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Chemisorption of alkenes on copper-exchanged ZSM-5 zeolite

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On Cu-ZSM-5 zeolite at room temperature, propane is physisorbed, while propene shows characteristics of chemisorption. The chemisorption mode has certain advantages for the catalytic control of automotive emissions. Alkane and alkene adsorption equilibria and kinetics are compared on Cu-ZSM-5 and on ZSM-5 free of alumina. The results are discussed in terms of the Langmuir adsorption isotherm.

Keywords: alkene chemisorption; olefin adsorption; propene; propylene; Cu-ZSM-5; ZSM-5; silicalite

1. Introduction

The zeolite H-ZSM-5 has a medium-pore 10-member-ring structure classified under the pentasil group [1,2]. This molecular sieve, after metal-ion exchange, has been recognized as an effective catalyst for the selective reduction of nitric oxide by hydrocarbons (HCs) in excess oxygen [3–6]. Results from studies of NO_x (NO and NO_2) reduction under overall oxidizing conditions suggested to us that Cu-exchanged ZSM-5 (Cu-ZSM-5) preferentially adsorbs alkenes over their alkane counterparts. To scrutinize this phenomenon, adsorption of propene and butene on Cu-ZSM-5 is compared with propane and butane adsorption. Results are also correlated with adsorption data obtained on silicalite, a ZSM-5 material consisting essentially of pure silica.

At least two aspects of the different adsorption modes examined here are of interest for the control of automotive emissions. One consideration is the influence of the increased HC adsorption strength on the mechanisms governing activity and selectivity of catalytic reactions. Of particular current interest for automotive emission control is the selective reduction of NO by HCs in the presence of excess oxygen. A second aspect for automotive emission control is the use of ZSM-5, or other molecular sieves, as a temporary trap for HC cold-start emissions, which are to be released later after the catalyst temperature is sufficiently high to effect HC oxidation. Zeolites are desirable adsorbents because of their large surface area associated with an extensive network of cavities and channels of molecular dimensions. The harsh environment of automotive exhaust is less bothersome for chemically stable zeolitic adsorbents compared to active carbons, which are more commonly employed for many adsorption applications. Furthermore, the observations reported here can serve as the basis for the formulation of other materials practical for the selective condensation of HCs that contain an olefinic bond. Such HCs, alkenes, are by a factor of ten or more reactive than their alkane counterparts and thus have a much stronger effect on the chemistry of atmospheric reactions.

2. Experimental

2.1. MATERIALS

A Cu-ZSM-5 powder with a silicon/aluminum ratio of 15 was obtained from Universal Oil Products (UOP). The material contained 2.47 wt% copper, which had been exchanged into the zeolite from an aqueous solution of copper acetate. The extent of ion-exchange was about 94%. The sample was calcined in air at 550°C for 4 h. Further treatment, including reduction in hydrogen, took place in a reactor used for analysis by TPD (temperature programmed desorption). The silicalite powder was the same material employed in a previous investigation [7]; it was manufactured by Union Carbide.

2.2. PROCEDURES

Two approaches were employed to measure and evaluate adsorption characteristics. A dynamic flow reactor was used for the TPD experiments. The Cu-ZSM-5 powder was packed inside a quartz reactor between two buttons of an inert ceramic monolith. Quartz wool separated the powdered sample from the buttons. The powder was first reduced in hydrogen at 450°C to produce its ultimate adsorption capacity.

A first adsorption mixture consisted of 500 ppm propene, 500 ppm NO, and 3% O_2 in nitrogen. This mixture was selected to represent the reactants that control the catalytic reduction of NO from lean-burning engines over Cu-ZSM-5. The gas passed over 0.50 g of the Cu-ZSM-5 sample at a flow rate of 300 cm^3/min. After the adsorption equilibrium had been reached, the reactor was heated at a rate of 15°C/min. The propene concentration was measured continuously by an FID detector (Beckman model 400A). The amount of desorbed C_3H_6 was calculated from the area under the desorption peaks. In some cases HC analysis by FID was supplemented by mass spectrometry.

To exclude the presence of nitric oxide as a key component in the adsorption process, additional TPD experiments were carried out with 500 ppm of propene, or propane, in helium over 0.25 g of Cu-ZSM-5 at a flow rate of 250 cm^3/min. Gas desorption was analyzed by mass spectrometer.

In a second approach, a Cahn microbalance, attached to a vacuum system, served to measure adsorption isotherms in a controlled atmosphere. Furthermore, this equipment was used to evaluate adsorption and desorption kinetics as a function of temperature. Results from an earlier investigation of HC adsorption on silicalite [7], a ZSM-5 consisting essentially of pure silica free of alumina [8], provide additional data for a broader comparison.

3. Experimental results and discussion

3.1. THERMODYNAMIC CONSIDERATIONS

Fig. 1 shows equilibria for propene and propane adsorption on Cu-ZSM-5 by open and filled circles, respectively. At a pressure of 10 Torr (1.33 kPa), the Cu-ZSM-5 powder adsorbs about twice as much propene than propane. The difference becomes larger at lower pressures. For example, below 1 Torr, in the linear region of the adsorption isotherm, Cu-ZSM-5 holds at least three times the amount of propene compared to propane.

It was of interest to compare Cu-ZSM-5 and silicalite (ZSM-5) as adsorbents. Both materials have essentially the same crystal structure; they differ, however, in chemical composition. The Al/Si ratio of H-ZSM-5 can be up to 0.15. Silicalite (ZSM-5) represents the lower limit of this range; it is essentially free of alumina and, accordingly, lacks ion-exchange sites. Fig. 1 shows propene and propane adsorption isotherms on silicalite [7] by the dotted and dashed lines, respectively. A small excess of propane adsorption on Cu-ZSM-5 (filled circles), as compared to

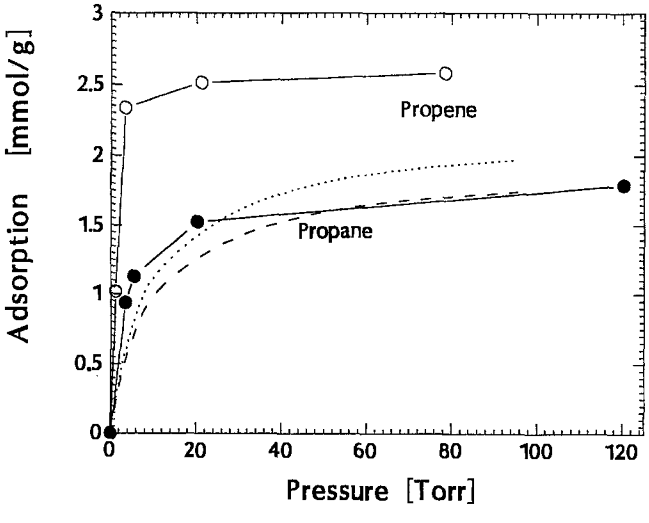

Fig. 1. Adsorption of propene and propane on Cu-ZSM-5 (–○– and –●–) and ZSM-5 (silicalite) (· · · and – – –), respectively, at 24°C.

silicalite (dashed line), disappears above 50 Torr, where propane adsorption on the two adsorbents is the same within experimental error.

The Langmuir isotherm is suited for a simple, but physically meaningful description of HC physisorption on silicalite below atmospheric pressure [7]. In the present work, the adsorption of alkenes on Cu-ZSM-5, which differs from the physisorption of alkanes, as explained below, was equally well described by the Langmuir isotherm

$$\frac{p}{m} = \frac{p}{m_s} + \frac{c}{m_s} . \tag{1}$$

In this linear representation, the ordinate intercept is

$$k_0 = \frac{c}{m_s} \tag{2}$$

and the slope is

$$k_1 = \frac{1}{m_s} . \tag{3}$$

The fractional coverage Θ ($0 \leqslant \Theta \leqslant 1$) is given as the ratio of moles m adsorbed at pressure p and the maximum adsorption capacity m_s that defines saturation coverage at $\Theta = 1$. The coefficient c, a constant at a fixed temperature, is described by

$$c = \frac{c_d}{c_a} \exp\left(\frac{q}{RT}\right) = \frac{k_0}{k_1} , \tag{4}$$

where c_d and c_a are coefficients of desorption and adsorption respectively, q is the heat of adsorption; R and T are the gas constant and the absolute temperature, respectively.

Table 1 shows numerical values of selected HC adsorption data for the slope k_1 and ordinate intercept k_0. The adsorption capacity limit, derived from the recipro-

Table 1
Parameters of Langmuir isotherms

	k_0 (Torr g/mmol)	k_1 (g/mmol)	Maximum capacity (mmol/g)	Capacity at 1 Torr (mmol/g)	k_0/k_1 (Torr)
Cu-ZSM-5					
propane, 24°C	1.98	0.54	1.85	0.40	3.67
propene, 24°C	0.40	0.38	2.63	1.28	1.05
propene, 154°C	0.35	0.48	2.08	1.20	0.73
butene, 24°C	0.26	0.58	1.72	1.19	0.45
silicalite (ZSM-5)					
propane, 24°C	4.68	0.52	1.92	0.19	9.00
propene, 24°C	4.11	0.46	2.17	0.22	8.93
butane, 24°C	2.53	0.62	1.61	0.32	4.08

cal slope of the Langmuir isotherm at room temperature, is the same for propane adsorbed on silicalite and on Cu-ZSM-5, as expected. The maximum adsorption capacity for a given alkene molecule, as a rule, exceeds that of its alkane counterpart. For example, the propene adsorption maximum on silicalite exceeds that of propane by 14%. A difference of 6% is expected based on the relative size of propane and propene molecules, derived from their liquid densities. The ratio $k_0/k_1 = c$ (table 1 and eq. (4)) is a rough measure for adsorbate volatility [7] or, in its reciprocal form, for HC adhesion. Thus, the coefficient c can be used for a cursory comparison of adsorption trends.

In fig. 2, the adsorption equilibrium of propene on Cu-ZSM-5 is plotted for the parameters of the Langmuir isotherm at two temperatures, 24 and 154°C. A correlation coefficient of 0.9999 indicates an excellent linear fit of each data set. Fig. 2 also shows that the change in adsorption capacity with temperature is relatively small. Thus, the maximum adsorption capacity, as defined by the reciprocal slope of the propene adsorption isotherms in fig. 2, decreases by 21% (cf. table 1). The difference in adsorption capacity at lower pressures is even smaller. For example, at 1 Torr the adsorption equilibria at the two temperatures of fig. 2 differ by less than 10%. The temperature change in silicalite adsorption capacity is considerably larger. Thus, butane adsorption on silicalite at 1 Torr decreased by 84% when the temperature was increased from 23 to 104°C [7]. The data listed in table 1 for butane and butene show that the salient features derived from the comparison of propane and propene adsorption hold also for butane and butene. Thus, while the maximum adsorption capacity for butane on silicalite and butene on Cu-ZSM-5 agrees within 7%, the adsorption equilibrium at 1 Torr favors propene on Cu-ZSM-5 by a factor of four.

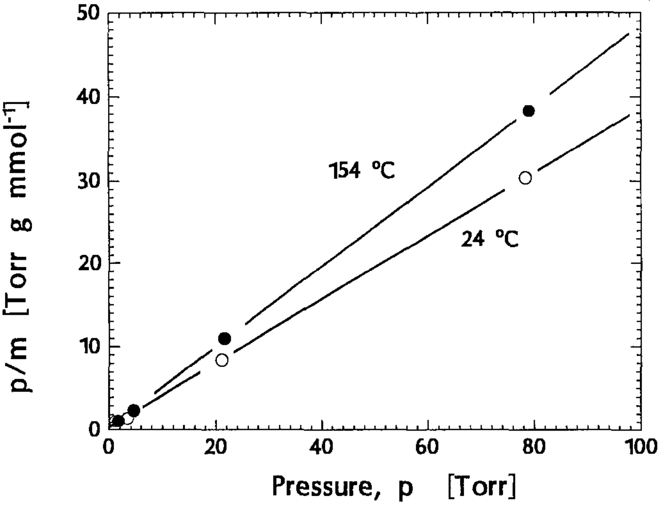

Fig. 2. Adsorption of propene at 24 and 154°C in terms of the coordinates of the Langmuir isotherm.

3.2. KINETIC CONSIDERATIONS

Another parameter of interest is the time required to reach adsorption equilibrium. Cold-start emissions, which are limited to the firsts few minutes of engine operation, must be trapped quickly. Fig. 3 is selected as an example to illustrate that the rate associated with the enhanced propene adsorption mode on Cu-ZSM-5 does not worsen mass-transfer limitations. The same equilibrium coverage holds for the adsorption of 1.8 Torr of 1-butene on Cu-ZSM-5 (circles) and 18 Torr of *n*-butane on ZSM-5 (dashed line). At first, however, adsorption is much faster on Cu-ZSM-5, according to the initial slopes of fig. 3, marked by solid and dashed lines, respectively. Disregarding the first adsorption point at 1 min, which is ill-defined because of the disturbance generated by adsorbate rushing into the balance system at time zero, the adsorption rates are 0.12 and 0.05 mmol g^{-1} min^{-1}, respectively, for the adsorption of 1.8 Torr 1-butene on Cu-ZSM-5 and 18 Torr butane on ZSM-5 in the interval between 2 and 3 min.

Physical adsorption and desorption equilibria of HCs on ZSM-5 were typically complete within 20 to 60 min [7]. While the adsorption on Cu-ZSM-5 is at least as fast, the desorption of alkenes from Cu-ZSM-5 at room temperature was too slow to be measured. The desorption characteristics of propene on Cu-ZSM-5 were therefore evaluated by TPD.

3.3. EVALUATION OF ADSORPTION MODES

The two prominent desorption peaks of propene are shown in fig. 4. At a heating rate of 15°C/ min a smaller portion of the adsorbate is released at the first maximum at 70 ± 5°C. This peak was also found when propane was the adsorbate. A second desorption maximum appeared at 253 ± 5°C for propene, but not for pro-

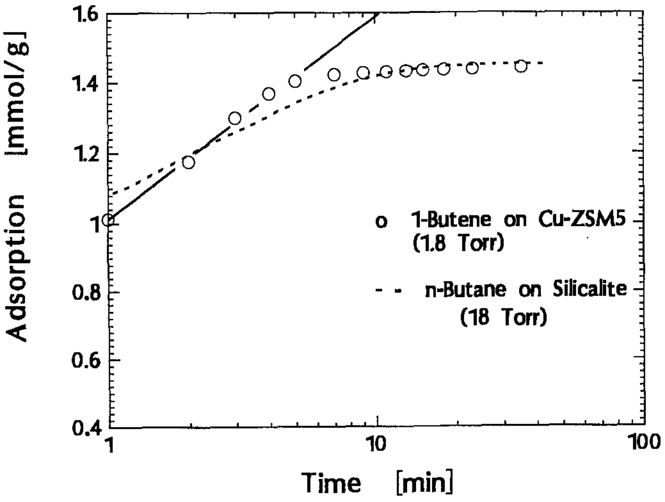

Fig. 3. Adsorption kinetics of 1.8 Torr 1-butene on Cu-ZSM-5 and 18 Torr *n*-butane on silicalite.

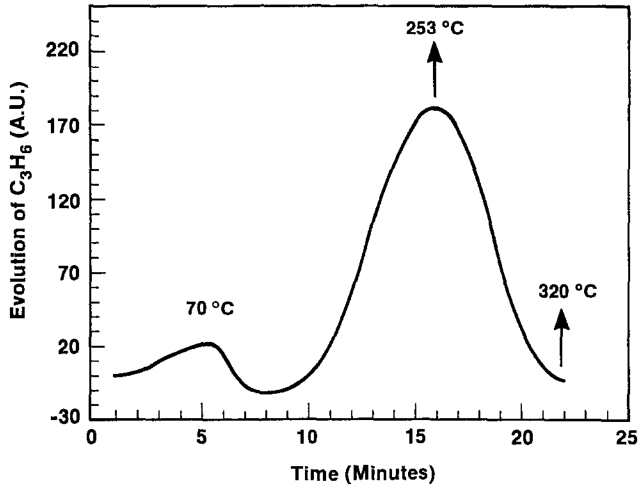

Fig. 4. Temperature-programmed desorption of propene from Cu-ZSM-5.

pane. Propene desorption was complete at 320°C. The two desorption peaks at 70 and 253°C in fig. 4 are thought to represent adsorbate portions associated with physisorption and chemisorption, respectively.

The distinction between physical and chemical adsorption is based on the definitions given by Howard and Trapnell [9]. Accordingly, physical adsorption is essentially nonactivated and is characterized by a low heat of adsorption (typically 4–6 kcal/mol per surface contact of the adsorbate species). Appreciable physical adsorption exists only near or below the boiling point of the adsorbate.

The first peak in fig. 4 always accounted for 5% or less of the total adsorption and is considered to reveal physisorption, although very weak chemisorption cannot be ruled out. The reality of propene chemisorption, manifested by adsorption far above the boiling point of propene (–47°C), is supported by additional evidence. Thus, a mass spectrometric analysis of the gas components released at 270°C disclosed minor m/e peaks at 55 and 56. These peaks signify polymerization of propene molecules. A product containing four carbon atoms clearly requires a chemisorbed precursor. An upper limit of the polymerized fraction of propene can be calculated from a comparison of propene disappearing from the gas stream upon adsorption and propene released under the two desorption peaks of fig. 4, measured by $m/e = 41$. According to this analysis, at least 69.5% of the adsorbed propene was desorbed as such. Considering that $m/e = 43$ (C_3H_7) also represents a non-polymerized species derived from propene, and because of other uncertainties, it is estimated that polymerization involves about 25% or less of the adsorbed alkene.

4. Conclusions

While adsorption of alkanes, such as propane, on Cu-ZSM-5 exhibits the characteristics of physisorption, adsorption of alkenes is substantially stronger and is judged to be chemisorption. A strengthened adsorption on Cu-ZSM-5, compared to silicalite, is also noticeable for alkanes, albeit to a much smaller degree. The chemisorption of alkenes can be expected to be a dominating process in the reaction profile of alkane–alkene mixtures over Cu-ZSM-5. Initial reduction of Cu-ZSM-5 after calcination appears to maximize propene adsorption at a given temperature and pressure. Subsequent presence of oxygen during propene adsorption did not cancel the promoted adsorption.

The results reported here are consistent with an investigation of copper and silver Y-zeolites by Huang [10] who studied adsorbed ethene complexes by infrared spectroscopy. These complexes are characterized by a strong interaction with Ag(I) and Cu(I) ions resulting in dπ bonding, while Cu(II) interacts with ethene only by van der Waals forces. Huang reports an isosteric heat of about 16 kcal/mol for Cu(I)Y. If the heat of (nonactivated) propene physisorption (or weak chemisorption) associated with the first desorption peak at 70°C in fig. 4 is assumed to be 9.5 ± 1 kcal/mol [11] it is estimated that the second desorption peak at 253°C corresponds roughly to an activation energy of desorption of about $9.5 \times (253+273)/(70+273) = 15$ kcal/mol consistent with the isosteric heat value. It is assumed here that the activation energy of adsorption is small when compared to the heat of adsorption. Alkene chemisorption on ZSM-5 zeolites is apparently not limited to copper ions, as a heat of ethene adsorption of 13 kcal/mol on H-ZSM-5 was measured by Stach et al. [12]. For comparison, heats of chemisorption of short alkene chains, such as C_2H_4 and C_3H_6, on Cu and Cu_2O are typically 18 and 20 kcal/mol, respectively [9].

It is of interest to know to what degree other ions in ZSM-5 besides Cu^+ (or Cu^{2+}) enhance alkene adsorption. A comparison of alkene adsorption on Cu-ZSM-5 and H-ZSM-5 is informative, as well. Dr. J.S. Hepburn of Ford Research Laboratory recently observed in bench tests that propene adsorption on H-ZSM-5 persists at temperatures exceeding the desorption temperature of physically adsorbed propene. However, according to the concentration trace of propene released upon heating, Cu-ZSM-5 substantially exceeds the adsorption capacity of H-ZSM-5 (by roughly 50%).

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