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Support Effects on CO Hydrogenation over Ru/Zeolite Catalysts

Y. W. CHEN,[1] H. T. WANG,[2] AND JAMES G. GOODWIN, JR.[3]

Department of Chemical and Petroleum Engineering, University of Pittsburgh,
Pittsburgh, Pennsylvania 15261

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Hydrogenation of carbon monoxide at 101.3 kPa has been studied over a series of ion-exchanged Ru catalysts supported on NaX, NaY, KL, Na mordenite, and HY zeolites. The type of zeolite had pronounced effects on the activity and selectivity of the Ru. The specific activity would appear to be related to the dispersion of reduced ruthenium in the zeolite. Methane selectivity, however, seems to be strongly influenced by the type and concentration of alkali cations remaining in the ion-exchanged zeolite. These cations appear to promote chain growth much as traditional alkali promoters would, though perhaps more indirectly. Due to bifunctional properties of the zeolite-supported catalysts, a significant fraction of C_4 was in the form of isobutane. Formation of isobutane seems to be related to either the Si/Al ratio in the zeolites or the concentration of the remaining alkali cations, but not to the OH concentration. In addition, H_2 chemisorption at 25°C was increasingly suppressed as the Si/Al ratio of the zeolite support increased. Both the formation of isobutane and the suppression of H_2 chemisorption may be related to the acid strength of the OH groups present, which is a function of the Si/Al ratio of the zeolite.

I. INTRODUCTION

Recent studies have shown that ruthenium catalysts are very active for the water–gas shift (*1*), ammonia synthesis (*2*, *3*), hydrogenation of benzene (*4*), hydrogenolysis of propane (*5*), higher alcohol synthesis (*6*), Kolbel–Engelhardt reaction (*7*), and Fischer–Tropsch synthesis (*8*). In the Fischer–Tropsch synthesis, ruthenium has the ability to produce hydrocarbons up to heptane even at a pressure of only 1 atm. In addition, it is considerably easier to reduce than other Fischer–Tropsch metals, such as Fe and Co, and is not converted to a carbide under F-T reaction conditions. While silica, alumina, and other metal oxides have been widely used as supports for transition metals, the use of zeolite supports has been fairly limited except in hydrocracking catalysts. Due to their high surface area, shape-selective character, acidic nature, ion-exchange properties, and well-defined structure, zeolites have a great potential in Fischer–Tropsch catalysis. The large surface area allows a high degree of metal dispersion in the zeolite. While the acidity, cation-exchange properties, and shape selectivity can significantly affect the selectivity of the catalysts.

In assessing metal–support interactions, it is important to consider both electronic effects, where the support can donate or extract charge density from the metals, and bifunctional effects, where sites on the support and on the metal particles act somewhat independently on the reactants and intermediates. The behavior of transition metals in zeolites is complex and not fully understood at this time. Jacobs *et al.* (*9*, *10*) have reported that, for Ru ion-exchanged with a wide variety of zeolites, the activity for methanation increased by a factor of 3 as the Si/Al ratio of the zeolite support decreased, provided the temperature of reduction was only 300°C. Accompanying this decrease in Si/Al ratio was also a shift in product selectivity toward higher hydrocarbons. Few results on F-T activities and selectivities were given. Fajula *et*

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[1] Current address: Department of Chemical Engineering, National Central University, Taiwan.

[2] Department of Chemistry.

[3] To whom correspondence should be addressed.

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al. (*11*) have reported that the activity for methanation on Pd/HY is much higher than that on Pd/NaY catalyst. They concluded that interactions between the partially hydrogenated reactant species and the acid groups on the support result in an enhancement of the reaction rate.

The present studies were undertaken to investigate the effects of various aspects of zeolite supports on Ru catalysts for the Fischer–Tropsch synthesis. These catalysts were supported on NaX, NaY, KL, Na mordenite, and HY.

II. EXPERIMENTAL

Materials. The zeolites were obtained from Strem Chemicals (NaX, NaY, and KL) and Norton (Na Zeolon = large port Na mordenite). The composition and properties of the zeolites are listed in Table 1. HY was prepared by ion exchange of NaY to form NH_4Y. The extent of exchange was 84%. The Ru zeolites were prepared by a conventional ion-exchange technique using $Ru(NH_3)_6Cl_3$ which was obtained from Strem Chemicals.

For preparing the ion-exchanged catalysts, $Ru(NH_3)_6Cl_3$ was dissolved in a weakly acidic hydrochloride solution (pH 4.5). This solution was then mixed with the zeolite and stirred continuously for 50 h at ambient temperature. Excess solution was used to maintain an approximately constant pH during ion exchange. After the ion-exchange reaction, the catalysts were filtered and washed several times in deionized water and dried in air overnight at 40°C. The catalysts were usually decomposed slowly under vacuum (ca. 4×10^{-5} Pa) by heating to 420°C (0.5°C/min) and holding at that temperature for 2 h. Otherwise, the catalysts were decomposed under a flow of H_2 by heating slowly in a stepwise fashion to 420°C and holding for 2 h. No significant differences in catalytic behavior were found to result from these different decomposition procedures. During the decomposition procedure the NH_4Y support was converted to HY.

Catalyst characterization. The reduced catalysts were characterized by H_2 and CO chemisorption (static gas volumetry), AA, ir, and ESCA. The gas chemisorption measurements were conducted at ambient temperature in a glass adsorption system capable of achieving a vacuum of ca. 4×10^{-5} Pa. Total chemisorption of hydrogen or carbon monoxide was determined by extrapolation of the linear part of the first isotherm to zero pressure. A second isotherm was measured after evacuation of the sample for 2–3 min following the first isotherm. The second isotherm provided a measure of the reversibly bound hydrogen or carbon monoxide (both chemisorbed and physisorbed). The differences between the two isotherms gave the amount of irreversibly chemisorbed hydrogen or carbon monoxide.

The Ru metal loadings of the catalysts were determined by AA. Infrared spectroscopy was used to study CO adsorption on Ru. The ir cell was constructed of Pyrex and had KCl windows. The cell had vacuum stopcock valves at both ends to pro-

TABLE 1

Chemical Composition and Physical Properties of the Zeolites (*32*)

Zeolite	Chemical composition	Si/Al Ratio	Diameter of free apertures (nm)	Void volume (cm^3/cm^3)
NaX	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}].264H_2O$	1.23	0.74	0.50
NaY	$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}].25OH_2O$	2.41	0.74	0.48
KL	$K_9[(AlO_2)_9(SiO_2)_{27}].22H_2O$	3.0	0.71	0.32
Na mordenite	$Na_{8.7}[(AlO_2)_{8.7}(SiO_2)_{39.3}].24H_2O$	4.52	0.67 × 0.70	0.28

vide gas flow in and out. The catalyst was ground slightly in an agate mortar and then compressed under 207 MPa into a self-supporting disk having a diameter of 2.5 cm and a weight between 30 and 50 mg. Following catalyst pretreatment and adsorption of CO, spectra were recorded at 25°C. ESCA data were taken (via a sealable probe) of catalysts which had been reduced but not exposed to air. An AEI ES200 ESCA spectrometer with an Al anode was used.

Reaction studies. Kinetic measurements were made at 101.3 kPa total pressure using a $\frac{3}{8}$-in. (1 in. = 2.54 cm) stainless-steel tubular reactor that contained approximately 0.3 g of catalyst. The reactant gases used were H_2 (99.999%), He (99.997%), and a H_2/CO mixture ($H_2/CO = 1$, 99.9% pure), which were purified by passing through drierite and 5-Å molecular sieve traps to remove water and metal carbonyl contaminants. Prior to passage through the molecular sieve trap, the hydrogen was passed through a Deoxo unit from Air Products. The flow rate of each gas was controlled by a micrometering valve and measured by a bubble-flow meter. The product gas was transferred from the reactor to the sampling valve of the gas chromatograph via a heated transfer line and was analyzed by a Perkin–Elmer Sigma 1 gas chromatograph. Products were separated using a 6-ft. × $\frac{1}{8}$-in. stainless-steel column (1 ft. = 30.48 cm) packed with Porapak Q and were detected by a thermal conductivity detector. A 0.5-cm^3 gas sample was injected into the column and its temperature was held at 50°C for 2 min. The column oven was then programmed to go to 180°C at 15°C/min. The hydrogen bracketing technique, which gave the catalyst a 30-min H_2 exposure after every kinetic measurement, did an exceptionally good job of maintaining a clean Ru surface and yielded reproducible initial activities and selectivities. In order to make sure that there was no hydrocarbon produced due to the mixing of pure H_2 and the reaction mixture by gaseous diffusion during the initial period of each reaction run, both flows were separated by a short flow of He. The CO conversion was kept below 5% to minimize the effects of heat and mass transfer. Reproducibility of results was ±3%.

III. RESULTS AND DISCUSSIONS

Infrared Spectroscopy

The ir investigation of CO adsorption on these Ru zeolite catalysts at 25°C produced spectra similar to those previously reported and discussed (*12, 36*). These results showed that, in general, as the Si/Al ratio of the support increased the frequency of the absorbed CO also tended to increase indicating weaker CO chemisorption. The one case that deviated slightly from this trend was that of RuKL. It is felt that the slight deviation to lower CO vibrational frequencies was due to presence of K^+ in the L zeolite as opposed to Na^+ in all the other zeolites studied. This would seem to be reasonable given the relatively greater ability of K compared to Na to destabilize CO in alkali-promoted F-T catalysts.

ESCA

ESCA spectra from the reduced catalysts indicated a fairly complex structure. In all cases, there were 3 resolvable peaks in the Ru $3p_{3/2}$ region. In general, the ESCA data did not show a great difference among the various catalysts. From the results, one could conclude that in every case very small particles of Ru were predominately present and were in a number of different environments. The resulting species seemed to be cationic Ru possibly located in the sodalite cages, small reduced Ru particles, and small reduced Ru particles, probably located in the super cages, which appeared to be affected strongly by the zeolite (*13*). An in-depth discussion of these results will be given in a series of upcoming articles (*33, 34*).

Chemisorption

From H_2 chemisorption at 25°C, average

Ru particle diameters and dispersions were calculated (Table 2). It would appear that as the Si/Al ratio of the zeolite support increases larger average particle diameters result. However, it becomes apparent from a consideration of the CO/H ratios that suppression of hydrogen chemisorption took place on the Ru catalysts with higher Si/Al ratios (it is impossible for 1 Ru atom to bond to 12 CO ligands). The amount of such suppression was directly related to the Si/Al ratio. Since the stoichiometry of CO adsorption on Ru is determined by the metal particle size (*14*), it is difficult to use CO to determine metal surface areas. However, CO chemisorption can at least serve to compare relative metal dispersions. The CO/Ru_T ratios in Table 2 would seem to indicate that the Ru dispersions in the various catalysts were similar and probably on the order of 70–90%.

Catalytic Activity

The F-T synthesis was carried over a range of temperatures. Table 3 shows typical results for the various catalysts at a reaction temperature of 250°C. As can be seen in Table 3, the specific rate of reaction of CO varied by a factor of 2. Specific rate is used due to the uncertainty in the determination of the number of Ru surface sites as a result of various degrees of hydrogen chemisorption suppression at 25°C. However, these specific rates should vary approximately in the same way as the turnover number (TON) since these catalysts appear to have similar dispersions as measured by CO chemisorption.

TABLE 2

Catalyst Characteristics Based on Chemisorption

Catalyst	d_p[a] (nm)	D[a] (%)	CO/H_{ir}	CO_{ir}/Ru_T
2.5% RuNaX	1.0	83	2.98	2.47
3.1% RuNaY	1.6	51	4.59	2.24
2.8% RuKL	2.6	32	9.88	3.16
2.2% RuNaM	3.9	22	12	2.64

[a] Determined from irreversible H_2 chemisorption.

TABLE 3

Effect of the Support on F-T Synthesis

Catalyst	$-r_{CO}$ (mol/s · g cat)	CH_4 (wt%)	Olefin fraction in C_2–C_4 (wt%)
2.5% RuNaX	2.46	47	0.49
3.1% RuNaY	1.21	73	0.53
3.0% RuHY	1.23	97	ca. 0.59
2.8% RuKL	2.20	54	0.56
2.2% RuNaM	1.06	83	ca. 0.38

Note. Reaction conditions: 250°C, $H_2/CO = 1$, 1 atm, GHSV = 1800 h^{-1}. Products determined by TCD through C_5 (little HC above C_5).

Jacobs *et al.* (*9, 10*) reported that for catalysts prepared by ion exchange of $Ru(NH_3)_6Cl_3$ with a wide variety of zeolites the activity for methanation decreased with increasing Si/Al ratio of the zeolite support, provided the temperature of reduction was only 300°C. Due to the high metal loading used (5.6 wt% Ru), the Ru was not highly dispersed in these catalysts. This is indicated by the fact that the CO/Ru ratios were less than unity.

Coughlan *et al.* (*15–18*) previously reported the exchange of $[Ru(H_2O)_6]^{3+}$ into several zeolites. They (*17*) reported that the turnover number for the hydrogenation of benzene increased smoothly with increasing metal surface area and was independent of the type of the zeolite. Their catalysts were prepared, however, at a pH of 6.5, where $[Ru(H_2O)_6]^{3+}$ is unstable and polymerized hydroxy species are known to occur (*19*). This would result in the formation of large Ru particles on the external surface of the zeolite support. King (*20*) did not see any differences between the specific activities of NaX- and NaY-supported Ru catalysts for CO hydrogenation. The starting material was $Ru(NO)(NO_3)_3$ and a high metal loading was used in his catalysts. As a result, the formation of large Ru metal particles on the external surfaces of the zeolites would have been likely. In addition, the reaction was not operated in a differential mode and secondary reactions were probably also significant.

In this study, the observed differences in specific activity do not seem to be related to any of the known characteristics of the zeolites, such as Si/Al ratio, OH concentration, and remaining alkali concentration. The differences might be due to the particle size effect or the degree of reduction of the Ru. From an intensive study of Ru/NaY catalysts (*21*), it has been found that turnover number is a strong function of average particle size. However, based on the CO chemisorption results, we hypothesize that the average particle size of all the catalysts in this study were approximately the same. Therefore, it would seem that the particle size is not the only important variable affecting activity.

Suzuki *et al.* (*22, 23*) have reported that the activity of zeolite-supported Ni for several reactions is proportional to the dispersion of reduced nickel. The degree of nickel ion reduction and the dispersion state of the reduced nickel were found to be affected by the type of zeolite support and the extent of nickel exchange. It is well known that one of the main factors determining the metallic dispersion is the strength of interactions between the metallic particles and the support. In the case of zeolite carriers, the electron-deficient character of small metallic particles has been shown, by XPS and ir, for several Pd/NaY (*24*) and Pt/NaY (*25*) catalysts. This was explained by the withdrawal of electrons from the metal particles by electron-acceptor sites of the support. In a recent paper Fajula *et al.* (*11*) found the activity for methanation on Pd/HY to be much higher than that on Pd/NaY catalysts. They postulated that methanation on supported palladium proceeds mainly through direct CO hydrogenation with the participation of acid sites on the support. In this study, however, no differences were found in the rate of CO conversion over the ruthenium catalysts under F-T conditions which followed changes in OH concentration. It must be concluded therefore that rate of reaction is a complex function of a number of factors such as particle size, zeolite–metal interaction, etc.

Catalytic Selectivity

Olefin fraction. The data in Table 3 show that the olefin fraction of C_2–C_4 hydrocarbons was approximately constant for all the supports used. The values that deviate the most from 0.53 do so due to the fact that mostly methane was produced in those cases, hence the error in calculation of the C_2–C_4 olefin fraction was much greater.

Methane. There were very large differences in the selectivity for methane. Since particle size has been found not to be a factor in determining this quantity for NaY zeolite-supported Ru (*21*), one must look to characteristics of the zeolite supports which might affect it. Three of the most likely candidates are Si/Al ratio, OH concentration in the reduced catalysts, and the concentration and type of alkali cations remaining after ion exchange. One or more of these characteristics might cause a given effect on selectivity by affecting the Ru directly via some type of metal–support interaction or by interacting directly with primary or secondary reaction products. These characteristics are related by

$$N_H = \frac{1}{r+1} N - N_{Na}$$

where

$N_H = f\,N_{Al}$

N_H = estimated concentration of OH groups (mol/g)

N_{Al} = concentration of Al in zeolite (mol/g)

N_{Na} = concentration of Na^+ remaining (mol/g)

N = total concentration of Si and Al (mol/g)

f = fraction of exchange of Na^+ or K^+ by Ru cations

r = Si/Al ratio

Thus, the Si/Al ratio, concentration of OH groups, and remaining alkali cation concentration are complex functions of each other. Figure 1 shows a plot of methane selectivity versus Si/Al ratio. As can be seen, Si/Al ratio does not appear to correlate very well to the results found. Figure 2 shows a plot of methane selectivity versus estimated OH concentration resulting from reduction of the Ru cations, as calculated from the amount of Ru exchanged and the assumption of the formation of 3 OH groups per Ru cation reduced. For the HY supported catalyst, 84% of the cations present were assumed to be H^+. The OH concentration too does not appear to greatly affect methane selectivity. However, methane selectivity appears to be a strong function of the concentration of the residual neutralizing alkali cations (Fig. 3). This should not be surprising considering that alkali species are well-known promoters of the F-T synthesis and tend to increase chain growth probability and, thereby, to decrease the methane selectivity. The only catalyst that deviates greatly from the linear relationship in Fig. 3 is RuKL. This deviation is most likely due to the fact that this zeolite contains K^+ instead of Na^+ like the others. If Na^+ in a zeolite does have a promotion function, then K^+ should have an even greater one since most results in the literature show K compounds to be better promoters of chain growth than Na compounds. This is in fact, what is observed for RuKL. The result for RuKL lies well below the line connecting the points for the other catalysts and has a much lower methane selectivity than it would if it were on that line. However, the seeming effect of these cations may be produced in quite a different manner than that of regular alkali promotion. In addition, it is possible that these cations may act in an indirect manner upon the Ru, affecting such things as the electrostatic field in the zeolite.

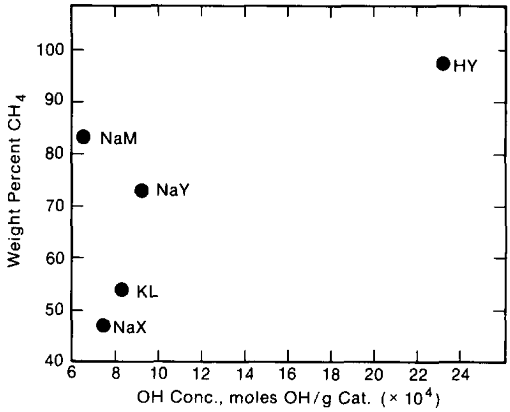


FIG. 2. Methane selectivity versus catalyst OH concentration.

While the NaM-supported Ru exhibited the greatest amount of hydrogen chemisorption suppression at ambient temperature, it also gave the highest selectivity for

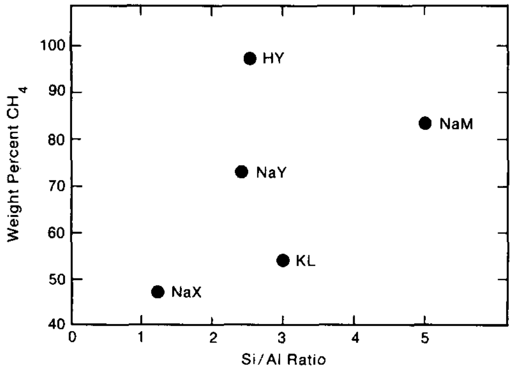


FIG. 1. Methane selectivity versus catalyst Si/Al ratio.

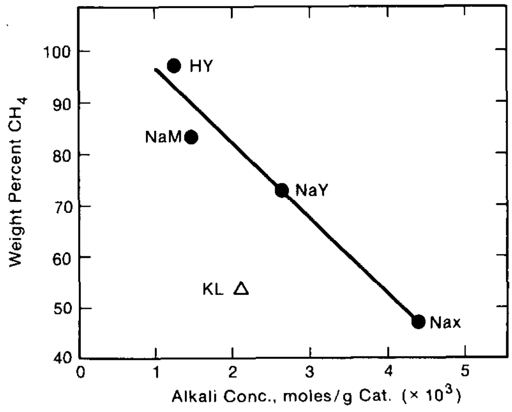


FIG. 3. Methane selectivity versus residual alkali cation concentration.

CH_4 of the alkali-containing zeolite based catalysts. These results point out the complexity of the F-T system of reactions and the difficulty in applying adsorption characteristics of a catalyst at lower temperatures to the understanding of events occurring on the catalyst surface at F-T conditions. It is thus more important to understand the quality of the catalyst that gives rise to the H_2 chemisorption ability and how it may affect other surface steps during F-T than to understand such an isolated event, since it is the relative rates of reaction of the various steps (adsorption, surface reaction, desorption) which determine product selectivity. More work is needed before such an understanding is possible.

Isobutane. A significant fraction of C_4 was in the form of isobutane for a number of the catalysts. Due to bifunctional properties of zeolite-supported catalysts (*26–28*) it is not surprising that branched hydrocarbons would be found in the product stream. However, as can be seen in Fig. 4, OH concentration did not appear to play a role in producing isobutane. Both the Si/Al ratio (Fig. 5) and residual alkali concentration (Fig. 6) seemed to be related to the formation of isobutane if one neglects RuHY due to relatively large Ru particles formed.

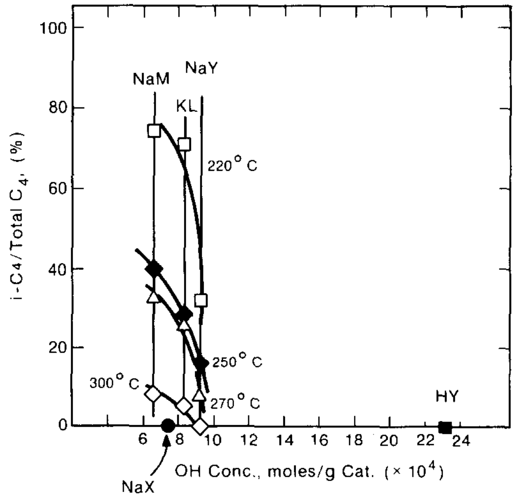


FIG. 4. Isobutane selectivity versus OH concentration.

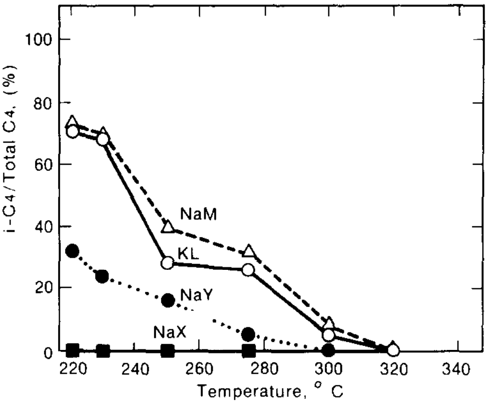


FIG. 5. Isobutane selectivity versus temperature.

King (*20*) explored F-T synthesis over a group of Ru catalysts having NaX, NaY, and silica–alumina as supports. He found that the Si/Al ratio appeared to be important in affecting the fraction of isobutane formed. Our results are in accord with his. Based on a previous study of the effect of preparation method on the F-T properties of NaY-supported Ru (*21*), only catalysts prepared by ion exchange produced isobutane. Catalysts prepared by vapor impregnation with $Ru_3(CO)_{12}$ and having similar Ru dispersions as the ion-exchanged catalysts, the same Si/Al ratio, higher concentrations of Na^+, and no significant concentration of OH groups did not produce any isobutane. Thus, the Si/Al ratio, by itself,

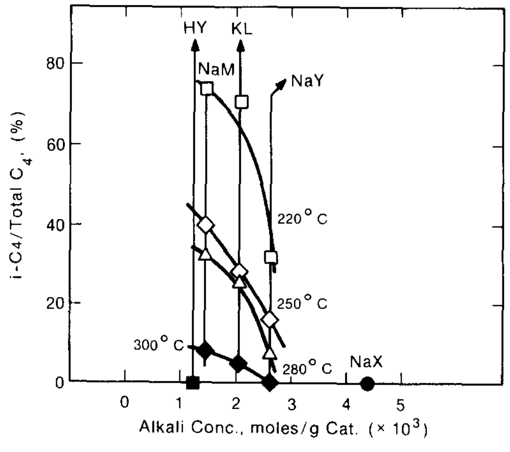
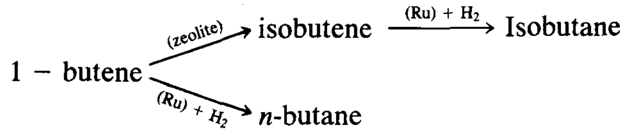


FIG. 6. Isobutane selectivity versus residual alkali cation concentration.

does not directly affect this production. However, since the acid strength of the OH groups increases with an increase in the Si/Al ratio, it is suggested that the combination of presence of OH groups and their strength may influence the formation of isobutane. It has also been suggested that this combination may be the cause of H_2 chemisorption suppression (*35*). The relationship of isobutane formation to residual alkali concentration may be only coincidental, due to the fact that, for the same Ru loading, the residual alkali concentration decreases as the Si/Al ratio increases. This is because, for higher Si/Al ratios, the initial alkali cation concentrations are less.

The role of mass transport in polyfunctional catalysis has been considered in detail by Weisz (*29*). Diffusional kinetics are likely to be particularly important for the production of isobutane in the present system. The formation of isobutane can be described by the following mechanism



Weisz (*29*) has derived a general criterion to check for the absence of mass transport limitations, and many researchers (*27, 28, 30*) have used this criterion with zeolite catalysts. Therefore, Weisz's criterion (*29*) was applied to give an indication of the presence or absence of mass transport limitations in this study. The criterion for the absence of mass transport limitations is

$$\Phi = \frac{dn}{dt}\frac{1}{[\mathrm{B}]_{\mathrm{eq}}}\frac{R^2}{D} \ll 1$$

where

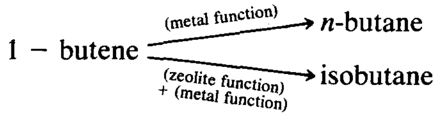
Φ = Weisz's number
dn/dt = reaction rate for isobutane formation per unit volume catalyst
$[\mathrm{B}]_{\mathrm{eq}}$ = concentration of isobutene at equilibrium
R = radius of zeolite particle
D = diffusivity of isobutene

From the observed conversion, the rate of isobutane formation per unit volume of catalyst was calculated to be 0.5×10^{-8} mol s^{-1} cm^{-3}. Due to the complexity of the C_4 species, we were not able to calculate $[\mathrm{B}]_{\mathrm{eq}}$ exactly. The maximum possible concentration was estimated to be about 50% of isobutane; for steady state operation $[\mathrm{B}]_{\mathrm{eq}}$ would be thus about 0.25×10^{-8} mol cm^{-3}. The effective diffusivity of isobutene in NaY has been reported to be 1.0×10^{-6} cm^2 s^{-1} at 250°C (*31*), and the radii of the zeolite particles were about 0.01 cm (100–120 mesh). Applying Weisz's criterion, one obtains $\Phi \gg 1$ this indicates that the reaction was probably substantially constrained by diffusion limitations. In this study the residence time of 1-butene in a zeolite particle would have been approximately:

$$t = \frac{L^2}{2D} = \frac{(0.02)^2}{(2)(1.0 \times 10^{-6})} = 200 \text{ s.}$$

This is long enough to produce the isomerization reaction within the same zeolite particle.

The observed reaction temperature effect on isobutane selectivity can be interpreted by the assumption of competing reactions, as shown in the scheme:



Selectivity would be dependent upon the relative effectiveness factors, which are determined by diffusion criteria. Isobutane formation normally decreases with increasing temperature of the reaction, as can be seen in Fig. 5. Since the hydrogenation activity of Ru is expected to be greater at higher temperatures and the residence time of 1-butene is decreased with increasing temperature, the isomerization activity is greatly reduced at higher temperatures.

CONCLUSIONS

A series of ion-exchanged zeolite-supported Ru catalysts have been studied. The results of this study suggest that the type of zeolite support has pronounced effects on the activity and selectivity of Ru for CO hydrogenation. The specific activity appears to be related in part to the dispersion of reduced ruthenium in the zeolite. The degree of ruthenium ion reduction and the dispersion of the reduced ruthenium are probably affected by the type of zeolite support. Olefin selectivity does not seem to vary greatly with the different supports. Methane selectivity, however, appears to be strongly related to the concentration of the alkali cations remaining in the zeolite. As far as is known, this is the first time that chain growth promotion in F-T synthesis by the neutralizing alkali cations in zeolites has been suggested. It is not yet known whether this is due to direct or indirect interaction.

Formation of isobutane is perhaps related to either the Si/Al ratio or the concentration of remaining alkali cations, but it is not related to the OH concentration. It is suggested, however, that this formation may be related to the acid strength of the OH groups present, which is a function of the Si/Al ratio. Although CO diffusion does not significantly affect the specific activity of CO conversion, the diffusion of 1-butene plays an important role in the formation of isobutane.

It is important to keep in mind that there are a large number of factors which may affect the properties of a zeolite-supported metal. Some of them are metal particle size and geometry, metal reducibility, location of metal, pore structure, OH concentration and strength, Lewis acidity, neutralizing cations present and their concentration, interaction of the metal with the zeolite (OH's, L.A. sites, cations, structural oxygen), defect structure, and presence of impurities. Different catalyst preparation methods (*21*), pretreatment conditions, etc., may cause different factors to be important in determining catalytic properties.

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