Diffusion effects in the hydrogenation of 3-methyl crotonaldehyde over zeolite-supported Ru

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The activity and selectivity in gas-phase hydrogenation of the unsaturated aldehyde 3-methyl crotonaldehyde (UAL) over zeolite-supported Ru was found to depend markedly on the partial pressures of the two reactants in the gas phase, with the rate increasing as the ratio P_{UAL}/P_{H_2} decreased. Anomalously low apparent activation energies were found compared to the same reaction over Ru/SiO_2, and secondary reactions to produce the totally hydrogenated product occurred much more readily in the zeolite-supported Ru. These observations led to the suggestion that these reactions were under diffusion control.

Keywords: Diffusion controlled hydrogenation; crotonaldehyde hydrogenation; rhuthenium catalyzed hydrogenation

1. Introduction

The selective hydrogenation of α, β-unsaturated aldehydes to produce unsaturated alcohols has recently attracted attention because of its importance in the fine chemicals industry [1–10]. In recent studies we have investigated how the use of zeolites as supports affects selectivity in hydrogenation reactions over metals such as Ru [2,3]. Depending on the steric and electronic constraints of the particular organic substrate, the use of zeolites as supports may provide a means of obtaining desired product selectivities difficult to achieve without microporous supports. In liquid-phase reactions, geometric influences of the zeolite pore structure as well as electronic effects of the nature of the zeolite compensating cation were observed. Steric constraints dominated for bulky, rigid molecules such as cinnamaldehyde, while for 3-methyl crotonaldehyde the selectivity for hydrogenation was most influenced by the type of alkali cation in the zeolite structure. Increased selectivity to the unsaturated alcohol was observed when Na^+ was exchanged for K^+, and this trend also held in gas-phase

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reactions over the same Ru/NaY and Ru/KY catalysts. It was also observed, however, that the gas-phase reactions exhibited a transient initial period in which both activity and selectivities were found to vary widely until steady state was finally reached. The present study was undertaken to examine the effects of varying the partial pressures of the reactants and the reaction temperature and in particular to explore the extent to which diffusion processes may influence reaction rates and selectivities.

2. Experimental

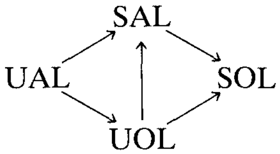
Materials. Ultrahigh purity H_2, He, and Ar (Linde, 99.995%), and commercial purity CO (Linde, 99.5%) gases were used in all pretreatments, characterization experiments and reactions studies, and all gases were further purified by molecular sieve traps. An oxygen removing unit (Deoxo) was also placed in the hydrogen line prior to the molecular sieve trap. 3-methyl crotonaldehyde was used as received (Alpha Products, 97% purity) and was stored under refrigeration.

Catalyst preparation. NaY zeolite was used as received and was also modified by ion exchange with potassium nitrate (Aldrich Chemicals, ultrapure) to produce the KY support (92% exchange) as previously described [3,11]. Preparation and pretreatment of the Ru-loaded zeolites has also been described [3]. Briefly, ion-exchange with $Ru(NH_3)_6Cl_3$ (Alpha Products) to a loading of 2.3% Ru was followed by treatment in flowing He at 0.5 K/min to 673 K and holding there for 2 h. Reduction was accomplished by switching from He to H_2 and holding for 2 h at 673 K. Catalysts were cooled in inert gas and stored in air until use. As reported previously [3], results from characterization of metal particle sizes by hydrogen chemisorption and transmission electron microscopy was consistent with the metal particles being located primarily within the supercages of the zeolites.

Reaction studies. Continuous flow, gas-phase hydrogenation of 3-methyl crotonaldehyde was carried out in a stainless steel system with a pyrex reactor. About 0.1 g of the catalyst was placed in the reactor and pretreated at 673 K for 4 h after ramping at 0.5 K min^{-1}. After cooling the catalyst to reaction temperature in flowing H_2, the organic substrate was admitted to the reactor in a stream of He gas bubbled at 20–100 ml min^{-1} through the liquid in a gas saturator kept at 298 K, giving substrate flow rates between 7 and 35 μmol min^{-1}. The flow rate of hydrogen varied between 100 and 180 ml min^{-1} (4.5–8 mmol min^{-1}), at a constant total gas flow rate of 200 ml min^{-1}. This allowed us to study an order of magnitude variation in the molar ratios of substrate to hydrogen. Reaction rates and product selectivities were measured at temperatures between 313 and 373 K and products were analyzed by GC. Reaction rates are reported as turnover frequencies based on exposed Ru surface area as measured by hydrogen chemisorption [3].

3. Results and discussion

The reaction network for the hydrogenation of 3-methyl crotonaldehyde is shown below, where UAL refers to the unsaturated aldehyde substrate, SAL and UOL are the two half-hydrogenated products, saturated aldehyde and unsaturated alcohol, and the total hydrogenation product is the saturated alcohol, SOL:



A previous discussion of these gas-phase reactions over Ru/Y catalysts at 313 K focussed on product selectivities obtained during steady-state reaction, where it was found that the selectivity towards UOL increased from 30% to near 60% when the Na^+ cation of the zeolite was replaced with K^+. However, the steady-state rate and product selectivities were established only after a period of approximately 100 min during which the initially high conversion of UAL to the three products (up to 20%) fell off with time to less than 3%.

A mass balance for the reactant UAL and the products could not be established during the early stages of the reaction over either Ru/NaY or Ru/KY, indicating that there was a significant uptake of 3-methyl crotonaldehyde by the catalyst early in the reaction. Fig. 1 demonstrates this for the reaction over Ru/KY at 313 K and $P_{UAL}/P_{H_2} = 0.009$. Blank experiments with the pure KY support showed that, while it exhibited no catalytic activity, the support took up UAL from the gas phase for about 100 min before the gas-phase flow of UAL at the initial feed concentration was finally re-established in the exit stream. This uptake of 3-methyl crotonaldehyde suggests that the zeolite pores were steadily filled by the substrate during its initial exposure to the catalyst. Table 1 gives an estimate of the amount of UAL in the catalyst pores during reaction over Ru/KY, calculated from integration of the area under curves such as that shown in fig. 1. The total amount of UAL adsorbed or condensed on the catalyst surface at steady state was found to depend on the partial pressure of the unsaturated aldehyde in the gas phase, ranging from 0.3 to 1.5 mmol/g catalyst. The calculations in table 1 show that the amount of UAL far exceeds monolayer coverage of the exposed metal sites and that it is greater than the total surface area of the zeolite as well. The uptake at the lowest P_{UAL}/P_{H_2} corresponds to 75% of the pore volume of the zeolite. Under the conditions of the highest UAL partial pressure, intraparticle condensation

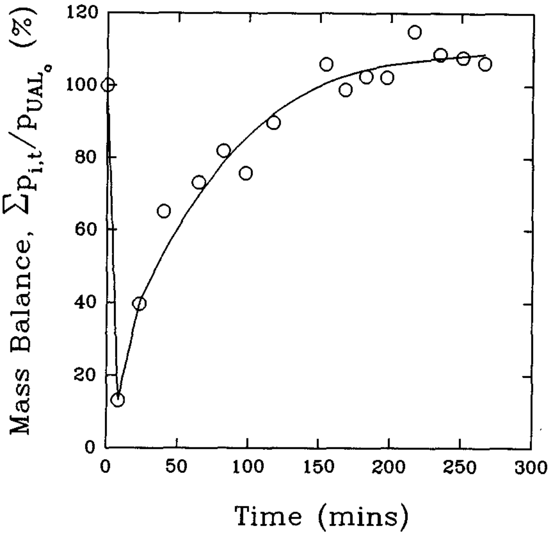


Fig. 1. Mass balance for reactant UAL and products (nomenclature defined in text) as a function of reaction time for Ru/KY at 313 K and $P_{UAL}/P_{H_2}=10^4$, based on the summation of the partial pressures of each component in the exit stream. Y-axis $=\Sigma(P_{UAL}+P_{SAL}+P_{UOL}+P_{SOL})_t/P_{UAL_0}$.

of UAL must occur in addition to the filling of the pores. Observations of pore-filling in gas-phase reactions in zeolites have been made previously, and models which treat adsorption and reaction in zeolite pores containing an adsorbed condensed phase have been developed [12–14].

Table 1
Estimate of UAL surface coverage on Ru/KY from adsorption uptake during reaction

	P_{UAL}/P_{H_2} ($\times 10^4$)	
	10	100
mmol/g cat [a]	3	15
molecules UAL/Ru_s [b]	28	140
no. monolayers UAL [c]	1.8	9
% pore volume occupied by UAL (liquid) [d]	75	375

[a] Uptake of UAL estimated from integrating the concentration of UAL remaining in the effluent stream during the inital adsorption period before mass balance was established, i.e. before $[UAL]_{in}=[UAL]_{out}$.

[b] Assuming adsorption of UAL on metal sites only; Ru_s = number of surface Ru atoms estimated from hydrogen chemisorption.

[c] Assuming flat adsorption of the UAL molecule covering an area of 50 $Å^2$/UAL molecule and zeolite surface area of 500 m^2/g.

[d] Liquid density of UAL = 0.85 cc/g and pore volume of zeolite estimated to be 0.4 cc/g.

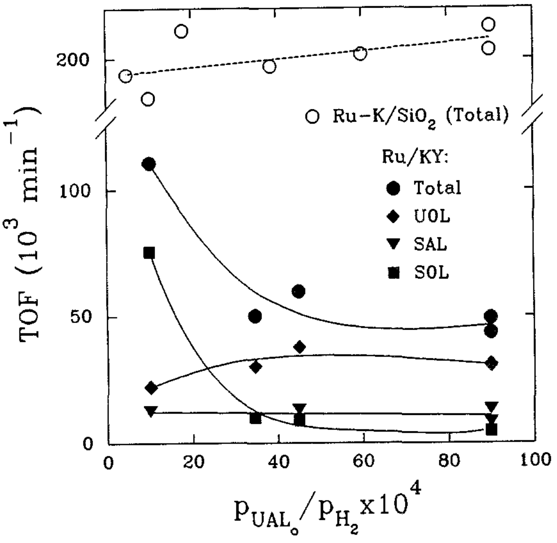


Fig. 2. Steady-state reaction rates over Ru/KY at 313 K as a function of partial pressures of the reactants. TOTAL = sum of product rates; UOL, SAL, SOL are rates of formation of the individual products. Plotted for comparison (dashed line and open circles) is the TOTAL = sum of product rates for reaction over Ru-K/SiO$_2$ at 313 K as a function of partial pressure of reactants (from ref. [10].

Experiments were carried out to study the effects of the relative concentrations of the substrate UAL and hydrogen, and these results suggest that diffusion limitations were important in these reactions. The combination of low substrate and high hydrogen concentrations led to pronounced increases in the overall reaction rate and strong shifts in product selectivity at steady state for both catalysts and is illustrated in fig. 2 for Ru/KY. This figure shows clearly that the increase in overall rate may be attributed almost totally to an increase in the rate of formation of the total hydrogenation product, SOL. These results are in direct contrast to those from reactions carried out under identical conditions over potassium-promoted Ru supported on a non-porous SiO$_2$ support, where neither the reaction rates nor product selectivities were influenced by similar changes in reactant partial pressures [10]. This result for Ru-K/SiO$_2$ is shown in fig. 2 for comparison. Over the whole range of P_{UAL}/P_{H_2}, the reaction rate for Ru-K/SiO$_2$ was about twice the highest value for the Ru/KY catalyst obtained at low P_{UAL}/P_{H_2}.

This increase in reaction rate may represent the response of a hydrogen-starved catalyst surface to changes in conditions which provided it better access to hydrogen. The observation of a large initial consumption of substrate suggests that at steady state a significant liquid film covered the surface within the catalyst pores. A decrease in the gas-phase concentration of the substrate may result in a decrease in the thickness of this film and hence might increase the

Table 2
Activation energies for gas-phase hydrogenation of α, β-unsaturated aldehydes

Catalyst	Activation energy (kcal/mol)	Condition	Ref.
Ru/NaY	2.1	a	this study
Ru/KY	1.5	a	this study
Ru/SiO_2	11.7	b	[10]
Ru-K/SiO_2	7.2	b	[10]
Pt supported on			
SiO_2, Al_2O_3, TiO_2	3–8	c	[4]

[a] Reaction of 3-methyl crotonaldehyde at 313–373 K; substrate:$H_2 = 1:10^4$.
[b] Reaction of 3-methyl crotonaldehyde at 313–393 K; substrate:$H_2 = 1:10^3$.
[c] Reaction of crotonaldehyde at 313–373 K; substrate:$H_2 = 1:22.7$.

rate of diffusion of hydrogen from the gas phase through the liquid layer to the active sites on the catalyst surface. Increasing the partial pressure of hydrogen would also bring about an increase in rate by increasing the concentration of hydrogen in this liquid layer.

If diffusion limitations were minimized at the conditions of low substrate/high hydrogen concentration, the measured rates would correspond to the intrinsic reaction rates expected in a system where pore diffusion was not an important concern. In that case the only significant resistance for hydrogen to adsorb on the active sites would come from competition with other adsorbed species. However, additional experiments provide important evidence suggesting that the influence of diffusion within the pores remained significant under all conditions employed in these studies. Apparent activation energies were measured by carrying out reactions over both Ru/NaY and Ru/KY at temperatures between 313 and 373 K under the conditions of low substrate/high hydrogen concentration where diffusion effects should be minimized. These values are compared in table 2 with values obtained in other gas-phase studies of aldehyde hydrogenation over non-zeolite-supported metals. The values of 2.3 and 1.5 kcal/mol measured for Ru/NaY and Ru/KY respectively were lower by about a factor of five than those measured for the same reaction over Ru/SiO_2 in recent work by our group [10]. They were also lower than values obtained in another study of the hydrogenation of crotonaldehyde over Pt supported on various non-zeolite supports [4]. Such significantly different activation energies suggest a different rate limiting process for the zeolite-supported catalysts. The very low values for E_a indicate that this process was less temperature-sensitive than are intrinsic reaction rates, which is a feature of diffusion-controlled processes. Hence, even at the lowest concentration of substrate it appears that the rate of reaction was mass-transfer limited.

The shift in product selectivity towards the total hydrogenated product under conditions of low substrate/high hydrogen concentration is also consistent with strong pore diffusion limitations. No such change in selectivity with reactant concentrations was observed in the case of the Ru supported on a non-porous SiO_2, as mentioned above, where diffusion limitations were assumed to be absent. In those studies, in fact, the production of the total hydrogenation product SOL was very low under all conditions of reactant concentrations and reaction temperature. It appears that not only was the availability of hydrogen important in controlling activity, but also the opportunity for prolonged adsorbed substrate–hydrogen contact due to significant residence time within the catalyst pores played a role in determining selectivity. Readsorption and secondary reactions of the half-hydrogenated products within the pores were more significant in the zeolite-supported systems than for catalysts where diffusion limitations were absent.

4. Conclusions

Gas-phase hydrogenation of 3-methyl crotonaldehyde over Ru supported on NaY and KY zeolites showed that activity and selectivity depend markedly on changes in substrate and hydrogen concentrations. The highest activity was observed at low substrate/high hydrogen concentrations, and the increase in overall rate was accompanied by a shift in selectivity to the production of the saturated alcohol SOL. There was a large uptake of the reactant by the catalyst at the beginning of the reaction under all conditions of reactant partial pressures which, along with anomalously low activation energies, implied a diffusion-controlled rate. The change in activity and selectivity under conditions of low substrate/high hydrogen concentrations was attributed to better access of hydrogen to the catalyst sites and increased secondary reactions of the half-hydrogenated products within the pores.

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