elemental analysis of purified, untreated clay samples.

% oxide	Na	Fe	Ni	Al	Si	Mg	Ti	Ca	K	L.O.I.*
	1.8	8.2	0.3	13.5	50.8	5.3	1.3	5.7	2.8	10.3

* Loss on ignition

various temperatures (150, 250, 350, 500, 700 and 900°C) using a tubular quartz electric oven.

Methods of characterization

Elemental analysis. A 0.200 g sample of bentonite was digested in a solution containing 5 cm³ of HF, 2.5 cm³ of 25% HCl_(aq.) and 2.5 cm³ of 25% HNO_{3(aq.)} at 70°C for 2 h, 50 cm³ of 4% H₃BO_{3(aq.)} and 10 cm³ of distilled water were then added. The elemental analysis of diluted solutions was carried out via atomic absorption spectroscopy (Pye-Unicam, SP 9).

BET surface area measurement. Single-point BET surface area measurements were carried out in a N₂ adsorption glass apparatus designed in our laboratories after Johnne and Severin (1965). The results were shown to be accurate and reliable when compared with results obtained from a Micromeritics instrument. The relative pressure of N₂ in our experiments was ~0.26, lying within the desired linear range between 0.05 and 0.35 (Brunauer *et al.*, 1938). Before measurement, the sample was degassed under vacuum at 250°C for 3 h, to ensure a clean surface.

Surface acidity measurement. The number and strength of the acidic sites on the bentonite surface were determined by non-aqueous titration of bentonite samples suspended in dry benzene with benzenic solution of *n*-butylamine as a titrant using various indicators [methyl red (pKa = 4.8), methyl orange (pKa = 3.6), bromocresol green (pKa = 2.9) and thymol blue (pKa = 1.2)]. At the end point of titration, the number of acidic sites having an acid strength H_o < pKa is determined, where H_o is the Hammett acidity function defined as

$$H_o \equiv -\log a_{H^+} \cdot f_B / f_{BH^+} = pKa + \log \frac{[B]}{[BH^+]} \text{ for Brönsted acids} \quad (1)$$

or

$$H_o \equiv -\log a_A \cdot f_B / f_{AB} = pKa + \log \frac{[B]}{[AB]} \text{ for Lewis acids} \quad (2)$$

where a_{H^+} is the activity of H⁺ (Brönsted acid); a_A is the activity of Lewis acid, A; [B] is the concentration of neutral Brönsted or Lewis base, B; [BH⁺] is the concentration of the corresponding conjugate acid of the Brönsted base, B; [AB] is the concentration of Lewis acid-base complex; and f_i values are the activity coefficients.

H_o is a measure of the acid strength; the smaller the H_o value, the stronger the acid. The details of this technique are to be found in Tanabe (1970).

Catalytic activity. The acid-catalyzed debutylation of 2-tert-butylphenol was considered in this work as a test reaction to investigate the catalytic activity of pretreated Jordanian bentonite. The debutylation reaction was carried out under two different sets of conditions: (1) debutylation of neat 2-tert-butylphenol at 125°C (2.5 cm³ of liquid reactant over 0.500 g of bentonite in a 50 cm³ two-necked round-bottom flask supplied with a 40 cm long condenser and heated in an oil bath); (2) debutylation of a 2.0 M solution of 2-tert-butylphenol in CCl₄ at 76°C (10 cm³ of solution over 0.500 g of bentonite in two-necked round-bottom flask heated at the reflux temperature of 76°C). Samples were taken at 5 min intervals and analyzed by gas chromatography (Pye-Unicam with a flame ionization detector (FID)) on a 1.5 m × 6 mm outer diameter stainless steel column, packed with 10% silicone 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 cm³ min⁻¹. The injector, detector and column temperatures were 250, 300 and 150°C, respectively.

RESULTS AND DISCUSSION

Thermal treatment

The catalytic activity (expressed as the conversion of 2-tert-butylphenol after 10 min of reaction) and the surface acidity of Jordanian bentonite samples treated with 1.0 M H₃PO₄ and calcined at various temperatures are presented in Table 2. Obviously, the maximum catalytic activity was obtained after calcination at 250°C and could be correlated to the surface acidity. For calcination temperatures at and below 250°C, no change in the total surface acidity (H_o < 4.8) was observed. However, the concentration of 'strong' acidic sites (H_o < 3.6; H_o < 2.9; H_o < 1.2) was found to increase with increasing calcination temperature, going through a maximum at 250°C, before decreasing at higher temperatures. As a consequence, the observed increase in the number of strong acidic sites in the calcination temperature range at and below 250°C must have occurred at the expense of the weak acid sites, since the total acidity (H_o < 4.8) in the above-mentioned range remains constant. Such behavior was observed in related systems, *e.g.* in the Peruvian Ca-montmorillonite studied by Mokaya and Jones (1995) who reported a monotonic decrease in the concentration of Brönsted sites ($\nu = 1540 \text{ cm}^{-1}$ in the pyridine IR spectrum) of the acid-activated clay with increased calcination temperature, whereas the concentration of Lewis sites ($\nu =$

Table 2. Effect of calcination temperature on surface acidity and catalytic activity of acid-treated Jordanian bentonite samples (all clay samples were treated with 1 M H₃PO₄; the reaction temperature was 150°C).

Calcination temperature (°C)	Acid amount (mmol H ⁺ /g clay)				Conv.% after 10 min at 150°C
	H _o < 4.8	H _o < 3.6	H _o < 2.9	H _o < 1.2	
25	0.35	0.15	0.08	0.06	86
150	0.35	0.17	0.09	0.06	94
250	0.35	0.19	0.12	0.08	97
350	0.30	0.17	0.08	0.07	87
500	0.27	0.14	0.06	0.05	2

1440 cm⁻¹) was found to peak at 250°C. Similar results were also obtained in other systems such as NiSO₄·xH₂O (Hattori *et al.*, 1971), showing the generally greater thermal stability of Lewis acid sites (Adams and Voge, 1957). Since sorption on unsaturated metal cations is usually stronger than sorption on hydroxyl groups, the Lewis acid sites are expected to be stronger than the Brönsted ones, which would explain the observed increase in the concentration of strong acid sites mentioned above.

On the other hand, calcination temperatures >250°C were found to lead to a decrease in the catalytic activity and to a loss in both strong and total acid sites. Moreover, calcination at temperatures >500°C makes the bentonite sample completely inactive. This behavior is attributed to the strong loss in surface acidic sites and to the observed drastic decrease in the surface area of the bentonite catalyst (down to 10 m²/g after calcination at 900°C). These observations can be explained by the well known fact that clay minerals are thermally unstable above 200°C, suffering from interlayer collapse due to elimination of interlayer water (Pinnavaia, 1983). Under these conditions, only the external surface of the clay with rather small surface area can be effective for catalytic reaction, since a proportion of acid sites on the clay sheets becomes inaccessible to the base (Izumi *et al.*, 1992). Much higher calcination temperatures would probably lead to a complete structural collapse producing new phases as could be detected in the thermal transformation of kaolin to mullite, γ-Al₂O₃ and/or Al-Si spinel (Brown *et al.*, 1985; Watanabe *et al.*, 1987; Sanz *et al.*, 1988).

Acid treatment

The effect of the type of acid treatment on the physical properties and catalytic activity of Jordanian bentonite is summarized in Table 3 where it can be recognized that the variety of acid and acid concentration play an important role in modifying the clay properties. When treating Jordanian bentonite samples with 0.1 M HCl, 0.1 M H₂SO₄ or 0.1 M H₃PO₄, differently activated clay samples were produced, with the conversion after 10 min (measure of catalytic activity) being 92%, 82% and 29%, respectively. On the other hand, acid treatment with 6.0 M H₂SO₄ deactivated the bentonitic sample completely, whereas

the treatment with 6.0 M HCl or 6.0 M H₃PO₄ reduced the conversion drastically to ~8%, but it did not completely diminish its catalytic activity. These observations indicate that the nature of the acid used (*e.g.* its strength, nature of anion) does play an important role in the activation process, in agreement with the conclusion of Komadel *et al.*, 1996 who found that the dissolution rate of hectorite decreased in the order HCl ≥ HNO₃ > H₂SO₄ at the same concentrations.

It is noteworthy that the acid activation by 0.1 M H₃PO₄ is much less than that by HCl or H₂SO₄ of the same concentration, which may be attributed to the fact that H₃PO₄ is a weak acid, while HCl and H₂SO₄ are strong acids. High concentrations of H₂SO₄ and H₃PO₄ (6–12 M) seem to act differently when compared to HCl at the same concentration, leading to an obvious decrease in the BET surface area of the activated catalyst. This may be attributed to the presence of oxyanions, which may have caused co-precipitation of the leached cations.

On the other hand, acid concentrations as low as 0.1 M were found experimentally to enhance significantly the catalytic activity of Jordanian bentonite (Table 3). Moreover, the bentonite samples experience a strong reduction in their activity upon pretreatment with high acid concentrations (6–12 M). The optimum acid concentration that produces maximum activity was 0.1 M in the case of HCl and 1.0 M for H₂SO₄ and H₃PO₄. The observed enhancement of catalytic activity upon acid treatment can be explained by the increased amount of surface acidity as evident from Table 3 (as will be discussed below, a strong correlation between the catalytic activity and surface acidity was in fact obtained only for the strong acid sites).

The modification of surface acidity upon pretreatment with acids is, however, a rather complicated process that depends largely on the extent of the treatment. When bentonite is treated with acids, the protons released replace the cations on the interlamellar surfaces of the clay. This decationation leads to an increased number of Brönsted sites. However, in the case of bentonite, whose major constituent is montmorillonite, an enhancement of catalytic activity due to decationation only is not expected. This is because montmorillonite is an 'octahedrally charged' silicate, *i.e.* with Mg²⁺ and Al³⁺ substitutions mostly in the

Table 3. Effect of acid pretreatment on surface acidity, surface area and catalytic activity of Jordanian bentonite (all clay samples were calcined at 250°C; the temperature of debutylation reaction was 125°C).

Treatment	Conc. (mol/L)	Acid amount (mmol H ⁺ /g clay)				BET SA (m ² /g)	% conv. after 10 min
		H _o < 4.8	H _o < 3.6	H _o < 2.9	H _o < 1.2		
HCl	0	0.1	0.0375	0.0225	0.0225	134	0
	0.1	0.385	0.205	0.17	0.0975	231	92
	1.0	0.37	0.185	0.155	0.09	242	87
	6.0	0.275	0.08	0.035	0.025	269	8
	12.0	0.2	0.0675	0.0325	0.0225	299	0
H ₂ SO ₄	0	0.1	0.0375	0.0225	0.0225	134	0
	0.1	0.385	0.155	0.125	0.085	222	82
	1.0	0.375	0.230	0.195	0.12	260	94
	3.0	0.325	0.085	0.06	0.05	282	39
	6.0	0.25	0.0525	0.035	0.025	267	0
H ₃ PO ₄	0	0.1	0.0375	0.0225	0.0225	134	0
	0.1	0.37	0.11	0.09	0.072	219	29
	1.0	0.35	0.185	0.12	0.0825	233	81
	6.0	0.25	0.075	0.035	0.025	302	8
	12.0	0.2	0.075	0.025	0.0125	225	0

octahedral sheets and only very limited substitution in the tetrahedral sheets. Consequently, the released protons will migrate via the hexagonal hole and become attached to the OH-groups located below the hole producing Brönsted acid sites (... OH₂⁺ ...) which have been verified to be energetically most favorable from the results of CNDO/2 calculations (Akama *et al.*, 1986). Such acid sites are, however, inaccessible to the reactant and indicator molecules since the entrance diameter of the hexagonal hole is as small as an oxygen atom (Izumi *et al.*, 1992).

The extent of dealumination was determined experimentally by elemental analysis of acid-pretreated bentonite samples. The results are presented in Figure 1a. Obviously, the higher the concentration of the acid, the larger is the extent of dealumination. It can be recognized that some dealumination is needed in order to activate the bentonite samples and that strong

dealumination makes the bentonite samples completely inactive (Figure 1b). It is believed that an opening of the clay structure by an initial acid treatment increases the number of accessible Al³⁺ ions, although the total amount of Al present decreases. In fact, it was reported that dealumination by acid treatment must be kept below 50% to ensure that the activation of the clay by acid treatment is not reduced (Mokaya and Johns, 1995).

Kinetic measurements

Debutylation of 2-tert-butylphenol in CCl₄ was carried out at 76°C over the following acid-treated bentonite samples (classified according to the acid treatment): 1.0 M H₂SO₄; 0.1 M H₂SO₄; 1.0 M HCl and 0.1 M HCl (Table 3). In addition to phenol, the direct product of debutylation, 4-tert-butylphenol and the di-substituted phenols (2,4-Di-tert-butylphenol and 2,6-Di-tert-butylphenol) were also formed under the

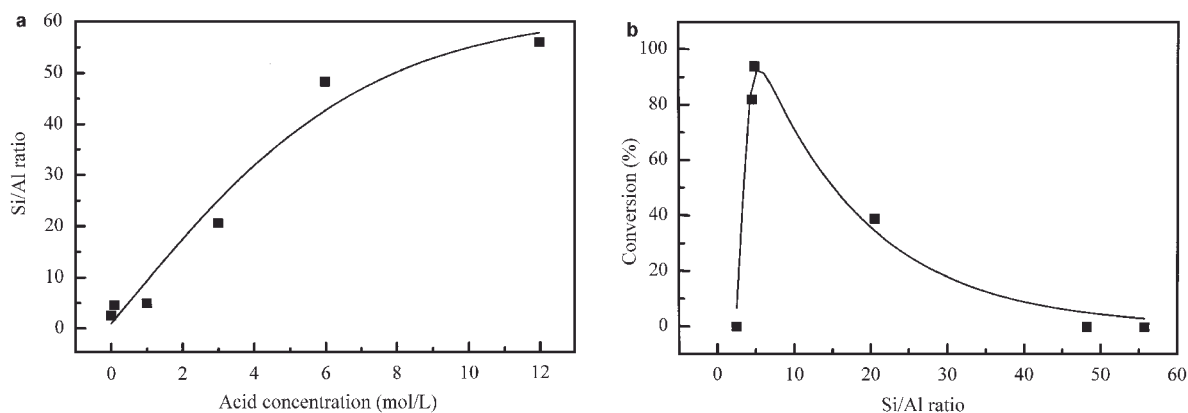


Figure 1. (a) Si/Al atomic ratio of Jordanian bentonite as a function of H₂SO₄ concentration in the acid pretreatment. (b) Relationship between the catalytic activity of Jordanian bentonite (expressed by conversion % after 10 min) and Si/Al atomic ratio.

above conditions as a result of the consecutive butylation of phenol and 2-tert-butylphenol, respectively, thus complicating a detailed kinetic study. The mechanism (involving a carbonium ion intermediate) and products obtained in this reaction are in agreement with our previous reports concerning the conversion of 2-tert-butylphenol over Jordanian bentonite and some other clays (Saleh and Mahmoud, 1998; Mahmoud and Saleh, 1999). Nevertheless, the debutylation of 2-tert-butylphenol was found to follow simple first-order kinetics as obtained from a plot of \ln concentration vs. time, with a correlation coefficient better than 0.996 (e.g. for the debutylation over Jordanian bentonite pretreated with 0.1 M H_2SO_4). The experimentally determined rate constant of debutylation is shown in Figure 2 as a function of the amount of acidic centers of the four bentonite samples. While no correlation between the rate constant and the total number of acidic centers (i.e. those with $H_o < 4.8$) could be observed, on the other hand a strong one was obtained for the strong acidic sites (e.g. $H_o < 1.2$; $H_o < 2.9$) indicating that weak acidic centers do not catalyze the debutylation of 2-tert-butylphenol at 76°C effectively.

In principle, the apparent rate constant (k) can be divided into several contributions according to the following equation:

$$k = k_0 + k_1[\text{H}^+]_1 + k_2[\text{H}^+]_2 + k_3[\text{H}^+]_3 + k_4[\text{H}^+]_4 \quad (3)$$

where k_0 is the rate constant of the uncatalyzed reaction, k_1 , k_2 , k_3 and k_4 are the catalytic constants of the acidic sites with acidic strengths $H_o < 1.2$, $1.2 < H_o < 2.9$, $2.9 < H_o < 3.6$ and $3.6 < H_o < 4.8$, respectively, and $[\text{H}^+]_1$, $[\text{H}^+]_2$, $[\text{H}^+]_3$ and $[\text{H}^+]_4$ are the corresponding numbers of these sites, respectively. k_0 is very small at 76°C and can be ignored, thus $k_0 = 0$; k_4 is also equal to zero, since no correlation between the apparent rate constant and weak acidic centers with $3.6 < H_o < 4.8$ was observed as explained in Figure 2. Solving the reduced form of

equation 3 for k_1 , k_2 and k_3 gives values of 0.408, 0.205 and 0.0024 g/(min mmol), respectively. The latter ($k_3 \approx 0$) explains why the dependence of k on the amount of acidic sites with $H_o < 3.6$ is almost the same as that for the acidic sites with $H_o < 2.9$, but shifted to larger numbers of acidic sites (Figure 2). Clearly, acidic centers with $2.9 < H_o < 3.6$ are almost inactive in the debutylation process. The different values of k_1 and k_2 ($k_1 > k_2$) explain the different slopes observed in Figure 2 for acidic sites with $H_o < 1.2$ and $H_o < 2.9$ indicating that the stronger the acidic site the more efficient it is in the debutylation process.

These kinetic results of the debutylation in CCl_4 at 76°C were found to be applicable to the debutylation of the neat 2-tert-butylphenol over Jordanian bentonite at 125°C. Figure 3 shows $\ln(1-x)$ vs. the amounts of acidic centers, where (x) is the conversion of 2-tert-butylphenol after 10 min, which is used in this work as a measure of the catalytic activity. Since the time, t , is constant for all points shown in Figure 3, $\ln(1-x)$ is proportional to $(-k)$. We therefore obtain the same dependence as in Figure 2, supporting the conclusion that even at 125°C only acidic sites with $H_o < 2.9$ are effective in the debutylation reaction.

CONCLUSIONS

Acid-treated bentonite samples possess more acidic sites than the untreated ones. The maximum number of acid sites ($H_o < 4.8$) was obtained when Jordanian bentonite was treated with 0.1 M H_2SO_4 , H_3PO_4 or HCl , while a maximum concentration of strong acidic sites ($H_o < 3.6$; $H_o < 2.9$) was obtained when the clay samples were treated with 1.0 M H_2SO_4 , 1.0 M H_3PO_4 , or 0.1 M HCl . Higher acid concentrations were found to induce strong dealumination causing the surface acidity to decrease. For H_2SO_4 and H_3PO_4 , high acid concentrations also caused a significant decrease in the BET surface area, whereas no similar effect was observed for

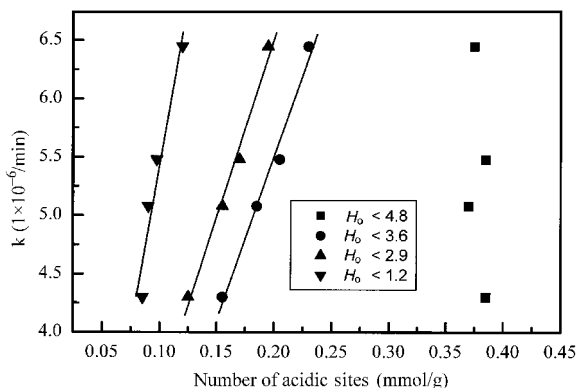


Figure 2. Debutylation of a 2.0 M solution of 2-tert-butylphenol in CCl_4 over Jordanian bentonite at 76°C showing the dependence of the apparent debutylation rate constant on the number of acidic sites with different acidic strengths. (Data for bentonite samples calcined at 250°C after pretreatment with 1.0 M H_2SO_4 , 0.1 M H_2SO_4 , 1 M HCl and 0.1 M HCl .)

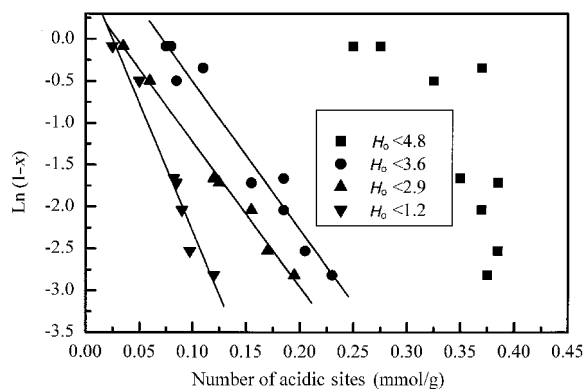


Figure 3. Debutylation of neat 2-tert-butylphenol over Jordanian bentonite at 125°C. Correlation between catalytic activity and the number of acidic sites with different acidic strengths. x is the conversion after 10 min.

HCl. Maximum acidity was also obtained upon calcination at 250°C. Higher calcination temperatures lead to a decrease in both surface acidity and surface area.

De-tert-butylation of 2-tert-butylphenol was chosen in this work to test the catalytic activity of Jordanian bentonite. A correlation between catalytic activity and surface acidity could be established. It was found that weak acid sites ($H_o > 2.9$) do not catalyze the debutylation reaction effectively. Only strong acid sites with ($H_o < 2.9$) are able to produce appreciable enhancement of the debutylation rate.

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