

Gas phase hydrogenation/hydrogenolysis of benzaldehyde and *o*-tolualdehyde over Ni/SiO₂

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Abstract

The gas phase hydrogen treatment of benzaldehyde and *o*-tolualdehyde was studied over a Ni/SiO₂ catalyst prepared by homogeneous precipitation/deposition. The reactions were conducted in the absence of diffusion limitations and reproducible turnover frequencies are presented. The products generated resulted from the hydrogenation and hydrogenolysis of the substituent C=O bond and from the hydrogenolysis of the aryl–carbonyl C–C bond, the aromatic ring remaining intact. The temperature dependencies of the rate constant and product selectivity are illustrated and apparent activation energies for hydrogenation to the aromatic alcohol are given. The influence of the *ortho*-substituted methyl group on the reactivity of the carbonyl function is discussed. The reaction of benzyl alcohol and 2-methylbenzyl alcohol over the same catalyst was investigated and the overall reaction pathway is identified.

Keywords: Ni/SiO₂; Benzaldehyde; *o*-Tolualdehyde; Hydrogenation; Hydrogenolysis; Electronic effects

1. Introduction

The selective hydrogenation of organic compounds that possess C=O and/or C=C bonds is an area of catalytic research that has lately received considerable attention [1]. In the hydrogenation of aromatic aldehydes either or both the benzene ring and the substituent carbonyl group may be reduced. The simplest aromatic system, benzaldehyde, has been selectively hydrogenated to benzyl alcohol using ruthenium complexes in homogeneous applications [2,3]. Aldehydes are also known to undergo electrochemical reduction where the aromatic forms are more prone to glycol formation than the

aliphatic counterparts [4]. In addition, the liquid phase heterogeneous hydrogenation of benzaldehyde over rhodium clusters [5], hectorite-incalated rhodium complexes [6] and Raney nickel [7] have been reported. Acetal formation occurs when benzaldehyde is reduced in methanol, the degree of hydrogenation depending on the purity of the solvent [8]. All substituent groups, with the exception of acid, ester and amide functions are hydrogenated in preference to the benzene ring over Raney nickel in the temperature range $373\text{ K} \leq T \leq 423\text{ K}$ [9]. Selective reduction of aromatic carbonyl compounds is problematic in that concurrent ring hydrogenation and/or hydrogenolysis can occur. Different metal catalysts, operating under various experimental conditions are favoured depending on the function to be reduced; palladium is consid-

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ered the best agent for side chain reduction to the alcohol or hydrocarbon while rhodium, ruthenium and platinum are suitable for ring hydrogenation [10,11]. In general, homogeneous catalysts exhibit little or no hydrogenolysis activity and supported palladium and Raney nickel have certainly been the preferred catalysts for use in hydrogenolysis studies [12]. Substituted benzenes are now regarded as choice model compounds to evaluate hydrogenolysis versus ring hydrogenation [13,14]. In the reduction of benzaldehyde using nickel 2-ethylhexanoates– Et_3Al , hydrogenolysis to toluene and disproportionation to benzylbenzoate have been shown to occur in addition to benzyl alcohol formation [15]. To date, heterogeneous catalytic studies of benzaldehyde hydrogenation have largely been devoted to liquid phase systems and the author could find no documented investigation of gas phase applications using supported nickel catalysts. Reproducible specific activity data for the hydrogen treatment of benzaldehyde in the temperature range $383 \text{ K} \leq T \leq 573 \text{ K}$ over Ni/SiO_2 are presented in this paper. The relative rates of $\text{C}=\text{O}$ hydrogenation, $\text{C}=\text{O}$ hydrogenolysis and $\text{C}-\text{C}$ hydrogenolysis are presented and the effect of methyl substitution in the *ortho* position on overall activity and selectivity is considered.

2. Experimental

2.1. Catalyst preparation, activation and characterization

A nickel-dilute catalyst was prepared by the homogeneous precipitation/deposition of nickel onto a non-porous microspheroidal Cab–O–Sil 5 M silica of surface area $194 \text{ m}^2 \text{ g}^{-1}$. The silica support was washed with triply deionized water and dried in air for 20 h at 375–383 K before use. The precipitation was carried out in a 2 dm^3 three-necked round-bottomed flask fitted with a Citenco motor driven stirrer. A sample of urea (Aldrich Chem., 99 + %) was added

to a 1.5 dm^3 aqueous suspension of Cab–O–Sil 5M in nickel nitrate (Aldrich Chem., 99.999%) at $290 \pm 2 \text{ K}$, where the molar ratio of the nitrate to urea was 0.36. The suspension was slowly heated under constant agitation (600 ppm) to $361 \pm 3 \text{ K}$ and held at this temperature for 6 h. Temperature control was maintained using an oil bath equipped with a heating element and mechanical stirrer to ensure good heat transfer. The pH of the suspension was preadjusted (with nitric acid) to 2.8 to prevent premature hydrolysis and the pH was observed to increase to 5.3 on completion of the precipitation step. The suspension was then filtered and the filtrate washed with $4 \times 400 \text{ cm}^3$ hot deionized water and air-dried in an oven at 375–383 K for 20 h. The nickel loading was determined by atomic absorption (Perkin–Elmer 360 AA spectrophotometer) using the experimental procedure described elsewhere [16] and the water content of the catalyst precursor was measured by thermogravimetry [17]. The hydrated catalyst precursor was reduced, without a precalcination step, by heating in a $150 \text{ cm}^3 \text{ min}^{-1}$ stream of hydrogen at a fixed rate of 5 K min^{-1} to a final temperature of $723 \pm 1 \text{ K}$ which was maintained for 18 h. The hydrogen gas (99.9%) was purified by passage through water (activated molecular sieve type 5A) and oxygen (1% Pd on WO_3) traps which were connected in series. Nickel metal dispersions, before and after the catalysis step, were determined by carbon monoxide chemisorption at 273 K as described in detail elsewhere [18].

2.2. Catalytic procedure

All the catalytic reactions were carried out under atmospheric pressure in a fixed bed glass reactor (i.d. = 15 mm) over the temperature range $383 \text{ K} \leq T \leq 573 \text{ K}$. The catalyst was supported on a glass frit and a layer of glass beads above the catalyst bed ensured that the aromatic reactant reached the reaction temperature before contacting the catalyst. The reactor temperature was monitored by a thermocouple

inserted in a thermowell within the catalyst bed; reactor temperature was constant to within ± 1 K. A Sage pump (model 341 B) was used to deliver the aromatic feed via a syringe at a fixed rate which had been carefully calibrated. The aromatic vapour was carried through the catalyst bed in a stream of purified hydrogen, the flow rate of which was set using mass flow controllers. The reactant (benzaldehyde, benzyl alcohol, *o*-tolualdehyde and 2-methylbenzyl alcohol) concentration was in the range 2.2×10^{-3} – 7.3×10^{-3} mol h⁻¹, at a 720 Torr partial pressure of hydrogen and a space velocity of 2×10^2 h⁻¹ (STP). The W/F values were in the range 22–69 g mol⁻¹ h where W is the weight of activated catalyst and F is the flow rate of aromatic. A methanolic solution of 2-methylbenzyl alcohol was used as feed. Activity and selectivity measurements were made using four separate batches of the catalyst sieved in the mesh ranges 75–125, 125–150, 150–300 and 300–800 μm to gauge the contribution of internal diffusion to the catalytic measurements. The values of the Weisz criterion [19] for the conversion of benzaldehyde and *o*-tolualdehyde were less than 10^{-4} . Steady state conversion was kept below 25 mol% by varying the catalyst weight in order to minimize heat and transfer effects. However, the conversion of both benzyl alcohol and 2-methylbenzyl alcohol was higher due to the higher reactivity of these compounds in addition to the need to operate the reactor at temperatures above the condensation temperatures in order to maintain a vapour phase reaction. The reactor effluent was either sampled on-line via a 20 μl sampling valve or was frozen in a dry ice/acetone trap for subsequent analysis. Product analysis was made using a Varian 3400 GC chromatograph equipped with a flame ionization detector and employing a 30% Silicone SF96 on 60/80 mesh acid washed Chromosorb W (6 ft \times 1/8 in.) stainless steel column; data acquisition and analysis were performed using the GC Star Workstation. Product identification was achieved by comparison of the retention times with those of known stan-

dards (Aldrich). The overall level of hydrogenation/hydrogenolysis was converted to a mol% conversion of each reactant using detailed (at least 30 point) calibration plots which covered the range of possible reactant/product mixtures. Each reactant (benzaldehyde/benzyl alcohol 99 + % and *o*-tolualdehyde/2-methylbenzyl alcohol 98%, Aldrich) was thoroughly degassed by purging with purified helium followed by a series of freeze/pump/thaw cycles and was stored over activated molecular sieve type 5A.

3. Results and discussion

The catalyst precursor has a nickel loading of 1.5% w/w and low water content ($< 1\%$ w/w). It may be noted that Ni/SiO₂ catalyst precursors prepared by homogeneous precipitation/deposition (HPD) exhibit stronger nickel/support interactions than is the case with impregnated precursors and the metallic phase supported on the activated HPD carrier is in the form of smaller crystallites which are characterized by a narrow size distribution [18]. The nickel metal dispersion, obtained from CO chemisorption (reproducible to better than $\pm 3\%$), expressed as $(\text{Ni}_{\text{surface}}/\text{Ni}_{\text{total}}) \times 100\%$ equals 73%. The average nickel particle size is estimated to be 1.4 nm according to the relationship [20] $d = 101/D$, where D is the dispersion or percentage of exposed nickel atoms and d is the surface weighted average crystallite diameter assuming (spherical) particles ≤ 1 nm to be 100% dispersed. A value of 0.633 nm² for the average surface nickel atom [21] yields a surface area of 74 m² g⁻¹. Repeated use of the catalyst did not result in any change in the dispersion or dimensions of the supported nickel crystallites.

The hydrogen treatment of benzaldehyde in the presence of Ni/SiO₂ at 383 K $\leq T \leq$ 573 K yielded benzyl alcohol as the only hydrogenated product; aromatic ring reduction was not observed. Toluene and benzene, generated via the hydrogenolysis of the substituent C=O and car-

bonyl C-aromatic C bonds, respectively, formed the remainder of the product mixture. Passage of benzaldehyde in a stream of hydrogen over the silica support did not result in any measurable conversion of the aromatic. All the activity data presented in this paper were obtained at steady state and represent the average of at least six separate test samples where reproducibility was better than $\pm 4\%$. The experimental conditions were chosen so that the reaction rate was not influenced by external or internal diffusion. The possible contribution of external diffusion was monitored by independently varying W and F and establishing that the measured rate was constant at a constant value of W/F . A representative case is illustrated in Fig. 1 where reaction rates of 4×10^{-4} and 12×10^{-4} mol h^{-1} obtained using two benzaldehyde feed rates correspond to W/F values of 22.6 ± 0.4 and 67.9 ± 0.8 g mol^{-1} h, respectively. The reactor can certainly be considered to operate with negligible external diffusion retardation within these W/F values which represent the extremes within which all subsequent catalytic measure-

ments were made. In a separate set of experiments the role of intraparticle diffusion was probed by varying the catalyst particle size, in the mesh ranges 50–125, 125–150, 150–300 and 300–800 μm while maintaining W/F constant and representative data are presented in the inset to Fig. 1. The reaction rate was essentially independent of particle size in the range 50–300 μm but was somewhat lower for particles greater than 300 μm wherein the reaction can be considered to be controlled to a certain extent by transport limitations. There are however negligible internal diffusion constraints in the intermediate 125–150 μm range which was chosen for subsequent rate measurements.

The effect of temperature on the turnover frequency (TOF), the number of molecules converted per metal site per second, of benzaldehyde to the three identified products is illustrated in Fig. 2a. At $T < 490$ K, benzyl alcohol was the principal product and its rate of formation passed through a maximum (T_{max}) at 433 K. The degree of hydrogenolysis of benzaldehyde to toluene also passed through a maxi-

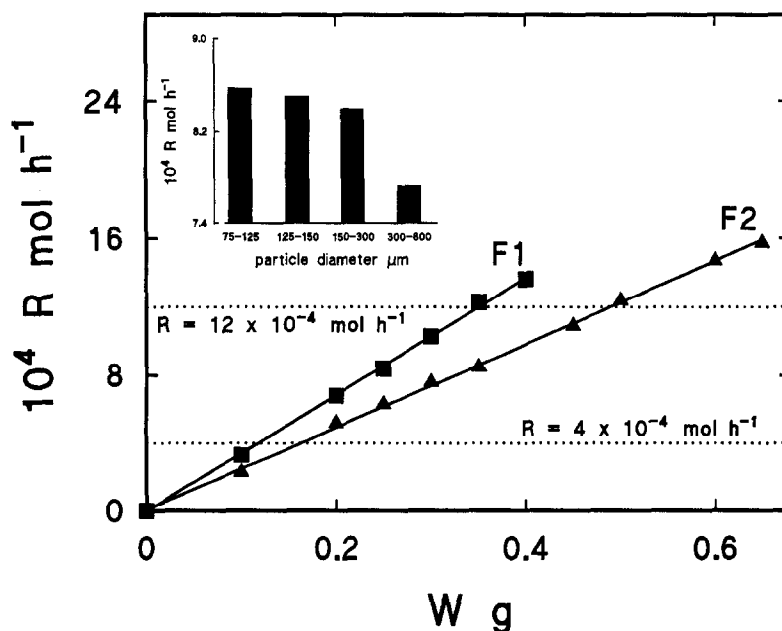


Fig. 1. The variation of reaction rate at 408 K with catalyst weight for two benzaldehyde feed rates: F1 = 5.1×10^{-3} mol h^{-1} ; F2 = 7.3×10^{-3} mol h^{-1} . Inset: The influence of catalyst particle diameter on the reaction rate.

mum but at a higher temperature ($T_{\max} = 473$ K) while benzene formation only became appreciable at $T > 473$ K and increased markedly with increasing temperature to ultimately become the major product. The variation of the TOF of *o*-tolualdehyde with temperature, illustrated in Fig. 2b, exhibits the same basic trends. Reduction of the substituent carbonyl group produced 2-methylbenzyl alcohol while the aromatic ring again remained intact. The hydrogenation TOF profile is, however, characterized by a higher T_{\max} (453 K) than that observed for the benzaldehyde feed. Hydrogenolysis of the C=O bond to form *o*-xylene likewise attains a maximum at 473 K and the hydrogenolysis of the C–C bond to form toluene was again the predominant process at higher temperatures, i.e. $T > 500$ K.

The dependence of the rate constant (k , units of s^{-1}) for the three catalytic processes on temperature is illustrated in Fig. 3 for both aromatic feeds. Maintenance of activity was verified by ascending and subsequent descend-

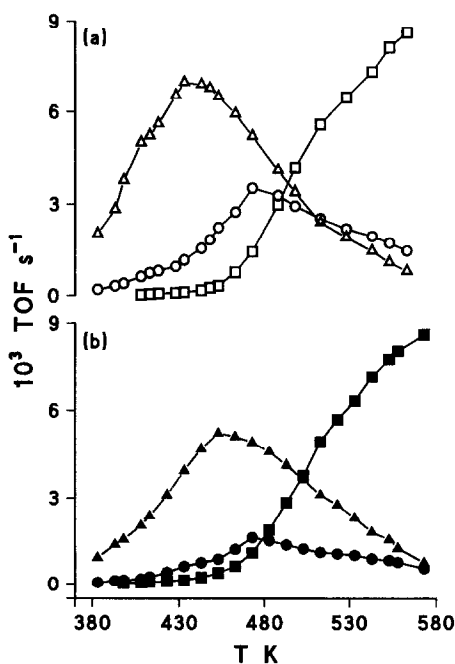


Fig. 2. The temperature dependence of the turnover frequency of (a) benzaldehyde to benzyl alcohol (Δ), toluene (\circ) and benzene (\square) and of (b) *o*-tolualdehyde to 2-methylbenzyl alcohol (\blacktriangle), *o*-xylene (\bullet) and toluene (\blacksquare).

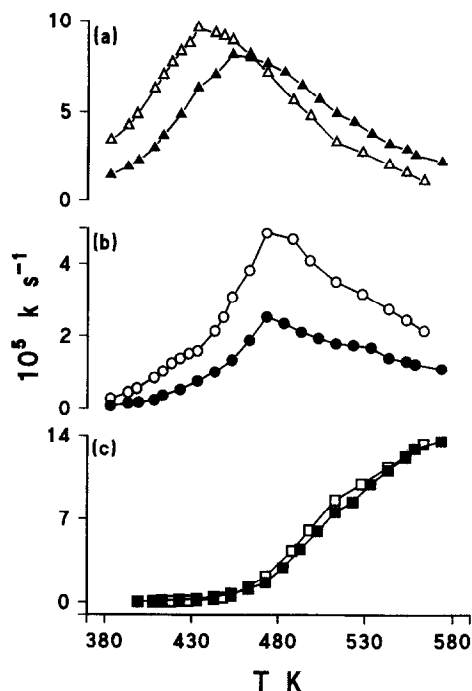


Fig. 3. The variation of the reaction constant, k , with temperature for: (a) the hydrogenation of benzaldehyde to benzyl alcohol (Δ) and *o*-tolualdehyde to 2-methylbenzyl alcohol (\blacktriangle); (b) the hydrogenolysis of benzaldehyde to toluene (\circ) and *o*-tolualdehyde to *o*-xylene (\bullet); (c) the hydrogenolysis of benzaldehyde to benzene (\square) and *o*-tolualdehyde to toluene (\blacksquare).

ing temperature sequences over the entire temperature interval. The experimentally determined k values for the hydrogenation of the aldehyde to the alcohol are greater for benzaldehyde at $T < 463$ K. In the temperature range $383 \text{ K} \leq T \leq 423 \text{ K}$ the corresponding k values for C=O and C–C hydrogenolysis were less than $1 \times 10^{-5} \text{ s}^{-1}$ and $2 \times 10^{-6} \text{ s}^{-1}$, respectively, and the variation of the rate constant for the surface controlled hydrogenation of both aromatic aldehydes with temperature yields valid apparent activation energies (E_{app}). The Arrhenius plots (correlation coefficients > 0.99) gave a computed E_{app} for the hydrogenation of benzaldehyde equal to 30.9 kJ mol^{-1} with a 95% confidence limit of $\pm 1.6 \text{ kJ mol}^{-1}$ which is appreciably lower than the value of $42.2 \pm 3.9 \text{ kJ mol}^{-1}$ recorded for *o*-tolualdehyde. The apparent activation energies for the hydrogenation of the aromatic ring over the same catalyst [22],

i.e. $49.2 \pm 2.0 \text{ kJ mol}^{-1}$ ($393 \text{ K} \leq T \leq 473 \text{ K}$) and $63.6 \pm 2.9 \text{ kJ mol}^{-1}$ ($383 \text{ K} \leq T \leq 463 \text{ K}$) for benzene and toluene, respectively, are considerably higher which may account for the preferential hydrogenation of the carbonyl group. It can be concluded that the carbonyl function of *o*-tolualdehyde is less reactive than that of benzaldehyde under the same reaction conditions. The source of this increased stability may be attributed to the presence of the *ortho*-methyl substituent where the effect is electronic in nature. It is known that the presence of methyl substituents on the benzene ring stabilizes the adsorbed π -complex with the resultant introduction of a higher energy barrier for aromatic ring hydrogenation [23–27]. In the case of the carbonyl double bond the mobile π cloud is pulled strongly toward the more electronegative oxygen atom with the result that the carbonyl carbon is electron-deficient and the polarized group is therefore highly reactive. It is well established that, compared to a hydrogen atom, an alkyl group tends to release electrons [28]. The *ortho*-substituted methyl group in *o*-tolualdehyde must act to release electrons to the aromatic ring which are distributed to the carbonyl carbon, thereby reducing its positive charge. Such a dispersal of charge stabilizes the carbonyl function with the result that *o*-tolualdehyde is more resistant than benzaldehyde to reduction to the aromatic alcohol. Both plots of the temperature dependence of C=O hydrogenation exhibit a maximum due to the increasing competitive rate of C=O hydrogenolysis with temperature, as shown in Fig. 3b. The greater stability of the carbonyl function in *o*-tolualdehyde is manifest in the higher T_{max} for the hydrogenation reaction and the lower rate of hydrogenolysis over the entire temperature interval. Fission of the C–C bond by hydrogen requires more severe reaction conditions and is only initiated at temperatures in excess of 430 K but is clearly accelerated as the temperature is increased with the result that the extent of C=O hydrogenolysis begins to decrease after passing through a maximum at 473

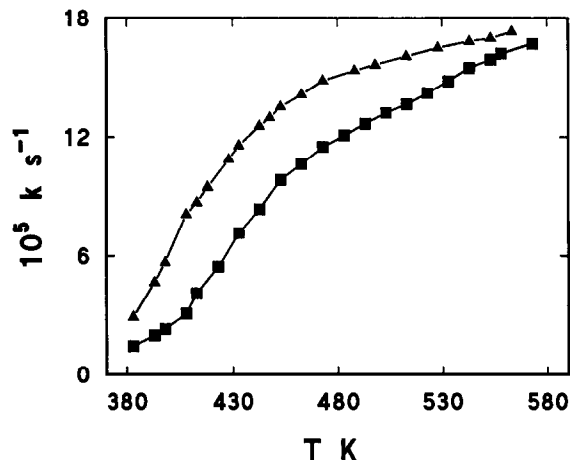


Fig. 4. The variation of the overall rate constant, k , with temperature for the conversion of benzaldehyde (▲) and *o*-tolualdehyde (■).

K. However, the rate constants for C–C hydrogenolysis are essentially the same for both aromatic aldehydes. The inductive effect of the *ortho*-substituted methyl group therefore has little bearing on the stability of the aryl carbon/carbonyl carbon bond.

The effect of temperature on the overall rate constant for the conversion of both aromatic aldehydes is illustrated in Fig. 4. Reactivity is clearly modified by the presence of the *o*-CH₃ substituent and the rate of conversion of *o*-tolualdehyde is markedly lower where $383 \text{ K} \leq T \leq 533 \text{ K}$. At higher temperatures, C–C hydrogenolysis is the overwhelming reaction and any effect of electron delocalization on reactivity is rendered negligible. The fact that the aromatic nucleus is unreactive while the carbonyl substituent undergoes either or both hydrogenation and/or hydrogenolysis suggests that the aromatic aldehyde interacts principally with the catalyst via the carbonyl function. Kuiper et al. [29] have provided spectroscopic evidence that benzaldehyde adsorbs on alumina as a benzoate. The author could find no spectroscopic study of benzaldehyde on nickel or silica. The silica support alone did not induce any hydrogenation or hydrogenolysis of either aldehyde but ‘spillover’ hydrogen from the nickel

metal may attack an analogous benzoate type structure adsorbed on the silica support. Alternatively, the aromatic aldehyde can bind to the nickel metal via the oxygen lone pair electrons. Benzene is known to adsorb on nickel through π -bond interactions in which the ring lies parallel to the active surface [30–32]. It may be assumed that in the adsorption of benzaldehyde on Ni/SiO₂ the plane of the aromatic ring again lies parallel to the surface of the catalyst, bringing the substituent carbonyl function close enough to the active surface to allow for orbital interaction. The dissociated hydrogen preferably attacks the carbonyl group due to the lower energy barrier for the reaction. It is not possible, from the presented catalytic data alone, to differentiate the contribution of steric constraints from the electronic inductive effect due to the neighbouring methyl group in the conversion of *o*-tolualdehyde. The author could find no spectroscopic study of *o*-tolualdehyde adsorption in heterogeneous systems. The repulsive potential due to the *ortho*-methyl group must cause this function to bend away from the plane of the carbonyl/catalyst interaction in order to relieve steric strain. The consequent distortion of the aromatic ring suggests that *o*-tolualdehyde has to overcome a larger barrier than benzaldehyde at the adsorption step and the adsorption energy must be greater for the former reactant. The higher energy of interaction with the surface may be accompanied by a decrease in reactivity with the result that steric hindrance may also contribute to the lower reactivity of *o*-tolualdehyde.

The temperature dependence of molar selectivity (S) in terms of product x , where $S = m_x/m_{\text{tot}}$ and m_{tot} is the total moles of product, is best illustrated in Fig. 5. Both aromatic feeds exhibit a decrease in the selective formation of the alcohol with increasing temperature. The carbonyl group in *o*-tolualdehyde is hydrogenated with a higher degree of selectivity (at $T > 413$ K) than is the case for benzaldehyde. Indeed, the rate of C=O hydrogenation, as the temperature was increased from 383 K to 573

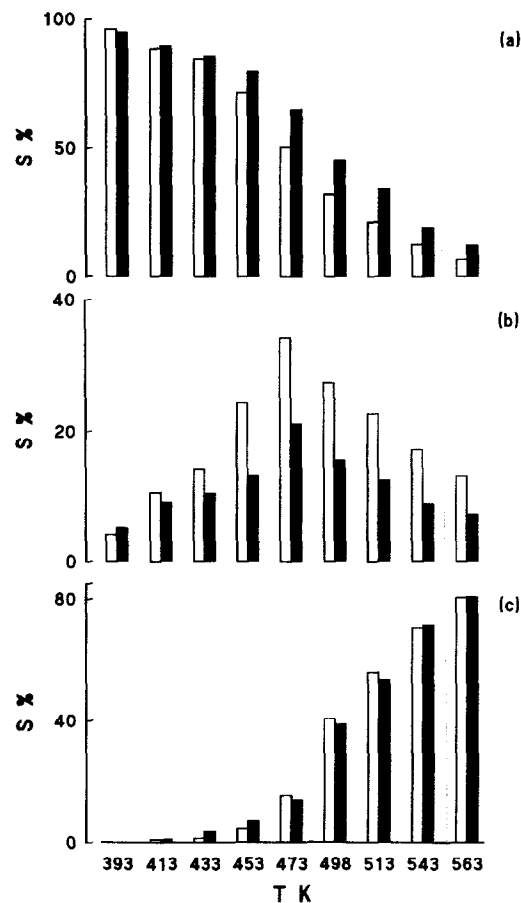


Fig. 5. Percentage molar selectivity in the conversion of benzaldehyde (open bar) and *o*-tolualdehyde (solid bar) in terms of (a) C=O hydrogenation, (b) C=O hydrogenolysis and (c) C–C hydrogenolysis at representative temperatures.

K, was 10.2–0.5 times and 18.3–2.0 times that of C=O hydrogenolysis for benzaldehyde and *o*-tolualdehyde, respectively. The selective hydrogen cleavage of the substituent carbonyl bond passes through a distinct maximum at 473 K in both systems but is clearly preferred to a greater extent in the conversion of benzaldehyde. Selectivity in terms of C–C hydrogenolysis is essentially the same for both feeds and exceeds 80% at the highest temperature that was studied. The progressive shift in process selectivity from C=O hydrogenation to C=O hydrogenolysis to C–C hydrogenolysis with increasing temperature is evident in the hydrogen treatment of benzaldehyde. The increased stability of the

C=O bond in *o*-tolualdehyde results in the carbon/oxygen linkage exhibiting a greater resistance to hydrogen cleavage with the result C=O hydrogenation is preferred to C=O hydrogenolysis at every temperature. Under identical reaction conditions, benzyl alcohol as feed yielded toluene and benzene as the sole products while 2-methylbenzyl alcohol likewise generated *o*-xylene and toluene as the result of C–OH and C–C hydrogenolysis. The ratio of the specific rates of substituent to substituent/aromatic bond hydrogenolysis for the two sets of alcoholic and aldehydic reactants at representative temperatures is given in Table 1. It can be seen that the distribution of products resulting from the aromatic alcohols is quite different from that produced by the aromatic aldehydes. The degree of substituent hydrogenolysis is considerably greater for the alcohol feed, no doubt as a result of the relative ease of C–OH cleavage. The extent of C–C hydrogenolysis in both alcohols also increases with increasing temperature but remains lower than that observed for the aromatic aldehydes. In view of the marked difference in hydrogenolysis selectivity exhibited by the alcohol, the formation of toluene and benzene from benzaldehyde must occur via the direct hydrogenolysis of benzaldehyde and not as a result of a further conversion of benzyl alcohol. The same observation holds true for *o*-tolualdehyde. Methyl substituted benzene systems have been shown

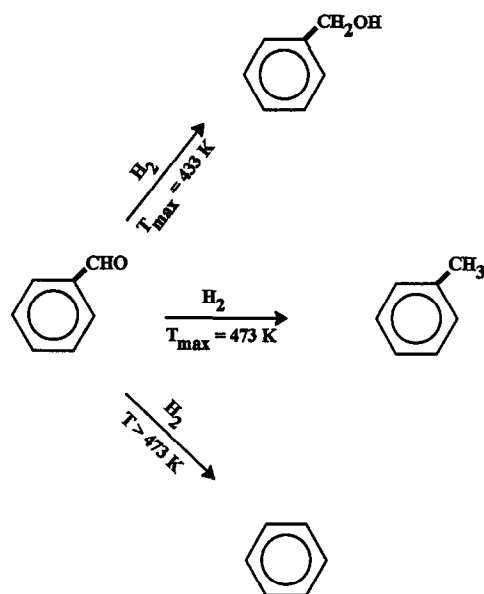


Fig. 6. Temperature dependence of the reaction pathways involved in the conversion of benzaldehyde over Ni/SiO₂.

[22] to exclusively undergo ring hydrogenation over the same catalyst at temperatures lower than 523 K and in view of the absence of ring reduction in the present applications, *o*-xylene and toluene may be discounted as reactive intermediates. Therefore, the reaction products are the direct result of a concerted attack of dissociated hydrogen on the adsorbed aromatic aldehyde. The reaction pathways for the hydrogen treatment of benzaldehyde is illustrated in Fig. 6 and the temperature dependency of each pathway is summarized.

Table 1

The temperature dependence of the relative specific rate of C=O/C–C and C–OH/C–C hydrogenolysis in the hydrogen treatment of benzaldehyde, *o*-tolualdehyde, benzyl alcohol and 2-methylbenzyl alcohol

T (K)	TOF _{C=O} /TOF _{C–C}		TOF _{C–OH} /TOF _{C–C}	
	C ₆ H ₅ - CHO	<i>o</i> -CH ₃ C ₆ H ₅ - CHO	C ₆ H ₅ CH ₂ - OH	<i>o</i> -CH ₃ C ₆ H ₅ - CH ₂ OH
413	12.1	3.4	49.9	44.4
443	7.9	2.5	24.4	21.0
473	2.2	1.5	5.8	5.3
503	0.6	0.3	3.0	2.8
533	0.3	0.2	1.4	1.3
563	0.2	0.1	0.7	0.7

4. Conclusions

Passage of benzaldehyde or *o*-tolualdehyde in flowing hydrogen over Ni/SiO₂ in the temperature range 383 K ≤ T ≤ 573 K resulted in the hydrogenation and hydrogenolysis of the substituent C=O bond and hydrogenolysis of the aryl–carbonyl C–C bond. The benzene ring is not reduced in either case. Methyl substitution at the *ortho* position is observed to lower the overall reactivity of the aromatic aldehyde

by stabilizing the carbonyl function. The *o*-tolualdehyde reaction is characterized by a higher E_{app} and T_{max} for the hydrogenation reaction, a greater selectivity for hydrogenation and a lower rate of hydrogenolysis over the entire temperature interval. Hydrogen scission of the C–C bond to give benzene and toluene, respectively, from benzaldehyde and *o*-tolualdehyde requires more severe reaction conditions but at $T > 500$ K is the principal process where methyl substitution has little effect on the rate or selectivity. It is concluded that the principal interaction of both aldehydes with the catalyst is through the carbonyl function, the aromatic alcohols or methyl aromatics that are formed do not act as reactive intermediates in either reaction and the hydrogenolysis products result from the direct cleavage of C=O and C–C bonds in the aldehyde feed.

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