International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:12, No:1, 2018

Basicity of Jordanian Natural Clays Studied by Pyrrole-tpd and Catalytic Conversion of Methylbutynol

M. Z. Alsawalha

***Abstract*—**The main objective of this study is to investigate basic properties of different natural clays, by two methods. The first method is a gas phase conversion of methylbutynol (MBOH). The second method is the application of Pyrrole-tpd. Based on the product distribution from the first method, the acidic, basic and coordinately unsaturated sites were differentiated. It was shown that both the conversion and the selectivity for basic products did not change with reaction time. Nevertheless, a deviation from the stoichiometric ratio *R* of formed acetylene to acetone was observed (R=0.8…0.97). The conversion normalized to the surface area was used for establishing the activity sequence: White kaolinite > red kaolinite > bentonite > zeolite > diatomite. In addition, the results were compared with synthetic amorphous alumosilicates and typical basic materials like MgO and ZnO. The basic properties were characterized using the Pyrrole-tpd. The Pyrrole-tpd results showed the same basicity sequence as the MBOH gas phase reaction.

***Keywords*—**Alumosilicates, basic surface properties, natural clays, normalized conversions with acetylene and acetone, pyrrole-TPD adsorption

I. Introduction

CLAYS consist mainly of silica, alumina and water, frequently with small quantities of iron, alkalis and earth alkali ions. It is important to know more about their physical and chemical features because they contribute an important function in widely environmental and industrial applications [1]-[5]. One class of clay minerals is known as montmorillonite group. These types of clay are most desirable because they show faster reactions and have a higher degree of basic reactivity [6]. Some studies were performed for modifying clays for organic reaction purposes [7]-[9]. Obviously, both physical and chemical properties of the clay minerals are very important to give proper judgment on their utilization in different industrial applications [10]. One of these methods is the conversion of 2-methyl-3-butyn-2-ol (MBOH) as presented in Fig. 1 [11]-[13]. Based on the MBOH reaction model, samples are transformed into different products as shown in Fig. 1. The MBOH conversion happens in different pathways depending on the existing active sites of the sample. For example, 3-methyl-3-buten-1-yne (MBYNE) product is obtained through isomerization of alcohol MBOH when the sample has an acidic reactivity, while acetone and acetylene products are obtained from the MBOH decomposition when sample has a basic reactivity. Finally, coordinately unsaturated sites are represented by two products, 3-methyl-3-butyn-2-on (MIPK) and 3-hydroxy-3-methyl-2-butanone. The gas phase reaction proved its capacity to identify different properties of solids: basic and acidic sites [14]-[20]. Fig. 1 presents the path of MBOH conversion. In addition, other methods like temperature-programmed desorption of carbon dioxide was utilized to measure the total density and the strength of the basic sites on the solid surface.

M. Alsawalha is with the Department of Chemical & Process Engineering Technology, Jubail Industrial College, Jubail Industrial City, PO Box 10099, 31961, KSA (phone: + 966 13 342 5427; fax: + 966 13 340 9903; e-mail: murad_s@jic.edu.sa).

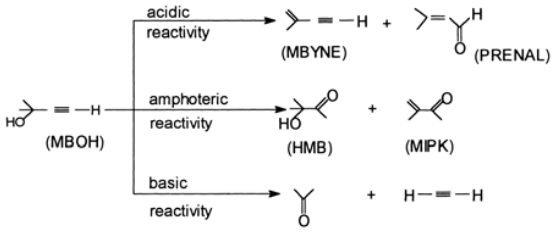

Fig. 1 Possible three pathways reactivity of MBOH [20], [21]

The basic properties of potassium oxide supported on Zeolite Y were studied using both the MBOH gas phase reaction and the pyrrole-tpd methods [20]. Moreover, after a thorough literature review on the subject [11]-[15], it was observed that investigations of natural Jordanian clays were characterized by MBOH gas phase reaction but not by the pyrrole-tpd method. This article will focus on the use of MBOH in the classification of the basic characteristics of natural Jordanian clays. In this paper, some commercial samples with different SiO_2/Al_2O_3 ratios and typical basic materials like MgO and ZnO were studied using the MBOH gas phase reaction at 180 ºC. Moreover, the pyrrole-tpd technique is applied to enhance the information and database about the basic strength sequence of the investigated samples. Consequently, in this paper, studies of certain clays; namely bentonite, white kaolinite, red kaolinite, zeolite and diatomite were conducted using both the MBOH gas phase reaction and the pyrrole-tpd method.

II. Experimental

A. Materials

Natural Jordanian clays such as bentonite, white kaolinite, red kaolinite, zeolite and diatomite were provided by the Resource Authority of Jordan. The phase and the chemical

compositions of these clays were reported in the literatures [21]-[24]. Other materials like manganese and zinc oxides with a purity of 99.0% were obtained from Sigma Aldrich.

B. Characterization Methods

MBOH was performed at different temperatures: 120 °C and 180 °C. Correlations of MBOH conversions with the ratio of acetylene to acetone were studied using 0.2 g of each sample. Previous activations of the sample were conducted under nitrogen stream for three hours.

Pyrrole-tpd Adsorption

The weight of each studied natural samples is 0.2 g with a particle size of 200-300 µm. The experiments started by heating the samples from 25ºC to 600ºC in one-hour duration at a heating rate of 10 $K \cdot min^{-1}$. Helium was used as a carrier gas.

III. Results and Discussions

A. Gas Phase Reaction

The higher conversion of the MBOH was found to be over natural zeolite with 58% while the lowest conversion was on white kaolinite 18%, after 120 min. time on-stream (t.o.s). It was also noticed that the conversion was not changed over reaction time for all natural samples. In contrast to samples with dominating acidic properties [25], no significant deactivation was observed. A slight increase of activity was observed for bentonite and red kaolinite. Swelling of these layered compounds can be possibly explained by penetration of polar molecules like water and/or acetone formed during the reaction, into the interlayer space. The catalytic activities of MBOH and acetylene conversions were calculated as acetylene, which indicate the basic character of the surface. Therefore, a specific conversion was calculated as the ratio of conversion to a specific area (Table I).

TABLE I
Correlation between Surface Areas and Catalytic Activities of MBOH (T=120 °C)

Sample	SiO_2/Al_2O_3	Surface area, m^2/g	Spec. conv.	Na+K*	Ca+Mg*
White kaolinite	1.3	24	0.89	1.9	0.4
Red kaolinite	1.9	32	0.86	3.1	1.5
Bentonite	2.8	50	0.78	2.5	5.6
Zeolite	3.3	82	0.50	4.6	15
Diatomite	6.3	23	0.31	7.2	1.5

Time on Stream; T.O.S. = 117 min., 0.5 g

From Table I, it can be observed that lower specific conversions were obtained for zeolites and diatomites which have higher alkali or alkaline-earth content. In addition, the significant content of iron ions also seems to influence the basic properties. Furthermore, the influence of other non-silicatic basic impurities in the different minerals cannot be excluded. The resulted specific conversion appeared as the following sequence: White kaolinite > red kaolinite> bentonite > zeolite > diatomite. Typical reaction products were both from the acidic (MBYNE and Prenal, see Fig. 1) and basic (acetone and acetylene) path of conversion of MBOH. Here, we will focus entirely on products formed on basic centers. Fig. 2 presents the selectivity of the basic sites to form acetylene on different natural clay samples. The selectivity shows a nearly constant behavior. White kaolinite has the highest selectivity while diatomite has only 15%.

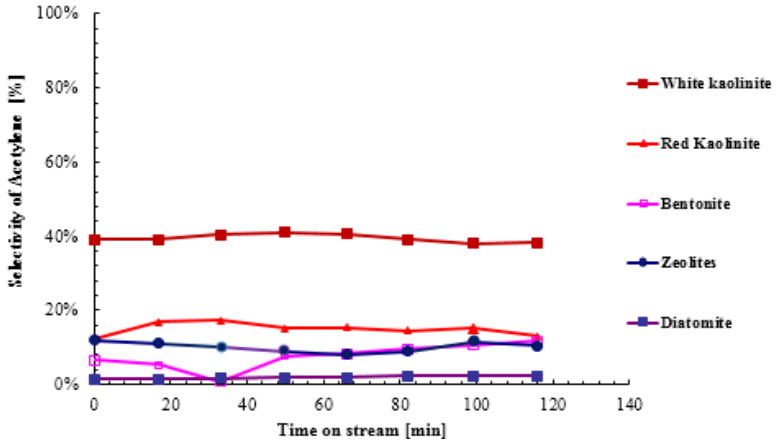

Fig. 2 Selectivity of basic site, acetylene formation on different natural clays at T=120 °C

According to the stoichiometry of the decomposition of MBOH the ratio (R) acetylene to acetone equals R=1. If R > 1, the lack of acetone could be explained by oligomerization by aldol condensation. If R < 1, a conversion of acetylene took place (polymerization). Table II presents the specific conversion values, and basic products of MBOH conversion at higher reaction temperature.

It is noteworthy that the color of the samples after the reaction was grey to black as indicated on coke deposition, but no change in the value of R was observed for natural clays. A decrease of the specific conversion and a dependence on the moduli were observed. Taking into account the basic products, the ratio of acetylene to acetone changes in the range from R = 0.8-0.97 (Table III). This could be explained in terms of

conversion of acetylene on acidic centers. Note that even for typical basic materials like MgO, R< 1. On the other hand, Table III demonstrates the ability of the conversion of MBOH to analyze basic properties of surfaces. Compared to other test reactions, i.e. conversion of i-propanol, it could be applied to broad range of materials. In contrast to the conversion of i-propanol, decomposition of MBOH does not depend on the presence of transition metal ions. So it was shown that the formation of acetone, claimed as evidence for basic sites, rather correlates with the redox than with basic properties.

TABLE II
CORRELATION BETWEEN SiO_2/Al_2O_3 AND BASIC PRODUCTS OF MBOH CONVERSION AT 180 °C

Sample	SiO_2/Al_2O_3	Surface area, m^2/g	Spec. conv.	Acetylene	Acetone
Syn.#5	0.05	115.8	0.56	1.94	3.0
Syn.#10	0.11	134.8	0.46	4.80	5.9
Syn.#20	0.24	183.2	0.43	41.4	42.5
Syn.#40	0.63	223.2	0.41	0.36	0.34

B. Pyroll-TPD Adsorption

Figs. 3-7 present the pyrrole tpd adsorption over various natural samples: White kaolinite, red kaolinite, bentonite, zeolite and diatomite, respectively. The highest pyrrole tpd adsorption was revealed over red Kaolinite while the lowest was over diatomite sample. The maximum pyrrole tpd adsorption was investigated at different temperatures, ranging from 90 to 200 °C. The literature described basics sites on other different samples utilizing pyrrole method [26], [27]. For natural Jordan clays, this technique illustrates a good agreement in terms of the basic strength sequence when it is compared with the conversion of MBOH gas phase reaction. It confirms again the quality of results.

TABLE III
CORRELATION OF MBOH CONVERSIONS (X) WITH THE BASICITY PRODUCT RATIO (ACETYLENE TO ACETONE) AT 180 °C

Samples	X	Ratio of Acetylene to Acetone (R)
Al_2O_3	77.4	0.97
ZnO	61.6	0.93
MgO	45.3	0.93
Syn.#5	26.1	0.80
Syn.#10	29.7	096
Syn.#20	91.6	0.93
Syn.#40	92.7	0.97
Bentonite	71.8	0.97
Red Kaolinite	64.6	0.93
White kaolinite	55.3	0.93
Diatomite	52.1	0.80

Time on Stream; T.O.S. = 117 min

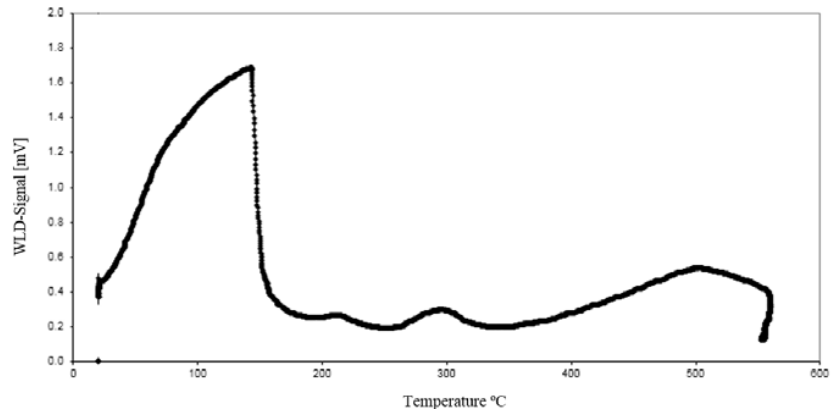

Fig. 3 Profile of pyrrole adsorption over White natural kaolinite

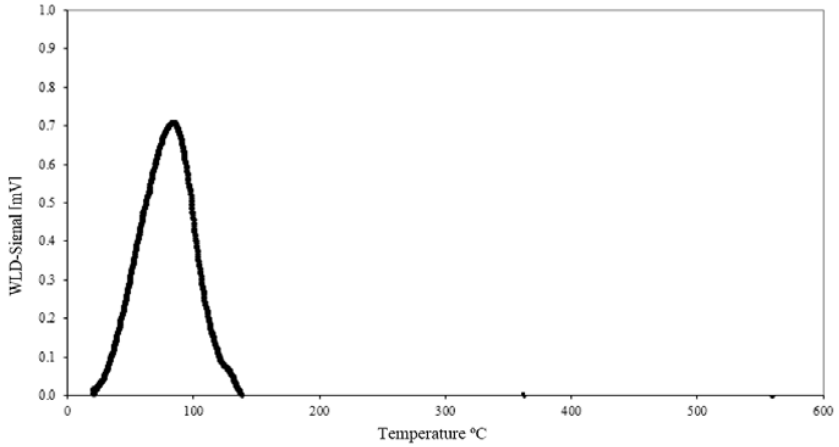

Fig. 4 Profile of pyrrole adsorption over Red natural kaolinite

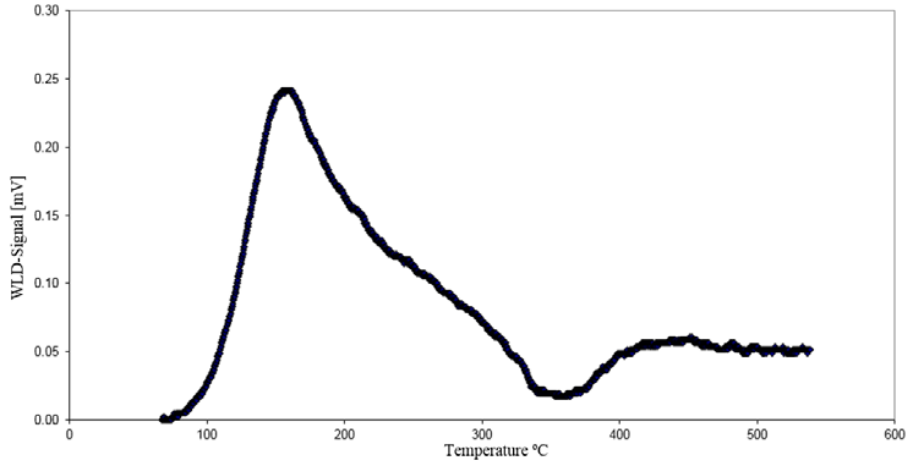

Fig. 5 Profile of pyrrole adsorption over natural Bentonite

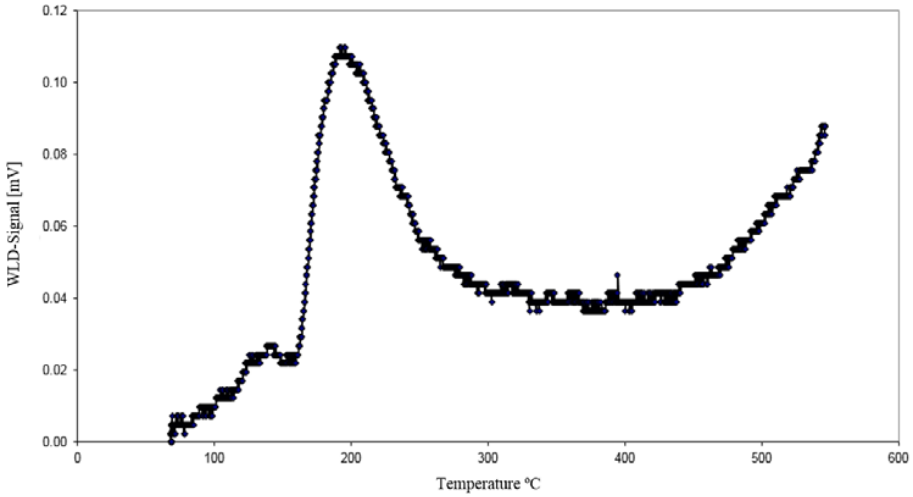

Fig. 6 Profile of pyrrole adsorption over natural Zeolite

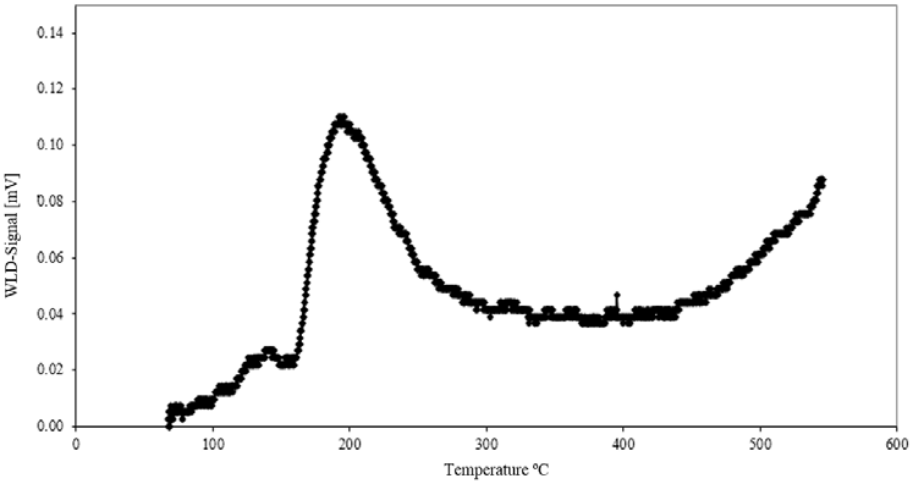

Fig. 7 Profile of pyrrole adsorption over natural Diatomite

IV. Conclusions

The conversion of MBOH was applied to study basic sites of different Jordanian clays. Analyzing the product distribution, the parallel presence both of acidic and basic sites was detected. The normalization of the conversion to the surface has shown the sequence: White kaolinite> red kaolinite> bentonite> zeolite >diatomite. Since the clays are layered materials, the intercalation would open the access to the internal surface. Consequently, the yield of basic products would be expected in the same order of magnitude as for materials with high surface area.

Focusing on the basic products, it was shown that for all studied materials the stoichiometric ratio of acetylene was lower than one, R=0.8-0.97 and is independent on the reaction time. Here, coke formation could not be excluded. Nevertheless, no deactivation regarding the formation of basic products was observed. Probably, the reaction of acetylene took place on residual acidic centers. If these centers have Brönsted or Lewis character could not be decided in frame of the entirely catalytic reaction. Moreover, the Pyrrole-typed method found same basic strengths sequence as obtained by the MBOH gas phase conversion.

Acknowledgments

Many thanks for Professor Frank Roessner at the University of Oldenburg (Germany), Industrial Chemistry. In addition, many thanks to Oldenburg research facilities. The author is also grateful to Industrial College, for the continuing support. Furthermore, M. Z. Alsawalha would like to express his sincere to Mr. Edwin Calicdan Obra, Mr. Mohammed Francis and to the Jordanian Resource Authority, for all given support.

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