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Catalytic Hydrogenation of Carbon Monoxide on Ruthenium Y-Zeolites

Effect of Support on Activity and Selectivity

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The specific activity of ruthenium supported on zeolite Y in the hydrogenation of carbon monoxide is enhanced when the charge-compensating sodium ions are replaced by multivalent cations or protons. This effect is attributed to an increase in electron deficiency of the metal crystallites owing to an electron transfer from the metal to electron-acceptor sites in the support. Hydrogen then competes more successfully with carbon monoxide for available surface sites, resulting in an increased hydrogenation activity. This conclusion is supported by the marked decrease in the selectivity to olefins which is observed. The electronic influence of the support is greater for small metal particles. © 1985 Academic Press, Inc.

INTRODUCTION

An important goal in recent research on hydrocarbon synthesis by the catalytic hydrogenation of carbon monoxide has been that of selectivity control. Depending on particular requirements, this may be in the direction of gasoline or diesel fractions as alternative fuels or toward low-molecular-weight olefins for use as chemical feedstocks.

The state of dispersion of the catalytically active metal is evidently (*1*) an important factor in controlling hydrocarbon chain length. Considerable shifts in selectivity have been reported for supported metal catalysts possessing a narrow distribution of particle sizes such as exists for metals encapsulated in zeolite supports. For example, ruthenium in zeolite Y is reported to be selective (*2*) for the synthesis of hydrocarbons in the C_1–C_{10} range, while an appropriate treatment of cobalt-exchanged zeolite A yields propylene as the only hydrocarbon product (*3*). Using iron, cobalt, and ruthenium carbonyl complexes deposited in zeolite Y as catalyst precursors, short-chain hydrocarbons in the C_1–C_9 range are obtained (*4*).

However, the influence of the support in altering the catalytic behavior of a metal extends beyond purely dispersional effects. Strong interactions between small metal clusters and the support can modify the electronic structure of the metal with concomitant effects on catalytic behavior. Titania-supported nickel, palladium, and ruthenium, for example, possess activities and selectivities in the hydrogenation of carbon monoxide (*5–7*) which differ significantly from conventional silica- and alumina-supported catalysts. These effects have been attributed to a strong metal–support interaction, although the precise nature of this interaction remains unclear.

The electronic structure of small metal clusters encaged in acidic zeolite supports is modified (*8*) by the interaction of the metal with the strong electron-acceptor sites which exist in these materials. Platinum particles in Y-type zeolite, for instance, are electrophilic in character (*9*) owing to a partial electron transfer to the

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support, and exhibit anomalously high specific activities (*10*) for hydrogenation, isomerization, and hydrogenolysis reactions. Palladium supported on zeolite Y exhibits (*11*) similar behavior.

In the present study, the influence of zeolite support interactions on the catalytic behavior of ruthenium in the hydrogenation of carbon monoxide was investigated. Apart from the effect of metal dispersion on hydrocarbon chain length, attention was given to the influence of electronic interactions between the metal and support on specific activities and product distribution.

TABLE 1

Composition of Supported Ruthenium Catalysts

Catalyst	Na^+ % of c.e.c.[a]	M^{n+} % of c.e.c.[a]	Ru mass %
RuNaY-I	76	—	1.44
RuMgY-I	22	53	1.84
RuLaY-I	27	63	0.85
$RuNH_4Y$-I	7	80	1.28
RuNaY-II	93	—	0.71
RuMgY-II	27	70	0.65
RuLaY-II	27	67	0.80
$RuNH_4Y$-II	8	85	0.75

[a] Cation exchange capacity.

EXPERIMENTAL

Materials. The zeolite support materials were prepared from the parent NaY zeolite (Linde LZ-Y52) by exchanging part of the Na^+ ions with NH_4^+, Mg^{2+}, and La^{3+} using conventional ion-exchange techniques. Ruthenium was introduced into these zeolites by two methods. The first series of catalysts, designated Y-I, was prepared by stirring the zeolite at ambient temperature for 12 h in a 3×10^{-3} mol dm^{-3} aqueous solution of ruthenium trichloride (Johnson Matthey Chemicals) to yield a ruthenium content of approximately 1 mass%. The second series, designated Y-II, was prepared by ion exchange for 12 h at ambient temperature using a 2×10^{-3} mol dm^{-3} aqueous solution of $Ru(NH_3)_6Cl_3$ (Strem Chemicals). In both cases the pH of the suspension was in the range 5 to 6. Following introduction of the ruthenium, the zeolites were filtered, washed free of chloride, air-dried, and subsequently stored over saturated calcium nitrate solution. The chemical compositions of the catalysts are given in Table 1. The catalyst powder was pressed into wafers and crushed, the 180- to 250-μm fraction being retained for further use.

Hydrogen of 99.999% purity, supplied by Afrox, was further purified by passage through a Deoxo unit (Engelhard Industries) followed by a 5A molecular sieve trap maintained at 77 K. Matheson grade carbon monoxide (99.99%) was passed through an activated-charcoal trap before use. Helium of 99.995% purity, supplied by Air Products, was further purified by passage through a 5A molecular sieve trap at 77 K followed by an Oxy-trap (Alltech Associates), while argon of 99.999% purity, supplied by Afrox, was passed through a 5A molecular sieve trap at 200 K followed by an Oxy-trap.

Apparatus and procedure. Kinetic measurements were performed on 0.2-g samples of catalyst supported on a porous quartz frit in a downflow quartz tubular microreactor operating at atmospheric pressure. CO conversions were kept below 3% so that the reactor operated under differential conditions, thus minimizing the effects of heat and mass transfer. Standard catalytic runs were performed at 493 K using an $H_2:CO$ ratio of 2. Product analyses were carried out on-line using a Hewlett–Packard 5836A reporting gas chromatograph equipped with TCD and FID detectors. A Porapak Q column was used with helium as carrier gas. To achieve steady-state operation, the synthesis gas was flowed over the catalyst for 15 min before a sample was taken for analysis. A bracketing procedure similar to that described by Sinfelt (*12*) was used to maintain a clean metal surface; the reactant stream was replaced by pure hydrogen and the catalyst heated to and maintained at 623 K for a period of 1 h.

Standard catalyst pretreatment consisted of vacuum outgassing of the sample in 100 K steps at a heating rate of 1.5 K min^{-1} and holding the temperature at each step for 1 h, until a final temperature of 673 K was attained. The catalyst was held at this temperature for approximately 6 h, cooled to 623 K, and reduced in flowing hydrogen at a flow rate of 40 ml min^{-1} for 10 h. The catalyst was then cooled to the desired reaction temperature in flowing hydrogen. To investigate the effect of the presence of water vapor during reduction on the metal dispersion, samples of RuNH$_4$Y-II were also outgassed at 300 K for 15 min followed by heating to 623 K in moist flowing hydrogen at a flow rate of 20 ml min^{-1} for 6 h. Reduction in dry flowing hydrogen was then continued for a further 10 h.

Metal dispersions for both the freshly reduced and spent catalysts were calculated from hydrogen chemisorption data obtained by temperature-programmed desorption (TPD). The quantity of hydrogen chemisorbed during cooling of the reduced catalyst overnight in flowing hydrogen from 623 K to ambient temperature was measured by desorption to 623 K. A distinct minimum in the hydrogen desorption spectrum occurred at this temperature and, following Verdonck *et al.* (*13*), the hydrogen recovered up to this point was attributed to irreversibly chemisorbed hydrogen.

The possible contribution of hydrogen adsorbed on ruthenium atoms in the sodalite cages or of subsurface hydrogen, both of which desorb above 623 K, was excluded from the measurement in the following way. Hydrogen was first desorbed to 723 K, the catalyst was cooled to 623 K, and hydrogen was then readsorbed by flowing the gas over the catalyst as it cooled to ambient temperature. No migration of the hydrogen present in the high-temperature desorption states to the low-temperature state occurred following desorption to 723 K and all of the readsorbed hydrogen was recovered below 623 K.

The apparatus used was similar to that described by Robertson *et al.* (*14*). One-gram samples of catalyst were contained in a reactor identical to that employed in the catalytic studies and desorption was carried out at a heating rate of 5 K min^{-1} in an argon flow of 20 ml min^{-1}. Physisorbed hydrogen was first removed by flowing argon through the reactor at ambient temperature for 1 h. Spent catalysts were rereduced in flowing hydrogen at 623 K for 4 h prior to the desorption experiment.

RESULTS

Hydrogen chemisorption data on both the freshly reduced and used catalysts are given in Table 2. Catalysts prepared by ion

TABLE 2

Hydrogen Chemisorption on Supported Ruthenium Catalysts

Catalyst	Hydrogen uptake (mol g catalyst^{-1} × 10^6)		H[a]/Ru	Average crystallite size (nm)	
	Fresh	Used		Fresh	Used
RuNaY-I	13.2	14.1	0.20	4.9	4.6
RuMgY-I	19.0	16.7	0.18	4.3	4.9
RuLaY-I	18.3	19.3	0.46	2.1	2.0
RuNH$_4$Y-I[b]	14.6	18.2	0.28	4.0	3.2
RuNaY-II	27.0	15.6	0.45	1.2	2.0
RuMgY-II	20.7	11.4	0.35	1.4	2.6
RuLaY-II	21.7	17.5	0.44	1.6	2.0
RuNH$_4$Y-II[b]	14.5	19.7	0.53	2.3	1.7

[a] Based on H_2 chemisorption on the used catalyst.

[b] Converted to protonic form.

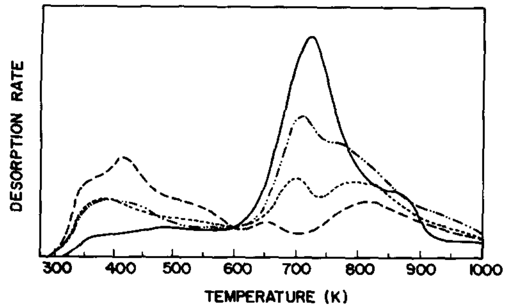

FIG. 1. Temperature-programmed desorption of hydrogen from RuNH$_4$Y-II (—), RuMgY-II (–·–·–), RuLaY-II (– – –), and RuNaY-II (— — —).

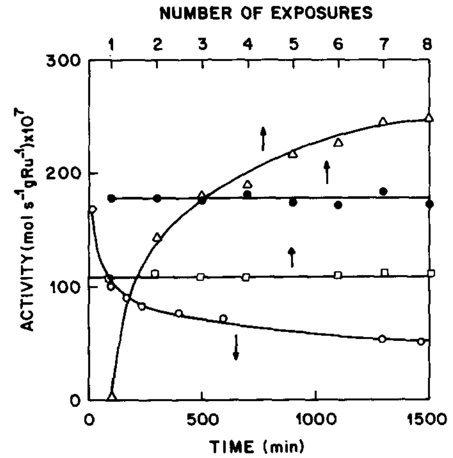

FIG. 2. Effect of time on stream or number of exposures to synthesis gas on activity of RuMgY-I (○, ●), RuNH$_4$Y-II (△), and RuNH$_4$Y-II reduced in moist hydrogen (□).

exchange using Ru(NH$_3$)$_6$Cl$_3$(Y-II) resulted in a higher ruthenium dispersion upon reduction than was the case for the catalysts prepared using ruthenium trichloride (Y-I). However, this dispersion decreased following exposure of the catalyst to synthesis gas and regeneration in hydrogen. In the case of ruthenium supported on the ammonium form of the zeolite, an apparent increase in the ruthenium dispersion accompanied the synthesis reaction.

The TPD spectra of hydrogen from the freshly reduced Y-II series of catalysts exhibited two broad high-temperature maxima at around 700 and 800 K, respectively. The intensity of the 700 K peak varied with the nature of the exchange cation and showed a maximum intensity for the RuNH$_4$Y-II catalyst (Fig. 1). Only the 800 K peak was present in the high-temperature region in the desorption spectra of the Y-I catalysts.

The activity of the Y-I catalysts decreased by some 70% during the first 24 h of continuous exposure to synthesis gas. However, using the bracketing technique described above, the initial activity levels were reproducibly maintained. This is illustrated typically for RuMgY-I in Fig. 2. In contrast, the activity of the Y-II catalysts increased markedly following the first exposure of the catalyst to synthesis gas and subsequent hydrogen treatment. The activity leveled off eventually after about nine exposures to synthesis gas, as shown in Fig. 2 for RuNH$_4$Y-II. The Arrhenius plots shown in Fig. 3 confirm the stability of the catalysts following several reaction–regeneration cycles. Exposure of the freshly reduced catalyst to carbon monoxide alone followed by hydrogen treatment in the standard way did not result in an enhancement in activity.

Turnover numbers for carbon monoxide conversion over RuNH$_4$Y-II were calculated from hydrogen chemisorption data obtained after completion of a number of reaction-regeneration cycles and are sum-

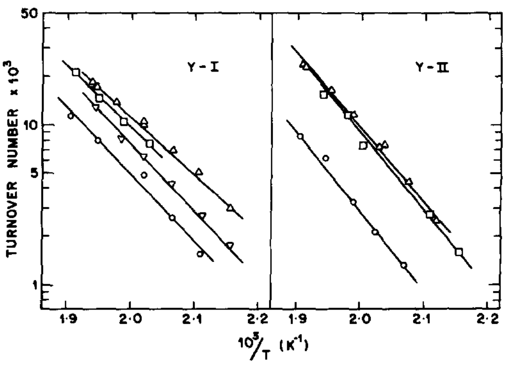

FIG. 3. Arrhenius plots for CO conversion over ruthenium on various zeolite supports. ○, NaY; △, MgY; □, LaY; ▽, NH$_4$Y.

TABLE 3

Hydrogen Chemisorption and Turnover Number (*N*) for CO Disappearance on $RuNH_4Y$-II

Number of exposures to synthesis gas	Hydrogen uptake (mol g^{-1} × 10^6)	H/M	N[a] (s^{-1} × 10^5)
0	14.5	0.39	6.8
1	14.2	0.38	380
3	15.1	0.41	470
6	19.6	0.53	470

[a] Number of CO molecules converted per second per surface ruthenium atom.

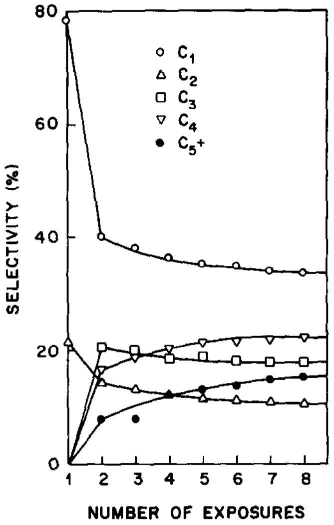

FIG. 4. Effect of number of exposures to synthesis gas on selectivity of $RuNH_4Y$-II.

marized in Table 3. A sharp increase in specific activity after the first cycle was followed by a more gradual increase and a constant activity was obtained after about four cycles. Kinetic data for both the Y-I catalysts and the Y-II catalysts in their stabilized state are summarized in Table 4. An increase in turnover number for carbon monoxide conversion by a factor of two to three occurred when the sodium cations in the zeolite support were extensively replaced by multivalent cations or protons.

The product of carbon monoxide hydrogenation on the freshly reduced Y-II catalysts was mainly methane with small amounts of ethane. In subsequent runs following intermediate hydrogen treatment, the product spectrum shifted towards higher hydrocarbons as illustrated in Fig. 4 and included substantial amounts of olefinic hydrocarbons. The product spectrum observed for the Y-I catalysts ranged from C_1 to C_6 and remained essentially unchanged during repeat runs. Samples of $RuNH_4Y$-II catalysts preheated in moist hydrogen showed similar behavior. Selectivity data for all the catalysts studied at similar conversion levels are given in Table 5. A higher proportion of C_1–C_3 hydrocarbons was obtained on the Y-II series of catalysts than on the Y-I series, for which the product distribution was shifted in the direction of longer hydrocarbon chains.

The olefin-to-paraffin ratio of the C_3 fraction gives a good indication of the olefin-forming ability of the catalysts. This ratio was highest when the sodium form of the zeolite was employed as the support and decreased markedly on replacement of the sodium cations by multivalent cations or protons. The extent of chain branching in the product was also strongly influenced by the nature of the majority exchange cation and this effect is illustrated in Table 5 by the isobutane content of the C_4 fraction. No isobutane was obtained when the sodium form of the support was used but it was

TABLE 4

Activity Data for Supported Ruthenium Catalysts

Catalyst	Activity[a] (mol s^{-1} g Ru^{-1}) × 10^7	N[b] (s^{-1} × 10^3)	Activation energy (kJ mol^{-1})
RuNaY-I	72.9	3.7	79.8
RuMgY-I	160.2	8.8	69.5
RuLaY-I	339.6	7.5	73.6
$RuNH_4Y$-I	163.8	5.8	79.8
RuNaY-II	91.9	2.1	94.2
RuMgY-II	245.2	7.0	89.7
RuLaY-II	284.8	6.5	92.7
$RuNH_4Y$-II	247.6	4.7	—

[a] Reaction temperature, 493 K; $H_2 : CO = 2$; pressure 101 kPa.

[b] Number of CO molecules converted per second per surface ruthenium atom; based on H_2 chemisorption on used sample.

TABLE 5

Selectivity[a] of Supported Ruthenium Catalysts

Catalyst	CO conversion (%)	C_1	C_2	C_3	C_4	C_{5+}	C_3^{2-}/C_3^{-}	i-C_4H_{10}/ Total C_4
RuNaY-I	2.0	23.1	9.5	20.5	27.6	19.2	3.8	0.1
RuMgY-I	3.8	24.3	8.0	13.6	30.6	23.4	1.8	0.75
RuLaY-I	3.1	22.8	7.4	8.9	36.0	24.8	1.8	0.89
$RuNH_4Y$-I	2.4	25.5	8.5	14.1	27.5	24.5	1.5	0.75
RuNaY-II	0.7	40.9	15.2	24.9	12.9	6.2	4.4	0.00
RuMgY-II	2.0	40.5	12.7	17.8	18.0	10.9	1.1	0.62
RuLaY-II	2.5	40.4	14.3	15.2	19.9	10.2	0.8	0.78
$RuNH_4Y$-II	2.3	33.6	10.7	18.0	22.4	15.4	1.8	0.64
RuNaY-II + LaY	0.5	45.6	17.7	19.1	13.3	4.4	3.0	0.60

[a] Mole percentage CO converted into stated product.

present in considerable quantities on the protonic and multivalent cation exchanged forms.

To check the influence on product distribution of the acidic support alone, the synthesis reaction was performed on an intimate mixture of equal amounts of RuNaY-II and a 70% exchanged lanthanum Y-zeolite which is well known to possess strongly acidic properties. The product distributions given in Table 5 indicate that isomerization of the C_4 product occurred, as would be expected in the presence of a strongly acidic catalyst. However, the C_3 olefin selectivity remained considerably higher than that obtained using the RuLaY-II catalyst.

DISCUSSION

Variations in catalytic activity attributable to a support effect can arise from a variety of phenomena, the two most commonly discussed effects being metal particle size effects and those arising from electronic interactions between the metal and the support. The hydrogenation of carbon monoxide to hydrocarbons is a structure-sensitive reaction (*2*, *15*) so that to separate possible electronic influences from dispersional effects, the reaction must be performed on metal crystallites of comparable size.

The state of dispersion of ruthenium in zeolites is influenced not only by the pretreatment conditions (*13*) but also by the method of introduction of the metal. "Ruthenium trichloride" is known (*16*) to consist of a mixture of Ru(III) and Ru(IV) and is extensively hydrolyzed in aqueous solution. It is to be expected therefore that at the pH at which the ruthenium was introduced into the zeolite by this method, some deposition of the metal on the external surface of the zeolite occurs. This would account for the poorer ruthenium dispersion observed in the Y-I catalysts; nevertheless the average crystallite sizes obtained were comparable for the various cationic forms of the zeolite and remained reasonably stable during the course of the reaction–regeneration cycles.

The average sizes of the ruthenium crystallites formed in the freshly reduced catalysts prepared by ion exchange are within the limit of the diameter of the supercage in zeolite Y. X-Ray studies on a vacuum-pretreated RuNaY catalyst prepared in a similar way have shown (*17*) that following reduction, approximately 19% of the ruthenium is located in the sodalite cages. This ruthenium is inaccessible for hydrogen chemisorption so that the initial metal dispersion is in reality considerably higher than the calculated value.

The high-temperature peak at 700 K observed in the TPD spectra of hydrogen from the freshly reduced Y-II catalysts may also be explained by the presence of a substantial fraction of ruthenium in the sodalite cages. The poorly dispersed Y-I catalysts which contain mainly larger metal crystallites on the external surface do not exhibit this peak in their desorption spectra.

Hydrogen (kinetic diameter, 0.289 nm) adsorbed on ruthenium atoms in the sodalite cages during reduction would be expected to require a higher temperature to desorb through the 0.22-nm aperture of the sodalite cage than would be necessary for desorption from ruthenium crystallites in the supercages. Furthermore, this hydrogen is not readsorbed at ambient temperature following desorption. The small amounts of hydrogen recovered around 800 K are attributed to hydrogen dissolved in subsurface layers of the ruthenium crystallites, in agreement (*13*, *18*) with other workers.

Approximately 2.5 times as much hydrogen is desorbed above 623 K from freshly reduced $RuNH_4Y$-II than from a similarly prepared and pretreated RuNaY catalyst. This suggests that up to 50% of the ruthenium in the $RuNH_4Y$-II catalyst is located in sodalite cages. Thus the ruthenium crystallites which are accessible to reactant molecules will have an average diameter of about 1.2 nm, which allows them to be located inside the supercage. Furthermore, the almost exclusive formation of methane during the initial exposure of the catalyst to synthesis gas indicates (*2*) a much smaller crystallite size than that calculated from the hydrogen chemisorption data.

The decrease in the ruthenium dispersion during regeneration of the catalysts in hydrogen is probably due to the influence of water formed during the synthesis reaction and subsequently adsorbed in the zeolite. Agglomeration of zeolitic ruthenium into larger particles during reduction in the presence of water vapor has been noted (*13*) previously. The crystallites formed are larger than can be accommodated in the supercages; however, this does not necessarily imply that the ruthenium has migrated to the external surface of the zeolite. Verdonck *et al.* (*13*) and others (*19*) have suggested that larger metal particles exist in holes in the zeolite crystals, possibly created by a partial hydrolysis of the framework aluminum. Indeed, for the low ruthenium loading used in the present work, comparatively few of these holes would be required to accommodate the 2.0- to 2.5-nm particles obtained. Alternatively larger metal particles could be formed which protrude into several supercages while still remaining accessible to reactant molecules.

Attempts to differentiate between supercage ruthenium, ruthenium in holes, and ruthenium on the external surface from the positions (*13*) of the peak maxima in temperature-programmed oxidation of the metal, proved unsuccessful. Using this technique, no evidence was found for external ruthenium in Y-II catalysts, which contrasts with the Y-I catalysts where a broad maximum at 746 K was observed.

Migration of ruthenium from inaccessible positions in the sodalite cages leads to an increase in the number of particles able to chemisorb hydrogen and accounts for the apparent redispersion observed following several catalytic cycles on $RuNH_4Y$-II even though, by comparison with the other catalysts in the series, some sintering of the particles has occurred.

The low initial activity of the Y-II catalysts is indicative of a high ruthenium dispersion and contrasts with the Y-I series of catalysts where the larger ruthenium crystallites result in a much higher activity. The marked increase in specific activity of the Y-II catalysts following the first exposure to synthesis gas and subsequent regeneration in hydrogen is followed by a more gradual increase after further reaction–regeneration cycles and a subsequent leveling off in activity. This 50- to 100-fold increase in turnover number is associated with a decrease in the ruthenium dispersion and is further evidence for the demanding nature of the synthesis reaction. Overall increases in activity of the same order of magnitude, rapid at high dispersions and more gradual as the dispersion decreased, were also observed by Kellner and Bell (*20*) for ruthenium-on-alumina catalysts. This activity increase was ascribed to an increase in the fraction of suitably reactive sites on the ruthenium surface as the dispersion decreased.

The fact that treatment of the catalyst with carbon monoxide alone produced no marked increase in activity indicates that sintering in the presence of water vapor during hydrogen regeneration is responsible. An alternative explanation that the surface becomes activated by the formation of some surface carbidic species appears to be ruled out. The higher initial activity of the catalyst reduced in the presence of water vapor also supports this conclusion. The leveling off in activity following several exposures to synthesis gas suggests that the metal dispersion has stabilized following this treatment. A stable metal dispersion was also obtained upon reduction of the catalyst in the presence of water vapor. The lower activity in this case may be explained by the formation of larger metal crystallites following this treatment.

Replacement of the charge-balancing sodium ions in the zeolite by multivalent cations or protons resulted in a two- to threefold enhancement in the stabilized specific activity of ruthenium for carbon monoxide hydrogenation. Such an enhancement in activity may be attributed to differences in the metal dispersion or alternatively, it may result from an electronic interaction between the metal crystallites and the support. An explanation based on dispersional effects is considered less likely in this case since the ruthenium dispersions within the two series of used catalysts were comparable irrespective of the nature of the exchange cation in the support. Furthermore in the case of RuLaY-II and $RuNH_4Y$-II, where the dispersion was either identical to or higher than that of RuNaY-II, the change in activity is opposite to what would be predicted had a dispersional effect alone been involved. Similar increases in activity were also observed with the Y-I series of catalysts even though the ruthenium dispersion was lower in some cases.

Exchange of sodium ions in zeolite Y by multivalent cations or protons is known to enhance its acidic (*21*) and electron-acceptor character (*22, 23*). Hence small metal particles encaged in these zeolites might be expected to become electron-deficient either as a result of a partial electron transfer between the metal and electron-acceptor sites in the support or owing to a perturbation of the electronic structure of the metal by the high electrostatic fields associated with the multivalent cations. Small platinum clusters encaged in Y-zeolites exhibit (*9*) an electrophilic character, while for ruthenium dispersed in zeolite Y, recent X-ray photoelectron spectroscopy studies indicate (*24*) that the metal clusters are also electron-deficient.

The adsorption of carbon monoxide on electron-deficient palladium crystallites on amorphous silica–alumina and on zeolite Y has been studied (*11*) by infrared spectroscopy. The observed shift toward higher frequencies of the CO band as the metal becomes more electron-deficient reflects a decrease in π bonding between the metal and adsorbed carbon monoxide and hence a decrease in electron density on the oxygen. Similar shifts have been observed (*25*) for carbon monoxide adsorbed on ruthenium as the acidity of the support increases. Following the correlation of Joyner and Roberts (*26*) relating oxygen (1*s*) binding energies in carbon monoxide to its heat of adsorption on a variety of metals, it is expected that carbon monoxide will adsorb less strongly on ruthenium as the metal particles become more electron-deficient and the extent of back-bonding decreases. Hydrogen will then compete more successfully with carbon monoxide for the available adsorption sites, resulting in an increased surface concentration of hydrogen and an enhanced reaction rate. This pattern is also consistent with the suggestion by Vannice (*27*) that a weakening of the metal–carbon monoxide bond results in a higher activity for carbon monoxide hydrogenation.

The selectivity data in Table 4 show that the methane selectivity is a function of the ruthenium dispersion and appears to be independent of the nature of the exchange cation in the zeolite. The high methane selectivity of the freshly reduced Y-II catalysts (Fig. 4) is further evidence of a high initial ruthenium dispersion. The decrease in dispersion during the course of several reaction cycles results in a selectivity shift toward higher hydrocarbons. The methane selectivity of the Y-I series of catalysts is considerably lower as would be predicted for the larger metal crystallites and in addition a further shift in the product distribution toward longer hydrocarbon chains is observed. Variations in product composition, dependent on metal particle size, were also obtained by Nijs *et al.* (*2*).

The increased selectivity toward branched-chain hydrocarbons as the acidity of the support is increased, as evidenced by the isobutane selectivity, is to be expected from the known isomerization activity of acidic zeolites. The isomerization of the product obtained from RuNaY-II in the presence of LaY indicates that isomerization occurs subsequent to initial product formation.

The olefin selectivity of the various catalysts reflects the electronic properties of the ruthenium crystallites and provides further evidence for the existence of an electronic metal–support interaction. The high olefin selectivity obtained with the physically mixed catalyst consisting of RuNaY-II and LaY rules out the possibility that the secondary reaction of the product on the acidic support accounts for the lower olefin selectivity obtained with the range of acidic supports investigated. As discussed above, an increase in the electrophilic character of the metal particles will be expected to enhance the hydrogenation activity of the catalyst. Thus for the more electron–deficient metal particles formed on the acidic supports, the enhanced secondary hydrogenation of the primarily formed olefins results in a sharp decrease in the olefin fraction in the product. This conclusion is fully supported by the finding (*28*) that if the ruthenium crystallites are made less electron-deficient by the introduction of large alkali metal cations into the support, a marked increase in olefin selectivity is observed.

The absence of olefins in the product obtained from the freshly reduced Y-II catalysts indicates that the electronic influence of the support is greater for very small metal particles.

CONCLUSIONS

The activity of zeolite-supported ruthenium catalysts for the hydrogenation of carbon monoxide increases markedly with decreasing ruthenium dispersion. At the same time the hydrocarbon product distribution shifts in the direction of longer hydrocarbon chains.

The nature of the exchange cation in the zeolite support also influences the catalytic activity. Replacement of the sodium ions by multivalent cations or protons results in a two- to threefold increase in specific activity. This activity increase is attributed to an electronic metal–support interaction which increases the electron-deficient character of the metal crystallites.

The resulting enhancement in the hydrogenation activity of the catalyst causes a decrease in the olefin selectivity owing to the increased secondary hydrogenation of the primarily formed olefins. Isobutane is present in the product in considerable quantities when the acidic forms of the zeolite are used as support.

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