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Geometric and Electronic Effects in the Selective Hydrogenation of α, β-Unsaturated Aldehydes Over Zeolite-Supported Metals

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The hydrogenation of two α, β-unsaturated aldehydes, cinnamaldehyde and 3-methylcrotonaldehyde was investigated over Ru, Pt, and Rh. The use of zeolite supports was compared with activated carbon for Ru, and the effect of changing the neutralizing cation in the Y zeolite was compared for all three metals. Selectivity to the unsaturated alcohol could be influenced by both geometric and electronic effects, and the relative importance of these effects was found to depend on the nature of the organic substrate.

INTRODUCTION

The role of heterogeneous catalysis in the production of fine chemicals is becoming increasingly more important, as attested by a number of recent symposia on this topic (*1*). One important reaction is the selective hydrogenation of α, β-unsaturated aldehydes (UAL) to unsaturated alcohols (UOL). While there are reports of catalysts that can achieve high UOL selectivity (*2*), much remains to be understood about these reactions. Three metals with much potential are Pt, Ru, and Rh. On inert supports, all three metals tend to be intrinsically more selective to the saturated aldehyde (SAL) than to UOL, the desired product. However, in the hydrogenation of cinnamaldehyde, they were shown to be capable of giving enhanced selectivity toward cinnamyl alcohol with changes in the nature of the support (*3*), in the presence of promoters (*4*), or with changes in the metal particle size and morphology (*5*). The capacity of these metals to be "tuned" to give enhanced UOL selectivity encourages further study of these effects.

In the present paper, Ru, Pt, and Rh were supported on activated carbon and on NaY and KY zeolite supports and were studied in the high-pressure, liquid-phase, batch hydrogenation of two organic substrates, cinnamaldehyde and 3-methyl crotonaldehyde. Zeolites were compared to activated carbon as an inert, amorphous support. Earlier work by this group (*6*) showed that the microporous structure of Y zeolite imposed molecular constraints on the mobility of the organic substrate within pores containing metal clusters and favored adsorption at the C=O bond, increasing its probability of being hydrogenated. By contrast, the inert carbon support imposed no geometric or electronic constraints on the reactions (*3*).

Zeolite supports introduce the possibility of metal-support interactions in addition to shape selectivity or geometric considerations. NaY and K-exchanged NaY were chosen in the present study to investigate the effect of the type of neutralizing cation on the UOL vs SAL selectivity. Cation effects in Ru/Y zeolites have been observed

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in CO hydrogenation reactions (*7*), where increased basicity of the cation resulted in a decrease in the capacity for C=C hydrogenation of primary olefinic products.

Finally, two organic substrates with different steric constraints were used to explore how the environment of the C=C bond may affect its hydrogenation capacity relative to the C=O bond. The bulky phenyl group in cinnamaldehyde places constraints on how the molecule may enter small pores or adsorb on metal sites within the pores. An aliphatic substrate such as 3-methylcrotonaldehyde may rotate more easily in the zeolite cage and may be adsorbed in a number of orientations. The selectivity of hydrogenation in this case may be less dependent on steric considerations than it would be for a bulkier molecule.

EXPERIMENTAL

Catalyst preparation. Activated carbon (CECA 50S) was pretreated in HCl solution to eliminate impurities and in NaClO solution to increase the number of acidic surface groups (*3*). NaY zeolite (Strem Chemicals) was used as received and was also modified to produce the KY support. In this modification, the NaY was exhaustively ion-exchanged with potassium nitrate (Aldrich Chemicals, ultrapure) as described in Ref. (*8*) Chemical analysis (Galbraith Laboratories) revealed that 92% of the Na was exchanged for K in this procedure.

Ru-loaded activated carbon and Ru-, Pt-, and Rh-loaded zeolite catalysts were prepared by ion exchange of the NaY and KY supports with $Ru(NH_3)_6Cl_3$ (Alpha Products), $[Pt(NH_3)_4]$ (Strem Chemicals), and $[Rh(NH_3)_5Cl]Cl_2$ (Strem Chemicals to a nominal weight loading (wet basis) of 3%. Chemical analysis for Ru/NaY and Ru/KY (Galbraith Laboratories) revealed that the Ru weight loadings were 2.31 and 2.23 wt%, respectively.

Pt and Rh samples were pretreated by heating first in flowing O_2 at 0.5 K/min (1 min = 60 s) to 673 K, holding there for 2 h. After flushing in He, the samples were treated with flowing H_2 at 673 K for 2 h. The Ru catalysts were treated as described above except that the samples were initially heated in flowing He rather than O_2 to prevent volatilization of RuO_2. The catalysts were passivated and stored in air until use.

Catalyst characterization. Reduced samples were studied by transmission electron microscopy using a JEOL 100 CX equipped with high-resolution pole pieces. Samples were made from ultramicrotome cuts of each catalyst embedded in an epoxy resin. This technique reveals the presence of metal particles internal to the zeolite, either within the cavities or occluded in the zeolite bulk (*9*). Ru/NaY and Ru/KY dispersions were determined by hydrogen chemisorption in a standard glass high-vacuum system capable of 10^{-6} Torr.

Reaction studies. The high-pressure, liquid-phase hydrogenation reactions were carried out in a well-stirred batch autoclave under 4 MPa H_2 (l'Air Liquide, 99.995% purity) using 0.1 mol of the unsaturated aldehyde and about 0.6 g catalyst. Isopropanol (50 cc) was used as a solvent. The catalyst was activated by stirring under 4 MPa H_2 pressure at 373 K for 2 h prior to introduction of the UAL reactant. Reactions with Ru and Rh catalysts were carried out at 373 K, while reaction with the Pt catalyst took place at 343 K under constant stirring at a rate at which bulk diffusion is negligible (*10*). However, other considerations such as configurational diffusion within the zeolite pores may still affect reaction rates. Reaction results are given in terms of percentage yield vs percentage conversion so that catalysts may be compared at a given conversion level even if they exhibit different reaction rates. The reaction products were monitored by repetitive sampling and gas chromatographic analysis.

RESULTS

Figure 1 shows transmission electron micrographs of Ru supported on activated carbon, NaY, and KY supports. In all three cases the metal particles were well dis-

TABLE 1

Chemical Formulas of Organic Substrates and Products

	UAL
Cinnamaldehyde (3-Phenyl-2-propenal)	$C_6H_5-CH=CH-CH=O$
3-Methylcrotonaldehyde (3-Methyl-2-butenal)	$(CH_3)_2-C=CH-CH=O$
	SAL
Hydrocinnamaldehyde (3-Phenylpropanal)	$C_6H_5-CH_2-CH_2-CH=O$
3-Methylbutanal	$(CH_3)_2-CH-CH_2-CH=O$
	UOL
Cinnamyl alcohol (3-Phenyl-2-propen-1-ol)	$C_6H_5-CH=CH-CH_2-OH$
3-Methylcrotyl alcohol (3-Methyl-2-buten-1-ol)	$(CH_3)_2-C=CH-CH_2-OH$
	SOL
3-Phenyl-1-propanol	$C_6H_5-CH_2-CH_2-CH_2-OH$
3-Methyl-1-butanol	$(CH_3)_2-CH-CH_2-CH_2-OH$

persed and were on the order of 1 nm in diameter. In the case of the zeolite-supported Ru, the ultramicrotome cuts allowed observation of the zeolite bulk, suggesting that the metal particles observed were contained within the supercages. Micrographs of the zeolite-supported Pt and Rh also showed small metal particles in the range 1–1.5 nm, indicating that for these catalysts also the metal was located primarily in the supercages.

Hydrogen chemisorption on Ru/NaY and Ru/KY gave metal particle sizes of 1.4 and 1.9 nm respectively, based on the irreversible hydrogen chemisorption and on the assumption of a five-sided cube for particle morphology. The fact that the micrographs show particles smaller than that calculated from hydrogen chemisorption suggests that a small fraction of the metal may be trapped in the sodalite cages where it is inaccessible to hydrogen. However, metal particles internal to the zeolite may also grow to this size by extending from one supercage into a neighboring one, or by being occluded in the zeolite bulk (*11*).

The names and chemical formulas of the two organic substrates as well as their partial and total hydrogenation products are listed in Table 1. Figures 2–7 and Tables 2 and 3 present results of UAL hydrogenation for all three metals.

Cinnamaldehyde hydrogenation. Figure 2 compares product yields as a function of conversion up to about 40% for carbon-, NaY-, and KY-supported Ru. Selectivity to UOL was greatly enhanced when either zeolite was used as a support compared to the carbon. The rate of conversion of UAL, however, was faster for the carbon-supported Ru compared to both zeolite-sup-

TABLE 2

Hydrogenation of α, β-Unsaturated Aldehydes over Supported Ru Catalysts

Catalyst	Cinnamaldehyde	3-Methylcrotonaldehyde
	UOL Selectivity (%) at 25% conversion	
Ru/C	30	26
Ru/NaY	63	10
Ru/KY	67	35
	Reaction time (min) to attain 25% conversion	
Ru/C	218	100
Ru/NaY	1180	49
Ru/KY	1228	80

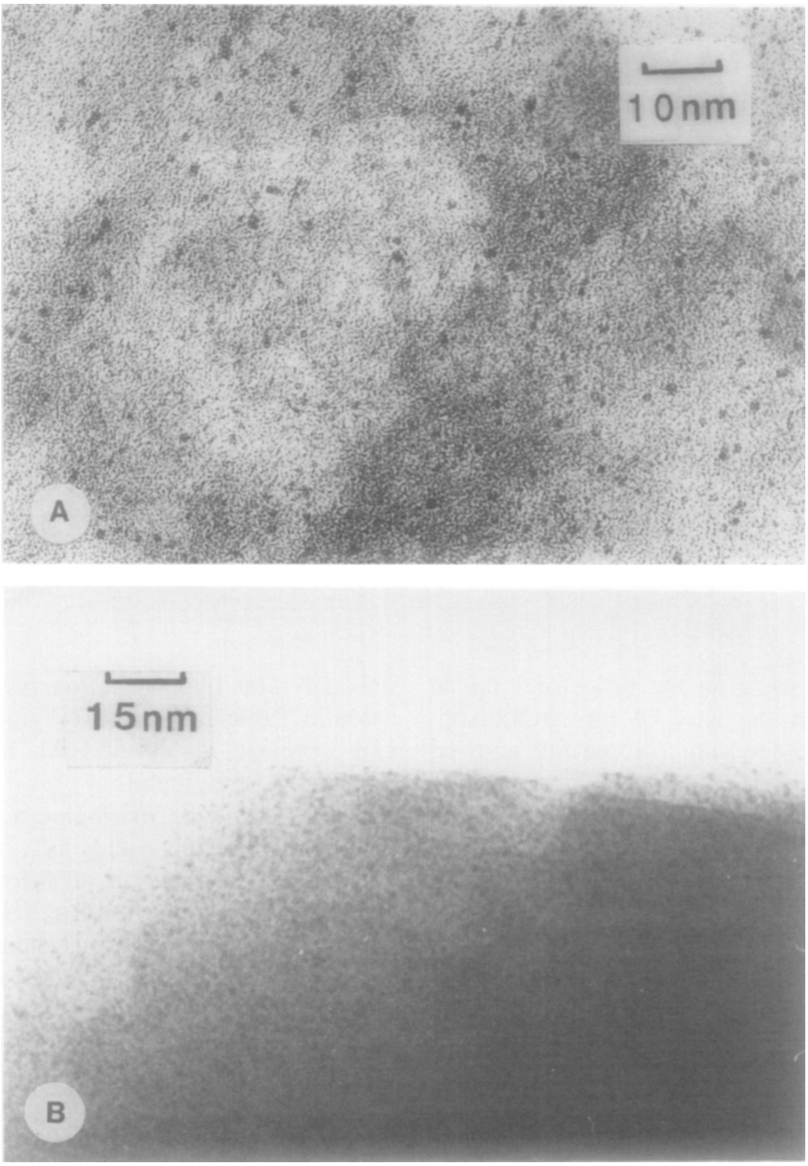


Fig. 1. Electron micrographs of Ru catalysts supported on (A) carbon, (B) NaY zeolite, Ru/NaY; and (C) K-exchanged NaY zeolite, Ru/KY.

ported Ru catalysts, as is shown in Table 2. The selectivity to UOL was also seen to increase with increasing conversion, particularly for the zeolite-supported Ru.

The results for Pt and Rh supported on the two zeolites were similar to Ru, as is shown in Fig. 3 and 4 and in Table 3. There was little difference between the two types of Y zeolite for UOL selectivity, suggesting that the zeolite pore structure—and not electronic properties dictated by the type of cation—was the important factor for achieving high UOL selectivity with cinnamaldehyde as the organic substrate.

3-Methylcrotonaldehyde hydrogenation. Figure 5 and Table 2 present data for the

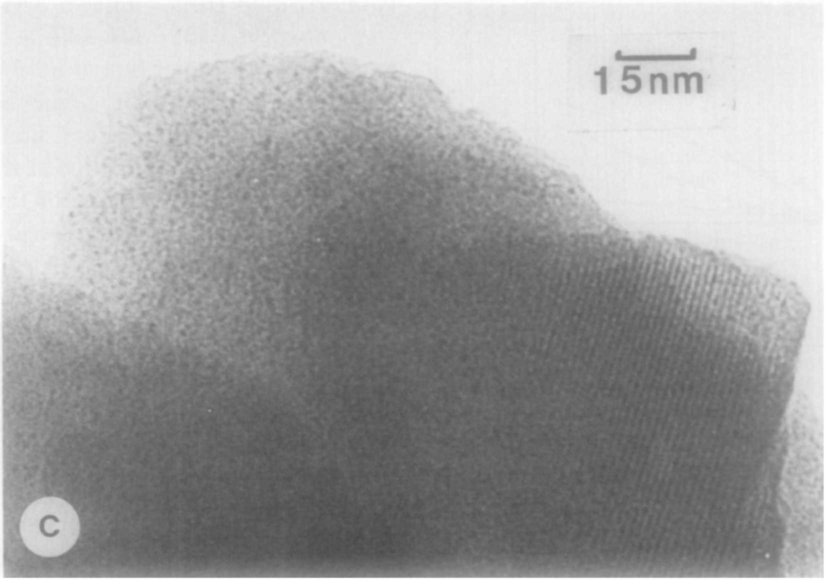


Fig. 1—*Continued*

reaction of 3-methylcrotonaldehyde over the three Ru catalysts. The overall reaction proceeded much faster over all three catalysts than did the cinnamaldehyde reaction, although UOL was not the dominant product in any case. In contrast to the results for cinnamaldehyde, however, there was a striking difference between the NaY- and the KY-supported Ru for UOL selectivity from 3-methylcrotonaldehyde. Ru/KY produced UOL three times as selectively as Ru/NaY. Hence, the question of whether the zeolite cation can affect UOL selectivity was found to depend on the organic substrate employed in the reaction.

TABLE 3

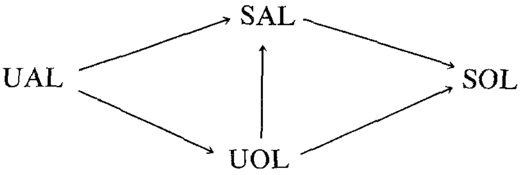
Hydrogenation of α, β-Unsaturated Aldehydes over Supported Pt and Rh Catalysts

Catalyst	Cinnamaldehyde	3-Methylcrotonaldehyde
UOL Selectivity (%) at 25% conversion		
Pt/NaY	68	42
Pt/KY	60	56
Rh/NaY	30	6
Rh/KY	33	10
Reaction time (min) to attain 25% conversion		
Pt/NaY	3571	3888
Pt/KY	544	4254
Rh/NaY	483	45
Rh/KY	215	76

Results for 3-methylcrotonaldehyde hydrogenation over the zeolite-supported Pt and Rh catalysts shown in Fig. 6 and 7 and in Table 3 also demonstrate the effect of the type of zeolite cation. Again the KY catalyst produced an amount of UOL relatively higher than that of NaY, although on Rh the amount of UOL formed was small for both samples.

DISCUSSION

The reactions of unsaturated aldehydes may be described as a parallel-consecutive network (*12*) in which one or both of the unsaturated functionalities may be hydrogenated:



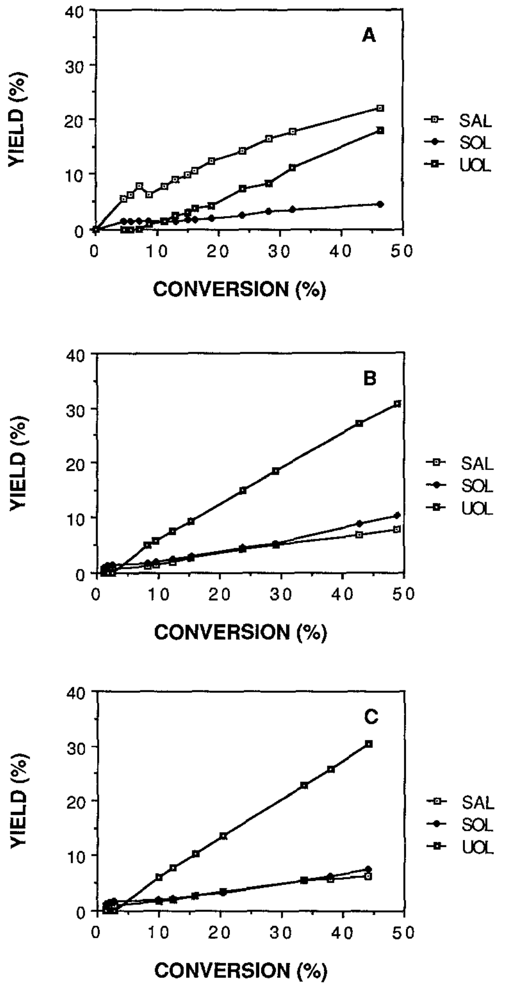


Fig. 2. Product yield vs conversion in the hydrogenation of cinnamaldehyde over supported Ru catalysts. (A) Ru/C, (B) Ru/NaY, (C) Ru/KY.

Isomerization from UOL to SAL has also been observed (*13, 14*). While the C=C bond energy is lower than that of C=O, the actual product selectivity achieved depends significantly on parameters including the type of metal and the nature of the support (*3, 6, 15–17*), the structure of the reactant (*18, 19*), and concomitant steric and electronic factors involved in adsorption of the reactant on the catalyst surface. All of these clearly came into play in the present work, with different factors dominating under different circumstances.

The shape-selective effects of zeolite catalysts have been well-documented. Earlier work by this group (*6*) showed that selectivity to cinnamyl alcohol could be enhanced for metals in zeolite micropores, both for Pt, which exhibits moderate selectivity to UOL, and for Rh, which is usually quite unselective to UOL. This work extends that finding to include Ru, comparing the zeolite-supported catalyst to Ru supported on an inert, amorphous carbon. Cinnamaldehyde can only enter the 0.74-nm zeolite pore opening end-on, and its mobility once inside the 1.33-nm-diameter supercage is constrained because of the rigidity of the side chain, the bulkiness of the phenyl group, and the fact that a significant portion of any supercage where hydrogenation can occur is occupied by a metal particle. The cinnamaldehyde molecule can easily adsorb onto the metal particle only through

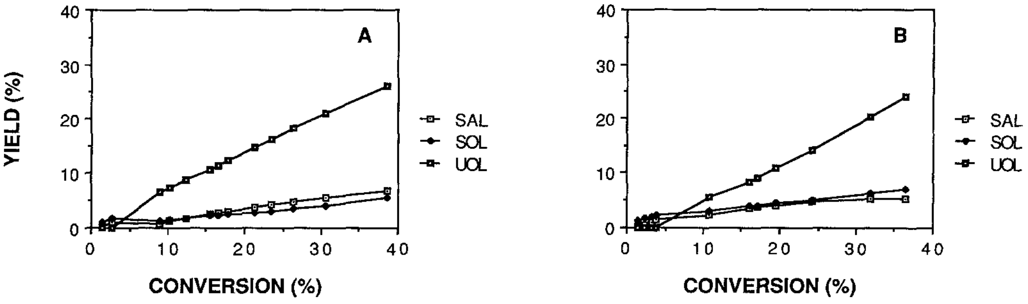


Fig. 3. Product yield vs conversion in the hydrogenation of cinnamaldehyde over supported Pt catalysts. (A) Pt/NaY, (B) Pt/KY.

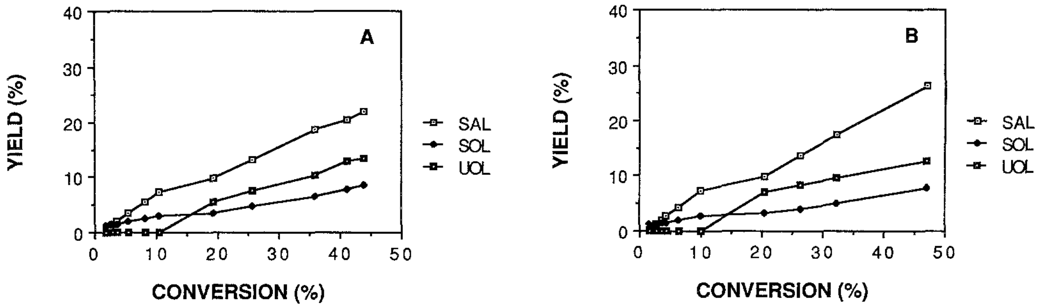


Fig. 4. Product yield vs conversion in the hydrogenation of cinnamaldehyde over supported Rh catalysts. (A) Rh/NaY, (B) Rh/KY.

the carbonyl group on the tip of the aromatic side chain because an approach to the metal surface near the C=C bond is sterically hindered. In contrast, on Ru/carbon the absence of the steric constraints of the zeolite pores means that other modes of adsorption are available to cinnamaldehyde, including adsorption of the planar molecule parallel to the surface. Hence in the case of Ru/carbon, the intrinsic catalytic properties of Ru dominate over any steric constraints imposed by the support. For zeolite-supported Ru, the molecular constraints of cinnamaldehyde within the zeolite pores predominate over other potential effects such as the electronic environment of the Ru particles in the zeolite pores and any changes that occur when K^+ replaced Na^+ in the zeolite framework. This work shows that for Pt and Rh catalysts as well the geometric effect of the zeolite pores predominates over electronic considerations in cinnamaldehyde hydrogenation.

The results for 3-methylcrotonaldehyde hydrogenation over these same zeolite-supported Ru, Pt, and Rh catalysts preclude reaching a general conclusion about the importance of geometric vs electronic effects based on the cinnamaldehyde reaction results alone. For the aliphatic substrate, the nature of the zeolite cation significantly affected the UOL selectivity on all three metals. Similar cation effects have been observed in studies of other reactions, including hydrocarbon cracking (*20*) and de-

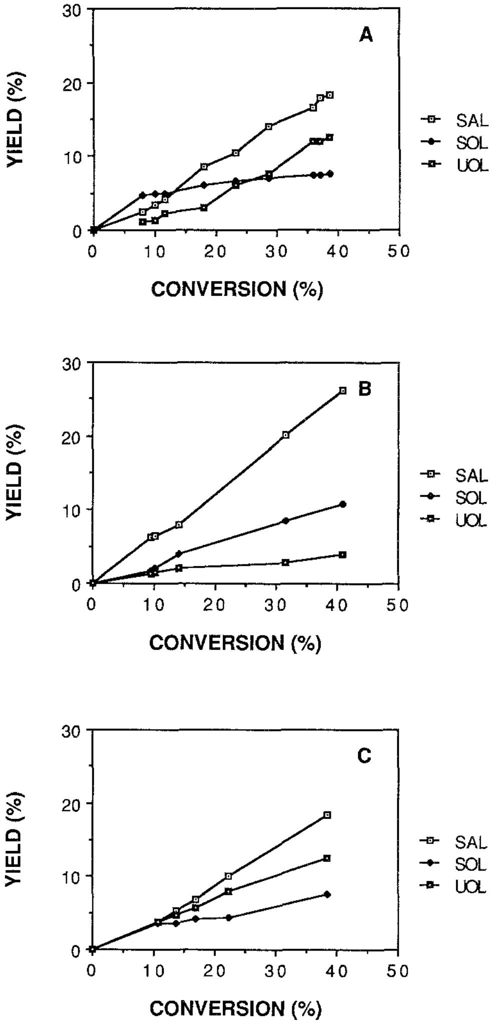


Fig. 5. Product yield vs conversion in the hydrogenation of 3-methyl crotonaldehyde over supported Ru catalysts. (A) Ru/C, (B) Ru/NaY, (C) Ru/KY.

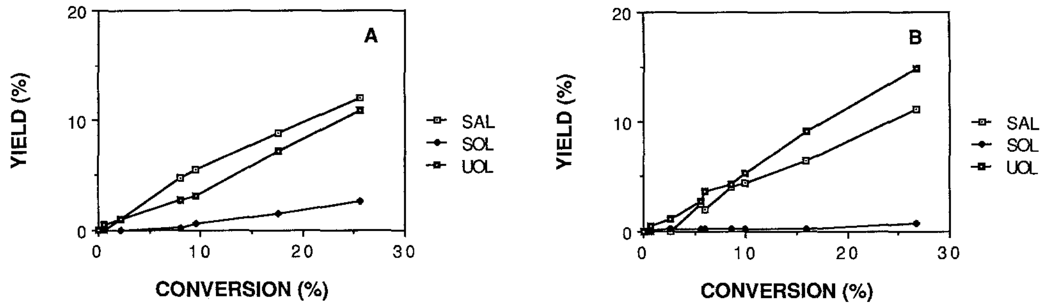


Fig. 6. Product yield vs conversion in the hydrogenation of 3-methyl Ru crotonaldehyde over supported Pt catalysts. (A) Pt/NaY, (B) Pt/KY.

hydrogenation (*21, 22*) as well as other hydrogenation reactions (*7, 23*). In Fischer–Tropsch reactions, the exchange of K^+ for Na^+ as neutralizing cations in Y zeolites resulted in a suppression of the hydrogenation of olefins that are formed as primary products (*7*). The acid strength of the protons in Y zeolite decreases as the alkali cation is changed from Li through Na, K, Rb, to Cs. This decrease in acidity results in greater electron density on the small metal particles within the zeolite pores (*9, 24*). An increase in charge density of the metal may cause a suppression in the C=C hydrogenation rate by enhancing the delocalization of electrons in the adsorbed conjugated substrate. Selectivity to UOL would thus be increased. This "through-metal" effect has been suggested from a number of different studies in which the support (*3*), promoter species (*4*), and a second metal (*16, 17*) have all been implicated in electron transfer to the metal. The present study offers the first evidence that changing from a less basic to more basic cation in Y zeolite may increase UOL selectivity in a similar manner by modifying the electronic properties of encapsulated metal particles. This cation effect operates for all three metals, although it is more pronounced for Ru and Pt than it is for the intrinsically nonselective Rh.

Other suggestions have been made to describe the apparent electronic effects of alkali species on adsorption and reaction on metal catalysts. Electrostatic interactions have been proposed in several theoretical studies to explain observed changes in CO adsorption on alkali-promoted metals (*25–27*). In these models, the electrostatic field of the alkali species act "through space" directly on the CO function to stabilize

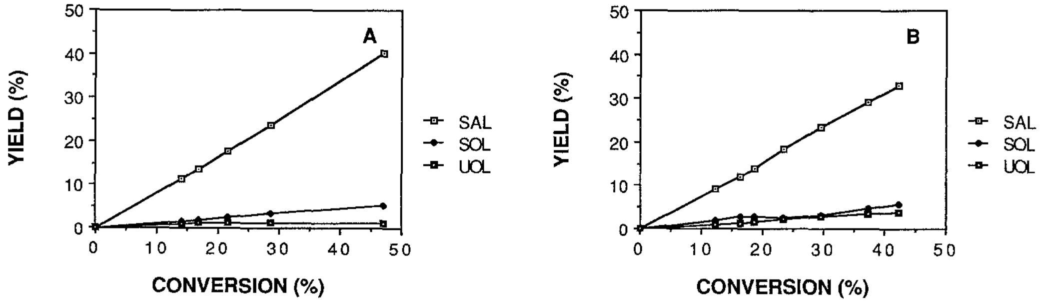


Fig. 7. Product yield vs conversion in the hydrogenation of 3-methyl Ru crotonaldehyde over supported Rh catalysts. (A) Rh/NaY, (B) Rh/KY.

metal–carbon bonding while weakening the C=O bond. It was suggested (*27*) that this electrostatic interaction might be a more realistic model for alkali promotion on single-metal crystals or larger supported metal particles than is the through-metal electronic effect described above, because the observable effect of an alkali-to-metal shift of electron density might be negligible for single crystals of metal or for large supported metal particles where large numbers of metal atoms are involved. For the zeolite-encapsulated metal particles of the present study, however, the number of metal atoms per particle is fewer than ca. 40 as shown by radial electron distribution studies (*28*), and an increase in electronic charge on the metal should be observable in the chemisorptive properties of the metal.

Metal-support interactions resulting in enhanced UOL selectivity were reported for the hydrogenation of crotonaldehyde over Pt/TiO_2 (*15*), a catalyst well-documented for its strong metal support interaction (SMSI) in CO hydrogenation reactions. This effect was attributed not to an electronic effect of the support on the Pt particles, but instead to a direct interaction between the oxygen of the C=O functionality of UAL and the TiO_2, increasing the polarization of the adsorbed reactant. Recent studies of CO adsorption on alkali-promoted metals have suggested similar C=O–alkali interactions (*29–32*). Effects of alkali promotion on CO adsorption and reaction become more significant in the order from Li to Cs (*32–34*). If such a direct organic substrate–cation interaction occurred within the zeolite pores of the catalysts in the present study, it would be expected that KY would show enhanced UOL selectivity over NaY. However, if this C=O activation is the predominant effect, one might also expect to observe an increase in the overall rate of UAL conversion. Table 2 shows that the rate of UAL conversion in the reaction of 3-methylcrotonaldehyde decreased slightly for Ru/KY compared to Ru/NaY. The higher selectivity to UOL may be due to the combination of an increase in the C=O hydrogenation rate due to direct C=O–KY interactions and a decrease in the C=C hydrogenation rate due to suppression of C=C–Ru interaction because of increased electron density of the metal particles.

Selectivity to UOL increased with increasing conversion of UAL for both substrates, as has been observed previously (*35*). The accumulation of products in the reaction medium during reactions carried out in batch may affect the reaction rate and product selectivity if certain products compete with the reactants for surface sites. In studies of cinnamaldehyde hydrogenation (*35*), it has been shown that SAL added to the reaction medium acted as an inhibitor for UAL conversion. SAL produced in the course of the reaction may remain adsorbed on the metal. UOL selectivity may then be altered either by a steric effect, in which the UAL substrate is forced to adsorb end-on via the C=O group, or by an electronic effect in which the adsorbed SAL causes an increase in charge density on the metal, lowering the probability for C=C bond activation. Either case would result in an increase in UOL selectivity.

Studying the overall rate of consumption of UAL may provide some clues about the nature of the predominating effect in a particular case. For example, the hydrogenation of cinnamaldehyde proceeds much faster over the carbon-supported Ru than over Ru on either of the zeolite supports. Since in this case the geometric effect of the zeolite pores on the bulky organic substrate governs the product selectivity over both zeolites, it is not surprising to find that the reaction of cinnamaldehyde proceeds much more slowly for these cases where the substrate must find its way to sites inside the pores and adsorb in a particular conformation in order to react. In the case of 3-methylcrotonaldehyde hydrogenation, however, molecular constraints are less important and the overall rate over the zeolites and the carbon support are much closer in magnitude. Geometric or steric considerations, concerning both the catalyst and the organic substrate, appear to be first-order effects; when these constraints are relaxed, electronic effects may come into play.

CONCLUSIONS

The hydrogenation of two α, β-unsaturated aldehydes was investigated over transition metals supported on activated carbon and NaY and KY zeolites. The pore structure of the zeolites led to higher selectivity toward the unsaturated alcohol in the case of cinnamaldehyde, where steric constraints of the reactant prevented adsorption at the C=C bond on metal sites within the pores, but not in the case of 3-methylcrotonaldehyde, where the mobility and orientation of the molecule was not inhibited by the zeolite pores. UOL selectivity could be increased for 3-methylcrotonaldehyde, however, by replacing Na^+ compensating cations in the zeolite with K^+ cations. This modification brought about a decrease in C=C hydrogenation attributed to enhanced metal electron density combined with an increase in C=O hydrogenation due to an interaction between the carbonyl function and the more basic zeolite cation. The relative importance of geometric/steric and electronic effects for different systems was discussed.

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