

## Research Article

# Properties of Raw Saudi Arabian Grey Kaolin Studied by Pyrrole Adsorption and Catalytic Conversion of Methylbutynol

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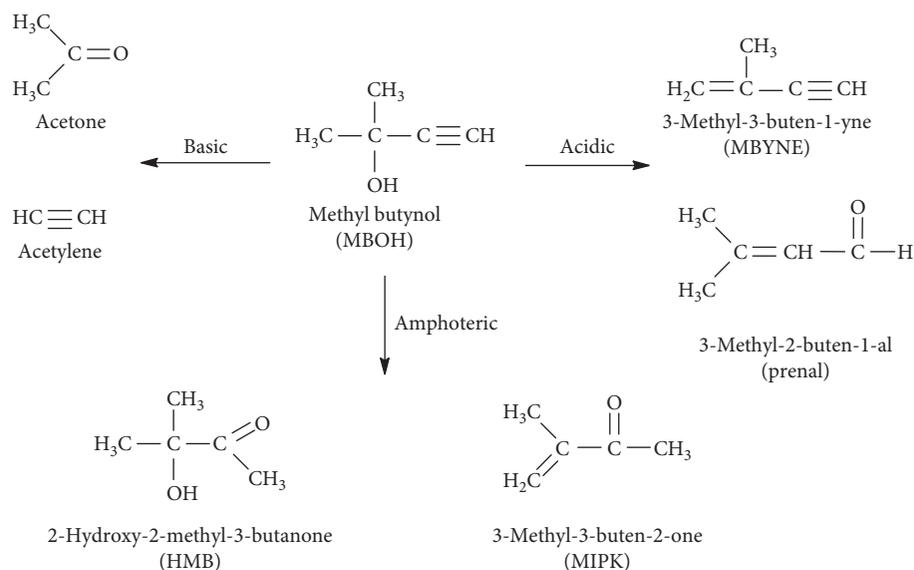
This current article demonstrates how X-ray fluorescence spectroscopy (XRF) was employed to reveal the major constituents of a sample of natural grey Saudi kaolin. The XRF results showed that it contained 52.90 wt.% silica together with 14.84 wt.% alumina. Additionally, this paper presents a study on the effect of holding times (i.e., 6, 12, 18, and 24 h) using pyrrole adsorption and methylbutynol test reaction (MBOH) on the Saudi grey kaolin (raw material). Temperature-programmed desorption of pyrrole (pyrrole-TPD) results indicated that increases in thermal conductivity detector (TCD) signals are directly proportional to increases in the heat activation holding time. Notably, a raw Saudi grey kaolin sample heated at a holding time of twenty-four hours resulted in the most intense TCD signal. Further, the MBOH transformations produced 3-methyl-3-buten-1-yne (MBYNE), as the main product, indicating the dehydration of MBOH due to the acidic sites of Saudi grey kaolin. The basic catalysis route was operative at the beginning of the reaction as acetone was observed only during the initial thirty-five minutes of the reaction then later dispersed entirely. Its disappearance is attributed to the high silica content of the test sample.

## 1. Introduction

In terms of their various industrial applications, clay materials play an important role in the production of ceramics, cement [1–3], environmental protection, and wastewater treatment [4, 5]. In order to clearly understand the uses of clay materials, researchers investigate their properties [6, 7] and endeavor to identify and explain their characteristics at their models level: micro and nano [8, 9]. A number of characterizations methods such as differential thermal analysis (DTA), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray fluorescence (XRF), and X-ray diffraction (XRD) are employed to examine the properties, morphological structures, and the chemical compositions of different clays [10–12]. Moreover, the gas phase reaction of methylbutynol (MBOH) is also studied to provide information about acidity and basicity features [13]. MBOH decomposition will lead to the formation of acetone and acetylene with respect to the basic properties of the

material. Conversely, the formation of 3-methyl-3-buten-1-yne (MBYNE) and 3-methyl-2-buten-1-al (prenal) products is due to dehydration of MBOH on weak acid sites of the material and MBOH isomerization on its strong acid sites, respectively. Other products like 2-hydroxy-2-methyl-3-butanone (HMB) and 3-methyl-3-buten-2-one (MIPK) are produced over amphoteric sites of the investigated materials [14–18]. The MBOH reaction is widely used to differentiate acidic and basic sites for the materials. The predominant three possible reaction pathways are presented in Scheme 1 [15].

Furthermore, another technique called pyrrole adsorption is also widely utilized for characterization of the clays. The reactive pyrrole-TPD techniques validate the basic properties of the material. The pyrrole aromatic compound is considered as an amphoteric molecule which gives an access for a hydrogen bonding through its NH group allowing it to react with the Lewis basic sites of the material sample [13, 14]. Saudi grey kaolin has been characterized



SCHEME 1: Different reaction pathways for catalytic conversion of methylbutynol [15].

using the following techniques: differential thermal analysis (DTA), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray fluorescence (XRF), and X-ray diffraction (XRD). To the best of our knowledge, none of the techniques reported in the literature makes use of the pyrrole-TPD and methylbutynol test reaction (MBOH) methods to investigate the properties of raw Saudi grey kaolin. In the present study, the pyrrole-TPD technique was used to investigate the basic properties of Saudi grey kaolin, while the MBOH conversion reaction was employed to study the catalytic performance of the clay.

## 2. Materials and Methods

**2.1. Material.** The sample was collected from the “Al Shammar” mountain in Al Medina at the western region of KSA, approximately 749 kilometers from the capital city of Riyadh. The chemical composition of the sample was then analyzed using XRF-Philips PW 2400.

**2.2. Sample Preparation.** Natural Saudi grey kaolin was heated in furnace from room temperature up to 200°C with a heating rate of 20°C, at various holding times (6, 12, 18, and 24 h). Each sample with the specific holding period was then tested separately for its properties by two methods: temperature-programmed desorption of pyrrole (pyrrole-TPD) and MBOH conversion.

**2.3. Pyrrole-TPD.** Table 1 summarizes the experimental conditions of the pyrrole-TPD analysis.

**2.4. MBOH Transformation over Grey Kaolin.** The reaction was conducted in a fixed bed reactor controlled by a bench unit. 0.3 grams of grey kaolin with a particle size of 250–350 μm was subjected to a temperature of 400°C, under a nitrogen flow of 15 ml/min, at different holding times (6,

12, 18, and 24 h) before starting the MBOH catalytic reaction. A mixture of MBOH and toluene (96%:4%), respectively, was placed in a storage vessel and cooled to 14°C. A vapor of the mixture was then applied under a nitrogen pressure of 1 bar and a flow rate of 0.01 mL/min into the evaporator. A HP 8090 series II gas chromatograph with a 60 m Optima Wax capillary column with a 0.25 μm wax film ( $T_{\text{max}} = 250^\circ\text{C}$ ) [17, 19] was used for the product analysis. The calculation of MBOH conversions and selectivity was based on the literature [13].

## 3. Results and Discussion

**3.1. Chemical Composition.** Table 2 presents the chemical composition of the “Al Shammar” grey kaolin sample as determined using XRF with an ignition loss of 800°C. The major content included 52.90 wt.% silica and 14.84 wt.%  $\text{Al}_2\text{O}_3$ . The results shown in Table 2 were found to correlate well with results reported in the literature [10].

It is also noteworthy that the clay contains substantial amount of iron oxide (10.2 wt.%). It has been reported that iron oxide mineral affects the physical features of clays, particularly their basicity [14].

**3.2. Pyrrole-TPD Chemical Composition.** The basic strength properties of the grey kaolin sample were investigated, after heating at different holding times, using the pyrrole adsorption method. The pyrrole-TPD profiles of grey kaolinite at various holding times are shown in Figure 1. The results show that the most intense TCD signal is produced when the sample is heated at a holding time of 24 h. By considering all profiles in Figure 1, it can be observed that increases in the holding time produces higher pyrrole-TCD signals. In other words, the amount of adsorbed pyrrole is directly proportional to the holding time period.

The hydrogen bonding facilitated by pyrrole can be used as a probe to estimate the basic properties on the sample

TABLE 1: Experimental conditions of pyrrole-TPD.

Pyrrole-TPD conditions	Description
Sample amount and particle size	0.3 g with a particle size distribution of 150–250 $\mu\text{m}$
Instrumented detector	Thermal conductivity detector (TCD)
Conditioning flow	Helium was utilized as carrier gas (50 mL/min), heated to 270°C, with a heating rate of 15°C/min. After that, a helium flow filled with pyrrole at 30°C was passed over the conditioned sample at a flow rate of 50 mL/min, for 30 min
Temperature-programmed desorption of pyrrole	Sample was then investigated up to 270°C with a heating rate of 15°C/min

TABLE 2: Chemical composition of analyzed Saudi grey clay.

Material	Chemical composition of grey kaolinite (KSA), wt.%	
	Current results	Reference [10]
SiO <sub>2</sub>	52.90	53.77
Al <sub>2</sub> O <sub>3</sub>	14.84	15.84
Fe <sub>2</sub> O <sub>3</sub>	10.2	9.01
TiO <sub>2</sub>	0.98	0.93
MnO	0.15	0.15
MgO	2.36	2.47
CaO	1.3	1.08
Na <sub>2</sub> O	0.74	0.68
K <sub>2</sub> O	1.45	1.82
P <sub>2</sub> O <sub>5</sub>	0.32	0.34
SO <sub>3</sub>	0.1	0.08
K <sub>2</sub> O	1.93	1.82
Cl	0.12	0.14
LOI	12.51	12.50
Total	99.89	99.81

surface [18]. The hydrogen bonding between pyrrole and the clay surface can be exhibited in two possible forms [20], as shown in Figure 2.

The results in Figure 1 can be explained in several plausible ways. The adsorption of pyrrole can be through Lewis acid-base interactions of pyrrole and the clay oxygen, respectively, as shown in Figure 3(a). The enhancement of pyrrole adsorption by a specific temperature at longer time periods is likely due to activation of strong Lewis acid sites on the surface of the grey kaolin [12, 21]. Heating may cause partial disintegration of the acidic bridging (structure I) and lead to formation of silanol and trigonal aluminum. The latter could act as a strong Lewis acid for adsorbing pyrrole and pyrrolate anion (Figure 3(b)).

Moreover, two available forms of amorphous silica-alumina (ASA) and their levels of acidity are described in the literature [22]. The first is the weaker form related to alumina five-domain-coordinated bonds and which constitute the interface between these domains and the ASA interface. The second is the stronger form appearing

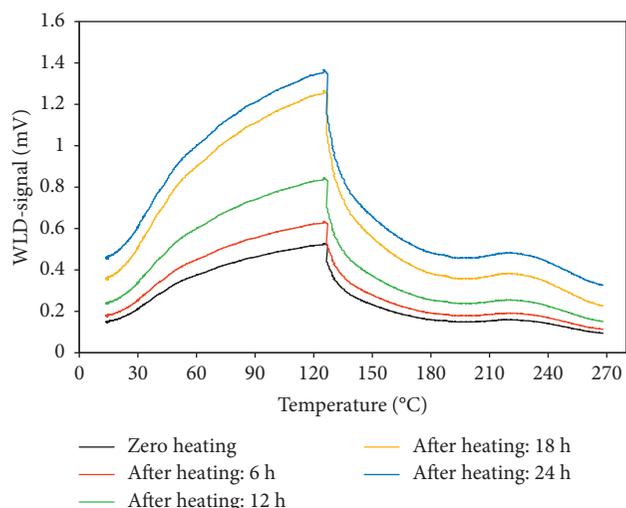


FIGURE 1: Experimental findings of TPD peaks of pyrrole on grey kaolin samples heated to 150°C at different holding times.

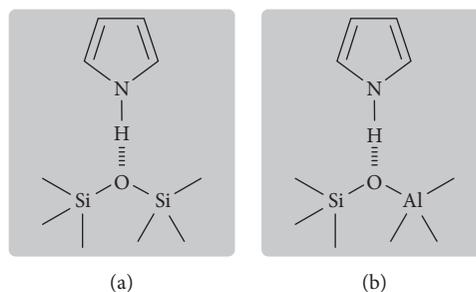


FIGURE 2: Possible hydrogen bonding interactions between pyrrole and Saudi grey kaolin: (a) predominant silica surface; (b) mixed silica/alumina surface.

below the coordinated Al sites and spliced into the silica surface [22].

**3.3. Catalytic Conversion of MBOH.** The conversions of MBOH as a function of time over grey kaolin at reaction  $T=130^\circ\text{C}$  and different holding times are shown in Figure 4. The results show that, at a reaction temperature of 130°C, MBOH conversion increases proportionally with the activation/holding time period. Accordingly, the highest conversion of MBOH over the raw grey kaolin sample was observed when the sample was calcined for 24 h. Decline in the rate of conversion by all grey kaolin samples was observed after a forty-minute time period on stream. This reduction is attributed to the existence of metal oxides that cause deactivation of MBOH conversion at the beginning of the reaction [14, 15]. Furthermore, small amount of acetone product (approximately 5% yield) was only observed during and up to the first 35 minutes of the reaction.

**3.4. Selectivity of the MBOH Conversion Reaction.** The MBOH conversion reaction was quite selective in favor of

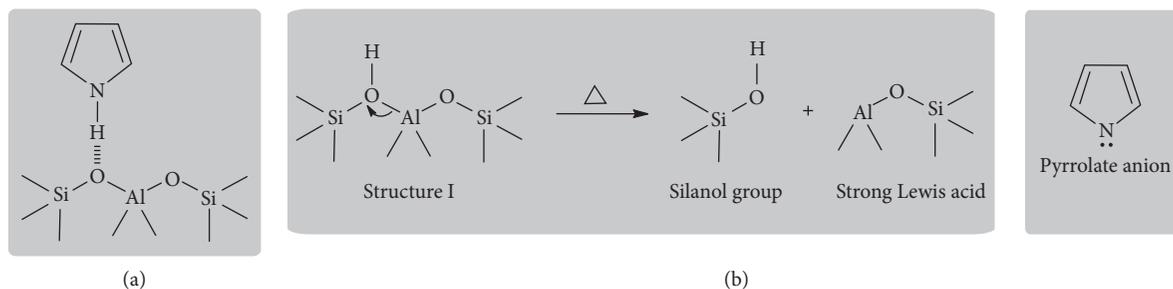


FIGURE 3: Different ways by which pyrrole can be adsorbed by the Saudi grey kaolin: (a) by the lattice oxygen as a Lewis base; (b) by aluminum acting as a Lewis acid.

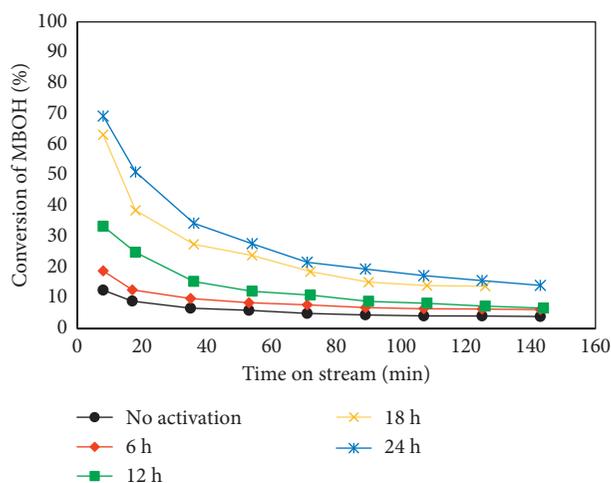


FIGURE 4: Conversions of the MBOH over grey kaolin heated to 400°C, under nitrogen stream, and subjected to different holding times (6 h, 12h, 18 h, and 24 h), at a reaction temperature of 130°C.

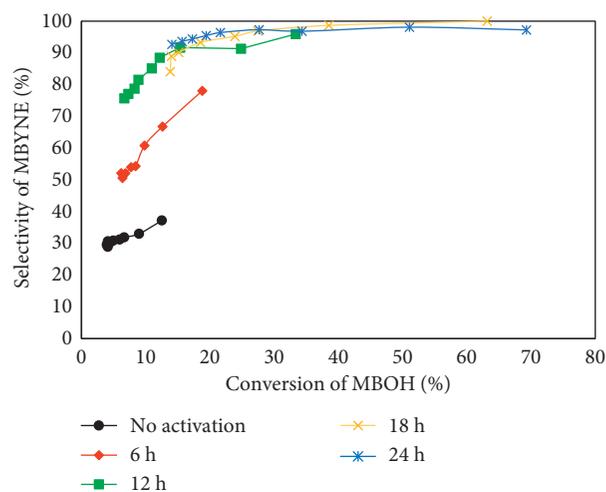


FIGURE 5: Product selectivity of the MBOH conversion at a reaction temperature of 130°C (clay preheated before starting the MBOH catalytic reaction at 400°C under nitrogen stream with different holding times: 6, 12, 18, and 24 h).

MBYNE. Figure 5 shows an increasing selectivity preference for the MBYNE product with an increase in the MBOH conversion.

Small amount of the acetone product (approximately 5% yield) was only observed during and up to the first 35 minutes of the reaction. This indicates that the acidic sites are dominant which is in a good agreement with previous study [17]. A higher amount of the MBYNE product was formed over grey kaolin heated for 24 h, 18 h, and 12 h. In general, acidic sites increase if the content of silica is higher than that of alumina [23] which explains the formation of the acid-catalyzed MBYNE product during the reaction with the Saudi grey kaolin. Accordingly, this will result in a lower electron density causing the protons to be more loosely linked to oxygen [24].

In general, results in this current article show the existence of acidic features in grey kaolin and are comparable with other studies, independent of the characterization methods employed [7, 14, 17, 25, 26]. Researchers studied the acidic features of the pillared clays using the potentiometric titration method in order to determine their acidic characteristics (pH 4 to 6) [26]. A previous finding [27] also observed that acid-based properties vary depending on the ionic type inserted into the material. Ken-ichi and coworkers [28] tested the properties of clay using the advantageous method of

acylation of cyclohexanol with acetic anhydride reaction and found the highest Lewis acidity revealed on the clay type montmorillonite exchanged with iron oxide ( $\text{Fe}^{3+}$  mont.). Similarly, the high percentage (10.2 wt.%) of iron oxide ( $\text{Fe}_2\text{O}_3$ ) present in the Saudi clay may contribute to its acidic properties as determined in our study. There seem to be some discrepancies in the results we obtained regarding the basic properties of grey kaolin using the MBOH conversion method compared with the use of other techniques such as temperature-programmed desorption of carbon dioxide since the basicity of natural grey kaolin was evident only through the acetone product during the MBOH conversion. However, it is understood that, in general, our results largely correspond to similar findings from the use of other techniques [29–31]. Lauron-Pernot [15] briefly explains that such appearing discrepancies were not due to the nature of the sites, but rather to the order of reactivity obtained on strongly basic solids. Furthermore, such reactivity does not correlate with the scale of basicity found using other techniques.

#### 4. Conclusions

Based on XRF results, the major content of the raw Saudi grey kaolin is silica at 52.90 wt.% followed by alumina at

14.84 wt.%. Pyrrole-TPD results showed an increasing TCD signal with increased holding times. This directly proportional relationship between TCD signals and holding time indicates similarity on the sequence order of the basic properties of raw grey kaolin samples. MBOH transformation results showed the same direct proportionality between the MBOH conversion and holding time. The selectivity of product of MBOH catalytic conversion over the clay was in favor of MBYNE indicating the activity of acidic sites. Acetone production was only observed in small quantity during the first 35 minutes of the reaction and then subsequently dissipated. The disappearance of the acetone product is attributed to the high silica content of the sample over the alumina content indicating predominant acidic sites. The acidity characteristic of the Saudi grey kaolin was evident by the formation of the MBYNE product. MBYNE was dominantly produced regardless of the activation time period.

### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

### Conflicts of Interest

The authors declare that there are no conflicts of interest.

### Acknowledgments

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