SURFACE PROPERTIES OF SEPIOLITE FROM AMBOSELI, TANZANIA, AND ITS CATALYTIC ACTIVITY FOR ETHANOL DECOMPOSITION

A. J. Dandy

School of Natural Resources, University of the South Pacific, Suva, Fiji

M. S. Nadiye-Tabbiruka

Department of Chemistry, Makerere University, Kampala, Uganda

Abstract—The catalytic activity of sepiolite from Amboseli, Tanzania, for the dehydration and dehydrogenation of ethanol at 150°–300°C has been studied using a flow reactor. Both reactions occur, but the catalyst activity decreases with use. The products include water, carbon dioxide, ethene, ethanal (acetaldehyde), diethyl ether, but-1,3-diene, but-2-enal (crotonaldehyde), and an unidentified aromatic compound. The proportions change with temperature, the dehydrogenation reaction being favored at the higher temperatures. The BET surface areas of the sepiolite are 316 m²/g (nitrogen adsorption at −197°C) and 212 m²/g (ethanol vapor adsorption at 25°C, assuming a molecular cross-sectional area of 24.6 Å²), indicating a possible greater penetration of pores and channels by nitrogen compared with ethanol vapor under these conditions. The pore-size distribution reveals that approximately 55% of the surface area measured by nitrogen adsorption is contributed by micropores.

Key Words—Adsorption, Catalysis, Ethanol, Pore size, Sepiolite, Surface area.

INTRODUCTION

Sepiolite is a hydrated magnesium silicate having an internal structure of channels which can accommodate zeolitic water and other molecules. On heating the structure loses water, resulting in a decrease in the surface area and micropore accessibility (Hayashi *et al.*, 1969; Martin Vivaldi and Fenoll Hach-Ali, 1969; Nagata *et al.*, 1974; Dandy and Nadiye-Tabbiruka, 1975; Fernandez-Alvarez, 1978; Serratosa, 1979). Sepiolite has a high adsorptive capacity for many gases and vapors (Barrer *et al.*, 1954; Dandy, 1968, 1969, 1971; Fenoll Hach-Ali and Martin Vivaldi, 1970; Serna and Fernandez-Alvarez, 1975; Serna and Vanscoyoc, 1979). Lopez-Gonzalez *et al.* (1978) studied the adsorption of aminobutane (n-butylamine) on acid-activated sepiolite as an indicator of surface acidity. Serna and Vanscoyoc (1979) showed that methanol and ethanol penetrate the internal channels of sepiolite, replacing zeolitic water, and hydrogen bond to coordinated water molecules; subsequently they replace part of this coordinated water.

Sepiolite has uses in gas chromatography (Manara and Taramasso, 1972) and as a catalyst and catalyst carrier; e.g., for the hydrorefining of hydrocarbons and fuel oils (Whittam, 1977; Inooka *et al.*, 1978a, 1978b; Ioka *et al.*, 1978) and the isomerization of methyl pentenes (Aldhouse *et al.*, 1969). In view of the interest in natural sepiolite as a catalyst and the use of synthetic magnesium silicates as catalysts for the dehydrogenation of ethanol (Niiyama *et al.*, 1972; Niiyama and Echigoya, 1972), a study of the interaction of ethanol with two types of sepiolite from deposits at Amboseli, Northern Tanzania, at 25°C and between 150°C and 300°C was undertaken. Nitrogen adsorption isotherms at −197°C were measured to give information on the surface area and porosity of this mineral.

MATERIALS AND METHODS

The sepiolite samples are from large deposits at the southern end of the Amboseli Basin in Northern Tanzania. The geology of this region has been described by Williams (1972) and by Stoessel and Hay (1978). In these deposits, two different forms of sepiolite have been identified and labelled sepiolite 1 and sepiolite 2 (meerschaum). The latter is lighter in color and denser than sepiolite 1 and consists of shorter laths; it is used for the manufacture of meerschaum pipes.

The samples were identified by X-ray powder diffraction (XRD) using Ni-filtered CuKα radiation and taking as references an orthorhombic sepiolite (JPDS index) and a sepiolite from Kenya (Brindley, 1959). Many of the diffraction effects are not well resolved, indicating that the samples are of imperfect crystallinity. In sepiolite 2, the presence of dolomite as a significant impurity was detected.

The samples were ground to 60–80 mesh and pressed into soft pellets. Ethanol (>99.5% purity) was boiled under vacuum and kept over Linde molecular sieve 4A before use. High-purity nitrogen was further purified with activated carbon at −197°C and stored over phosphorus pentoxide. A high-vacuum apparatus and a silica helix (McBain) arrangement was used for the gravimetric measurement of adsorption; the sensitivity of the helix was approximately 18.0 cm/g, measurements being made to an accuracy of 0.001 mm.

A flow reactor was used for the catalytic experiments. Ten grams of catalyst was contained in a glass tube reactor on a sintered glass disc. Temperature mea-
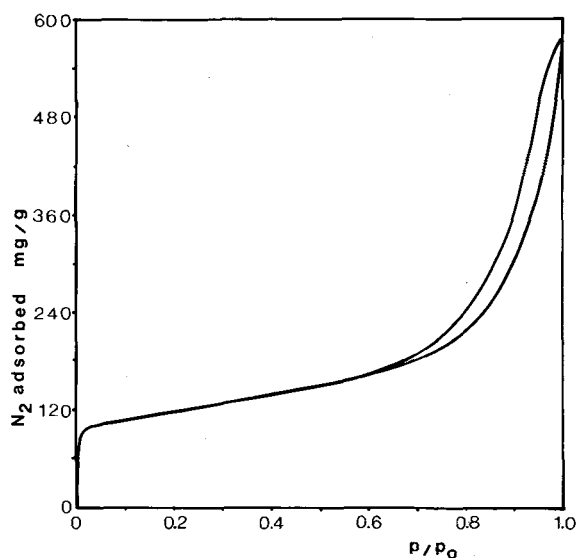
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Figure 1. Nitrogen adsorption on sepiolite 2 (meerschaum), Amboseli, Tanzania, at −197°C. Lower curve = adsorption; upper curve = desorption.

surements were made with a thermocouple placed next to the disc. Catalyst samples were initially heated in the reactor at 150°C in a stream of hydrogen for 3 hr, after which the reactor was set to the chosen reaction temperature. In between runs, the catalyst was maintained at 150°C in hydrogen for approximately 1 hr. Nitrogen carrier gas was bubbled through ethanol contained in an evaporator. Three gas channels and two sampling valve systems allowed sampling of the ethanol reactant and reaction products for direct analysis in a Perkin Elmer F11 gas chromatograph. Reaction mixtures were also frozen with liquid nitrogen for analysis by infrared (IR), ultraviolet (UV), and nuclear magnetic resonance (NMR) spectroscopy and by chemical means. For each experiment at a chosen reaction temperature, the carrier gas/ethanol vapor mixture at a constant flow rate was passed through the catalyst bed for 1 hr or more until a steady state was reached. Various flow rates between 0.2–1.3 cm³/sec were used in the experiments. The ethanol concentration at a constant flow rate was also varied by changing the evaporator bath temperature between 5°C and 25°C. Reaction products were analyzed at intervals of 30 min. The reactor temperature was increased from 150°C, by intervals of 50°C, to 300°C in each set of experiments using one catalyst sample.

RESULTS AND DISCUSSION

Adsorption experiments

Nitrogen at −197°C. Type II isotherms (Brunauer *et al.*, 1938) exhibiting hysteresis effects above a relative pressure of 0.5 were obtained from data of nitrogen adsorption on sepiolite 2 first outgassed (*in vacuo*) at 100°C (Figure 1). The BET surface area, S_{BET}, of sepiolite 2 calculated from the isotherm is 316 m²/g. The t-plot surface area, S_t (de Boer *et al.*, 1966) is 323 m²/g, in good agreement. These values are smaller than those obtained for Amboseli sepiolite 1, which are $S_{BET} = 364$ m²/g (Dandy, 1971) and $S_t = 380$ m²/g (Dandy and Nadiye-Tabbiruka, 1975). This difference may be a result of the poorer crystallinity of sepiolite 2 compared with sepiolite 1, and/or of the dolomite impurity.

Pore-size distribution analyses were made using the methods of Brunauer *et al.* (1967), as modified by Bodor *et al.* (1970) for wide pores (using the desorption branch of the isotherm), and Mikhail *et al.* (1968), as modified by Hagymassy and Brunauer (1970), for micropores. The volume of pores with radii greater than 15 Å is 0.61 cm³/g, contributing 147 m²/g to the surface area; the micropore volume (radii < 15 Å) is 0.025 cm³/g, with a surface area of 179 m²/g. The cumulative surface area is thus 326 m²/g, in good agreement with the S_{BET} and S_t values. Approximately 55% of the surface area of sepiolite 2 is due to the 'internal' (micropore) area. This result is similar to that obtained for Amboseli sepiolite 1 (Dandy and Nadiye-Tabbiruka, 1975). Serna and Vanscoyoc (1979) quoted a similar (theoretical) ratio for Vallecas sepiolite which has a measured S_{BET} (N₂) value of 321 m²/g.

Ethanol at 25°C. Ethanol adsorption on sepiolite 2 first outgassed *in vacuo* at 100°C yielded Type II isotherms (Figure 2), from which a S_{BET} value of 212 m²/g was calculated assuming a molecular cross-sectional area, σ, of 24.6 Å² for an ethanol molecule. This surface area value is much lower than that obtained from nitrogen adsorption isotherms, which indicates that nitrogen has greater access to the internal surface of sepiolite 2 than does ethanol, despite the strong polarity of ethanol molecules. However, this interpretation should be treated with caution. The orientation of the ethanol molecules on the surfaces of sepiolite 2 is not known, and the value of σ may be in error; other workers have used a value of $\sigma = 35.0$ Å² for ethanol on silica gel (Madeley and Sing, 1959), which would yield $S_{BET} = 301$ m²/g for sepiolite 2 if used here. This higher σ value is not preferred, because penetration of molecules of such size into channels of the solid is much more unlikely. A second reason for caution is related to the possibility of replacement of coordinated structural water molecules by ethanol; such replacement has been proposed for sepiolite by Serna and Vanscoyoc (1979). If this replacement occurs, the gravimetric measurements underestimate the adsorption of ethanol by the extent of water replacement and loss from the solid. IR measurements offer a more constructive approach to the question of penetration of internal surfaces by ethanol. Serna and Vanscoyoc showed that considerable penetration inside the channels does indeed take place.

Hysteresis effects are also evident (Figure 2) above

a relative pressure of 0.5, due to capillary condensation of adsorbate in the larger pores or corrugations of the solid. At low relative pressures the adsorption is not reversible, indicating that ethanol molecules may remain trapped in the channels.

Catalysis experiments

The reaction products obtained when ethanol vapor was passed over sepiolite 1 and sepiolite 2 at various temperatures are shown in Table 1. Results were also obtained for silica and for magnesia as catalysts and are included for comparison. In addition to the products listed, an unidentified aromatic compound was obtained at 250° and 300°C with both sepiolites as the catalyst. Because sepiolite 1 and sepiolite 2 behave similarly in these experiments, their catalytic activity will be discussed in terms of 'sepiolite' as a catalyst in this section. The products obtained indicate that sepiolite acts as a bifunctional catalyst, with activity for both dehydration and dehydrogenation reactions. The dehydration reactions: $C_2H_5OH = C_2H_4 + H_2O$, and $2C_2H_5OH = C_2H_5OC_2H_5 + H_2O$ are typical acid-catalyzed reactions and take place on catalysts with acid sites, such as alumina and silica.

Hydrogen and ethanal (CH_3CHO) may be produced by dehydrogenation:

$$C_2H_5OH = CH_3CHO + H_2.$$

This reaction occurs on basic sites on magnesia and synthetic silica-magnesia catalysts (Niiyama et al, 1972).

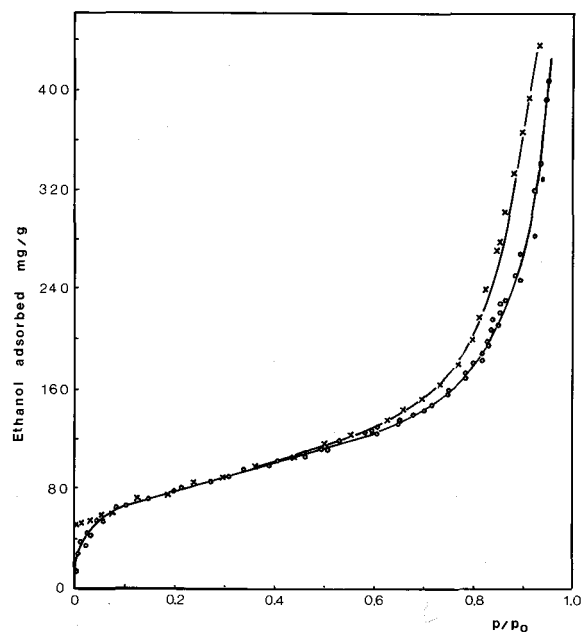At 150°C the reaction over sepiolite is predominantly one of dehydration, yielding water, ethene (C_2H_4), and

Figure 2. Ethanol adsorption on sepiolite 2 (meerschaum), Amboseli, Tanzania, at 25°C. o = adsorption; x = desorption.

diethyl ether ($C_2H_5OCH_2H_5$) as the main products. At 200°C and higher temperatures dehydrogenation also occurs, yielding ethanal (CH_3CHO); this process increases in importance, relative to dehydration processes, as the temperature is increased to 300°C. The amounts of ethanal are always small at varying reactant flow rates and partial pressures; at very large contact

Table 1. Products of the reaction of ethanol over sepiolite, silica, and magnesia catalysts.

Catalyst	Temp (°C)	H_2O	C_2H_4	$C_2H_5OCH_2H_5$	C_4H_6	CH_3CHO	CO_2	$CH_3CHCHCHO$
Sepiolite 1	150	*	*	*				
	200	*	*		*	*		(*)
	250	*	*		*	*	*	(*)
	300	*	*		*	*	*	(*)
Sepiolite 2 (meerschaum)	150	*	*	*	(*)			
	200	*	*		*	*		
	250	*	*		*	*	*	(*)
	300	*			*	*	*	(*)
Silica	150	*	*	*				
	200	*	*	*				
	250	*	*					
	300	*	*					
Magnesia	150	*	*	*				
	200	*	*		*	*		
	250	*			*	*		(*)
	300	*			*	*		(*)

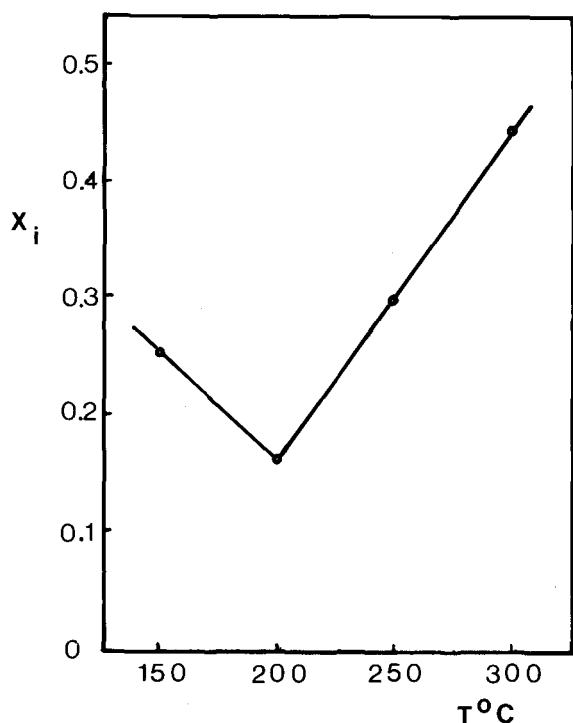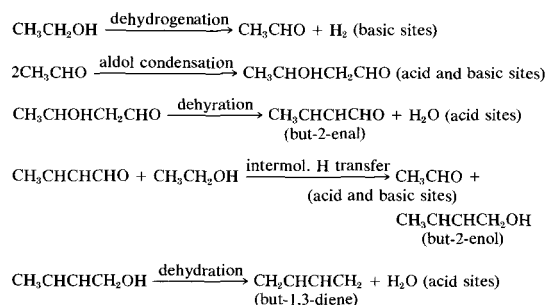* denotes product detected.
(*) denotes product detected in very small amounts.

Figure 3. Fractional conversion of ethanol over sepiolite 2 (meerschaum), Amboseli, Tanzania, X_i, vs. temperature, $T(°C)$, at constant reactant flow rate (0.67 cm³/sec, ethanol evaporator at 20°C, weight of sepiolite catalyst = 10 g).

Figure 4. Change of fractional conversion of ethanol, X_i, with: (a) flow of reactant; (b) reciprocal reactant feed rate (weight of sepiolite catalyst = 10 g).

times ethanal could not be detected. Thus, ethanal may be an intermediate in the reaction which yields but-1,3-diene.

Niiyama *et al.* (1972) used the following reaction scheme to explain the formation of but-1,3-diene from ethanol over synthetic silica-magnesia catalysts:

$$CH_3CH_2OH \xrightarrow{\text{dehydrogenation}} CH_3CHO + H_2 \text{ (basic sites)}$$

$$2CH_3CHO \xrightarrow{\text{aldol condensation}} CH_3CHOHCH_2CHO \text{ (acid and basic sites)}$$

$$CH_3CHOHCH_2CHO \xrightarrow{\text{dehyration}} CH_3CHCHCHO + H_2O \text{ (acid sites)}$$
(but-2-enal)

$$CH_3CHCHCHO + CH_3CH_2OH \xrightarrow{\text{intermol. H transfer}} CH_3CHO +$$
(acid and basic sites)
$$CH_3CHCHCH_2OH$$
(but-2-enol)

$$CH_3CHCHCH_2OH \xrightarrow{\text{dehydration}} CH_2CHCHCH_2 + H_2O \text{ (acid sites)}$$
(but-1,3-diene)

This scheme involves ethanal, but-2-enal (CH₃CHCHCHO), and but-2-enol (CH₃CHCHCH₂OH) as intermediates. To test its applicability in this study, reactant mixtures of ethanol + ethanal and ethanol + but-2-enal were passed over sepiolite. In both tests much more ethanol conversion was obtained than with ethanol alone, though the amount of ethanal in the product mixture remained small. The amounts of ethene and but-1,3-diene showed a marked increase with
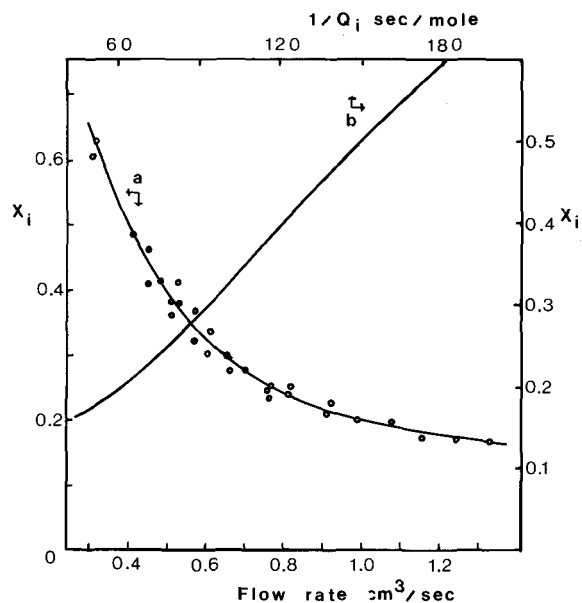
increasing contact time and with increasing partial pressures of ethanol reactant, which tends to confirm that they are final products rather than intermediates. These results support the scheme outlined above. The appearance of CO_2 at the higher temperatures may be due to the decomposition of dolomite impurity in the catalysts.

The change with temperature in the overall catalytic activity of sepiolite for ethanol decomposition is shown in Figure 3 as a plot of the fractional conversion of ethanol to products against reaction temperature for a constant reactant flow rate. The variation probably reflects the decreasing importance of dehydration and the increasing importance of dehydrogenation as the reaction temperature is increased. Schwab and Schwab-Agallidis (1949) found a similar temperature dependence of the competitive dehydration and dehydrogenation reactions of ethanol over α- and γ-alumina. They postulated that dehydration occurred in cracks and pores of the catalyst which were destroyed by heating at high temperature, whilst dehydrogenation occurred on the flat surfaces of the catalyst. A similar explanation was proposed by Pines and Manassen (1966) in their review of the dehydration of alcohols over aluminas. When sepiolite is heated in air at temperatures greater than 200°C, micropores are destroyed, and the surface area is decreased (Dandy, 1968). This process occurs at lower temperatures if the heating is carried out *in vacuo* (Dandy, 1971). In the reaction conditions employed in this study this process may account for the decline of the dehydration process above 150°C if the reaction

occurred in or near crevices, pores, or corrugations in the catalyst surface.

Because, in the temperature range studied, sepiolite catalyzes two types of reaction that are affected in different ways by change of temperature, a more detailed study is required to elucidate the kinetics of the individual reactions. However, an approximate value of the rate of reaction, r, at 250°C was obtained, assuming that at this temperature one reaction process (dehydrogenation) is predominant.

The change in fractional conversion of reactant with flow rate of reactant through the catalyst bed is illustrated in Figure 4a. The conversion increases with increasing contact time (decreasing flow rate). An equation suggested by Hougen and Watson (1943) for plug-flow reactor conditions may be used to calculate the differential rate of reaction:

$$r = 1/w[dX_i/d(1/Q_i)],$$

where w = weight of catalyst, X_i = fractional conversion of reactant, and Q_i = reactant feed rate (mole/sec). A plot of X_i against $1/Q_i$ for ethanol decomposition over sepiolite 2 at 250°C is shown in Figure 4b. Over most of the range, $r = 3.8 \times 10^{-8}$ mole/sec/g.

At all temperatures investigated there was great loss of activity with prolonged use of the sepiolite catalyst. This loss occurred more readily at the higher temperatures, possibly because of the higher conversions of reactant. The activity could be regenerated (though not completely) by evacuation of the catalyst at the reaction temperature, suggesting that the loss of activity may have been due to adsorbed compounds produced during the reaction which were removed by evacuation. Washing of used catalyst samples with organic solvents revealed the presence of an unidentified aromatic compound which was a product of side reactions probably involving polymerization and cyclization. These large molecules may be strongly adsorbed on the surface (by interaction of the OH groups of the catalyst with the π-bond electron system of the products) or block catalyst channels and prevent entry of more reactant molecules; both processes would lead to the observed decrease in catalyst activity with use.

ACKNOWLEDGMENTS

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Резюме—Исследовалась каталитическая активность сепиолита из Амбосели, Танзания, на дегидратацию и дегидрирование этаноля при 150°–300°C при помощи проточного реактора. Обе реакции происходят, но активность катализатора уменьшается со временем его использования. Продукты включают: воду, углекислоту, этен, этаноль (ацетальдегид), двухэфир, бут-1,3-диен, бут-2-енал, и неопределенное ароматическое соединение. Пропорции изменяются с температурой, реакция дегидрирования преобладает при больших температурах. Площади поверхности сепиолита, определенные методом БЭТ, равны 316 м²/г (адсорбция азота при −197°C) и 212 м²/г (адсорбция пара этаноля при 25°C), предполагая, что площадь молекулярного поперечного сечения равна 24,6 Å². Это указывает на возможное большое проникание азота в поры и каналы сепиолита по сравнению с прониканием пара этаноля при таких же условиях. Распределение пор по размерам указывает на то, что приблизительно 55% площади поверхности, измеренной адсорбцией азота, принадлежит микропорам. [E.C.]

Resümee—Die katalytische Wirkung des Sepiolith von Amboseli, Tanzania, bei der Dehydratation und Dehydrierung von Äthanol bei 150°–300°C wurde unter Verwendung eines Durchflußreaktors untersucht. Beide Reaktionen treten ein, aber die katalytische Wirkung nahm mit der Zeit ab. Die Produkte waren Wasser, Kohlendioxid, Äthylen, Äthanal (Acetaldehyd), Diäthyläther, But-1,3-Dien, But-2-Enal (Crotonaldehyd), und eine unidentifizierte aromatische Verbindung. Die Mengenverhältnisse veränderten sich mit der Temperatur, die Dehydrierungsreaktion wurde bei höheren Temperaturen begünstigt. Die BET-Oberfläche des Sepiolith beträgt 316 m²/g (Stickstoffadsorption bei −197°C) und 212 m²/g (Äthanoldampf-Adsorption bei 25°C), was auf eine molekulare Querschnittsfläche von 24,6 Å² schließen läßt. Außerdem deutet dies darauf hin, daß unter den gegebenen Bedingungen Stickstoff weiter in Poren und Kanäle eindringen kann als Äthanoldampf. Die Verteilung der Porengröße zeigt, daß etwa 55% der durch Stickstoffadsorption gemessenen Oberfläche von Mikroporen stammt. [U.W.]

Résumé—On a étudié avec un réacteur à flot l'activité catalytique de la sépiolite d'Amboseli, Tanzanie, pour la déshydration et la déshydrogènation d'éthanol à 150°–300°C. On observe les deux réactions, mais l'activité catalyste décroit avec l'emploi. Les produits comprennent l'eau, le carbone dioxide, l'éthène, l'éthanal (acétaldéhyde), l'éther diéthyl, but-1,3-diène, but-2-énal (crotonaldéhyde), et un composé aromatique non-identifié. Les proportions changent avec la température, la réaction de déshydrogènation étant favorisée à de plus hautes températures. Les aires de surface de la sépiolite sont 316 m²/g (adsorption de nitrogène à −197°C) et 212 m²/g adsorption (de vapeur d'éthanol) à 25°C, en supposant que l'aire moléculaire d'une section transversale est 24,6 Å², indiquant possiblement une plus grande pénétration possible de nitrogène dans les pores et les canaux en comparaison avec la vapeur d'éthanol sous les mêmes conditions. La distribution de tailles de pores révèle qu'approximativement 55% de la surface mesurée par l'adsorption par le nitrogène est contribué par des micropores. [D.J.]