

# Acidity of different Jordanian Clays characterized by TPD-NH<sub>3</sub> and MBOH Conversion

M. AlSawalha, F. Roessner, L. Novikova, L. Bel'chinskaya

**Abstract**—The acidity of different raw Jordanian clays containing zeolite, bentonite, red and white kaolinite and diatomite was characterized by means of temperature programmed desorption (TPD) of ammonia, conversion of 2-methyl-3-butyn-2-ol (MBOH), FTIR and BET-measurements. FTIR spectra proved presence of silanol and bridged hydroxyls on the clay surface. The number of acidic sites was calculated from experimental TPD-profiles. We observed the decrease of surface acidity correlates with the decrease of Si/Al ratio except for diatomite. On the TPD-plot for zeolite two maxima were registered due to different strength of surface acidic sites. Values of MBOH conversion, product yields and selectivity were calculated for the catalysis on Jordanian clays. We obtained that all clay samples are able to convert MBOH into a major product which is 3-methyl-3-buten-1-yne (MBYNE) catalyzed by acid surface sites with the selectivity close to 70%. There was found a correlation between MBOH conversion and acidity of clays determined by TPD-NH<sub>3</sub>, i.e. the higher the acidity the higher the conversion of MBOH. However, diatomite provided the lowest conversion of MBOH as result of poor polarization of silanol groups. Comparison of surface areas and conversions revealed the highest density of active sites for red kaolinite and the lowest for zeolite and diatomite.

**Keywords**—Acidity, Jordanian clay, Methylbutynol conversion, Temperature programmed desorption of ammonia

## I. INTRODUCTION

WIDE application of natural aluminosilicates and clays in the fields of catalysis, water treatment and desulfonation (petrochemistry) is caused by their surface active groups of different nature: acidic, basic and amphoteric, for example, protons, hydroxyls, SiOH, AlOH-groups, coordinately saturated and unsaturated cations. Characterization of acidic properties of inorganic solids is essentially for understanding of the behavior of catalysts in heterogeneously catalyzed reactions, as well as adsorption activity towards organic molecules in biochemical processes

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[1] and environmental application [2]. The acidity of aluminosilicates is characterized in terms of Brønsted and Lewis acid sites. Brønsted acid sites are formed by aluminum atoms connected to silicon by a so-called “bridging hydroxyl” Al-(OH)-Si where the negative charge generated is compensated for by a proton. Lewis acid sites are composed of aluminum with low coordination or  $\equiv\text{Si}^+$  ions formed from dehydroxylation in the thermal treatment at  $T > 773 \text{ K}$  [3]. Therefore, the acidity of an aluminosilicate is related to its silica and aluminum contents, and increases linearly with increasing silica to aluminum ratio in the sample.

Acidic and basic properties of porous materials such as zeolites, clays or mesoporous silica are usually determined by titration and spectroscopic techniques (FTIR, XPS, NMR) [4]-[6], together with temperature programmed desorption (TPD) of probe molecules such as NH<sub>3</sub> and CO<sub>2</sub> [7]-[9]. For the last decades catalytic test reactions have been intensively used as a tool for characterization of acid-basic properties of solids [10], [11] under real as practice-near as possible conditions. The first model reactions such as n-hexane conversion or but-1-ene isomerization were proposed to characterize acidity of solids to be used for petroleum chemistry [12]. Another powerful test reaction for clarification of structural questions like the conversion of 2-methyl-3-buten-2-ol (MBOH) was suggested and tested by [14]. According the acid-base properties of catalysts MBOH is converted to different products for each reaction pathway, namely 3-methyl-3-buten-1-yne (MBYNE) or 3-methyl-2-buten-1-al (Prenal) at acid sites and acetone together with acetylene at basic sites. Investigations on the MBOH conversion were performed on solids like zeolites [13], hydrotalcites [14], magnesium oxide catalysts [15], [16] and others.

The aim of this work was to determine the acidic properties of raw Jordanian clays containing zeolite, bentonite, kaolinite and diatomite and to find a correlation between TPD of NH<sub>3</sub> and catalytic test reaction of MBOH conversion.

## II. EXPERIMENTAL

### A. Materials

Five samples of Jordanian clays containing zeolite, bentonite, white kaolinite, red kaolinite and diatomite were collected from National Resource Authority, Jordan. Chemical

composition of these samples was determined by X-ray Fluorescence (XRF) method [17]-[19] and resulted in Table 1.

TABLE I  
CHEMICAL COMPOSITION OF JORDANIAN CLAYS CONTAINING ZEOLITE, BENTONITE, WHITE KAOLINITE, RED KAOLINITE AND DIATOMITE

Oxides (%wt.)	Zeolite (Tell Rmah) <sup>17</sup>	Bentonite (Al- Azraq) <sup>19</sup>	White Kaolinite <sup>19</sup>	Red Kaolinite (Batn el Ghoul) <sup>19</sup>	Diatomite (Al- Azraq) <sup>18</sup>
SiO <sub>2</sub>	42.0	55.7	48.0	47.6	72.0
Al <sub>2</sub> O <sub>3</sub>	12.8	20.1	36.3	24.9	11.4
Fe <sub>2</sub> O <sub>3</sub>	12.1	1.5	1.0	6.1	5.8
MgO	10.1	3.5	0.3	1.0	--
CaO	8.5	2.1	0.1	0.5	1.5
Na <sub>2</sub> O	4.0	0.1	0.1	0.8	7.2
K <sub>2</sub> O	0.8	2.4	1.8	2.3	--
TiO <sub>2</sub>	--	2.5	0.1	0.7	--

### B. Characterization methods

#### Temperature programmed desorption of ammonia (TPD-NH<sub>3</sub>)

Raw Jordanian clays samples were characterized by NH<sub>3</sub>-TPD with an apparatus constructed from Raczek analyze technical GmbH, Hannover. The apparatus consists of an adjustable oven to heat the sample, gas supplies for helium and a mixture of 5 vol.% NH<sub>3</sub> in argon (Messer-Griesheim) and a thermal conductivity detector (TCD) for gas analysis [15]. Prior to adsorption of ammonia 0.5 g of each samples was heated within a U-tube under He stream at a rate of 20 °C/min from room temperature up to 600 °C. Subsequently the sample was cooled down to 40 °C and saturated in flow of gas mixture containing 7 vol.% NH<sub>3</sub>/Ar for 30 min. The physically adsorbed ammonia was desorbed from the sample in a stream of He at 100 °C for 30 min. Desorption of the chemically adsorbed part of ammonia was realized by increasing temperature from 100 °C up to 500 °C at a rate of 20 °C/min.

#### Test catalytic reaction of MBOH conversion

The test reaction of MBOH conversion was carried out in a fixed-bed, automated bench unit [15]. Toluene was used as internal standard. Mixture of MBOH (95 vol.%) and toluene (5 vol.%) were cooled to 13 °C in a storage vessel. Applying a static nitrogen pressure of 202.65 kPa a constant flow of the mixture was forwarded through a capillary into the evaporator. A sample charge of 0.2 g with the fraction of 200–315 µm was placed in the centre of tubular reactor made from stainless steel. The catalyst activation procedure included oxidation step in the air flow at 550 °C for 1 hour and then in the flow of N<sub>2</sub> four 4 hours. Afterwards, catalyst sample was cooled down till the temperature of reaction 120 °C. The reaction products were analyzed on a Hewlett-Packard 5890 gas chromatograph equipped with a capillary column (Optima Wax, Macherey-Nagel). Correlation of the peak areas and response-factors of substances defined by gas chromatograph was experimentally determined in [15]. Conversion of MBOH ( $X_{MBOH}$  in mol.%), yield of products ( $Y_p$  in mol.%) and selectivities ( $S_p$ ) were calculated according to the following

equations:

$$X_{MBOH}(\%) = \frac{n_{MBOH,in} - n_{MBOH,out}}{n_{MBOH,in}} \cdot 100, \quad (1)$$

$$Y_p(\%) = \frac{A_p R_p / M_p}{\sum_k A_k R_k / M_k} \cdot 100, \quad (2)$$

$$S_p = \frac{Y_p}{X_{MBOH}}, \quad (3)$$

where  $n_{MBOH,in}$  and  $n_{MBOH,out}$  are the number of moles of MBOH at the input and outlet of reactor;  $A_p$ ,  $A_k$  and  $R_p$ ,  $R_k$  represent the peak areas and response factors of components  $p$  and  $k$ , respectively.  $M_p$ ,  $M_k$  are the corresponding molecular weights.

#### BET measurements

The surface area of samples was characterized by the BET method, performing adsorption of nitrogen at – 180 °C with the apparatus Quantachrome Autosorb-1. Data acquisition, reduction and calculating were performed by Quantachrome Autosorb software.

#### FTIR measurements

Analytical spectra were taken using a Shimadzu IR Prestige-21/FTIR-8400S spectrophotometer through the wave number range from 400 to 4000 cm<sup>-1</sup> using the KBr pellet technique. The spectra were collected using Shimadzu IR Prestige-21 Windows Software.

## III. RESULTS AND DISCUSSIONS

### A. FTIR-study of aluminosilicates

Experimental FTIR-spectra of the raw Jordanian clays can be characterized by three main adsorption regions, i.e. adsorption bands within the hydroxyl region 3400-3800 cm<sup>-1</sup>, OH-bending of physically adsorbed water at 1634 cm<sup>-1</sup> and low frequency range bands 400-1100 cm<sup>-1</sup> caused by structural aluminosilicate frameworks. Sharp bands at 3690 and 3614 cm<sup>-1</sup> are assigned to OH-vibrations of free Si-OH groups of diatomite and kaolinite [18], [20]. A band at 3620 cm<sup>-1</sup> on the zeolite spectra indicates on the acidic bridging hydroxyl Si-O(H)-Al. Wide bands at 3430 cm<sup>-1</sup> at all spectra correspond to OH-vibration of physically adsorbed water. A band at 1634 cm<sup>-1</sup> corresponds to deformation vibration of adsorbed water [21]. Vibration modes of siloxane (Si-O-Si) stretching are found to be around 1088 and 1026 cm<sup>-1</sup>. The bands of Si-O stretching are discerned for diatomite at 910 and 800 cm<sup>-1</sup>. For zeolite, bentonite and kaolinite the bands in the low frequency region are hard to discern, while for diatomite the

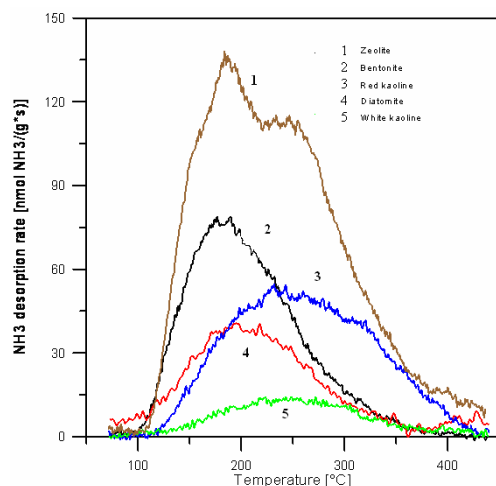


Fig.1 Profiles of temperature programmed desorption of ammonia for different Jordanian clay samples

peaks at  $466\text{ cm}^{-1}$  and  $524\text{ cm}^{-1}$  corresponded to a Si-O-Si and Al-O-Si deformation respectively [18], [20]. It worth mentioning that due to the analogical vibration frequencies of different surface hydroxyl groups and overlapping by the broad peak of the adsorbed water (with middle wave number at ca.  $3500\text{ cm}^{-1}$ ) it is difficult to distinguish the IR-spectra of aluminosilicates [22]. Relation between free and H-bonded hydroxyls and adsorbed water molecules is changed under different thermal treatment conditions and affect the number of acid sites on the aluminosilicate surface [23].

#### B. Temperature programmed desorption of $\text{NH}_3$

Experimental TPD- $\text{NH}_3$  profiles of raw Jordanian clays are shown in Fig. 1. It can be seen from fig. 1 that desorption of ammonia from the samples starts at  $100^\circ\text{C}$  and reaches its maximum at temperatures of about  $180^\circ\text{C}$  for zeolite and bentonite and about  $250^\circ\text{C}$  for white and red kaolinite. The maximum of  $\text{NH}_3$  desorption rate from zeolite surface is the highest and decreases from bentonite to white kaolinite in a row *zeolite > bentonite > red kaolinite > diatomite > white kaolinite*. The amount of acid sites on the clay surface were estimated by integration of the  $\text{NH}_3$  desorption peaks and resulted in Table 2. It follows from table 2 that order of the clays acidity shows good correlation to the amount of silica/alumina ratio in which the higher the ratio of silica to alumina in the sample, the higher is the amount of desorbing ammonia, except for diatomite. This behavior of diatomite is explained by the high Si/Al ratio resulting to formation of poorly polarized surface silanol groups due to low content of  $\text{Al}_2\text{O}_3$ . According the adsorption of pyridine studied by Raman spectroscopy, there are no acid sites detected in diatomite samples before thermal treatment [23]. However, thermal treatment of diatomite leads to condensation of surface silanols to siloxane groups and transforms hydrophilic surface into relatively hydrophobic one [24] resulting in low amount of ammonia adsorption.

TABLE II  
ACIDITY PROFILE RESULTED FROM TPD- $\text{NH}_3$  FOR DIFFERENT RAW JORDANIAN SAMPLES

Sample	$\text{SiO}_2/\text{Al}_2\text{O}_3$	Acidity amount ( $\mu\text{mol/g}$ )
Zeolite	3.28	130.0
Bentonite	2.67	59.4
Red kaolinite	1.91	56.9
White kaolinite	1.32	14.1
Diatomite	6.29	29.0

The fact that zeolite profile is characterized by two peak temperatures of ammonia desorption points to different strength of two acidic sites on the surface. The one recorded at higher desorption temperature corresponding to the stronger acid sites is usually attributed to the ammonia desorption from the Brønsted acid sites [3]. The lowest ammonia desorption rate and as a result the lowest acidity were found to be on Jordanian white kaolinite sample. Due to the low Si/Al-ratio of white kaolinite both SiOH and AlOH sites are centers responsible for the ammonia adsorption.

#### C. Conversion of MBOH on the surface of Jordanian clays

Catalytic reaction of MBOH conversion was utilized for direct characterization of acidic and basic properties of Jordanian clays. Fig. 2a and 2b summarize time dependences of MBOH conversions and selectivity of MBYNE during the catalytic reaction for zeolite, bentonite, diatomite, red and white kaolinite. Fig. 2a shows the highest conversion was obtained for zeolite and the lowest for diatomite. This leads to the conclusion that the amount of acid sites which are able to convert MBOH increases with Si/Al ratio and coincides with the sequence found by  $\text{NH}_3$ -TPD, except for diatomite. It is remarkable that zeolite and diatomite have relatively constant values of MBOH conversion through all the reaction process. On the contrary, for bentonite, red and white kaolinite conversion of MBOH increases on time. This fact can point to probable rearrangements of structure or framework of clay samples increasing the accessibility of acidic sites by the catalytic reaction. Performing the conversion of MBOH with the described clay samples, mainly MBYNE and acetone are detected as products of the acid and basic pathways of the conversion of MBOH, respectively.

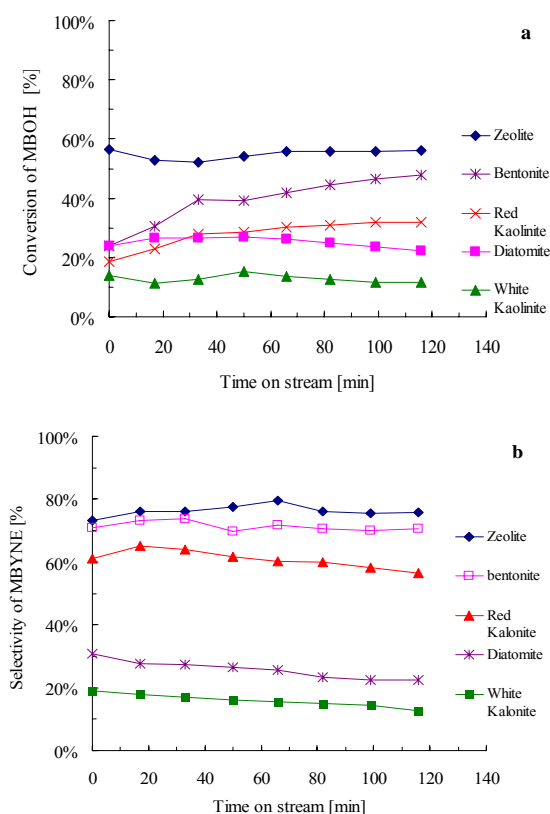


Fig. 2 Conversion of MBOH (a) and selectivity (b) over different Jordanian clays at reaction temperature 120°C

As can be seen from fig. 2b, the selectivity of MBYNE is significantly high, namely, between 60 and 80 mol.% for all samples except diatomite. Zeolite and bentonite samples indicated relatively constant selectivity of MBYNE, whereas one distinctly decreased in case of red and especially white kaolinite. This decrease in MBYNE selectivity is accompanied by the formation of acetone and acetylene with selectivity about 60 and 20 mol % respectively, which are products catalyzed by basic sites of catalyst, according the reaction mechanism. This fact points to deactivation of found by TPD- $\text{NH}_3$  strong acid sites of kaolinite on time. As a result, free silanol groups in kaolinite detected by FTIR become responsible for the formation of basic products. For the case of diatomite and pure silica [15] we have low conversion of MBOH together with low selectivity of MBYNE and high selectivity of acetone and acetylene. This fact is explained by weak polarized SiOH-groups of these silicas that are probably condensed partially to siloxane groups [24]. It is further noticed that Prenal is always a product and its selectivity ranges between 0.5 – 0.9 mol.%. The correlation between MBOH conversion and the surface area of the samples is illustrated in table 3. It is seen from table 3 that higher conversion of MBOH is caused both by higher surface areas and Si/Al ratio. However, the ratio X/BET shows that the

conversion per square meter declines in another sequence than Si/Al ratio or surface area:

*red kaolinite > bentonite > white kaolinite > zeolite > diatomite,*

i.e. the highest acidity per area unit is found for red kaolinite and the lowest for the diatomite. On the other hand, this row could point at the different type/strength of surface acid sites

TABLE III  
CORRELATION BETWEEN SURFACE AREA AND CONVERSIONS (X/BET) OVER JORDANIAN CLAY SAMPLES AT REACTION TEMPERATURES 120 °C

Sample	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	X <sub>after 100 min.</sub> %	BET <sub>before</sub> reaction m <sup>2</sup> /g (A)	BET <sub>after</sub> reaction m <sup>2</sup> /g (B)	X/BET <sub>af</sub> ter
Zeolite	3.28	55.80	96.35	87.20	0.64
Bentonite	2.67	44.60	70.21	50.20	0.89
Red kaolinite	1.91	30.90	45.21	32.25	0.96
White kaolinite	1.32	26.10	41.39	30.50	0.85
Diatomite	6.29	8.20	39.40	25.26	0.32

and their surface distribution. Similar values of X/BET<sub>after</sub> for bentonite and kaolinite mean probably that active sites are relatively equal accessible for MBOH molecules during the catalytic reaction. Low ratio of X/BET<sub>after</sub> for zeolite and diatomite can be caused by steric hindrance for MBOH molecules in pores of these samples. Moreover, adsorption of reaction product on the surface leads to decrease of BET surface area after the reaction and to deactivation of catalyst, especially at low reaction temperatures [25].

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