

The Role of the Zeolite in the Hydrogenolysis of C₂ and C₃ Hydrocarbons on RuNaY Catalysts

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The catalytic properties for the hydrogenolysis of ethane, propane, and cyclopropane of a series of highly dispersed RuNaY catalysts have been investigated. These catalysts have activities and selectivities for ethane and propane hydrogenolysis similar to other supported ruthenium catalysts. However, the activity of the RuNaY for cyclopropane hydrogenolysis is much higher than that of Ru on conventional oxide supports, while the selectivities remain in a range expected for well-dispersed ruthenium. The increase in activity for the RuNaY catalysts is due mainly to the presence of highly dispersed Ru particles made possible by the zeolite support. A destabilization of the cyclopropane ring by the electrostatic field of the zeolite, however, does not seem to contribute significantly to the observed rate increase. It appears that the ring opening of cyclopropane and the hydrogenolysis of cyclopropane to ethane and methane have a common intermediate, the formation of which is rate determining for both reactions. The discovery that on Ru the ring opening of cyclopropane is structure sensitive is surprising since this reaction is generally considered as a classic example for structure insensitivity. © 1986 Academic Press, Inc.

INTRODUCTION

Interactions between the metal and its support have been of interest in the field of catalysis for many years. The combination of high metal dispersions and the unique chemical environment provided by zeolites makes metal-loaded zeolite systems interesting candidates for investigating metal-support interactions. Hydrogenolysis reactions of hydrocarbons have found wide application for probing the catalytic behavior of metals (1, 2). The activities of hydrogenolysis catalysts appear to be very sensitive to the type of metal used as well as to the structural properties of the catalyst.

Hydrogenolysis reactions have been used extensively to study Ru catalysts (3-

16), and several of these reactions have been found to be structure sensitive. However, little work has been reported on the hydrogenolysis activity of zeolite-supported Ru (17). On the other hand, a number of hydrogenolysis studies have dealt with other zeolite-supported metals, in particular Pt (18-20). Tran Manh Tri *et al.* (19) correlated the *n*-butane hydrogenolysis activity with the electrophilic character of platinum in PtY. Neopentane hydrogenolysis and isomerization was one test reaction used by Dalla Betta and Boudart (18) to investigate the properties of PtY zeolite catalysts. They concluded that a support interaction leading to an apparent electron deficiency of platinum in multivalent cation zeolites was at least partially responsible for the increased activities. Naccache *et al.* (20) reported that the activity of platinum for ethane hydrogenolysis did not appear to depend upon whether the metal was supported on SiO₂ or Y zeolite. However, in cyclopropane hydrogenolysis, large activ-

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ity increases were observed on the PtY catalysts.

Hydrogenolysis of cyclopropane, propane, and ethane represent a suitable combination of catalytic reactions to investigate the structural and electronic properties of supported ruthenium. Cyclopropane undergoes three different primary reactions on ruthenium. Two of these reactions, namely ring opening to propane and hydrogenolysis of cyclopropane to ethane and methane in a 1:1 ratio are, according to previous work (8, 11) believed to be structure insensitive. However, the third possible reaction, which is the fragmentation of the cyclopropane ring into three molecules of methane, appears to be structure sensitive (8). The latter reaction has been observed only on Ru catalysts with relatively large particle sizes for temperatures higher than 110°C. Thus, changes in selectivity in the cyclopropane reaction may provide valuable insight concerning the properties of ruthenium catalysts. Propane hydrogenolysis complements the study of cyclopropane hydrogenolysis, providing a means for checking a possible onset of secondary reactions that may contribute to the observed selectivity patterns in cyclopropane hydrogenolysis. The well-known demanding nature of the ethane hydrogenolysis reaction permits one to probe the structure of the active sites.

The present study applies this set of hydrogenolysis reactions (cyclopropane, propane, and ethane) to a series of highly dispersed RuNaY catalysts with different Ru loadings in order to explore the effect of the zeolite support on C-C bond breaking in linear and cyclic alkanes. This is important in light of recent work on zeolite-supported Pt postulating a facilitation of cyclopropane-ring opening via an electrostatic field effect of the zeolite (20). In the case of platinum, only ring opening to propane occurs. Thus, any influence of the zeolite on product selectivity could not be explored in the previous study on platinum. For ruthenium, this limitation does not apply and a

TABLE 1
Catalyst Characterization Data

Catalyst	Dispersion (%)	S.A. ^a (m ² /g)	Treatment procedure ^b
3% RuNaY	65.5	9.56	a-b-c-d-e-f-g
1.5% RuNaY	55.3	4.03	a-b-c-d-g
0.76% RuNaY	77.4	2.86	a-b-c-d-e-f-g
0.19% RuNaY	95.8	0.89	a-b-c-d-e-f-g
1% Ru/NaY	77	4.12	h-b-g
3.86% Ru/SiO ₂	26	4.88	i-c-d-g

^a Ruthenium metal surface area per gram of catalyst, determined by H₂ chemisorption at 25°C. A stoichiometry of H/Ru_(s) = 1 was assumed for the irreversible uptake of hydrogen (26).

^b (a) Prepared by ion-exchange with Ru(NH₃)₆Cl₃; (b) decomposed under vacuum at 1°C/min up 400°C; (c) H₂ reduction at 450°C (P_{H₂} = 0.2 atm); (d) H₂ adsorption at 25°C; (e) desorption at 400°C for 2 h; (f) CO adsorption at 25°C; (g) exposed to air at room temperature; (h) prepared by Ru₃(CO)₁₂ vapor-phase deposition; (i) prepared by RuCl₃ · H₂O wet impregnation.

more complete picture of the role of the zeolite support in affecting both the activity and the selectivity of ruthenium can be obtained.

EXPERIMENTAL

The RuNaY zeolite catalysts used in this study were prepared by two methods. The first method consisted of ion exchanging Ru into NaY using an aqueous solution of Ru(NH₃)₆Cl₃. The exchanged [Ru(NH₃)₆]³⁺ complex was decomposed under a dynamic high vacuum of 10⁻⁶ Torr on heating the catalyst up to 400°C at a rate of 1°C/min. The metal was then reduced at 450°C in hydrogen and subjected to the various chemisorption characterizations as outlined in Table 1. Ru/NaY containing 1 wt% Ru was also prepared by vapor impregnation of NaY with Ru₃(CO)₁₂. Details of this preparation procedure are given by Goodwin and Naccache (21). For comparison, a conventional 3.86 wt% Ru/SiO₂ catalyst was used. The preparation method and characterization of the Ru/SiO₂ catalyst have been described previously (7, 9).

A flow reactor containing up to 100 mg of the catalyst having a grain size of about 0.1 mm was operated at atmospheric pressure (1 atm = 101.3 kPa) to obtain kinetic data on the catalysts. Prepurified hydrogen was

passed through a palladium/asbestos reactor maintained at 400°C. Ultrahigh-purity helium was passed over copper turnings maintained at 300°C. Each gas was then further purified using a molecular sieve trap maintained at liquid-nitrogen temperature. High-purity ethane, propane, and cyclopropane were used without further treatment.

The analysis of the products and the reactants was carried out by gas chromatography. The GC column was a 3-m copper tube filled with silica gel (100–120 mesh) and operated at 80°C.

Prior to pretreating the catalysts, the reactor was flushed with He at room temperature for 10 min. The catalysts were then slowly heated over a 2-h period from room temperature to 320°C in flowing H₂ and then held at this temperature in flowing H₂ for 19 h. Following reduction the reactor was cooled down to reaction temperature in flowing H₂.

In order to determine what activity the zeolite itself had for the reactions both NaY and HY zeolites were studied under reaction conditions. HY zeolites were studied in order to account for the possible activity of the acid sites in (ion-exchanged) RuNaY generated during the reduction of the Ru. The procedure outlined above was also used for NaY zeolite samples with the exception that He was substituted for the H₂. This was also done for NH₄Y to dehydrate it and to remove ammonia, in order to form the HY zeolite.

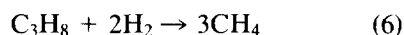
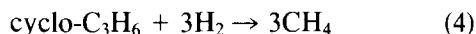
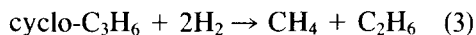
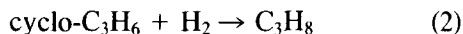
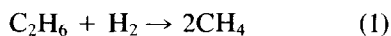
The typical experimental run consisted of passing the appropriate reactant mixture (typically containing 3% hydrocarbon, 20% H₂, and 77% He) over the catalyst and sampling the products after 120 s on stream. Immediately after sampling, the flow of hydrocarbon and He was stopped and H₂ was passed over the catalyst at 200°C for ½ h. The run was then repeated to check for deactivation. If signs of deactivation were observed, the catalysts were treated in flowing hydrogen overnight at 320°C. This procedure was sufficient to restore the initial activity. A number of runs were contin-

ued for longer periods of reaction time (up to 30 min) to study the deactivation characteristics of the catalysts. All the data used to calculate turnover frequencies and kinetic parameters were obtained at conversions of less than 10%. Rate orders were determined by varying the partial pressure of one of the reactants at constant temperature.

Thermogravimetric measurements on RuNaY, NaY, and HY zeolites were performed in a flow TGA system using a Cahn microbalance. The temperature range studied in the adsorption of cyclopropane was 25–110°C.

RESULTS

The following reactions were included in this study:



Reaction rates were determined using the expression

$$N_i = \frac{F_R}{A_s} \cdot \alpha_i, \quad (7)$$

N_i is the turnover frequency in molecules of hydrocarbon reactant converted per surface Ru site in one of the reactions i ($i = (1)$ through (6)). F_R represents the flow rate of the hydrocarbon reactant in molecules per second, A_s is the number of ruthenium atoms on the surface of the catalyst as determined by H₂ chemisorption, and α_i stands for the fraction of hydrocarbon reactant converted in reaction i .

Ethane Hydrogenolysis

Kinetic parameters for ethane hydrogenolysis were obtained for the RuNaY zeolites and the 3.86% Ru/SiO₂. The kinetic

TABLE 2
Kinetic Parameters for Ethane Hydrogenolysis on Ruthenium Catalysts

Catalyst	E_a (kcal/mol) ^a	Temp. range (°C)	$N_{160^\circ\text{C}} \times 10^{3b}$	n (H ₂ rate order)	m (C ₂ H ₆ rate order)	ln A
3% RuNaY	39 ± 3	162–179	2.93	-2.0	0.8	38 ± 3
1.5% RuNaY	39 ± 3	173–191	0.66	-2.0	1.1	37 ± 3
0.76% RuNaY	32 ± 3	160–178	3.5	-2.2	0.8	30 ± 3
0.19% RuNaY	30 ± 3	170–192	2.6	-1.6	0.9	29 ± 3
1% Ru/NaY	34 ± 3	173–194	3.9	-1.6	0.8	35 ± 3
3.86% Ru/SiO ₂	32 ± 3	156–183	1.9	-2.21	0.66	28 ± 3

^a 1 kcal = 4.186 kJ.

^b Molecules/Ru surface atom · s; the feed composition was 6% C₂H₆, 15.6% H₂, 78.4% He.

parameters are given in Table 2. The rate could be fitted to the power law equation

$$r = A \cdot \exp\left(-\frac{E_A}{RT}\right) (p_{\text{C}_2\text{H}_6})^m (p_{\text{H}_2})^n \quad (8)$$

The kinetic parameters are in good agreement with those reported in the literature (1–7, 14).

Cyclopropane Hydrogenolysis

In the cyclopropane hydrogenolysis, the RuNaY catalysts displayed much higher activities than Ru/SiO₂. Quantitative kinetic data under differential conversion conditions could only be obtained for the 0.19% RuNaY sample, the catalyst having the lowest metal loading (Fig. 1). All the other zeolite-supported Ru samples were so active that differential reaction conditions could not be achieved, even by lowering the reactor temperature to 0°C, increasing the flow rate to the maximum possible for the reactor system, and decreasing the amount of catalyst in the reactor to 10 mg. The high conversion over these catalysts was partly due to a significant exotherm observed once the conversion exceeded 50%. Figure 2 shows a comparison of the activities of 0.19% RuNaY with other ruthenium catalysts reported in the literature (8, 10). Apparent activation energies of 43 (±3) and 48 (±3) kJ/mol were found for reactions (2) and (3), respectively (Fig. 1).

In cyclopropane hydrogenolysis, the percentage selectivity (S_2) for propane formation via reaction (2) was determined using the expression

$$S_2 = \frac{N_2}{N_2 + N_3 + N_4} \cdot 100. \quad (9)$$

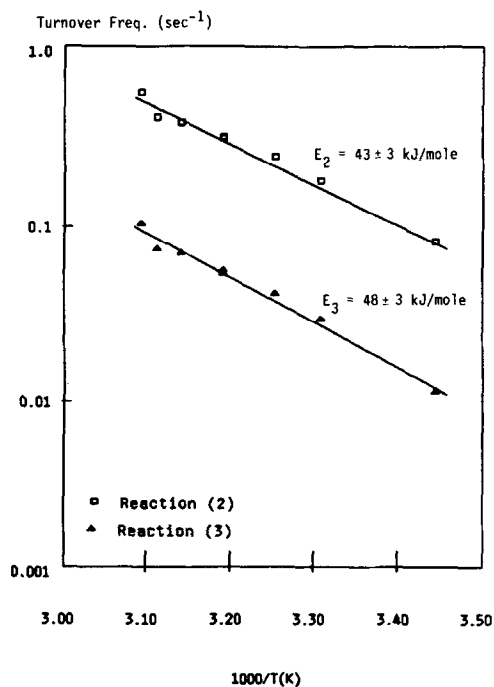


FIG. 1. Arrhenius plot for reactions (2) and (3) on 0.19% RuNaY.

In Figure 3, the selectivity S_2 for propane formation of two RuNaY catalysts is com-

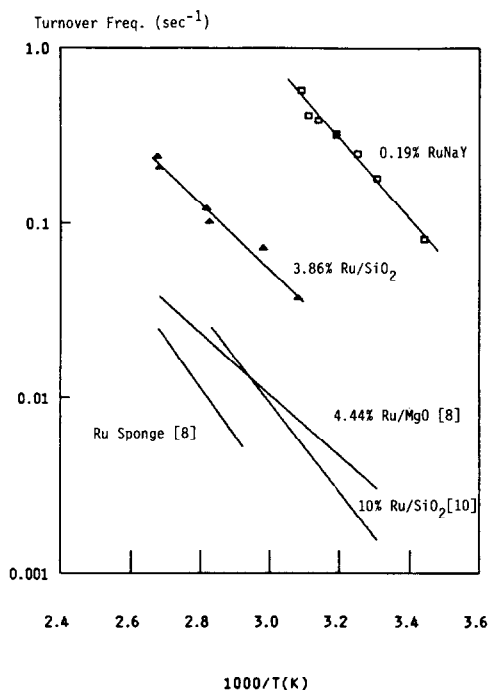


FIG. 2. Comparison of the activity of 0.19% RuNaY for reaction (2) with 3.86% Ru/SiO₂ and other previously reported Ru catalysts.

pared with that of the 3.86% Ru/SiO₂ catalyst, and two other catalysts (a Ru sponge with low dispersion, and a 0.6% Ru/SiO₂ catalyst with more than 65% dispersion)

taken from Ref. (8). The zeolite catalysts and the highly dispersed 0.6% Ru/SiO₂ maintained high propane selectivities and methane/ethane ratios close to unity up to 180°C. The two catalysts with low metal dispersions, namely the Ru sponge and the 3.86% Ru/SiO₂, had propane selectivity curves which showed a sharp decline as the temperature increased above 110°C. Their methane/ethane ratios exceeded unity in the higher temperatures regime above 110°C (8).

The activity of RuNaY for cyclopropane hydrogenolysis showed an induction period. When the reactant mixture (3% cyclopropane, 20% H₂, 77% He) was passed over any of the RuNaY catalysts and the product stream was sampled after 120 s on stream, the unreacted cyclopropane and all of the hydrogenolysis products leaving the differential reactor were less than the total amount of cyclopropane that was fed into the reactor. After a few minutes on stream, however, the carbon content of reactor inlet and outlet became balanced. At this point, no indications for mass transport limitations were evident for the reaction of cyclopropane in the differential reactor. No such induction period was observed in the ethane or propane hydrogenolysis experi-

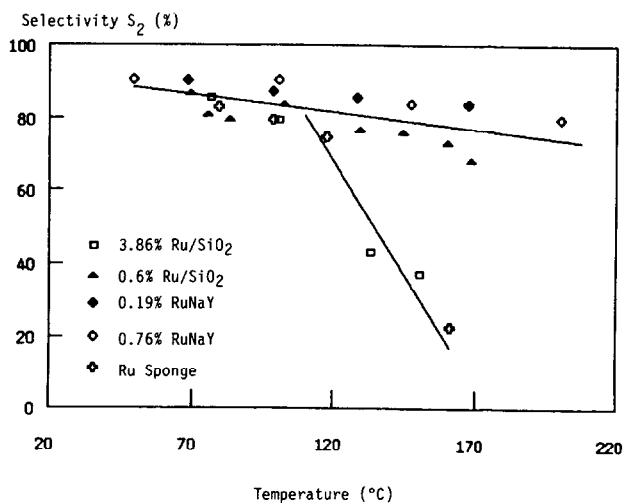


FIG. 3. Selectivity S_2 as a function of temperature. For comparison, data taken from Ref. (8) are included for a Ru sponge with low dispersion and a 0.6% Ru/SiO₂ catalyst with high dispersion.

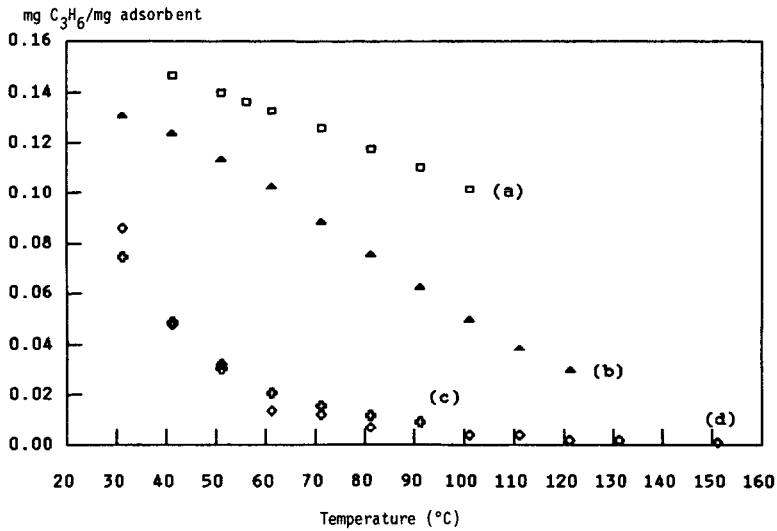


FIG. 4. Adsorption isobars of cyclopropane on NaY and 0.19% RuNaY during TGA at a total pressure of 1 atm. (a) Pure cyclopropane on NaY, (b) 10% cyclopropane in helium on NaY, (c) 3% cyclopropane in helium on NaY, (d) 3% cyclopropane in H₂/He mixture adsorbed on 0.19% RuNaY.

ments. Therefore, the catalyst seemed to be able to sieve a certain amount of cyclopropane out of the feed stream. A similar sieving effect was also observed on blank NaY and NY samples that had been subjected to the standard pretreatment in H₂ at 320°C.

The adsorption of cyclopropane in the zeolite can be seen in Fig. 4 which presents TGA results for NaY and RuNaY exposed to various concentrations of cyclopropane. Curves 4c and 4d indicate that there are

similar amounts of adsorption in both the NaY and the 0.19% RuNaY sample. All of these adsorbed species were only weakly bound and could be easily removed by evacuation. Although bulk diffusion appeared to control the rate of cyclopropane hydrogenolysis in the TGA reactor, the value and temperature dependence of selectivity, S_2 , for propane formation agreed with the results obtained in the differential reactor (Fig. 5).

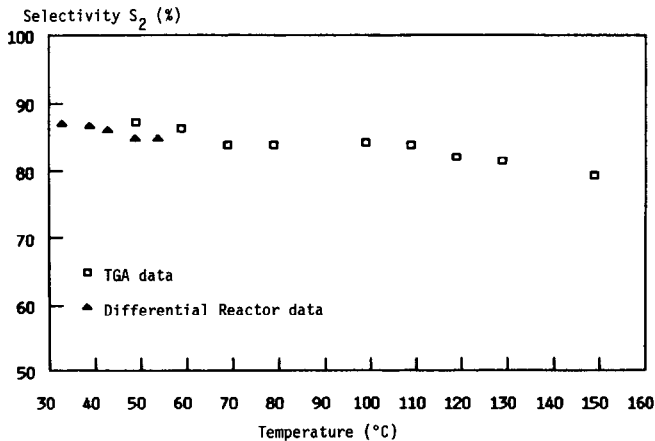


FIG. 5. Selectivity S_2 for propane formation as a function of temperature, comparing TGA data with results obtained in the differential flow reactor.

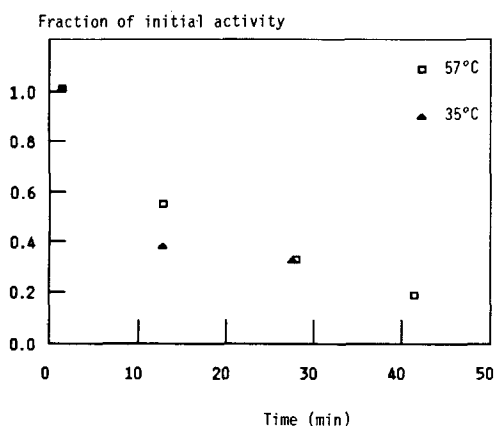


Fig. 6. Time dependence of the total cyclopropane conversion (relative to the total conversion after 120 s) for catalyst 0.19% RuNaY at two different temperatures.

The deactivation characteristics of 0.19% RuNaY catalysts in the cyclopropane hydrogenolysis reaction is presented in Fig. 6. The activity dropped and leveled off as a function of time on stream. However, the deactivation had no significant influence on product selectivity.

Propane Hydrogenolysis

Propane hydrogenolysis experiments were performed on the 0.76% RuNaY and the 3.86% Ru/SiO₂ catalysts. A comparison of these two catalyst's activities is shown in Fig. 7. The difference between the activities of the two catalysts is modest. The apparent activation energy was 130 ± 10 kJ/mol for the 0.76% RuNaY, which is in good agreement with previously published activation energy values for conventionally supported ruthenium (7). The rate order for hydrogen was also determined for 0.76% RuNaY. It was found to be -2.0 , similar to that previously reported for Ru/SiO₂ (7).

In the case of propane hydrogenolysis, the percentage selectivity (S_5) relating to ethane formation via reaction (5) was calculated by means of

$$S_5 = \frac{N_5}{N_5 + N_6} \cdot 100. \quad (10)$$

The selectivity behavior of the 0.76% RuNaY catalyst was different from that of the 3.86% Ru/SiO₂. As can be seen in Fig. 8, the selectivity S_5 on Ru/SiO₂ declined at higher temperatures, while the 0.76% RuNaY exhibited 100% S_5 selectivity over the entire temperature range studied.

DISCUSSION

Within the temperature range investigated in this work, blank NaY and HY supports proved to be inactive for ethane and propane hydrogenolysis. Also, no ring opening or isomerization of cyclopropane was observed up to a temperature of 160°C when a mixture of 3% cyclopropane and 97% helium was passed over HY at the same space velocities that were used for the cyclopropane hydrogenolysis experiments. HY was chosen for the blank test since its concentration of acid sites is greater than in RuNaY where some of the acid sites have been exchanged for Na. This indicated that the ruthenium surface provided the active sites for breaking the C–C bonds. To probe for a potential influence of the zeolite support on the properties of the active ruthenium sites, a comparison of the selectivity patterns of RuNaY catalysts with conventionally supported Ru catalysts was made.

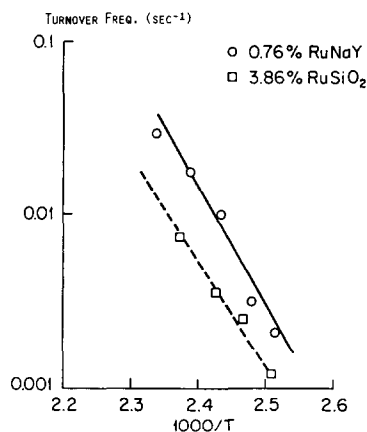


Fig. 7. Arrhenius plots for the propane hydrogenolysis reaction on 3.86% Ru/SiO₂ and on 0.76% RuNaY. The turnover frequency is given for total conversion of propane via reactions (5) and (6).

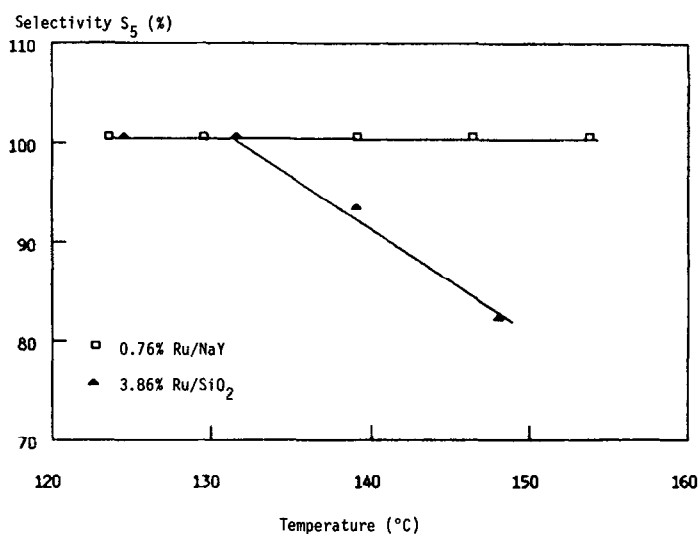


FIG. 8. Selectivity S_5 for propane hydrogenolysis as a function of temperature for catalysts 0.76% Ru/NaY and 3.86% Ru/SiO₂.

In propane hydrogenolysis, RuNaY showed 100% selectivity for ethane formation via reaction (5), while the selectivity of the 3.86% Ru/SiO₂ catalyst decreased at higher temperatures (Fig. 8) due to the onset of reaction (6). However, this difference in selectivity does not necessarily indicate an influence of the zeolite. It can adequately be explained on the basis of a particle size effect which was found in the previous study of propane hydrogenolysis on a series of conventionally supported ruthenium catalysts (7). Reaction (6), the exclusively methane producing reaction, becomes dominant on catalysts with low dispersions causing the selectivity S_5 to decrease.

In the case of cyclopropane hydrogenolysis, no significant difference in selectivity S_2 was found for RuNaY compared to other Ru catalysts in the low-temperature regime up to about 110°C (Fig. 3). However, recall that the activity of the zeolite catalysts was more than one order of magnitude higher than the previously studied Ru catalysts. It has been suggested (20) that the zeolite may facilitate the ring opening of the cyclopropane molecule, perhaps as a result of the electrostatic field acting as though it in-

serts a negative charge into a low lying unoccupied σ orbital. Such an effect would destabilize the strained cyclopropane ring. However, due to the previously discussed selectivity limitations on Pt catalysts Nacache *et al.* (20) could not judge whether or not the effect of the zeolite favors just ring opening to propane or also C-C bond scission leading to ethane and methane. In the case of zeolite supported Ru it is obvious that the selectivity S_2 remains unchanged despite the orders-of-magnitude increase in cyclopropane turnover numbers. It is apparent that both reactions (2) and (3) are accelerated by the same factor. Thus, reactions (2) and (3) on Ru would seem to proceed through a common intermediate, as previously suspected (8).

The high selectivity S_2 for propane formation observed in the low-temperature regime was also maintained in the high-temperature range (110–180°C) (Fig. 3). Such a selectivity behavior is typical for ruthenium catalysts having high dispersions. It was previously noted that the selectivity S_2 at temperatures greater than 110°C is dependent upon the ruthenium particle size (8). The onset of reaction (4) at temperatures greater than 110°C is responsible for the de-

cline in selectivity S_2 observed for Ru/SiO₂ and ruthenium sponge having low dispersions (Fig. 3). Reaction (4) was absent on the RuNaY catalysts within the temperature range studied. This was to be expected in view of the high ruthenium dispersion in the zeolite catalysts. For comparison, data for a highly dispersed 0.6% Ru/SiO₂ catalyst, taken from Ref. (8), are included in Fig. 3. This Ru/SiO₂ catalyst had ruthenium particle sizes smaller than 30 Å and did not give rise to reaction (4) even at the higher temperatures.

The catalytic activity of the RuNaY catalysts for ethane hydrogenolysis was very similar to the activity of Ru/SiO₂ (Table 2). These results are consistent with literature results for PtY catalyst where no significant difference between Pt/SiO₂ and PtY was detected for ethane hydrogenolysis (20). Similarly, the RuNaY samples showed no significant difference in propane hydrogenolysis activity compared to Ru/SiO₂ (Fig. 7).

While the RuNaY catalysts did not show any significant difference in activity for the hydrogenolysis of ethane or propane, a dramatic increase in activity was observed for both the ring opening of cyclopropane via reaction (2) as well as for the hydrogenolysis of cyclopropane via reaction (3). Obviously, the presence of the zeolite support did not change the intrinsic activity of the ruthenium surface sites for C–C bond hydrogenolysis in linear alkanes since the ethane and propane hydrogenolysis activities were unchanged compared to Ru/SiO₂ catalysts. The adsorption of hydrocarbons on zeolites is well documented (23–25), and no significant ethane or propane adsorption occurred on the zeolite support under our reaction conditions. The cyclopropane hydrogenolysis, however, was carried out in a temperature regime where cyclopropane did adsorb on the zeolite. Figure 4 shows the strong dependence of cyclopropane adsorption on the temperature and the partial pressure of cyclopropane. However, Figs. 4c and d indicate that there is no significant

effect of Ru on the amount of cyclopropane adsorbed by the zeolite. A comparison of Figs. 4a to d shows that, under our reaction conditions, the maximum adsorption capacity of the zeolite for cyclopropane is not attained. If there were an effect of cyclopropane adsorption by the zeolite on the reaction rate of cyclopropane, the effect should be most pronounced at the lowest temperatures. However, the Arrhenius plots (Fig. 1) show excellent linear correlations over the temperature regime where, according to Fig. 4d, the amount of adsorbed cyclopropane drops by a factor of 4. In addition, these Arrhenius plots yield apparent activation energies of 43 and 48 kJ/mol, values that are typical for Ru catalysts (8, 10). Thus, neither the adsorption of cyclopropane in the molecular sieve nor transport and diffusional limitations seem to exert a controlling influence on the cyclopropane hydrogenolysis rate. In view of these arguments, the electrostatic field effect suggested by Naccache *et al.* (20) might offer a viable alternative to explain the large increase in cyclopropane hydrogenolysis activity on the zeolite-supported Ru catalysts. However, recent cyclopropane hydrogenation data collected in our laboratories on Ru catalysts of widely varying dispersions surprisingly indicate that the activity depends strongly on Ru particle size. Figure 9 shows a clear trend of increasing turnover frequencies with increasing Ru dispersion. The RuNaY catalyst fits nicely into the qualitative trend of increasing turnover frequencies with increasing Ru dispersion. The Ru dispersion in the RuNaY catalysts is only a rough measure of particle size. In fact, in RuNaY catalysts some large metal particles tend to exist on the external surface of the zeolite crystallites, while a large portion of the metal exists as very small particles with diameters of less than 1.3 nm inside the zeolite supercages (26). The high turnover frequencies on the zeolite supported catalysts as compared to conventionally supported Ru catalysts (which, incidentally, had much lower

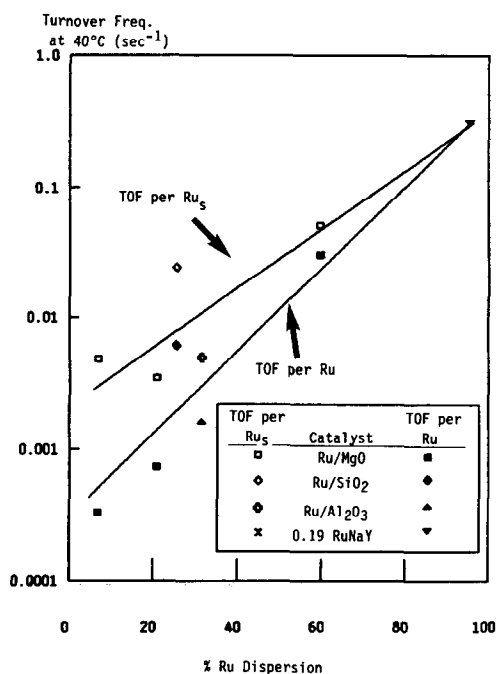


FIG. 9. Cyclopropane-ring-opening activity (reaction (2)) as a function of Ru dispersion on various supported Ru catalysts. Experimental conditions are: $p_{\text{cp}} = 0.03$ atm, $p_{\text{H}_2} = 0.2$ atm, $T = 313$ K. For each catalyst two points are plotted, one representing the turnover frequency per ruthenium surface atom (TOF per Ru_s), the other representing the turnover frequency per ruthenium atom in the catalyst (TOF per Ru).

metal dispersions) do not necessarily require one to invoke the electrostatic field effect of the zeolite, but could be explained by structure sensitivity of the cyclopropane reactions on Ru. Recent results on single-crystal Ni surfaces point also in the direction of structure sensitivity for cyclopropane hydrogenation (27). Both Ru and Ni, the two metals showing evidence for structure sensitivity of cyclopropane hydrogenation, can catalyze reactions (2), (3), and (4) between cyclopropane and hydrogen (8, 28). On Pt where the cyclopropane hydrogenation is clearly structure insensitive according to Boudart's classification (30), only reaction (2) takes place both on supported metal clusters (31, 32) as well as on large single crystals (33). These differences between Pt on one hand and Ni and Ru on

the other are probably related to the structure of the active sites and the ensemble requirements for the reaction intermediates.

While it cannot be excluded that the electrostatic field effect aids to some extent in the ring opening of cyclopropane, it appears that it is mainly the high dispersion of Ru in the zeolite catalysts that is responsible for the extremely high turnover frequencies. The selectivity S_2 on the zeolite-supported Ru catalysts shown in Fig. 3 has values typical for highly dispersed Ru indicating that both reactions (2) and (3) are boosted by the same order-of-magnitude. This lends further support to the hypothesis that on Ru the hydrogenation of cyclopropane via reaction (2) and the hydrogenolysis of cyclopropane via reaction (3) involve a common reaction intermediate, in contrast to the findings on Ni where the two reactions seem to proceed via different routes or intermediates (29).

The high temperature required for propane hydrogenolysis allows us to rule reaction (5) out as a secondary reaction in the cyclopropane experiments, at least under differential reaction conditions. Ethane hydrogenolysis (reaction (1)) would require an even higher temperature. Therefore, it is reasonable to assume that secondary reactions play a negligible role in the experimental results presented. This assumption is supported by a computer model of the kinetics of the reaction network for a worst case scenario (34).

CONCLUSIONS

RuNaY catalysts were investigated with respect to their activity and selectivity in the hydrogenolysis of ethane, propane, and cyclopropane. While the activity for ethane and propane hydrogenolysis appeared to be unaffected by the presence of the zeolite support, dramatic increases in activity were encountered in the hydrogenolysis of cyclopropane. It was found that substantial amounts of cyclopropane could be ad-

sorbed on the zeolite under reaction conditions. However, this adsorption phenomenon could not fully account for the order-of-magnitude increase in cyclopropane turnover numbers when compared to other Ru catalysts. The zeolite support seems to exert its effect mainly by stabilizing high Ru dispersions which in turn lead to high turnover frequencies of cyclopropane due to the apparent structure sensitivity of reactions (2) and (3). The selectivity patterns in the cyclopropane hydrogenolysis on Ru zeolites are unchanged compared to other Ru catalysts. This indicates that a common intermediate may exist for the hydrogenation and hydrogenolysis of cyclopropane on Ru. Finally, the structure sensitivity of reaction (4) follows an opposite trend as compared to reactions (2) and (3). The total cleavage of the cyclopropane ring into three molecules of methane via reaction (4) is favored on catalysts having large Ru particle sizes. These opposing trends lead to drastic changes in selectivity and activity patterns as a function of the microstructure and surface characteristics of the Ru catalysts with interesting implications for further investigations. In particular, a detailed study of the structure sensitivity of cyclopropane hydrogenation on supported Ru catalysts is currently under way.

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