N_2 taken up at −195° at $p/p° = 0.25$, is essentially unchanged by the acid extraction.

The ammonia chemisorption also decreases monotonically as the aluminum content decreases (Table 1). Of particular interest is the fact that the molar ratio (NH_3: Al) of ammonia chemisorbed relative to total aluminum in the sample is 1 ± 0.25 for all samples.

The following conclusions may be drawn from these data:

(1) If hydroxyl nests are formed in acid-extracted mordenites, they are not stable above 100°.

(2) Such hydroxyl nests, if initially formed during extraction, would play no role in catalytic reactions carried out at temperatures above 100°.

(3) Such hydroxyl nests, if initially formed during extraction, do not chemisorb ammonia at 250° and a partial pressure of 11.2 Torr.

(4) The amount of ammonia chemisorbed at these arbitrary conditions is roughly stoichiometric (1:1) with the total amount of aluminum present in the mordenite lattice.

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Rate Coefficients from Pulsed Microcatalytic Reactors—Nonlinear Kinetics with Linear Isotherms*

While the use of pulsed microcatalytic reactors has been widely used in many laboratories since its introduction (*1*) the extraction of quantitative rate coefficients from data obtained by this technique for systems with nonlinear kinetics and/or adsorption isotherms has been difficult. Previous consideration of this problem (*2*) has shown that by introducing (1) a dispersion column upstream of the catalyst bed and (2) concentration sensors immediately before and immediately after the catalyst bed, the problem of pulse dispersion could be circumvented and the resulting first-order differential equation could be solved numerically for nonlinear kinetics. In order to use the results of the calculation to extract rate coefficients, however, it is necessary to obtain the net linear velocity of the reactants (judged by the motion of the reactant pulse maximum through the catalyst bed), whereas it is the carrier gas velocity which is more commonly measured. In this note, we show that for the special case of a linear isotherm it is possible to use the numerical results (*2*) with only data on the carrier gas velocity

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(which is more easily obtained) even though the overall kinetics are nonlinear. As before, the catalyst bed is assumed to be isothermal, isobaric, and in plug flow.

For a reaction of the type, A → products, the mass balance for a nondispersing pulse in a differential element of reactor volume is given by:

$$\epsilon \frac{\partial C_A}{\partial t} + \rho_p(1-\epsilon)S\frac{\partial q_A}{\partial t} + \epsilon u \frac{\partial C_A}{\partial y} + \rho_p(1-\epsilon)SR_A = 0, \quad (1)$$

where:

ϵ is the external void fraction in the packed bed,
C_A is the reactant concentration in the gas phase (moles/cm^3),
t is the time (sec),
ρ_p is the apparent density of a single catalyst particle (g/cm^3),
S is the specific surface area of catalyst (cm^2/g),
q_A is the surface concentration of reactant (moles/cm^2),
u is the linear velocity of carrier gas through the voids of catalyst bed (cm/sec),
y is the axial distance along the bed (cm),
$-R_A$ is the specific reaction rate (moles/cm^2 sec).

The use of the linear isotherm after appropriate definition of nondimensional variables results in:

$$(\partial\phi/\partial\tau) + (\partial\phi/\partial Z) = [-\rho_p(1-\epsilon)S]/\epsilon \cdot L/u \cdot (R_A/C_A^\circ), \quad (2)$$

where

C_A° is the maximum concentration of the input pulse (moles/cm^3),
L is the total bed length (cm),
K_A is the slope of linear isotherm (cm^3 gas phase/cm^2 catalyst),
ϕ is the C_A/C_A°,
τ is the $\dfrac{t}{L}\dfrac{u}{(1+[\rho_p(1-\epsilon)/\epsilon]SK_A)}$,
Z is the $\dfrac{y}{L}$,

which is the same equation as Eq. (4) of Blanton *et al.* (*2*) except that the characterizing parameter is proportional to L/u rather than L/U_A where:

$$U_A = \frac{u}{1+[\rho_p(1-\epsilon)SK_A]/\epsilon}. \quad (3)$$

The quantity, U_A, is the velocity of the concentration pulse and u is the velocity of the carrier gas. Since the form of the rate equation is unspecified in Eq. (2), it follows that whenever the isotherm for the reactant is sufficiently linear, it is possible to use the previous numerical results (*2*) using the carrier gas flow rate instead of the volumetric reactant flow rate originally proposed. A simple empirical test for nonlinearity on a scale large enough to effect the shape of adsorption breakthrough curves and elution pulses has been given previously (*3*).

For clarity, we illustrate the use of Eq. (2) with simple power law kinetics.

$$R_A = -k_s q_A{}^n, \quad (4)$$

n is the order of reaction,
k_s is the specific rate coefficient [sec^{-1} (moles/cm^2)$^{1-n}$].

Substitution of the linear isotherm gives

$$R_A = -k_s K_A{}^n C_A{}^n, \quad (5)$$

and Eq. (2) becomes:

$$\frac{\partial\phi}{\partial\tau} + \frac{\partial\phi}{\partial Z} = \frac{-\rho_p(1-\epsilon)S}{\epsilon} \cdot k_s K_A{}^n C_A^{\circ\,n-1} \frac{L}{u}\phi^n, \quad (6)$$

and, thus, Fig. 1 of Blanton *et al.* (*2*) with an abscissa,

$$K = (VkC_0{}^{n-1})/Q, \quad (7)$$

may be used directly if

$$k = \{[\rho_p(1-\epsilon)S]/\epsilon\}k_s K_A{}^n,$$
$$Q = \epsilon a_s u, \quad (8)$$

where a_s is the reactor cross-sectional area.

Initially, one might question whether the assumption of a linear isotherm could possibly be reasonable for systems kinetically consistent with the highly nonlinear Langmuir–Hinshelwood (LH) equations. The point is that the linearity required is that which determines the axial mass transport of the reactant (i.e., U_A must be given by Eq. (3) which is independent of C_A). It is widely accepted, especially on heterogeneous surfaces, that it may be only a few sites having a rather narrow range of adsorption energies which are kinetically active. Thus, the adsorption coefficients deduced from the kinetic measurements could be quite different from the coefficients for the average adsorption site. It is this average adsorption site which influences axial transport and, thus, it is quite conceivable that the adsorptive retention characteristics of a catalyst might be consistent with a linear isotherm at conditions where the kinetically active sites are decidedly nonlinear. Furthermore, the general form of the LH rate equations is characteristic of many complex mechanisms and complexities in the surface chemistry could easily give rate equations similar to those based on LH mechanisms under conditions where the assumption of linear isotherms is quite valid.

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Correlation of Catalytic Oxidation Activity of Metal Macrocyclic Amine Complexes and Redox Potential

Introduction

A variety of metal salts are known to catalyze hydrocarbon autoxidation by inducing the catalytic decomposition of intermediate alkyl hydroperoxides to radicals. The commonly accepted mechanism for metal salt catalyzed hydroperoxide decomposition is the Haber-Weiss redox cycle (*1*, *2*).

$$\mathrm{ROOH} + \mathrm{M}^{n+} \rightarrow \mathrm{RO}\cdot + \mathrm{OH}^- + \mathrm{M}^{(n+1)+}$$
$$\mathrm{ROOH} + \mathrm{M}^{(n+1)+} \rightarrow \mathrm{RO}_2\cdot + \mathrm{H}^+ + \mathrm{M}^{n+}$$

Each step involves rapid complex formation between the hydroperoxide and the metal salt followed by decomposition of these complexes to free radical products. Several investigators have attempted to correlate the activity of metal complexes in catalyzing hydrocarbon oxidation with the standard redox potentials for the metal cations as measured in aqueous medium (*3*, *4*). In view of the sensitivity of redox potential to change in medium and to the nature of the ligands, it is not surprising that only qualitative correlations between oxidation activity and redox potential have been observed. A rigorous analysis of the role of redox potential requires that the redox potentials of the metal catalysts be known in the same solvent as used for the oxidations. Furthermore, the ligand must have a high stability constant so that it would not be displaced by other ligands during the course of the oxidation with the resultant change in redox potential of the metal cation. Recently the redox potentials of a series of macrocyclic tetradentate amine complexes which satisfy these two requirements have been measured (*5*). The redox potentials were measured in acetonitrile and the tetradentate ligand is extremely inert to displacement.

In the present study, the rates of cyclohexene oxidation catalyzed by Cu(II),