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Characterization of Acid–Base Catalysts by Calorimetric Titration

II. Effect of Poisoning on Titration Curves and Alcohol Dehydration Activity

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Several commercial aluminas, silica–aluminas and clays have been subjected to poisoning by ammonia and organic bases and subsequently characterized (1) by calorimetry, yielding the heat of adsorption of bases and acids as a function of coverage (2) activity in ethanol and methanol dehydration reactions. A correlation developed in the previous paper [Bakshi, K. R., and Gavalas, G. R., *J. Catal.* **38**, 312 (1975)] describing the activity of fresh catalysts in terms of their acidity and basicity distributions has been used to describe the activity of the poisoned catalysts. Certain rather subtle selectivity changes caused by poisoning have been explained by the corresponding changes in the acidity and basicity distributions.

NOMENCLATURE

A_i	Acidity in *i*th group defined by Table 3
B_i	Basicity in *i*th group defined by Table 4
f_i	Specific rate for *i*th group
r	Rate of product formation, mol product/hr-g catalyst
s_{ij}	Effective group density for *i*th group in *j*th catalyst, defined by Table 5
σ	Selectivity defined by Table 1
W	Amount of titer adsorbed, mmol/g catalyst
$-\Delta H$	Heat of adsorption, kcal/mol

INTRODUCTION

Most of the literature on catalyst poisoning has been concerned either with utilizing poison adsorption as a tool to elucidate reaction mechanisms or in relation to industrial catalytic processes. Thus the dynamics of poisoning and other deactivation processes in catalytic reactors and the resulting changes in activity and selectivity have all received considerable attention, see e.g., the review of Butt (*3*). Whether from the fundamental or applied standpoint, however, an investigation of catalyst poisoning brings to focus two important issues:

a. The change of the catalyst state brought about by poison adsorption.

b. The effect of the change in the catalyst state on the reaction kinetics; especially on the catalyst activity and selectivity.

These aspects of catalyst poisoning are intimately related to catalyst characterization, a very difficult problem at the center of current catalytic research.

In the case of acidic catalysts, acidity has provided a measure for character-

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ization and correlation with catalytic activity, Tanabe (9), Covini *et al.* (*4*). In the previous paper (*2*) we have used the heat of adsorption as a function of coverage to characterize the acidity and basicity distributions of a number of commercial aluminas. Almost all catalysts tested were found to possess nonuniform acidic and basic sites in agreement with similar behavior reported for other commercial catalysts, Hirschler (*6*), Tanabe (*9*). A group analysis involving determination of the relative activity of sites of different strengths was then developed to correlate the acid–base distributions with the activity of catalysts in alcohol dehydration reactions.

Since acidity and basicity distributions were found to be a suitable means of catalyst characterization, capable of describing the dehydration activity and selectivity of fresh catalysts, the present work is devoted to extend these results to poisoned catalysts. It includes a study of the effects of different poisons on the catalyst acidity and basicity distributions and attempts to explain quantitatively in terms of these distributions the activity and selectivity towards alcohol dehydration reactions.

EXPERIMENTAL METHODS

1. Reagents. All chemicals used in this investigation were high purity reagent grade and were used without further purification. Benzene used for calorimetric titrations was dried over molecular sieve before use.

2. Catalysts. Commercial catalysts used for this investigation were: KSFO montmorillonite clay obtained from Chemetron Corp.; Filtrol Grade 49 (F49) containing 4.5% MgO, 17.5% Al_2O_3 and 74% SiO_2 obtained from Filtrol Corp.; Aerocat Low Cracking (ALC) containing 13% Al_2O_3 and 87% SiO_2 obtained from American Cyanamid Co.

3. Catalyst pretreatment and poisoning. All catalysts were pretreated at 300°C for 5 hr in a dry nitrogen atmosphere before further use. The pretreated dry catalyst samples were partially poisoned by stepwise titrating at room temperature with a known amount of a standardized solution of an amine in dry benzene. The catalyst suspension was stirred during titration to obtain a uniform poisoning. The poisoned catalyst was dried at 200°C and stored under dry conditions before further use.

4. Activity measurements. Evaluation of the catalyst activity for alcohol dehydration was carried out in a differential microreactor suspended in a well-mixed air bath. The reactor temperature was maintained within ±0.2°C of the reported values by a proportional temperature controller. Alcohol, fed by a multispeed infusion pump, was vaporized and mixed with dry nitrogen to attain the desired feed concentration. The reaction products were analyzed by a flame ionization detector after separation on a 10% Carbowax 20 m column. The details of the experimental setup are described elsewhere (*1*).

5. Calorimetric titrations. Acidity and basicity distributions of both fresh and poisoned catalysts were carried out by calorimetric titrations described in the previous paper (*2*). The titrations were used to evaluate the heats of adsorption of *n*-butylamine and trichloroacetic acid as a function of coverage.

RESULTS

1. Activity measurements. Activities for alcohol dehydration of fresh and partially deactivated catalysts were determined under identical conditions and the observed rates of olefin and ether formation are given in Table 1. Poisoning was observed to affect both ether and olefin formation in all cases and as shown in Table 1, the decrease in the relative rates of olefin and ether formation depends on the poison used to deactivate the catalyst. Weak bases such as aniline, pyridine and ammonia affect ethylene formation more

TABLE 1

EFFECT OF PARTIAL CATALYST POISONING ON DEHYDRATION ACTIVITY AND SELECTIVITY[a]

Catalyst	Rate of formation: Ethylene ($r \times 10^4$)	Rate of formation: Ether ($r \times 10^3$)	Selectivity[b] $\sigma\%$
Group A			
KSFO	105.3	29.9	14.97
KSFO + aniline	46.08	11.57	16.61
KSFO + pyridine	28.56	9.96	12.53
KSFO + *n*-butylamine	48.0	8.61	21.80
KSFO + triethylamine	49.9	4.95	33.5
Group B			
F49	26.9	14.2	8.65
F49 + aniline	17.92	12.7	6.59
F49 + ammonia	12.78	9.94	6.04
F49 + pyridine	12.43	8.64	6.71
F49 + *n*-butylamine	10.74	2.64	16.9
F49 + triethylamine	11.58	3.08	15.8
Group C			
ALC	5.66	2.39	10.60
ALC + *n*-butylamine	0.987	0.828	5.62

[a] Run conditions: feed concn, 6.64×10^{-3} mol/liter; reaction temp, 200°C.

[b] σ = (amount of alcohol converted to ethylene × 100)/(total alcohol conversion).

than ether formation, thereby decreasing the selectivity σ of the fresh catalyst. Strong bases such as *n*-butylamine and triethylamine in most cases affect ether formation more than ethylene formation, resulting in a higher selectivity relative to the fresh catalyst. This behavior is not general, however, since the adsorption of *n*-butylamine on the ALC catalyst decreases the selectivity towards ethylene. These results suggest that the effect of poisoning on catalyst selectivity depends on the strength of the poison as well as the nature of the catalyst surface in its fresh state.

The changes in selectivity upon poisoning by weak bases such as pyridine and aniline follow the same trend as in the results of Figueras *et al.* (*5*) for ethanol dehydration and of Jain and Pillai (*8*) for isopropyl alcohol dehydration. The decrease in σ upon poisoning by weak bases is not surprising considering the stronger dependence of olefin formation on acidic strength compared to ether formation (*2*).

The change in selectivity upon poisoning by strong bases shows a more complex pattern. The rate data on the poisoned KSFO and F49 shown in Table 1 suggest that poisoning the catalyst by a fixed molar amount of either a weak or a strong base affects ethylene formation to the same extent. However, the reduction in ether formation is stronger so that the overall selectivity shifts in favor of ethylene formation. To investigate this rather unexpected behavior, the effect of *n*-butylamine poisoning on the selectivity of KSFO was tested at various poisoning levels. The results shown in Table 2 indicate that at all poisoning levels, ether formation is affected more than olefin formation. As the amount of adsorbed poison increases, the selectivity towards ethylene increases at first and then approaches a constant level.

2. Acidity and basicity distributions. The catalysts tested in this investigation have been characterized by their acidity and basicity distributions obtained by calorimetric titrations. The same characterization can be applied to the poisoned catalysts and the changes in their acidity and basicity distributions may be invoked to explain the unusual selectivity changes attendant upon poisoning.

The acidity distributions of KSFO, F49 and ALC catalysts in their fresh and poisoned states are shown in Figs. 1–3 in terms of their differential heat of adsorption curves obtained by calorimetric titra-

TABLE 2

EFFECT OF POISONING LEVEL ON DEHYDRATION ACTIVITY OF KSFO CATALYST

Poisoning level (mmol of *n*-butylamine/g catalyst)	Rate of formation: Ethylene ($r \times 10^4$)	Rate of formation: Ether ($r \times 10^3$)	Selectivity $\sigma\%$
0	105.0	29.90	14.97
0.0145	82.38	16.93	19.57
0.0909	60.22	8.57	26.00
0.1454	37.59	4.36	30.12
0.2000	16.22	1.94	29.48

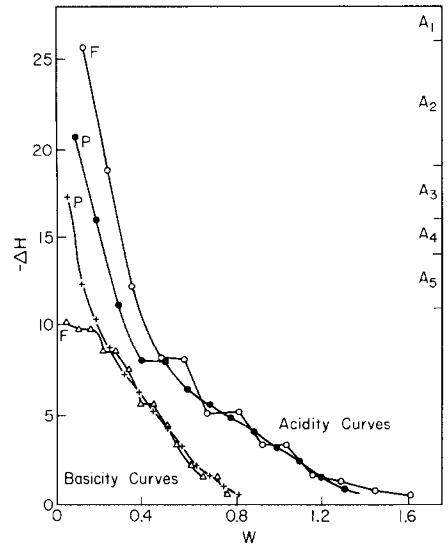

FIG. 1. Effect of *n*-butylamine poisoning on the heat of adsorption curves of KSFO: (○) fresh KSFO: acidity measurement; (●) poisoned KSFO: acidity measurement; (△) fresh KSFO: basicity measurement; (+) poisoned KSFO: basicity measurement.

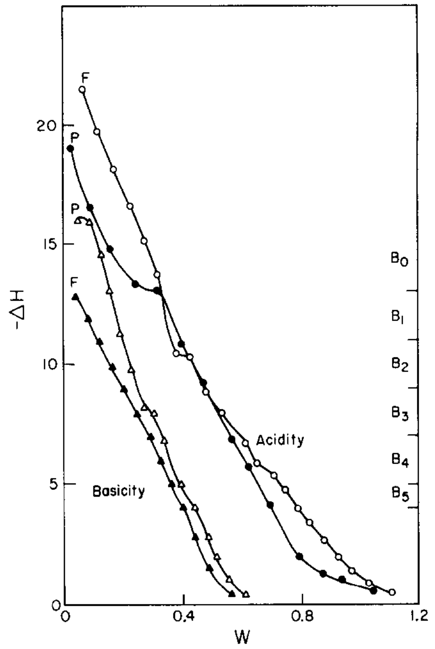

FIG. 2. Effect of *n*-butylamine poisoning on the heat of adsorption curves of F49: (○) fresh F49: acidity measurement; (●) poisoned F49: acidity measurement; (△) fresh F49: basicity measurement; (▲) poisoned F49: basicity measurement.

tions. The differential heat curves are divided into various groups bounded by heat of adsorption limits as indicated in Fig. 1 resulting in the distribution of Table 3. The corresponding group acidities in the strongest acidic group for the fresh and poisoned catalysts suggests that in all three catalysts tested, partial poisoning affects the stronger acidic sites preferentially and the loss in strong acidities determined by the calorimetric titrations is in good correspondence with the poisoning level.

The basicity distributions of the fresh and poisoned states of the three catalysts are shown in Figs. 1–3 in terms of their differential heat of adsorption curves. A comparison of these curves suggests that

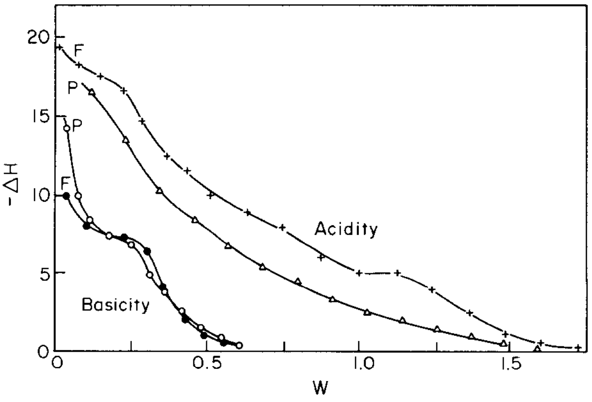

FIG. 3. Effect of *n*-butylamine poisoning on the heat of adsorption curves of ALC: (+) fresh ALC: acidity measurement; (△) poisoned ALC: acidity measurement; (●) fresh ALC: basicity measurement; (○) poisoned ALC: basicity measurement.

TABLE 3
ACIDITY DISTRIBUTION OF FRESH AND POISONED CATALYSTS

Catalyst[b]	Acidity[a] (mmol/g catalyst)				
	A_1	A_2	A_3	A_4	A_5
KSFO	0.0	0.24	0.05	0.04	0.06
KSFO + n-butylamine (0.12)	0.0	0.125	0.06	0.04	0.06
F49	0.0	0.136	0.104	0.06	0.09
F49 + n-butylamine (0.10)	0.0	0.03	0.09	0.08	0.16
ALC	0	0.02	0.22	0.08	0.13
ALC + $n$butylamine (0.10)	0	0	0.14	0.07	0.11

[a] Acidity groups are defined by heat of adsorption included between limits as follows: A_1: $26 < -\Delta H$; A_2: $19 < -\Delta H < 26$; A_3: $16 < -\Delta H < 19$; A_4: $14 < -\Delta H < 16$; A_5: $11 < -\Delta H < 14$.

[b] The numbers in parentheses represent poisoning level (mmol/g catalyst).

in all three catalysts, the maximum basic strength increases upon poisoning by n-butylamine. However, the total basicities obtained at the end of the calorimetric titrations are not affected by the adsorption of the poison. A division of the differential heat curves into groups of basicities as indicated in Fig. 2 leads to the basicity distributions given in Table 4.

A comparison of the basicity distributions for fresh and poisoned catalysts indicates that the adsorption of a strong base on an acidic site results in an increase in the strength of the neighboring basic sites for all three catalysts tested. The basicity distributions of the poisoned catalysts show an increase in the sites of the B_0 group at the expense of sites in B_1, B_2 and B_3 groups. Comparing the basicity distributions for the KSFO catalyst poisoned by a weak base such as pyridine with the basicity distribution of KSFO in its fresh state, it is apparent that there is a small increase in basicity although as shown by Table 4, the number of sites in each group remains essentially unaltered.

TABLE 4
BASICITY DISTRIBUTION OF FRESH AND POISONED CATALYSTS

Catalyst[b]	Basicity[a] (mmol/g catalyst)					
	B_0	B_1	B_2	B_3	B_4	B_5
KSFO	0.0	0.0	0.22	0.15	0.13	0.045
KSFO + pyridine	0.0	0.0	0.225	0.14	0.14	0.04
KSFO + n-butylamine	0.13	0.05	0.07	0.10	0.12	0.05
F49	0.0	0.11	0.09	0.09	0.06	0.025
F49 + n-butylamine	0.14	0.05	0.03	0.08	0.06	0.05
ALC	0.0	0.0	0.06	0.21	0.06	0.03
ALC + n-butylamine	0.05	0.015	0.03	0.16	0.06	0.05

[a] Basicity groups are defined by heat of adsorption included between limits as follows: B_0: $13 < -\Delta H$; B_1: $11 < -\Delta H < 13$; B_2: $9 < -\Delta H < 11$; B_3: $7 < -\Delta H < 9$; B_4: $5 < -\Delta H < 7$; B_5: $4 < -\Delta H < 5$.

[b] The poisoning levels are as in Table 3.

GROUP ANALYSIS

The acidity and basicity distributions of the fresh catalysts have been utilized in the previous paper (*2*) to develop a quantitative correlation for the rate of dehydration reactions. The group analysis attempted to determine the relative contribution of each group towards the total catalyst activity, and the specific rates were determined by least squares for both olefin and ether formation. The specific rates for the fresh catalysts are given in Table 5. Since the acid and base distributions of the poisoned catalysts are available, a group analysis may be attempted using these specific rates to predict the total catalyst activity for both ether and olefin formation. The effective group site densities s_{ij}, defined in

TABLE 5
SPECIFIC RATES FOR ALCOHOL DEHYDRATION[a]

Group	f_{ethylene}	f_{ether}
1	11933.7	914797.0
2	2379.0	32852.1
3	63.01	6322.86
4	5.608	2778.07
5	0.614	172.44

[a] Run conditions: feed concn, 6.64×10^{-3} mol/liter reaction temp, 200°C. Effective site density s_{ij} for jth catalyst is evaluated as follows: (a) ethylene: $s_{ij} = (A_i) \times (B_4 + B_5)$ for jth catalyst; (b) ether: $s_{ij} = (A_i) \times (B_4 + B_5) \times (B_1 + B_2) \times (A_4 + A_5)$ for jth catalyst. Specific rates obtained by Bakshi and Gavalas (*2*).

TABLE 6

GROUP ANALYSIS OF FRESH AND POISONED CATALYSTS[a]

Catalyst	Rate of formation				Percentage selectivity $\sigma\%$	
	Ethylene ($r \times 10^4$)		Ether ($r \times 10^3$)			
	Predicted	Observed	Predicted	Observed	Predicted	Observed
KSFO	100.52	105.30	32.04	29.90	13.56	14.97
KSFO + *n*-butylamine	51.23	48.00	9.40	8.61	21.41	21.80
F49	28.10	26.90	13.53	14.20	9.41	8.65
F49 + *n*-butylamine	8.51	10.74	3.00	2.64	12.42	16.90
ALC	5.58	5.66	2.60	2.39	9.72	10.60
ALC + *n*-butylamine	1.02	0.987	0.976	0.828	4.97	5.62

[a] The poisoning levels are as in Table 3.

Table 5 for both reactions, are estimated for poisoned catalysts using their acidity and basicity distributions. The evaluation of s_{ij} from the product of densities of acidic and basic sites possessing optimal strengths follows a correlation developed for fresh catalysts (*2*) and inherently assumes a random association of the acidic and basic sites on the catalyst surface. The rates predicted by group analysis are compared in Table 6 with the experimentally observed rates for all three catalysts in their fresh and poisoned states. The details of the group analysis are shown in Table 7 in terms of the actual contribution of each group for all the catalysts. A comparison of the various group contributions in the fresh states of KSFO and F49 catalysts indicates that the contribution from Group 2 is the most significant towards the rates of both olefin and ether formation. Upon poisoning by *n*-butylamine, part of the acidity in this group is lost with a simultaneous shift in the basicity distribution as shown in Table 4. The total change in weak basicities (B_4 and B_5) is insignificant with the result that olefin formation is affected in accordance to the loss of acidic sites. The effect of poisoning on ether formation is more pronounced since aside from affecting the strong acidic sites, there is a shift in the basicity distribution resulting in an increase in the B_0 group and a decrease in the B_1 and B_2 groups. Since the B_1 and B_2 basicity plays an important role in alkoxide formation (*2*) a decrease in the strong basicity affects ether formation more than olefin formation because the latter does not require an alkoxide intermediate.

In order to investigate the importance of the changes in basicity distribution upon poisoning by *n*-butylamine, two different models are employed to evaluate s_{ij} for the group analysis. Model A evaluates s_{ij} from the actual acid–base distributions obtained

TABLE 7

DETAILS OF GROUP ANALYSIS FOR VARIOUS CATALYSTS

Catalyst j	Product	Group contributions[a]				
		$f_1 s_{1j}$	$f_2 s_{2j}$	$f_3 s_{3j}$	$f_4 s_{4j}$	$f_5 s_{5j}$
KSFO	Ether	—	30.355	1.217	0.443	0.04
	Ethylene	—	99.92	0.56	0.04	0.006
KSFO + $BuNH_2$	Ether	—	8.377	0.78	0.241	0.02
	Ethylene	—	50.55	0.65	0.03	0.005
F49	Ether	—	11.393	1.677	0.44	0.35
	Ethylene	—	27.50	0.57	0.03	0.005
F49 + $BuNH_2$	Ether	—	1.675	0.914	0.391	0.045
	Ethylene	—	7.85	0.60	0.052	0.007
ALC	Ether	—	0.745	1.577	0.261	0.022
	Ethylene	—	4.282	1.25	0.042	0.006
ALC + $BuNH_2$	Ether	—	—	0.789	0.179	0.016
	Ethylene	—	—	0.970	0.045	0.007

[a] Total rate predicted by group analysis is given by $r_j = \Sigma_{i=1}^{5} f_i \cdot s_{ij}$ for jth catalyst.

from titrations of poisoned catalysts, whereas Model B evaluates s_{ij} by assuming that the poison decreases the acidity distribution by destroying an equimolar amount of strong sites and does not affect the basicity distribution of the fresh catalyst. Model B thus obtains the acid–base distributions of the poisoned catalyst state without an actual titration. The results of group analysis using these two models are shown in Table 8 for both dehydration products. Both models predict olefin formation rates satisfactorily with the predictions of Model A being slightly better based on overall least squares. In the case of ether formation, the predictions of Model B are good for catalysts poisoned by weak bases, in agreement with the fact that the basicity distribution is only slightly altered by weak bases as shown in Table 4. In contrast, the predictions of Model B for ether formation on catalysts poisoned by strong bases are high by a factor of two or so of the observed rates. Model A, on the other hand, provides satisfactory predictions for ether as well as ethylene formation independently of the strength of the adsorbed poison.

TABLE 8

Comparison of Group Analysis on Different Models' Observed Rates

	Rate of formation					
	Ethylene			Ether		
	Predicted by model			Predicted by model		
Catalyst[a]	A	B	Observed	A	B	Observed
KSFO + BuNH$_2$ (0.12)	51.23	52.71	48.00	9.40	17.56	8.61
KSFO + pyridine (0.17)	30.55	29.74	28.56	10.85	10.53	9.96
F49 + BuNH$_2$ (0.10)	8.51	6.60	10.74	3.00	4.66	2.64
ALC + BuNH$_2$ (0.10)	1.02	0.84	0.987	0.976	1.26	0.828

[a] The values in parentheses represent W (mmol/g catalyst).

DISCUSSION

The results of calorimetric titrations of a catalyst in its fresh and poisoned states reveal that chemisorption of a poison affects both acidity and basicity distributions. The change in the acidity distribution is predictable from the amount of adsorbed poison and does not specifically depend on the strength of the poison. The change in the basicity distribution, on the other hand, is more complex. The basicity distributions of all poisoned catalysts show an increase in number density of the B_0 group at the expense of the B_1, B_2 and B_3 groups. This behavior may be explained by surface induction phenomena whereby a base molecule adsorbed on an acidic site may affect the neighboring basic sites. The effectiveness of such induction depends on the strength of the chemisorbed poison and the proximity of basic sites to the poisoned acidic site. The data presented in Fig. 4 indicate that the effect of a weak base is indeed less pronounced compared to the effect of a strong base. To investigate the proximity requirement, the relative spacing between the active sites may be estimated by assuming a uniform distribution on the available catalyst surface. The maximum spacing between an acid site and its nearest base site for a catalyst with 1 mmol/g of total acid and base sites distrib-

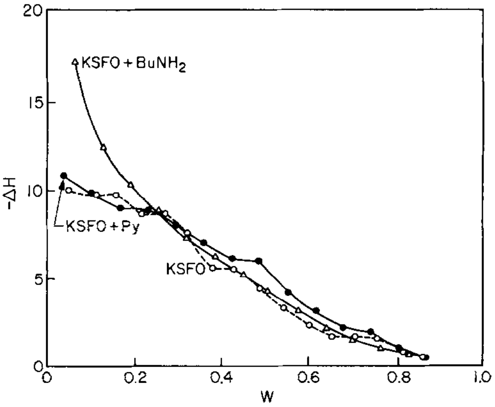

Fig. 4. Effect of various poisons on the heat of trichloroacetic acid adsorption curve for KSFO.

uted uniformly over 200 m^2/g of surface is about 6 Å. Although the maximum acid–base site spacing appears to be large, assumption of uniform distribution of the active sites is probably erroneous in view of the existence of patches of active sites observed by Hirschler (*7*) for alumina and silica–alumina catalysts. Invoking the existence of such clusters, the spacing between acid–base sites may be expected to be significantly less thereby providing the required proximity for surface induction.

As reported in our earlier investigation of the kinetics of dehydration reactions on fresh and poisoned F49 catalysts (*1*) the increase in the value of the "adsorption constant" for alcohol upon poisoning by *n*-butylamine could be explained by invoking a surface induction effect resulting in an increase in the strength of the basic sites. The results of titrations are in good agreement with such an inductive effect.

The importance of the change in basicity distribution by induction in correlating the catalyst activity for dehydration reactions is well established by the success of Model A over Model B in explaining the selectivity changes upon poisoning for all the catalysts tested. The change in basicity distribution explains the increase in the selectivity of KSFO and F49 catalysts upon poisoning by *n*-butylamine. The decrease in the ALC selectivity however indicates that the change in basicity distribution alone is not sufficient to explain the effects of poisoning by a strong base. The results of group analysis detailed in Table 7 show that the relative contributions of the various groups to the total activity play an important role. The main contribution to the KSFO and F49 activities are derived from Group 2 for both dehydration products. Poisoning of these catalysts by *n*-butylamine destroys acidic sites within this group such that olefin formation is affected almost proportionately to the level of poisoning. The effect on ether formation is more pronounced due to the decrease in the $(B_1 + B_2)$ group through surface induction. The overall effect is an increase in the selectivity.

In contrast, the acidity distribution of the fresh ALC catalyst shows higher number density in A_3 compared to A_2. However, as shown in Table 7, the main contribution to the activity for olefin formation still derives from Group 2 due to a considerable difference in the specific rates f_2 and f_3. Since poisoning completely destroys the acidic sites in Group 2 the activity for olefin formation decreases considerably. On the other hand, the main contribution for ether formation on fresh ALC catalyst derives from Group 3 because the relative values of activity constants k_2 and k_3 for ether formation do not compensate sufficiently for the higher number density in Group 3. Destruction of the contribution of Group 2 upon poisoning by *n*-butylamine results in a less pronounced effect on ether formation, thus resulting in a lower selectivity of the poisoned catalyst. This difference in behavior of the ALC and KSFO, F49 catalysts upon poisoning indicates that the detailed acid–base distributions of the fresh catalyst and the modifications due to poisoning are both important in determining the selectivity variations upon poisoning.

The evaluation of s_{ij} from specific models involving acid–base site pairs of specific strengths assumes a random distribution of the acidic and base sites on the catalyst surface. Such an assumption appears to lead to consistent results for fresh catalysts in as much as the s_{ij} determined by invoking this assumption leads to a successful quantitative correlation for the catalyst activities (*2*). Chemisorption of a strong base may lead to certain bias in the strengths of neighboring acidic and basic sites. The fact that the predicted activities for ether formation are somewhat higher than the observed values for all poisoned catalysts may arise from such a bias induced by the chemisorbed base.

CONCLUSIONS

A correlation developed in the previous paper (*2*) describing the dehydration activities of several commercial catalysts in terms of their acidity and basicity distributions has been found to provide good results for the catalysts poisoned by ammonia and organic bases. The adsorption of weak bases preferentially removes the strongest acidic sites but has little effect on the basicity distribution. The adsorption of strong bases in addition to removing the stronger acidic sites causes a shift in the basicity distribution towards higher strengths. This shift reduces the density of sites having an intermediate basicity responsible for ether production and hence increases the catalyst selectivity towards ethylene production. These results show that selective poisoning can be used to produce rather subtle selectivity changes for the catalysts studied.

REFERENCES

1. Bakashi, K. R., and Gavalas, G. R., *AIChE J.*, in press.

2. Bakshi, K. R., and Gavalas, G. R., *J. Catal.* **38,** 312 (1975).

3. Butt, J. B., *Advan. Chem. Ser.* **109,** 259 (1972).

4. Covini, R., Fattore, V., and Giordano, N., *J. Catal.* **9,** 315 (1967).

5. Figueras, F., Nohl, A., DeMourges, L., and Trambouze, Y., *Trans. Faraday Soc.* **67,** 1155 (1971).

6. Hirschler, A. E., *J. Catal.* **2,** 428 (1963).

7. Hirschler, A. E., *Prepr. Amer. Chem. Soc., N. Y. Meet.* **14,** No. 3, B-68 (1969).

8. Jain, J. R., and Pillai, C. N., *J. Catal.* **9,** 322 (1967).

9. Tanabe, K., "Solid Acids and Bases," Academic Press, New York, 1970.