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Amination of Butenes over Protonic Zeolites

M. Lequitte,* F. Figueras,*[,1] C. Moreau,* and S. Hub†

*Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618 CNRS/ENSCM, 8 rue de l'Ecole Normale, 34053 Montpellier Cedex, France; and †Centre de Recherches Rhône Alpes, ATOCHEM, 2 Rue H. Moissan, BP 20, 69310-Pierre Benite, France

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The reaction of 1-butene and isobutene with ammonia has been investigated, far from thermodynamic equilibrium, in the pressure range 1–6 MPa over a series of acidic zeolites. The kinetics are compatible with a Langmuir–Hinshelwood mechanism involving adsorbed species. The rates of amination increase with the Si/Al ratio of the solid. A small influence of the zeolite structure is noticed on the relative adsorption coefficients in the case of 1-butene but not in that of isobutene. The catalytic activity calculated per proton is higher on MFI than on BEA or HY zeolites, but this effect of the structure is less than an order of magnitude. Under the conditions of reaction used in this work large pore zeolites show a good resistance to deactivation. It is proposed that deactivation is mainly due to the formation of strongly basic polyalkylamines and not to coke.

INTRODUCTION

The direct amination of olefins with ammonia in the presence of zeolites is an attractive route for the synthesis of primary and secondary alkylamines and is one which has found industrial application, since BASF uses it to produce *t*-butylamine (1). High selectivities, about 95% for monoalkylamines, have been reported for alumino- (2), ferro- (3) and boro-pentasils (4), and a series of other zeolites (5–6). The addition of ammonia to olefins is an exothermic reaction, and the yield therefore decreases with increasing temperature (7). Moreover, both ammonia and olefins are nucleophiles, and due to the low reactivity thermodynamic equilibrium is reached at relatively high temperatures. Both kinetic and thermodynamic considerations then require high pressure, and in some cases pressures as high as 30 MPa have been used to reach yields of 13% in the case of isobutene (2–4). Under these conditions amination is very fast since thermodynamic equilibrium is reached, and any kinetic study is then impossible. All these technical problems probably explain why most of the results are to be found in the patent literature, and why the open literature is rather scarce in this field, except the pioneer work of Deeba *et al.* (7, 8).

Many important points are still obscure, in particular the influence of zeolite structure and composition on the catalytic properties and deactivation. For ethylene amination at 643 K under pressure, Deeba *et al.* (7) reported a linear correlation between the yield measured for a series of small-pore zeolites and the number of sites chemisorbing ammonia above 473 K, thus a constant turnover frequency. Owing to the larger critical dimensions of propylene and isobutene and their reaction products, the dependence for catalytic activity for the production of higher amines on acidity was difficult to deduce. By contrast, for the amination of isobutene at atmospheric pressure and in the presence of water, Mizuno *et al.* (9, 10) recently reported an increase of the turnover frequency with the Si/Al ratio for a series of zeolites including MFI, MOR, and FAU, independently of the zeolite structure. Catalytic activity was controlled by the chemical composition (Al content of the solid) with a maximum observed on MFI for a Si/Al ratio of 80, ascribed to an increase of the acid strength at this high Si/Al ratio.

In the reverse reaction of deamination of sec-butylamine a small effect of the structure was observed on the rate of deamination, with a higher activity for pentasil zeolites (11). Concerning the kinetics of amination, Deeba *et al.* (7) proposed a competitive adsorption of the reactants, whereas Mizuno *et al.* (9) report that ammonia saturates the surface and isobutene is weakly adsorbed. The real influence of pore size on deactivation is not very clear: Deeba and Ford (8) and Hölderich *et al.* (2–4) hypothesized that deactivation was related to coke formation from olefins. This reaction could be shape selective, since in the temperature range used for the reaction aromatics can be produced by cyclisation and hydrogen transfer. In the case of small pore zeolites (MFI, FER) these aromatics are excluded from the structure as proposed by Rollman and Walsh (12). This hypothesis accounts for the faster deactivation of HY zeolites compared to pentasils or offretite. However, Deeba (13) later reported an increased stability of dealuminated FAU zeolites, which are known to show a significant proportion of mesopores.

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[1] Present address: Institut de Recherches sur la Catalyse, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France. Tel: (33) 72 44 54 69, Fax: (33) 72 44 53 99, E-mail: figueras@catalyse.univ-lyon1.fr. Proofs to F. Figueras at the Villeurbanne address.

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It appeared then of interest to investigate the reaction of amination of isobutene on a series of zeolites and to compare the respective influence of the chemical composition and structure on activity, selectivity, and deactivation.

EXPERIMENTAL

Catalyst Preparation

All the samples used in this work were pure single phase zeolites, with no extraframework aluminum. Zeolite beta (BEA) was synthesized using tetraethylammonium hydroxide (TEAOH) as organic template, following the procedure described by Nicolle (14). The crystals appeared as spheroids with an average size of 0.6 μm. These samples were calcined at 773 K for 8 h under dry air (120 ml min^{-1}) and were then converted to the ammonium form by ion exchange in a 1 *M* NH_4NO_3 solution at 373 K.

A ZSM-5 sample (MFI) with a silicon to aluminum ratio of 14 was obtained from Conteka. A large port mordenite (MOR) with a Si/Al ratio of 6.9 was obtained from Norton. The ammonium forms of all samples were activated according to the procedure described above. Mordenite consisted of polycrystalline aggregates, with an average particle size of about 2 μm.

The Y zeolites (FAU) were Linde LZ-Y62 (Si/Al = 2.5), a sample obtained from this zeolite by Ce^{3+} exchange (percentage exchange 70%) and a dealuminated sample ZF515 obtained from Zeocat.

Catalyst Characterization

The chemical composition of the catalysts was determined by atomic absorption analysis after dissolution of the sample (SCA-CNRS, Solaize, France). The crystallinity of zeolites was checked by X-ray powder diffraction on a CGR Theta 60 instrument using Cu $K\alpha_1$ filtered radiation. Diffraction patterns showed a good crystallinity of the samples.

The size and morphology of the crystals were determined by electron scanning microscopy. The micropore volume and BET surface area were deduced from the isotherms of adsorption of nitrogen at 77 K.

Acid properties were determined by stepwise thermal desorption of ammonia. The catalyst was first activated in flowing nitrogen *in situ*, saturated with ammonia at 373 K, then swept by a flow of dry nitrogen while the temperature was raised by steps of 50 K. The amount of ammonia evolved by the solid was monitored by conductometry. The chemical compositions, the pore volumes, and the acid properties of these catalysts are reported in Table 1.

Catalytic Tests

Isobutene and ammonia of purity more >99.9% were supplied by Aga. Tests were performed in a flow reactor operated in the pressure range 1–10 MPa. The reactor was an inox tube (length 80 mm and diameter 21 mm) fitted with a fritted inox disk on which the catalyst was laid. A well enabled the measurement of the temperature in the center of the catalyst charge. Preheating was made in a tube 300-mm long and 8-mm diameter maintained at the reaction temperature. The zeolites were used in their powder form, and the size of the grains was that of the aggregates of crystals (a few microns). A quantity of 2 g of catalyst was first reactivated *in situ* in flowing air at 773 K for 6 h, and then the temperature was decreased to the desired value. Both reactants were stored as liquids in Grayel bottles and metered to the reactor as liquids using Gilson HPLC cryostated pumps. The liquids were vaporised in heated pipes before the reactor. The pressure in the reactor was controlled by a back pressure regulator (Kammer valve).

TABLE 1

Chemical Composition and Pore Volumes of the Catalysts Used Here

Sample	Source	Si/Al	Micropore vol. (ml · g^{-1})	Mesopore vol. (ml · g^{-1})	Acidity >523 K (meq/g)
HY2.5	Linde LZ62	2.5	0.36	0.04	1.5
HY15	ZF515	15	0.34	0.14	0.48
MOR6.9	Zeolon 100H	6.9	0.22	0.014	0.88
MFI	CBV3010	14	0.17	0.03	0.45
BEA	Home made	15	0.26	0.21	0.85

The composition of the effluent was determined by an on-line gas chromatograph equipped with two capillary columns (30 m × 0.75 mm ID) mounted in series: the first one was a polar CP Wax 51 for the separation of amines and the second one an apolar DB1 for the separation of olefins. The temperature program for chromatographic analysis was 6 min at 60°C, and then a ramp up to 200°C (10°/min). All connecting lines were heated to avoid condensation and adsorption of the reactants and products.

In a typical experiment, the reactants were introduced at the reaction temperature. When the desired pressure was reached the analysis was started, and this instant was considered as time zero for deactivation.

RESULTS

1. *Preliminary studies*. Several zeolites were compared in standard conditions (molar ratio ammonia/olefin = 1, total pressure 4 MPa) at different temperatures. The results are reported in Figs. 1 and 2. The major product of the reaction of isobutene (Fig. 1) is tert-butylamine, which is formed with high selectivity at low temperature (Fig. 3). In the conditions of reaction (4 MPa), the thermodynamic equilibrium at 523 K is about 20% conversion into tert-butylamine and therefore does not control the rate. At high temperature

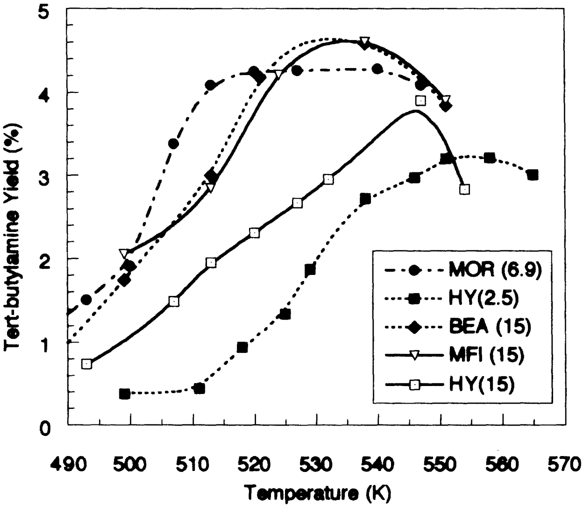

FIG. 1. Amination of isobutene over protonic zeolites: yield as a function of temperature for different zeolites. Total pressure 4 MPa; ammonia/olefin = 1.

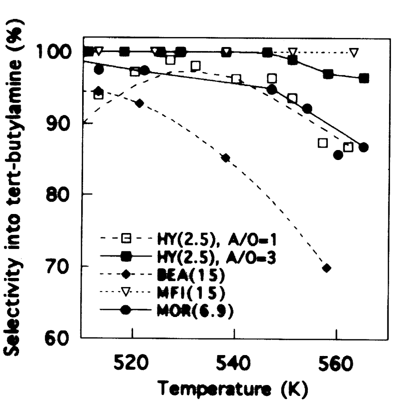

FIG. 3. Amination of isobutene; selectivity to tert-butylamine as a function of temperature for different zeolites, using a total pressure of 4 MPa and a ratio ammonia/olefin equal to 1, and effect of the ratio olefin/ammonia on HY2.5.

the selectivity decreases, which is indicative of secondary reactions.

In the conversion of 1-butene (Fig. 2), sec-butylamine is the major product. The selectivity is usually lower in this case and decreases at the higher temperatures by formation of di-sec-butylamine and olefinic oligomers (Fig. 4). 1-Butene is also isomerized to 2-butene in the course of the reaction. The position of the thermodynamic equilibrium depends on the degree of isomerisation of *n*-butenes, and is then more complex to compute: if we assume that the equilibrium between the *n*-butenes is reached, we obtain a conversion at equilibrium of 3.43% at 593 K, 2.52% at 613 K, and 1.76% at 633 K. The equilibrium is then reached with many zeolites.

At constant temperature the selectivity decreases with the conversion on mordenite, but remains high on MFI (Fig. 5). The decreased selectivity is due to a secondary reaction of the monoalkylamine, which can be either the alkylation of 1-butene by sec-butylamine, or the disproportionation to dialkylamine and ammonia, previously shown to be fast (9). The former study of the conversion of sec-butylamine on protonic zeolites showed that both reactions can occur; however, since mordenite and MFI were very selective for the decomposition of sec-butylamine into butene and ammonia, the consecutive alkylation of butene accounts for the decreased selectivity. BEA, on the other hand, was rather selective for disproportionation of

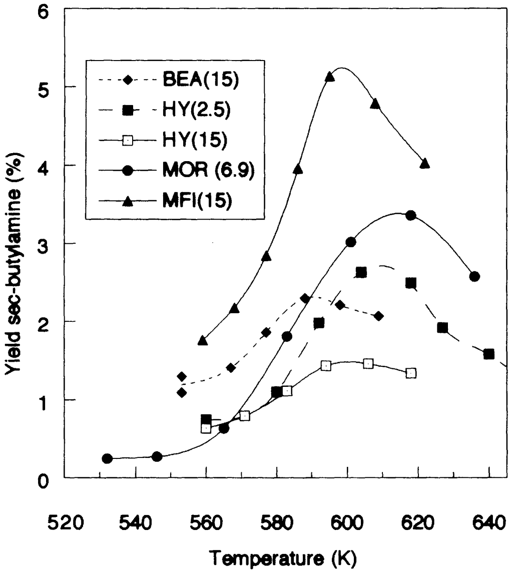

FIG. 2. Amination of 1-butene; yield as a function of temperature for several zeolites, at a total pressure of 4 MPa and a stoichiometric ratio ammonia/olefin = 1.

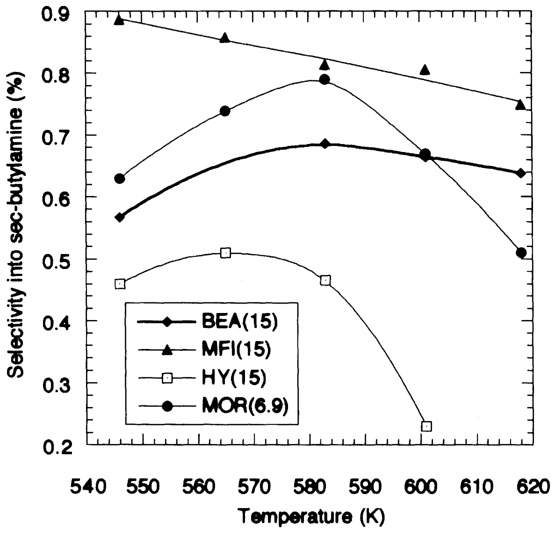

FIG. 4. Selectivity of the amination of 1-butene into sec-butylamine as a function of temperature for different zeolites, using a ratio ammonia/olefin = 1, total pressure = 4 MPa.

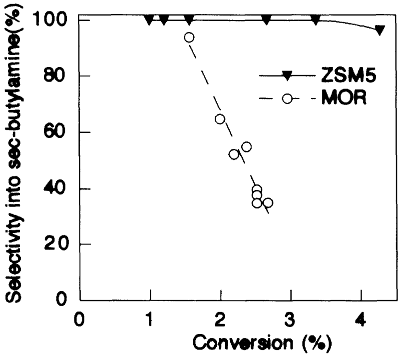

FIG. 5. Variations of the selectivity as a function of conversion for the amination of 1-butene on mordenite at 607 K and MFI at 499 K. The total pressure was 4 MPa.

sec-butylamine, which could be the secondary reaction observed here.

In these experimental conditions, the rate is independent of the flow of reactants, and therefore is not controlled by external mass transfer. Typical values of the rate of amine formation are 10^{-7} mol $\sec^{-1} \cdot g^{-1}$ over most zeolites, with average crystal sizes of about 1 μm, using a concentration of substrate of 10^{-4} mol ml^{-1}.

The criterion of Weisz (15),

$$\frac{dN}{dt}\frac{1}{C_0}\frac{R^2}{D_{\mathrm{eff}}} < 0.1,$$

predicts that the kinetics are then controlled by the chemical process and not by diffusion in the pores.

2. *Deactivation.* The stability of catalytic activity in isothermal conditions has been checked for BEA and MFI zeolites using isobutene as reactant. The results are represented in Fig. 6. After reaction the catalyst is grey or black and has, therefore, suffered some coke laydown. The carbon and nitrogen analyses of the solids after reaction are reported in Table 2 in terms of C/N ratios and show the presence of significant amounts of nitrogen on the solid.

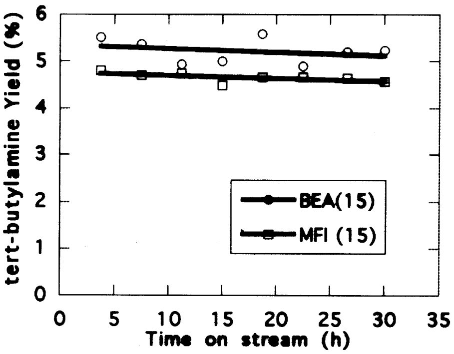

FIG. 6. Dependence of catalytic activity as a function of time for BEA and MFI zeolites of comparable composition using a ratio ammonia/olefin = 3, total pressure = 4 MPa. Temperatures of reaction: 543 K for BEA and 525 K for MFI.

TABLE 2

Chemical Analyses, in Terms of C/N Ratios of the Catalysts after the Conversion of 1-Butene and Isobutene

Zeolite	HY2.5	HY15	MOR6.9	MFI14	BEA15
C/N 1-butene	0.3	5.7	2	1.5	9.2
C/N isobutene	0.14	0.8	0.2	0.6	3.2

3. *Kinetics of the reaction.* At high ammonia pressure the rate of amine formation is proportional to the partial pressure of olefin, as illustrated in Fig. 7 for 1-butene and Fig. 8 for isobutene. Since when the pressure is changed, the new stationary state is reached after a certain time, only the points corresponding to longer times for the equilibration were selected in that case. Moreover, at the higher pressures of 1-butene deactivation increases; pressure cannot then be changed in a large range and it can be expected that the points at high pressure fall below the line. The selectivity to monoalkylamine increases with the partial pressure of ammonia (Figs. 3 and 9) in the case of HY zeolite, but it remains relatively constant in the case of MFI. This difference reflects changes of the adsorption coefficients of butylamines and ammonia related to the different acidities of the solids.

The mechanism proposed by Deeba *et al.* (7) involves the attack of the olefin forming a π-complex with surface protons and ammonium ions. In that case the kinetics should follow a Langmuir–Hinshelwood competitive mechanism, which can be written

$$r = k\frac{\lambda_{\mathrm{but}} P_{\mathrm{but}} \lambda_{\mathrm{NH_3}} P_{\mathrm{NH_3}}}{(1 + \lambda_{\mathrm{but}} P_{\mathrm{but}} + \lambda_{\mathrm{NH_3}} P_{\mathrm{NH_3}})^2}. \qquad [1]$$

In ammonia-rich mixtures, the rate equation is reduced to

$$r = k(\lambda_{\mathrm{but}}/\lambda_{\mathrm{NH_3}}(P_{\mathrm{but}}/P_{\mathrm{NH_3}})),$$

which agrees with the first order observed in these experimental conditions.

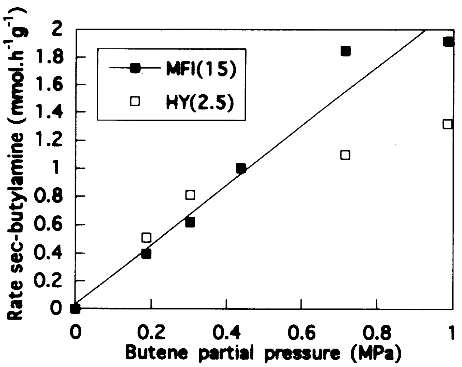

FIG. 7. Amination of 1-butene: variation of the rate of formation of sec-butylamine as a function of the partial pressure of olefin. Total pressure: 4 MPa, Temperature: 591 K.

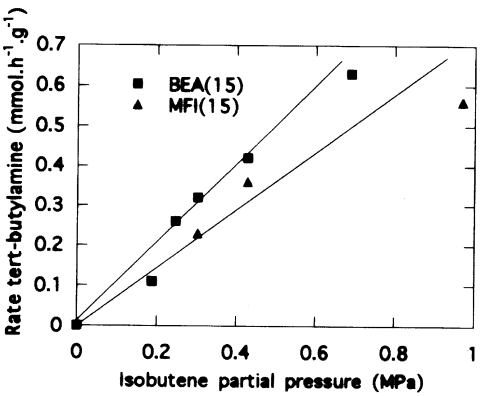

FIG. 8. Amination of isobutene: variation of the rate of tert-butylamine formation as a function of the composition of the feed, at a constant total pressure of 4 MPa. Temperature: 499 K.

In the general case, it can be assumed that the surface is covered either by ammonia or butene. Eq. [1] then becomes

$$r = k\frac{\lambda_{but}P_{but}\lambda_{NH_3}P_{NH_3}}{(\lambda_{but}P_{but}+\lambda_{NH_3}P_{but})}$$

and can be written

$$\sqrt{\frac{1}{r}\frac{P_{but}}{P_{NH_3}}} = \sqrt{\frac{\lambda_{NH_3}}{k\lambda_{but}}} + \sqrt{\frac{\lambda_{but}}{k\lambda_{NH_3}}}\left(\frac{P_{but}}{P_{NH_3}}\right).$$

A linearized form can then be obtained by plotting $\sqrt{(1/r)(P_{but}/P_{NH_3})}$ as a function of P_{but}/P_{NH_3}. A reasonable fit is then observed for several zeolites, independently of the total pressure (Fig. 10). From the slope and intercept at the origin of the linear part, the rate constant k and the ratio of adsorption coefficients $\lambda_{NH_3}/\lambda_{but}$ can be obtained (Table 3).

The apparent activation energies of reaction were deduced from the results reported in Figs. 1 and 2 using only the points at low temperature, far from equilibrium. The values for the two reactions are reported in Table 4. The activation energy determined for the deamination of sec-butylamine was 184 kJ/mol on HY2.5 zeolite, and 167 kJ/mol on mordenites (9). In principle the difference between the activation energies of the two reverse reactions of amination and deamination should be equal to the enthalpy of reaction. The enthalpy of reaction deduced from thermodynamic tables (16) is −58.5 kJ/mol and the difference between the activation energies is −50 kJ/mol for MOR and −59 kJ/mol for HY2.5. A reasonable agreement is therefore observed, which suggests that these activation energies are not affected by diffusional limitations.

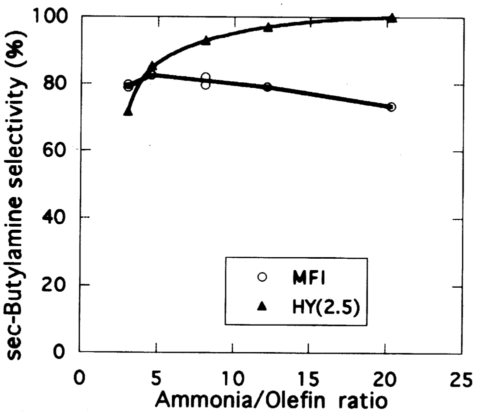

FIG. 9. Amination of 1-butene. Variation of the selectivity to sec-butylamine as a function of the composition of the feed at 591 K, total pressure 4 MPa.

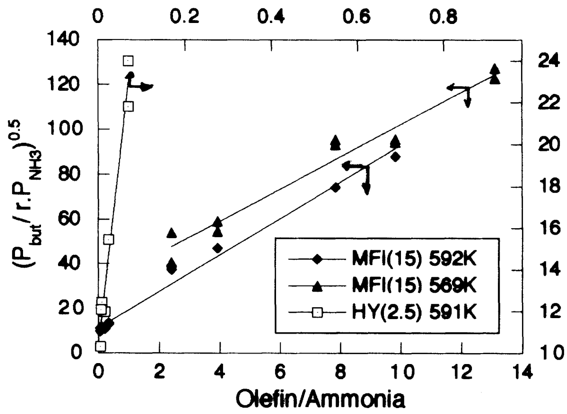

FIG. 10. Linearisation of the Langmuir–Hinshelwood equation as a function of the ratio olefin/ammonia using the results obtained for 1-butene with MFI at 592 and 569 K, and Y zeolites at 591 K.

DISCUSSION

The results of the kinetic study performed here, far from equilibrium conditions, support the hypothesis formulated by Deeba *et al.* (7) on the mechanism, suggesting a competitive adsorption of the reactants. Since the relative coefficients of adsorption of the olefin and ammonia are of the same order of magnitude, the bond between the olefin and the surface should be rather strong. However, this bond has

TABLE 3

Kinetic Constants Obtained for the Amination of Butenes of Ammonia

Zeolite	$\lambda_{NH_3}/\lambda_{but}$	k (mol/h · g)
	Amination of 1-butene at 591 K	
HY2.5	4.3	0.01
MFI	1	0.01
	Amination of isobutene at 499 K	
BEA and MFI	1	4×10^{-3}

Note. Both reactions were studied at 4 MPa, and a total flow rate of reactants of 0.133 mol/g_{cat}/h.

TABLE 4

Apparent Activation Energies for the Amination of 1-Butene and Isobutene on Various Zeolites

	Apparent activation energy (kJ/mol)					
	HY2.5	CeY	HY15	MFI	BEA	MOR
E*a* 1-butene	125	104	67	84	58	117
E*a* isobutene	137	129	63	133	220	104

to be covalent in order to permit a reaction with ammonium species. It has been proposed that olefins form not carbenium ions but alkoxide species by adsorption on zeolites (17–18). The interaction of such a covalent alkoxide with NH_4^+ ions is here proposed as the slow step of the reaction. In that case the reaction requires strong acidity to retain the alkoxide at the surface.

According to Rabo and Gajda (19), the rigidity of the lattice can affect the acid strength since it is well known that acidity is controlled by the Si–O–Al bond angle (20). Recent quantum chemical calculations demonstrate that deprotonation of the zeolite lattice leads to large local changes in geometry that change acidity (21). These calculations account for the modifications of the infrared spectrum of NH_4Y and HY zeolites related to the relaxation of the lattice when the proton is lost and then for the higher acidity, at the same Al content, of MFI zeolites which possess a rigid lattice, compared to more flexible systems composed of large cages such as BEA or FAU.

Some effect of the zeolite structure on the catalytic properties is then expected for those reactions catalyzed by protons, and so it was interesting to investigate the influence of the structure of the zeolite on the kinetic parameters of the reaction. Some differences could be expected when the substrate is changed since the coverage of NH_4^+ ions could then change and, thus, the acidity.

1-Butene is difficult to react and requires temperatures above 573 K. From the kinetic analysis it appears that $\lambda_{NH_3}/\lambda_{but}$ changes when the zeolite is changed from FAU to MFI. The change of the relative adsorption coefficient must reflect the higher acidity of MFI, which permits retention of the olefin at the high temperature required for the reaction. The reaction rate determined from this analysis is the same for the two zeolites. However, if we take into account the different numbers of acid sites, the rate constant per proton (turnover frequency) is higher on MFI, compared to HY zeolite. The difference, a factor of about 3, is consistent with the results previously reported for the reverse reaction of deamination.

The reaction of isobutene is much easier and proceeds at a lower temperature. In this case the relative adsorption coefficients $\lambda_{NH_3}/\lambda_{but}$ are comparable for MFI and BEA zeolites. The specific activities are similar, and MFI appears to be 2 times more active than BEA when the rate constant is calculated per proton.

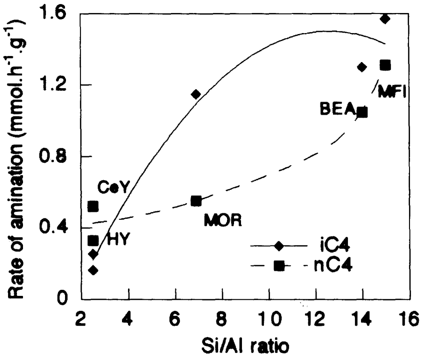

FIG. 11. Influence of the chemical composition and structure of the zeolites on the rates of formation of sec-butylamine from 1-butene measure at 583 K, and tert-butylamine from isobutene measured at 498 K under a pressure of 4 MPa, olefin/ammonia ratio = 1.

This kinetic study therefore suggests a small influence of the structure of the zeolite when considering **k**, which is an average over a large number of experiments on the same sample, and can then be affected by slow deactivation with time. The comparison of several zeolites of different structures with a ratio ammonia/olefin = 1 is reported in Fig. 11. It appears here also that the chemical composition of the solid is more important than the structure: at similar Si/Al ratios MFI and BEA show comparable activities for the amination of 1-butene or isobutene. Dealuminated Y has a lower activity for the formation of monoalkylamines because the secondary reaction of disproportionation is fast in that case. For the amination of isobutene, HY shows a low activity in spite of a great number of sites. If we consider turnover numbers, MFI is the most active zeolite for both reactions, but the difference with BEA or MOR is within a factor of 2.

By increasing the butene/ammonia ratio and contact time, conversions close to the thermodynamic equilibrium at 548 K can be reached (Table 5). These yields can be compared to those reported by Hölderich *et al.* (2–4) who used much higher pressures (30 MPa) and obtained yields of about 12–13%, corresponding also to the thermodynamic equilibrium in the same temperature range.

It is interesting to notice that the rate of amination is not proportional to the rate of deamination, when these

TABLE 5

Amination of Isobutene: Comparison of the Yields (%) Observed at 548 K, 4 MPa in the Presence of Different Zeolites

Zeolite	HY2.5	BEA15	MFI14	MOR6.9
Ratio NH_3/olefin = 1	2.3	4.6	4.5	4.3
Ratio NH_3/olefin = 3	3.2	8.2[a]	8.9	5.6
Selectivity	100	90	100	97

[a] Temperature 532 K, pressure 4.5 MPa.

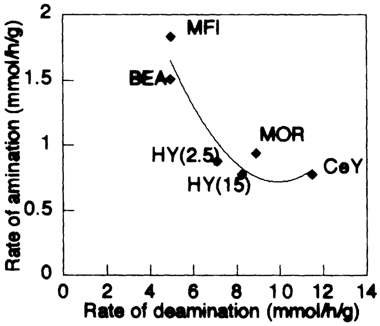

FIG. 12. Correlation between the rates of amination of 1-butene and deamination of sec-butylamine on a series of zeolites. Both rates are expressed in mmol $h^{-1} \cdot g^{-1}$.

two rates are measured in the kinetic regime (Fig. 12). At equilibrium these two rates must be equal, and the principle of microreversibility imposes that the reaction path is the same for the two reverse reactions. The mechanism of Hofmann degradation of amines can account for the reverse reaction of deamination and then for the reaction of amination. Far from equilibrium, the kinetics should be related to the reactivity of the two substrates, so this nonproportionality does not contradict the principle of microreversibility, since it simply implies that the different reactivities of sec-butylamine and 1-butene control the respective rates of reaction.

A very important point is the stability of catalytic activity. In the present work, a reasonable stability was obtained for both wide and small pore zeolites, suggesting that coke formation from olefins is not the main source of deactivation. Indeed the C/N ratios after reaction suggest that the surface is not covered by coke only, but at least partly by N-containing compounds. It is difficult to determine the chemical nature of the surface species since the solid is black and opaque in the infra-red. We can note, however, that the secondary reactions of the monoalkylamines yield dialkylamines. Secondary alkyalmines are stronger bases than ammonia and can then block the active sites. In this hypothesis diffusional limitations would play a decisive role in the stability of zeolites, since they favor these consecutive reactions. In that respect the stability of BEA would be accounted for by the small size of the particles which favors desorption of monoalkylamines before their reaction.

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