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Designing Zeolite Catalysts for Size- and Shape-Selective Reactions: Selective Hydrogenation of Acetylene in the Presence of Butadiene and Ethylene

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In the production of ethylene from the steam cracking of natural gas, small amounts of acetylene and butadiene are produced. Downstream, acetylene can present a hazard in a cryogenic separation process while nonselective hydrogenation removes acetylene as well as valuable ethylene and butadiene. With the aid of adsorption measurements, a selective hydrogenation catalyst has been designed. Small-pore zeolites, which serve as catalytic supports and provide reactant selective control, were ion-exchanged with Ni^{2+} and subsequently reduced. Compared to a commercial catalyst in which 60% of butadiene and all of the acetylene are hydrogenated, these new catalysts totally hydrogenate acetylene with only 10–20% hydrogenation of the butadiene and almost no hydrogenation of ethylene. To achieve selective hydrogenation, poisoning of the metal sites on the external zeolite surface is essential in order to obtain a product spectrum dominated by catalytic sites within the zeolite framework.

INTRODUCTION

In the production of polymer-grade ethylene from the steam cracking of natural gas, small amounts of acetylene and butadiene are by-products (*1*). Although acetylene, ~3500 ppm, and butadiene, ~6500 ppm, are present in low concentrations, the total volume per year makes their recovery very attractive economically. However, in a downstream cryogenic separation process, acetylene can pose a significant hazard due to the inherent danger of freezing followed by explosion. Therefore, acetylene is generally removed from the product stream by hydrogenation over a nickel or palladium catalyst depending on whether the removal occurs before ("front-end") or after product fractionation, respectively. In the case of front-end hydrogenation, a nickel catalyst operating at approximately 200°C is typically used. Since acetylene and butadiene are adsorbed much more strongly than ethylene, high selectivity toward hydrogenation of acetylene and butadiene with minimum loss of ethylene is achieved. Small amounts of H_2S are typically added to lower the catalyst activity and to further minimize the hydrogenation of ethylene (*1*).

A significant process improvement would eliminate acetylene from the product stream yet permit recovery of butadiene in addition to ethylene. As noted above, the catalysts are generally active metals which are supported on "inert" substrates. On such catalysts, both acetylene and butadiene are hydrogenated to a substantial degree. Therefore, in the development of a new front-end catalyst, one must consider:

- selective hydrogenation of acetylene versus butadiene and ethylene
- that hydrogenation of acetylene to ethylene is preferable
- minimal hydrogenation of butadiene and ethylene.

Furthermore, because of the economics of an existing plant, there should be no changes in reactor design or plant opera-

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tion, that is, no new investment. The net effect would be higher recovery of ethylene and butadiene and represent considerable cost savings.

One route to designing such a catalyst is to establish kinetic control over the hydrogenation. This can be accomplished by placing the active metal catalyst inside a support that takes advantage of the differences in size and shape of the acetylene, butadiene, and ethylene molecules. Zeolites with their high surface area and molecular sieving ability are excellent candidates as supports for such a shape-selective hydrogenation. Furthermore, zeolites can be ion-exchanged such that accessibility to the pore structure can be fine-tuned. Deposition of an active metal catalyst within the zeolite pore structure means that the molecular dimensions and configurations of the reactants and products would determine the reaction selectivity.

At least three types of reaction selectivity over zeolite catalysts have been described (*2*):

- Product selectivity: molecular sieving selectivity of the zeolite provides the basis for determining the product spectrum—molecules smaller than the pore openings can exit from the framework into the product stream while larger molecules are retained within the framework.
- Transition state selectivity: certain reactions are prevented because the corresponding transition state requires more space than is available within the framework of the zeolites.
- Reactant selectivity: only those components of the feed stream that are small enough to enter the pores can react while larger ones are excluded.

The difference in the molecular sizes of acetylene ~3.3 Å, ethylene ~3.9 Å, and butadiene ~4.2 Å, compared to the pore openings of various zeolites shown in Table 1, indicates potential for reactant selectivity. Butadiene, because of its larger size, could be excluded from entering the zeolite framework which would be accessible to the smaller acetylene and ethylene molecules. By choosing the smallest pore zeolite that permits acetylene and ethylene access to the intracrystalline voids and placing the active metal catalyst within those voids, diffusional limitations should result in improved hydrogenation selectivities over nonmicroporous supports. That is, acetylene will be hydrogenated within the framework at the active metal sites while butadiene, because it cannot enter the framework, passes through the bed unreacted. For the selective reaction of acetylene vs ethylene and butadiene, the eight-ring zeolites are preferred on the basis of size discrimination. Our studies, therefore, focused on zeolite A as a catalyst support because of its availability, cost, and its ability to be used as an ion-exchange substrate.

TABLE 1

Comparison of Sizes of Reactants and Sorption Probes and the Pore Dimensions of Zeolites

Reactant	Approx. size (Å)[a]	Sorption probe	Notation in text	Approx. size (Å)[a]
C_2H_2	3.3	CH_3OH	MeOH	3.7
C_2H_4	3.9	CH_3CH_2OH	EtOH	4.0
C_4H_6	4.2	$CH_3(CH_2)_2OH$	*n*PrOH	4.3

Zeolite	Number of *T*–O groups forming pores	Approx. pore dimensions (Å)[b]
Sodalite	6	2.8
A, ZK-5, Rho	8	4.3
ZSM-5, ZSM-11	10	6.3
X, Y	12	8

[a] Determined from space-filling models.

[b] Reference (*5*, p. 65).

Zeolite A is composed of four-, six-, and eight-membered rings of silicon and aluminum tetrahedra. Structurally, it can be described as a cubic arrangement of truncated octahedral units (sodalite or β-cages). These units, of free diameter 6.6 Å, are joined through oxygen bridges at the four-rings enclosing a cavity (α-cage) with a free diameter of 11.4 Å. Normally, zeolite A is synthesized in the sodium form. Other forms are prepared by conventional ion-exchange methods and many of their structures are known (*3*). From the crystal structures, it is known that divalent ions prefer a site associated with the six-ring. The monovalent ions reside primarily in the six-ring site as well as the eight-ring site. In a previous communication, we showed that by changing the size of the monovalent ion and hence partially blocking the eight-ring pore, the molecular sieving and hence reactant selectivity of the zeolite could be modified (*4*). In this paper, we describe the use of sorption measurements to fine-tune the design of a zeolite A-supported catalyst that permits selective hydrogenation of acetylene in the presence of butadiene and ethylene.

EXPERIMENTAL DETAILS

Catalyst Preparation

Samples of zeolite 5A were obtained from Linde. Zeolites 3A and 4A were obtained from Linde and Zeochem. Catalyst C-36, nickel supported on silica–alumina, was obtained from United Catalysts. Typically, samples of zeolite A powder were contacted with dilute solutions of $Ni(NO_3)_2$ at 90°C for 24 h. The resulting slurry was filtered, washed, and dried. Back-exchanges of alkali cations were performed by contacting samples of the Ni-exchanged zeolite A with solutions of the alkali metal carbonates at reflux. Surface treatments (other than those performed in the reactor) were performed by contacting the zeolite with the neat liquid, typically tetraethylorthosilicate and lead(II) 2-ethylhexanoate. The treatments and approximate unit cell compositions of the catalysts, as determined by chemical analysis (with oxygen content assumed), are given in Table 2.

Reactor Studies

Catalyst powders were pressed into wafers having a thickness of $\frac{1}{8}$ in. (0.3 cm) in a hydraulic press at 6000 psia (41,000 kPa). The resulting wafers were crushed and seived to 250 μm/425 μm (−40/+60 ASTM Std. sieve number). Hydrogenations were carried out in glass-lined $\frac{1}{4}$-in. U-tube reactors capable of holding 0.5 to 4 cc of sieved catalyst. Inside an explosion containment vessel, the reactors were heated to the desired temperatures. In a typical experiment, the catalyst (1 cc) was reduced under a flow of hydrogen at ~400°C for 2 to 14 h. Gas mixtures were simulated to those used in a typical front-end hydrogenation unit. A mixture of hydrogen (28%), ethylene (32%), acetylene (0.35%), butadiene (0.65%), and helium (balance) was fed through electronic flow controllers. Under actual plant operating conditions the balance is composed of a mixture of saturated hydrocarbons. Unless otherwise noted, experiments were conducted at atmospheric pressure with contact times of 0.5 to 1 s. Hydrogen sulfide, thiophene, and other potential pacifiers were metered to the reactor with flow controllers or with hypodermic needles through injection ports. Catalyst activity was controlled by careful addition of these pacifiers. The catalyst selectivity was determined at or near the acetylene breakthrough point (i.e., 99–100% acetylene hydrogenation). The product stream was analyzed on-line via a gas chromatograph.

Sorption Characterization

A full description of this method has been published previously (*5*). Essentially, a sample of the zeolite is put into a preweighed cell employing a leak-tight vacuum stopcock. The sample is heated to 425°C under vacuum to a residual pressure of $\sim 2 \times 10^{-5}$ mm, cooled, and weighed. Subtraction of the cell weight provides the weight of the dry, evacuated zeolite as well as its initial water content. The cell is then attached to a manifold where the zeolite is exposed to a solvent vapor at room temperature. Subtracting the cell and evacuated zeolite weights provides the weight sorbed by the zeolite in each cell. After correction for a small amount adsorbed on the surface of the zeolite particles, the amount sorbed per gram of dry zeolite is calculated. The

TABLE 2

Catalyst Descriptions

Catalyst designation	Starting zeolite	Contact solutions^a	Ion content^b
Ni,Ca-A(I)	5A^c	0.25 g/500 cc	$Na_{3.3}Ca_{4.5}Ni_{0.18}$
Ni,Ca-A(II)	5A^c	0.06 g/500 cc	$Na_{3.3}Ca_{4.6}Ni_{0.04}$
Ni,Na-A(III)	4A^c	0.275 g/500 cc	$Na_{9.6}Ni_{0.16}$
Ni,Na-A(IV)	4A^c	0.50 g/500 cc	$Na_{7.0}Ni_{0.34}$
Ni,Na-A(V)	4A^c	0.05 g/250 cc	$Na_{11.4}Ni_{0.013}$
Ni,K-A(VI)	4A^c	0.29 g/500 cc 4.4 g K_2CO_3/44 cc	$Na_{6.9}K_{5.0}Ni_{0.15}$
Ni,K-A(VII)	Ni,Na-A(III)	10 g K_2CO_3/100 cc	$Na_{3.9}K_{7.6}Ni_{0.17}$
Ni,K-A(VIII)	3A^c	0.275 g/500 cc	$Na_{4.0}K_{5.8}Ni_{0.20}$
Ni,K-A(IX)	3A^{c,d}	0.275 g/80 cc	$Na_{6.6}K_{4.2}Ni_{0.14}$
Ni,K-A(X)	Ni,Na-A(IV)	10 g K_2CO_3/100 cc	$Na_{2.1}K_{6.8}Ni_{0.31}$
Ni,K-A(XI)	3A^e	0.275 g/500 cc	$Na_{6.3}K_{4.8}Ni_{0.23}$
Ni,K-A/TEOS(XII)	Ni,K-A(VII)	100 cc TEOS^f	
Ni,K-A/Pb(XIII)	3A^g	0.75 g/333 cc 28.5 cc Pb(II)EH^g	$Na_{6.3}K_{4.8}Ni_{0.46}Pb_{1.1}$
Ni,Rb-A(XIV)	Ni,K-A(VI)	7.5 g Rb_2CO_3/44 cc	$Na_{7.6}Rb_{3.8}Ni_{0.46}$
Ni,Rb-A/TEOS(XV)	Ni,Rb-A(XIV)	100 cc TEOS^b	
Ni,Cs-A(XVI)	Ni,K-A(VI)	10 g Cs_2CO_3/44 cc	$Na_{8.1}Cs_{3.7}Ni_{0.21}$

[a] g $Ni(NO_3)_2 \cdot 6H_2O$/cc H_2O/10 g zeolite, 24 h at 90°C.

[b] Framework, $Si_{12}Al_{12}O_{48}$.

[c] Linde.

[d] Extrudate $\frac{1}{8}$ in.

[e] Zeochem.

[f] TEOS, tetraethylorthosilicate.

[g] Pb(II)EH, lead(II)2-ethylhexanoate.

correction for the amount adsorbed on a zeolite surface is nontrivial and the detailed procedure is included in a previous study (*5*). All of the data in Tables 3, 5, and 6 have been corrected for surface adsorption and represent the amounts sorbed into the zeolite frameworks.

ESCA

The ESCA data were obtained on an automated Du Pont 650 photoelectron spectrometer using Mg$K\alpha$ excitation (1254 eV) generated at 300 W. The powdered samples were packed into a cup sample holder. The data were collected using standard procedures and analyzed from areas of the pertinent photoelectron peaks using Scofield cross sections (*6*).

RESULTS AND DISCUSSION

Sorption Studies

Sorption measurements monitor changes in the accessible framework volume and the effective size of the eight-ring pore opening of ion-exchanged forms of zeolite A. The probe molecules chosen were methanol with a molecular dimension of ~3.7 Å, ethanol ~4.0 Å, and *n*-propanol ~4.3 Å. Methanol provides information of framework accessibility to acetylene while ethanol and *n*-propanol provide information on ethylene and butadiene accessibility. Results for a series of samples of exchanged zeolite A are given in Table 3. Also shown in Table 3 are the ratios of sorption values, for example, the amounts of sorbed ethanol to methanol. If the probe molecules pack as a liquid

TABLE 3

Sorption Results for Ion-Exchanged Zeolite A

	Ni,Ca (I)	Ni,Na (III)	Ni,K (VI)	Ni,K (VII)	Ni,Rb (XIV)	Ni,Cs (XVI)
Sorption data[b]						
MeOH, ~3.7 Å	21.9	19.5	17.0	16.5	14.6	10.6
EtOH, ~4.0 Å	19.9	16.3	11.4	1.7	8.6	0.19
*n*PrOH, ~4.3 Å	18.6	9.6	0.45	0.0	0.0	0.0
Ratio of amounts sorbed into frameworks						
EtOH/MeOH	0.908	0.836	0.666	0.106	0.589	0.018
*n*PrOH/EtOH	0.935	0.586	0.040	0.0	0.0	0.0
*n*PrOH/MeOH	0.849	0.490	0.027	0.0	0.0	0.0
Calculated framework sorption parameters						
FW	1695	1658	1791	1824	1953	2119
uc/g[a] 10^{20}	3.554	3.632	3.364	3.302	3.084	2.843
cc/g	0.665	0.679	0.629	0.617	0.577	0.532
g/cc	1.505	1.472	1.590	1.620	1.734	1.881
Voids/uc	934	926	883	867	878	860
Void f	0.500	0.495	0.472	0.464	0.470	0.460
Voids cc/g	0.332	0.336	0.297	0.286	0.270	0.244
Comparison of calculated and measured sorption values						
Acc vol (cc/g)	0.278	0.281	0.246	0.236	0.224	0.202
MeOH vol (cc/g)	0.277	0.246	0.215	0.208	0.184	0.134
Occupied fraction (%)	99.3	87.5	87.2	88.1	82.2	66.4

[a] Unit cell (uc) volume = 1870 Å^3.

[b] Grams sorbed into framework in 20 h per 100 g of dry sample.

and fill the same volume, these ratios should be close to 1.0 because their densities are so close. These ratios therefore provide a measure of packing constraints imposed on the molecules sorbed within the zeolite framework.

The following illustrates how the accessible pore volume may be calculated. From the chemical analysis of each sample shown in Table 2, a formula weight (FW) is calculated which, in turn, provides the number of unit cells per gram (uc/g) or 6×10^{23} uc ÷ FW g. Using 1870 Å^3 as the unit cell volume (*7*) yields the volume per gram of dry zeolite (cc/g) or the density (g/cc). The total void space in a unit cell (voids/uc) is obtained by subtracting the volume occupied by the TO_2 (T = Si or Al) groups and the cations. It is assumed that a TO_2 group occupies the same volume as that in quartz (~37.6 Å^3) and the volume of a cation is calculated assuming a sphere of known ionic radius (*8*). The total void space per gram (voids cc/g) is obtained by multiplying the volume per gram times the void fraction (which equals the voids/uc ÷ 1870). As noted earlier, the lattice contains sodalite or β-cages, volume ~151 Å^3, which cannot sorb methanol or larger molecules and this volume must be subtracted from the total pore volume. Consequently, the calculated accessible pore volume (Acc vol, cc/g) is corrected for this volume.

The volume occupied by methanol molecules (MeOH vol, cc/g) is calculated from the measured amount sorbed ÷ the density of liquid methanol using the assumption that methanol packs as a liquid. The occupied fraction is the volume occupied ÷ by the calculated accessible pore volume. To demonstrate how well this calculation estimates the accessible pore volume, Table 3 lists the calculated accessible volume (Acc vol) and the measured MeOH volume (assuming liquid packing). For sample Ni,Ca-A(I), the volume occupied by methanol is equal to the calculated value within experimental error and shows that Ca^{2+} ions do not constrain the packing of methanol in the framework. This agreement demonstrates the validity of the assumptions that were made and indicates that methanol packs as a liquid within the α-cages. The sorption values and ratios for this sample are higher than those for the other exchanged samples indicating that larger ions constrain the packing of methanol within the zeolite A framework. From the data presented in Table 3, it is apparent that the degree of exchange and the size of the cation have profound influences on the amounts sorbed by the framework.

Reduction in methanol sorption capacity indicates decreased internal pore volume and relates to the exchanged ionic size. The calcium form of zeolite A, sample Ni,Ca-A(I), as noted above, shows little differentiation for *n*PrOH, EtOH, and MeOH sorption which indicates that this sample should not be a reactant selective catalyst. Calcium ions site in the six-ring pores leaving the eight-rings open, and *n*-propanol easily enters the internal pores of the zeolite. Because it is smaller in size than *n*-propanol, butadiene should also access the internal framework of this sample. Therefore, if the active catalytic sites are within the framework, butadiene will also be hydrogenated.

Methanol occupancy depends on the size and amount of the cations in the framework. The occupied fraction is reduced depending on the charge compensating cations and indicates that these cations impose packing constraints on the methanol molecules sorbed in the framework. In fact, the bulkiness of the cesium ion has limited the methanol occupancy to two-thirds of the available volume. The effects on packing are much more pronounced for the larger probe molecules, ethanol and *n*-propanol.

In the sodium-exchanged form, Ni,Na-A(III), some pore narrowing has occurred (as evidenced by reduced *n*-propanol sorption) which should translate to reduced sorption by the framework for the butadiene molecule. In the cases of the K^+-, Rb^+-, and Cs^+-exchanged forms, essentially no *n*-propanol is adsorbed and these samples should show significant reduction in the hydrogenation of butadiene. However, ethanol sorption is significantly lowered for some samples. This observation suggests that ethylene, produced by the hydrogenation of acetylene within the framework, should have difficulty in migrating through the framework and entering the product stream. Thus, optimum catalyst design must take into account the effects of cation sizes, loadings, and the subtle changes in sorption behavior. Although sorption data are useful in demonstrating differences in molecular sieving from one exchanged form to the next, the data do not provide a measure of the catalytic activity of the external surface of the zeolite particles (vide infra).

Catalytic Results

As noted earlier, the objective of this study was to eliminate or reduce the hydrogenation of butadiene while completely hydrogenating acetylene under the same conditions. Total hydrogenation of acetylene is a requirement in plant practice because of safety reasons and butadiene recovery is important for economic reasons. As such, our studies were conducted using "acetylene breakthrough data" so that we were always in the regime where acetylene was almost, if not totally, reacted. We then explored ways to increase the amount of butadiene in the product stream. To compare the hydrogenation selectivity of different catalysts, we define a figure of merit, FM, as the ratio of hydrogenated acetylene to hydrogenated butadiene under the condition that ethylene passed through the bed unreacted. For the commercially available C-36 catalyst under plant conditions, about 60% of the butadiene and all of the acetylene in the feed is hydrogenated, yielding an FM ~ 1.6. As thiophene is added to the reactor feed, catalyst activity decreases much faster than changes in FM. This result demonstrates the accessibility of the catalytic sites to thiophene. Using Ni,Na-A, Ni,Ca-A, and Ni,K-A catalysts of varying nickel loadings produced no hydrogenation selectivity; i.e., acetylene, ethylene, and butadiene were totally hydrogenated, FM = 1. By a lowering of the nickel content, the catalyst activity and hence the degree of hydrogenation were decreased (ethylene and butenes appeared in the product stream), but FM was still 1. The catalytic sites are accessible to all reactants; consequently reactant selectivity is not in effect.

The lack of reactant selectivity suggests that the catalytic sites dominating the product spectrum must be located on the surface of the exchanged zeolites. Such metal sites on the external surface are more accessible in comparison to sites within the zeolite framework and can therefore override the contribution to the product spectrum made by sites within the zeolite framework. In order to limit the amount of active metal on the surface of the zeolite support, ion exchanges were very carefully performed. Since univalent exchanged forms of zeolites exhibit partial hydrolysis (*9*) in water suspension resulting in high pH, Ni^{2+} will hydrolyze causing formation of hydroxide species on the external surfaces of the zeolite crystallites (*10, 11*). Although dilute solutions were employed in the ion exchanges to minimize this hydrolysis, ESCA results given in Table 4 show the nickel to be concentrated on the external surface in the unused sample. Reduction of the sample leads to some apparent migration from the surface to the framework but the nickel is still concentrated on the external surface. These surface sites are accessible to all of the reactants and cause FM to be close to 1.

TABLE 4

ESCA and Chemical Analysis Results for Ni,K-A(XI)

	Ni/Si(bulk)	Ni/Si(surface)	Surface/bulk
Unused	0.019	0.82	43.2
Reduced[a]	0.019	0.24	12.6
Used[b]	0.019	0.81	42.6
Regenerated	0.019	0.31	16.3

[a] 400°C, H_2.

[b] Two regenerations and three reductions.

As the ESCA results show that a small fraction of the metal catalyst was incorporated within the framework, we examined the possibility of eliminating the surface reactivity while maintaining active, internal catalytic sites. Catalytic poisons were used to reduce the contribution of the unselective surface sites to the product distribution. Initial attempts at treating the nickel-exchanged zeolites with H_2S led to complete deactivation of the catalyst because the H_2S sorbed into the framework and deactivated the sites within. The external catalytic sites, however, could be selectively poisoned by treatment with molecules, such as phosphine, which are too large to access the sites within the zeolite framework (*12, 13*). The results of such an addition of tri-*n*-propylphosphine, TPP, to the feed stream are illustrated in Figs. 1A and 1B. Upon injection of 1–5 cc of TPP to the feed stream, the activity of the Ni,Ca-A(II) catalyst decreases sharply from total hydrogenation of both acetylene and butadiene, FM = 1, to hydrogenation of 73 and 11%, respectively, FM = 6.6. Thus, poisoning of the catalyst sites on the exterior of the zeolite permits reactant selectivity to be imposed by the framework. After 6.25 h of reactor operation, catalyst activity increased yielding 100% acetylene and 28% butadiene hydrogenation, with FM = 3.6. Hydrogenation selectivity virtually disappeared as the run continued but, upon readdition of TPP, the initial high selectivity was again obtained. Similarly, phosphine

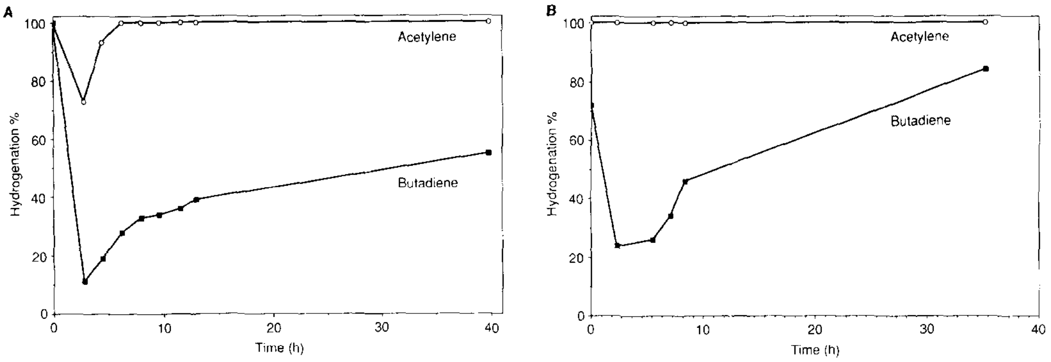

FIG. 1. (A) Effect of time on selectivity for Ni,Ca-A(II) treated with tri-*n*-propylphosphine. (B) Effect of time on selectivity for Ni,Na-A(IV) treated with tri-*n*-propylphosphine.

treatment of Ni,Na-A(IV) led to a very significant decrease in the butadiene hydrogenation from 100 to 24%, FM = 4.2. Again, hydrogenation selectivity, with time, was gradually lost. Other bulky phosphines such as tri-*n*-butylphosphine and tripentylphosphine were also used successfully as poisons to improve the selectivity. These results show that poisoning of the catalyst sites on the external surface is essential to obtaining the highly selective hydrogenation imposed by the framework. Apparently, during prolonged reactor operation, the phosphines may decompose and/or desorb from the metal sites on the surface of the zeolite particles making them active once again.

Thiophene, a sulfur-containing catalytic poison with a molecular dimension of about 5.4 Å (*14*) was added to the feed stream at levels of <100 ppm. The large size of thiophene precludes it from entering the framework of zeolite A. The catalytic and sorption data, for samples of exchanged zeolite A, are given in Table 5. For comparison, nickel supported on silica–alumina, C-36, without thiophene addition has FM ~ 1.5 and is virtually inactive with thiophene present. At similar exchange levels, as the size of the ion occupying the site in the eight-ring opening increases, selectivity, expressed as FM, also increases up to the Cs^+ material. Alcohol sorption amounts decrease steadily down the table indicating increased packing constraints imposed by the charge compensating cations. Complete inhibition of ethanol sorption indicates that ethylene generated by hydrogenation of acetylene at sites within the zeolite framework is not able to exit from the zeolite and enter the product stream. These ethylene molecules, because they are locked in the framework, will make it inaccessible for further adsorption and catalysis. Consequently, reactions at the surface will dominate the product spectrum; the reduced FM value for the Ni,Cs-A sample provides evidence of going too far in the degree of ion exchange and attempting to maximize size adsorption selectivity.

The trade-off in reactant selectivity (reaction at sites within the framework) versus reaction at sites on the external surface is typical in the design of zeolite catalysts. It is interesting to note that the degree of hydrogenation of the acetylene in the absence of ethylene is significantly greater over the silica-alumina support than over the zeolite support. Whereas 10 to 15% of the acetylene is converted to ethane over C-36, generally 5% or less is converted over the zeolite-based catalyst. This corresponds to less than 0.06% saturation of the ethylene and acetylene to ethane.

Product distributions can be influenced by other kinds of surface treatments, such as phosphorus, boron, aluminum, and silicon (*15*). Treating the exchanged zeolite

TABLE 5

Reactor Results (Thiophene Added)

Catalyst	Conversion of		Figure of merit (FM)	Sorption data[a]		
	C_2H_2 (%)	C_4H_8 (%)		MeOH	EtOH	*n*PrOH
C-36[b]	100	65	1.5			
	99.8	61	1.6			
Ni,Na-A(V)	100	39	2.6	20.0	18.3	11.8
$Na_{11.4}Ni_{0.013}$	99.4	31	3.2			
Ni,K-A(IX)	100	17	5.9	15.6	14.5	5.3
$Na_{6.6}K_{4.2}Ni_{0.14}$	99.7	12	8.3			
Ni,K-A(X)	100	20	5	16.3	10.3	1.5
$Na_{2.1}K_{6.8}Ni_{0.31}$	99.8	19	5.3			
Ni,Rb-A(XIV)	100	13	7.7	14.6	8.6	0.0
$Na_{7.6}Rb_{3.8}Ni_{0.46}$	99.4	11	9			
Ni,Cs-A(XVI)	100	23	4.3	10.7	0.2	0.0
$Na_{8.1}Cs_{3.7}Ni_{0.21}$	99.7	19	5.2			

[a] Grams sorbed into framework in 20 h exposure per 100 g of dry sample.

[b] Thiophene not added for this sample; addition of thiophene deadens the activity.

with tetraethylorthosilicate, TEOS, to deposit a silica coating generally produced higher selectivities as shown in Table 6. For example, after treatment of Ni,K-A(VII) with TEOS, FM increased to ~9.1 compared to an FM ~5.9 for the untreated catalyst. Similarly, TEOS treatment of Ni,Rb-A(XV) improved FM to ~10.0 compared to an FM ~7.7 for the untreated catalyst. For both of these samples, TEOS treatment did not alter the sorption data significantly. Thus, the TEOS treatment was mild enough such that the size of the zeolite pore openings was not affected. Therefore, the TEOS treatment provides a small amount of silica coating atop the surface metal sites thereby limiting their accessibility to the reactants.

TABLE 6

TEOS[a] Treatment of Catalysts

Catalyst	Sorption data[b]			FM
	MeOH	EtOH	*n*PrOH	
Ni,K-A(VII) (Control)	17.0	3.0	0.4	5.9
Ni,K-A/TEOS(XII)	17.1	5.0	0.6	9.1
Ni,Rb-A(XIV) (Control)	15.2	9.2	0.3	7.7
Ni,Rb-A/TEOS(XV)	15.1	8.6	0.3	10.0

[a] Tetraethylorthosilicate.

[b] Grams sorbed into framework in 20 h exposure per 100 g of dry sample.

Instead of adding catalytic poisons to the reactant stream, an attempt was made to deactivate the surface sites by adding lead(II), a well-known poison of active metal catalysts. Treatment of Ni-exchanged zeolites with lead-containing compounds larger than the pore opening should provide permanent deactivation of the surface sites. Such treatments, using lead(II) 2-ethylhexanoate, were successful and led to selective hydrogenation. At atmospheric pressure with no thiophene or H_2S addition to the feed stream, 29% of the butadiene was hydrogenated at 99.8% acetylene conversion, FM = 3.4, over Ni,K-A/Pb(XIII). Increasing the pressure to 220 psia did not

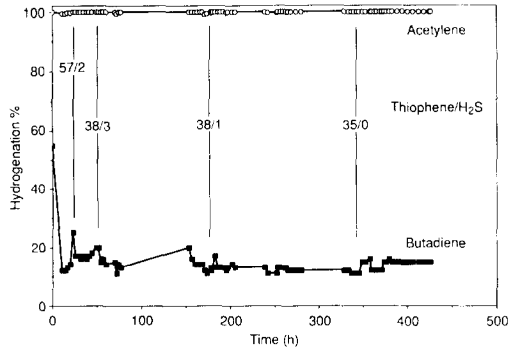

FIG. 2. Selectivity results from life studies for Ni, K-A/TEOS(XII). (Thiophene/H_2S ratio is ppm/ppm.)

alter the selectivity substantially, FM ~ 2.9–3.3. Upon addition of small amounts of a poison to the feed stream, FM increased to 5.0. This suggests that there may also be some active sites in surface micropores (>5 Å and not accessible to the large lead-containing poison). After 8 days on stream, both selectivity and activity showed no sign of deactivation. In another long-term (20-day) test using Ni,K-A/TEOS(XII), excellent selectivities could be maintained at atmospheric pressure by careful monitoring of the product stream and judicious control of the surface poisons (thiophene and H_2S) (Fig. 2). Similarly, Ni,K-A(VIII) was found to operate satisfactorily at atmospheric pressure with contact times of 0.5 to 1.0 s with thiophene added. Excellent selectivities were also obtained at 220 psia and the same contact times. Upon increasing the contact time to that commonly used in typical hydrogenation units (10 s), it was found that the selectivity was not maintained. However, by addition of H_2S in the range of 20 to 60 ppm instead of thiophene, the selectivity can be sustained at 99 to 100% acetylene hydrogenation with only ~20% butadiene loss, FM ~ 5.0. The catalyst gradually deactivates over a period of 30 days, but selectivity can be maintained by gradually reducing H_2S levels. After 30 days, regeneration is necessary. Calcination of the deactivated catalyst in air at 450°C is sufficient to return the catalyst to its original activity; however, selectivity was decreased to 99–100% acetylene hydrogenation and 25% butadiene loss, FM ~ 4.0. After 30 days, the catalyst again required regeneration and an additional 5% butadiene loss was realized. Thirty additional days resulted in selectivity losses to ~35% butadiene hydrogenation, FM ~ 2.9. The losses in selectivity are probably due to resiting of the nickel on and within the framework.

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