

Solid acid catalysts from clays: Acid leached metakaolin as isopropanol dehydration and 1-butene isomerization catalyst

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Received 17 September 1996; accepted 13 November 1996

Abstract

Some samples of acid leached kaolin were prepared by calcination of the natural clay at 873 K to obtain metakaolin followed by treatment at 353 K for 4 h with HCl or H₂SO₄ solutions of various concentrations. Some samples were washed with distilled water after the treatment. The modified clays were studied by chemical analysis, differential thermal analysis (DTA), and X-ray diffraction. The nature and strength of the acid sites was evaluated by FT-IR spectroscopy of adsorbed pyridine. All samples were tested as catalyst for the 1-butene isomerization and isopropanol dehydration. The sulfuric acid treated and washed MKH₂SO₄ 1 Mw sample resulted in a very active isopropanol dehydration catalyst. The MKH₂SO₄ 1 Mw sample and the two unwashed HCl treated samples MKHCl 2 M and MKHCl 6 M were found very active in the conversion of 1-butene to *iso*-products, which requires strong Brønsted acid sites. The well known K10 catalyst is less active in both reactions and the MKH₂SO₄ 1 Mw catalyst could be proposed as its suitable substitute.

Keywords: Kaolin; Metakaolin; Clays; Isopropyl alcohol; Dehydration; 1-butene; Acidity

1. Introduction

Solid acids find a wide range of catalytic applications in oil and chemical conversion processes [1,2]. In the last years there has been a renewed interest in the use of clay aluminosilicates, because the structure and dimension of their pores appeared more suitable, compared to zeolites, for the conversion of larger molecules [3].

The use of aluminosilicates in heterogeneous catalysis is almost as old as the catalytic concept itself. Among the earliest cracking catalysts were acid activated bentonites and kaolinite

clays [2,4,5]. The process by which bentonites are acid activated is known to involve the treatment of the uncalcined clay with sulfuric acid at 366 K for several hours. The treatment leads to aluminum leaching (and to a lesser extent silicon leaching) from the TOT layers. Increased surface areas and concentration of weak acid sites, together with a decrease in concentration of strong acid sites are the results. Calcination of kaolin at 823 K is known to lead to the formation of metakaolin by dehydroxylation of the crystalline clay [6,7]. Acid leaching of metakaolin gives a catalyst with activity comparable to that of acid activated montmorillonite at about one-half the fresh surface area [8]. The preparation of catalytic materials by acid-treat-

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ment of calcined kaolins in a wide range of conditions was described by Lussier [9]. A study on acid leached kaolins as Friedel–Crafts catalysts was published recently [10]. In this paper we discuss the preparation, the characterization and the use of acid leached metakaolin as isopropanol dehydration and 1-butene isomerization catalyst.

2. Experimental

2.1. Materials

The starting clay used in this study, Caolino G1-91, was a natural kaolin obtained from C. Laviosa (Leghorn, Italy). It is a well-crystallized kaolinite and it was used without further purification. The calculated unit-cell formula is: $(\text{Si}_{3.968} \text{Al}_{0.032})(\text{Al}_{3.930} \text{Fe}_{0.070})\text{O}_{10}(\text{OH})_8$. The montmorillonite K10 catalyst was supplied by Fluka. The chemical composition is reported in Table 1.

2.2. Preparation of catalysts

2.2.1. Preparation of metakaolin by calcination of kaolin clays

One hundred grams of kaolin (Caolino G1-91) were calcined for 18 h at 873 K in a ventilated oven.

2.2.2. Acid treatments of metakaolin

The metakaolin samples were suspended in the appropriate amount of HCl 2 M, HCl 6 M (samples MKHCl 2 M and MKHCl 6 M) or H_2SO_4 1 M, H_2SO_4 3 M, respectively (samples MKH_2SO_4 1 M, MKH_2SO_4 3 M). The suspensions were stirred at 353 K for 4 h and filtered. Some of the leached samples were washed free of chloride and sulfate anions (MKHCl 2 Mw and MKHCl 6 Mw, MKH_2SO_4 1 Mw, MKH_2SO_4 3 Mw). The resulting materials were air dried at 353 K and finely ground (> 40 mesh). All the clay samples were stored under vacuum in sealed glass vials.

2.3. Characterization methods

2.3.1. FT-IR measurements

IR spectral measurements were carried out in an evacuable Pyrex cell with CaF_2 windows. Pyridine adsorption experiments were performed as described by Occelli [11]. The clay samples were ground to a fine powder, pressed into self-supporting wafers and mounted in the holder of the IR cell, and degassed by heating at 673 K and 1.33 Pa. After cooling the wafers at room temperature, pyridine was adsorbed in the samples. The IR spectra were recorded, after degassing the wafers at 423 K and 1.33 Pa for 2 h [11], on a FT-IR Nicolet Magna-IR™ 750 spectrometer in the 1700–1400 cm^{-1} region.

2.3.2. Nitrogen adsorption / desorption

Adsorption/desorption experiments using N_2 were carried out at 77 K on a Carlo Erba Sorptomatic 1900. Prior to each measurement the samples were outgassed at 423 K and $1.33 \cdot 10^{-3}$ Pa for 6 h. Surface areas were obtained using the full BET equation.

2.3.3. X-Ray diffraction

X-Ray diffraction spectra were measured with a PW 1310 Philips diffractometer using the $\text{Cu K}\alpha$ radiation. The samples were pressed powders.

2.3.4. DTA differential thermal analysis

Differential thermal analysis experiments (DTA) were carried out on a Netzsh thermal analyzer heating the pretreated at 383 K samples at a scan rate of 10 K/min.

2.4. Catalytic measurements

2.4.1. Catalytic 1-butene isomerization

Catalytic 1-butene isomerization tests were performed in a tubular glass flow microreactor. Catalyst samples (250 mg) were pretreated for 2 h in an N_2 flow at 673 K. The experiments were performed at $\tau = 2.4 \text{ g}_{(\text{cat})} \text{ g}_{(1\text{-butene})}^{-1} \text{ h}$. The 1-butene was 5% in nitrogen and the time on

stream was 120 min. All the catalysts were tested for a total of 240 min of time on stream.

2.4.2. Catalytic dehydration of 2-propanol

Dehydration of 2-propanol was carried out in a tubular stainless-steel flow reactor interfaced to a gas chromatograph (HP 5890) equipped with a flame ionization detector (FID). Catalyst was pretreated for 2 h in an N₂ flow at 673 K. 2-propanol was vaporized into the carrier gas stream (He) using a thermostated saturator.

Typical experiment conditions: 300 mg of clay, total flow of reactants (N₂ and 2-propanol in helium) = 32.0 ml/min, alcohol concentration = 12000 ppm, $\tau = 5.35 \text{ g}_{(\text{cat})} \text{ g}_{(2\text{-propanol})}^{-1} \text{ h}$ and total pressure = 101.3 kPa. The reaction was monitored by GC with a 25 m wide bore CP Poraplot Q column working at 418 K.

3. Results and discussion

3.1. Surface areas and porosity

Kaolinitic clays undergo, by thermal treatment beyond 823 K, a partial collapse of the structure because of the octahedral layer dehydration. It was also demonstrated by ²⁷Al MAS NMR that the coordination number of the aluminum shifts from 6-fold to 5-fold and finally to 4-fold as the octahedral layer dehydroxylation proceeds [6,7]. The disordered structure of

metakaolin (Al₂Si₂O₇), stable in the 823–1223 K temperature range, is more readily attacked by mineral acids and higher surface areas and suitable pore geometries for catalysis are obtained.

Surface areas and chemical analysis of the acid treated metakaolin samples are reported in Table 1.

It can be easily noticed that the chemical and physical modifications of the surface induced by the acid treatment are strongly dependent on the nature of the acid and on the treatment length. In agreement with what was found by Lussier [9], hydrochloric acid, the anion of which does not complex the aluminum cation, caused a relatively fast aluminum release and surface area increase. Successive washings with distilled water appeared to induce only slight modifications of the surface areas.

On the other hand, the metakaolin samples treated with sulfuric acid, the anion of which is able to complex aluminum cations, showed a remarkable increase in surface areas and a modification of the chemical composition only after washing with distilled water. A mechanism of polymerization and readsorption was suggested to explain this behavior [9].

Differential thermal analysis (DTA) measurements provided further evidence of the presence of aluminum sulfate on the unwashed samples surfaces.

The DTA profiles of the MK H₂SO₄ 1 M

Table 1

Surface areas and chemical analysis of the metakaolin and acid leached metakaolin samples

	S.A. (m ² /g)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	Na ₂ O (%)	K ₂ O (%)	SiO ₂ /Al ₂ O ₃ (n/n)
MK	17	53.24	45.15	1.33	0.06	0.22	2.02
MKH ₂ SO ₄ 1 M	75	69.59	29.04	0.93	0.07	0.36	4.14
MKH ₂ SO ₄ 1 Mw	164	72.80	26.22	0.81	0.06	0.10	4.65
MKH ₂ SO ₄ 3 M	18	80.17	18.88	0.59	0.18	0.17	7.19
MKH ₂ SO ₄ 3 Mw	250	91.91	7.40	0.43	0.10	0.16	21.86
MKHCl 2 M	178	81.54	17.42	0.71	0.13	0.20	8.00
MKHCl 2 Mw	185	90.10	8.81	0.86	0.01	0.22	16.67
MKHCl 6 M	305	85.65	13.37	0.70	0.08	0.20	11.00
MKHCl 6 Mw	318	87.55	11.76	0.44	0.09	0.15	12.70

Samples were calcined at 1173 K prior to chemical analysis.

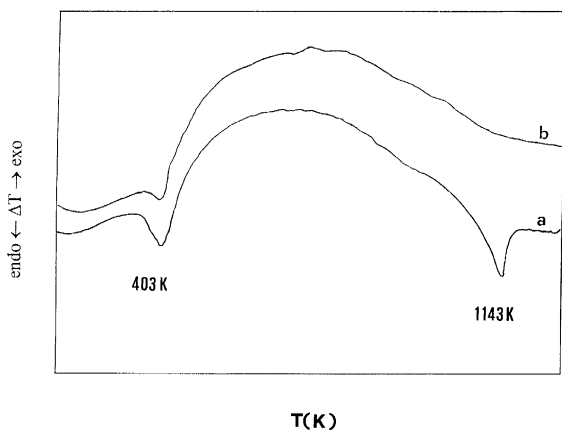


Fig. 1. Differential thermal analysis (DTA) curves of acid leached MK_2SO_4 (a) and $\text{MK}_2\text{SO}_4\text{w}$ (b) samples.

and $\text{MK H}_2\text{SO}_4$ 1 Mw are reported in Fig. 1.

The strong endothermic adsorption at 1143 K observable in the MKH_2SO_4 1 M thermal profile is in fact attributable to aluminum sulfate desulfuration and corresponds to 7% of the total weight loss [12].

The N_2 adsorption/desorption isotherms of some representative samples are reported in Fig. 2. The curve profiles appear typical of largely microporous materials, unlike what was reported by Lussier, who described his acid leached kaolin samples as mostly mesoporous materials [9].

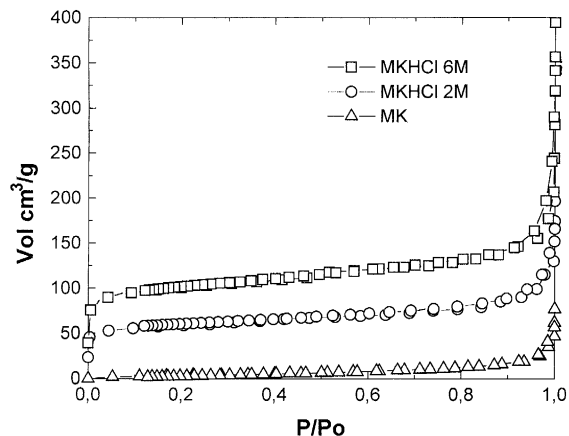


Fig. 2. N_2 Adsorption/desorption isotherms of metakaolin and some acid leached samples.

3.2. FT-IR measurements

Brønsted and Lewis acidity was evaluated from the IR spectra of the adsorbed pyridine [11,13,14].

Fig. 3 shows the infrared spectra in the region $1700\text{--}1400\text{ cm}^{-1}$ of the two representative H_2SO_4 1 M treated metakaolin samples MKH_2SO_4 1 M and MKH_2SO_4 1 Mw, following exposure to pyridine vapor and subsequent thermal treatment at 423 K under vacuum.

Both samples exhibit the typical bands that can be assigned to Lewis site-bonded pyridine

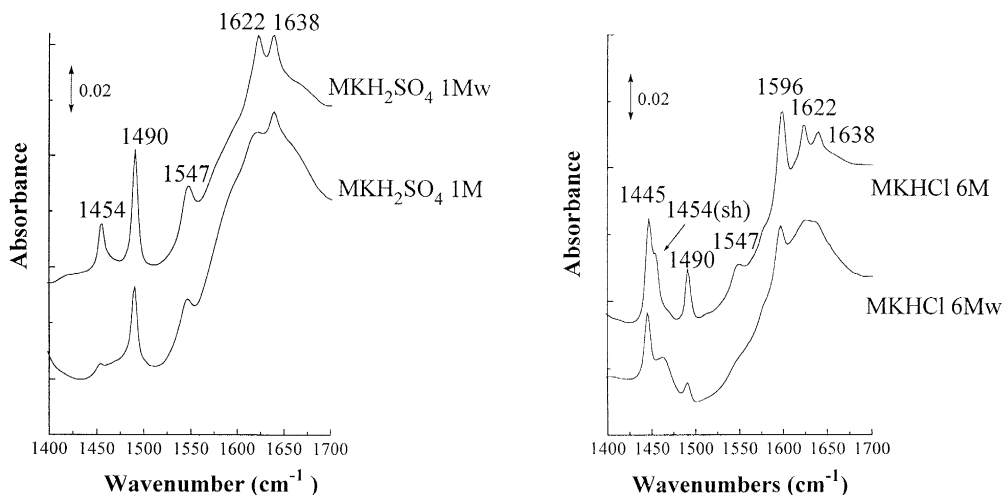


Fig. 3. Infrared spectrum of pyridine adsorbed on some acid leached metakaolin samples.

(1454 and 1622 cm^{-1}), Brønsted site-bounded pyridine (1547 and 1638 cm^{-1}), a band at 1490 cm^{-1} attributable to the pyridine molecule associated with both Brønsted and Lewis acid sites, and a shoulder at 1597 cm^{-1} related to weakly hydrogen bonded to the surface pyridine molecules. The bands related to Lewis-sites-bounded pyridine are much more pronounced on the MKH_2SO_4 1 Mw sample and consequently it can be deduced that while the washed sample has both Brønsted and Lewis acid sites, the unwashed sample ($\text{MK H}_2\text{SO}_4$ 1 M) appears to have mainly Brønsted acid sites.

On the other hand, the HCl 2 M sample surface appeared to be not modified by washings and the HCl 2 M and HCl 2 Mw spectra were found almost identical. On the contrary, treatment of the clay with 6 M HCl or 3 M H_2SO_4 followed by washing appeared to cause the complete disappearance of almost all strong acid sites from the surface.

3.3. Catalytic activity

3.3.1. 1-butene isomerization

The product distribution of the catalytic 1-butene isomerization is widely used to evaluate the acidity of heterogeneous catalysts [15,16].

The product distribution for 1-butene conversion is summarized in Table 2.

The reaction products can be divided into the following groups: (a) double bond isomerization products (*cis*-2-butene and *trans*-2-butene); (b) skeletal isomerization products (isobutene); (c)

hydrogenated products (*n*-butane and isobutane); (d) cracking products (C4-) (methane, ethane, ethylene, propane and propene); (e) surface carbon residue; (f) butadiene and higher molecular weight compounds.

It was reported that the formation of isobutene (skeletal isomerization) needs stronger Brønsted acid sites ($H_R < -6.63$) than those required by the geometric isomerization and the double bond migration ($0.82 > H_R > -4.04$) [16,17]. The reaction is thought to occur on Brønsted acid sites via carbenium ion intermediates by a three-step mechanism: protonation of the reactant, rearrangement of the carbenium ion formed, desorption of the products, with the rearrangement being the reaction rate limiting step. The hydrogenated C₄ compounds *n*-butane and isobutane were found among the other products. These compounds are usually generated by butene cracking and their presence can be explained by a cracking reaction of butene oligomeric carbenium ions or, alternatively, by a direct hydrogenation of the butene isomers through hydride transfer on the corresponding monomeric carbenium ions.

In order to have an idea of the skeletal isomerization activity of the catalysts, the amount of isobutene produced should be added to that of isobutane, assuming that the last originates from isobutene.

As shown in Table 2, the MKH_2SO_4 1 Mw sample was the most active catalyst for the 1-butene conversion and one of the more active in the skeletal isomerization, which requires

Table 2

Product distribution in 1-butene conversion at 400°C on the metakaolin acid leached samples (montmorillonite K10 was taken as a reference sample)

	Isobutane	<i>n</i> -butane	<i>Trans</i> -2 butene	1-butene	<i>Iso</i> -butene	<i>Cis</i> -2-butene	C4-
MK	0.00	0.00	30.38	44.62	0.61	24.15	0.00
MK H_2SO_4 1 M	0.17	0.16	39.55	17.96	8.91	29.93	1.88
MK H_2SO_4 1 Mw	1.76	1.35	37.66	9.96	16.16	26.94	4.03
MK H_2SO_4 3 M	0.04	0.23	40.10	25.56	2.68	30.38	0.15
MK H_2SO_4 3 Mw	0.00	0.00	38.20	30.62	0.56	30.16	0.03
MK HCl 2 M	0.87	0.64	32.13	15.87	21.54	24.60	0.99
MK HCl 6 M	0.47	0.13	32.81	16.03	24.26	25.29	0.50
Montmorillonite K10	0.00	0.11	42.00	22.00	4.04	31.59	0.00

stronger Brønsted acid sites. Moreover, 1 M H_2SO_4 acid leached samples produced more cracking (C4-) products (methane, ethane, ethylene, propane and propene). The 3 M H_2SO_4 acid leached samples showed a general decrease both of 1-butene conversion and isobutene formation activity. Only a negligible quantity of cracking products was detected on these samples. Leaching with HCl produced catalysts with a good 1-butene conversion activity that is independent from the acid concentration in the skeletal isomerization.

The *iso*-products production, that is related to the presence of strong acid sites, was observed to increase in the order MKH_2SO_4 1 Mw < MKHCl 2 M < MKHCl 6 M and dramatically dropped when the MKHCl 6 M sample was washed, confirming what was found by FT-IR of adsorbed pyridine. The complete disappearance of IR bands correlated to strong acid sites was in fact observed for the MKHCl 6 Mw washed sample while the surface area remained almost unaltered.

3.3.2. Dehydration of 2-propanol

Isopropanol easily undergoes dehydration in the presence of acidic catalysts [18]. The reaction occurs through a carbenium ion structurally similar to that formed during the isomerization of alkenes. The reaction, which does not need strong acid sites, can give ethers and olefins as products. The alkenes are presumably produced by simple proton catalyzed dehydration while the ethers formation must involve an intermolecular coupling reaction. The conversion of isopropanol is widely used as a test reaction to characterize acid–base or redox properties of catalysts [19–21]. The acid sites are known to lead essentially to the dehydration product, propene. A study of the isopropanol dehydration was undertaken on some selected acid treated metakaolin samples.

Activity data of the different catalysts in the isopropanol dehydration at 393 K are listed in Table 3.

All the acid treated samples showed some

Table 3

Surface areas, % conversion and normalized activity for the 2-propanol dehydration at 393 K over metakaolin (MK) and acid leached metakaolin samples (montmorillonite K10 was taken as a reference)

	S.A. ^a (m ² /g)	Conversion ^b (%)	Activity ^c ($\mu\text{mol}/\text{h}\cdot\text{m}^2$)
MK	17	0.0	0.0
MKH_2SO_4 1 Mw	164	99.4	18.85
MKH_2SO_4 3 Mw	250	55.8	6.94
MKHCl 2 M	178	32.8	5.73
MKHCl 2 Mw	185	26.1	4.37
MKHCl 6 M	305	69.8	7.12
MKHCl 6 Mw	318	40.8	3.99
Montmorillonite K10	260	65.5	7.54

^a S.A. = surface area.

^b Conversion % in moles.

^c Normalized activity in μmoles of 2-propanol converted per hour and per square meter.

catalytic activity while untreated metakaolin was totally inactive in the title reaction. The conversion and activity data appear to fit in the picture outlined by the preceding experiments. Washing appeared not to modify, modification being at most marginal, the surface areas values of the HCl treated samples, while an activity decrease, more dramatic for the more severely treated MKHCl 6 M sample, was observed, probably attributable to the modification of the surface Si/Al ratio. The highest conversion and activity values were found for the MKH_2SO_4 1 Mw sample, while the more severe treatment with 3 M H_2SO_4 caused almost the doubling of the surface area but a strong decrease of both conversion and activity.

4. Conclusions

Our data confirmed that leaching with mineral acids improves the catalytic activity of natural kaolin, increasing the surface area and the number of acid sites. The structurally disordered metakaolin phase resulted to be more readily attacked by acids than the crystalline mineral. Acid treatment of metakaolin was found to lead in our case to microporous materials

while the materials obtained by Lussier were mainly mesoporous [9]. The hydrochloric acid surface erosion mechanism must be very different from that of sulfuric acid. Treatment of metakaolin with hydrochloric acid caused a remarkable surface area increase and successive washings modified these values only slightly. On the contrary, washings with distilled water were found necessary to obtain an increase of the surface area by removal of the redeposited aluminum, when the metakaolin was treated with sulfuric acid. Catalytic activity must be strictly related to the chemical composition of the surface.

The excellent catalytic properties of the MKH_2SO_4 1 Mw sample shown on both the studied reactions are probably related to the high density of strong acid sites, generated on the catalyst surface by the mild acid treatment and the subsequent elution with water of the readsorbed aluminum sulphate. More severe acid treatments followed by washing to remove readsorbed aluminum species invariably led to less active species with larger surface areas but with a reduced number of acid sites.

The MKH_2SO_4 1 Mw catalyst appeared more reactive than the well known and widely used montmorillonite K10 based catalyst and could therefore be proposed as alternative to this reagent when an acceptable reproducibility of its preparation would be proved.

Acknowledgements

The financial support of M.U.R.S.T. (ex quota 40%) and of CNR (Progetto Strategico Tecnologia Chimiche Innovative. Sottoprogetto F) is acknowledged. The authors thank A. Talon for

the analytical determinations and T. Finotto for the XRD spectra.

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