

Relative Hydrogenation Rates of Carbon Monoxide, Hydrocarbons, and Oxygenates

A comparison of hydrogenation rates of various substrates over the same catalyst has sometimes been used to yield mechanistic information concerning the type of attack the substrate undergoes on the catalyst surface. Moreover, when two hydrogenable substrates and hydrogen are allowed in contact with the catalyst simultaneously, their relative conversions reflect the extent to which these reaction components compete for the active sites. We report herein on the relative hydrogenation rates, both of the individual substrates and of their mixtures with carbon monoxide, over the Cu/ZnO catalyst for methanol synthesis. A pattern which emerges for the Cu/ZnO catalyst is then compared with those for nickel, cobalt, and rhodium to demonstrate some significant differences in the function of these catalysts.

Using the Cu/ZnO = 30/70 catalyst described earlier (1), the substrates 1-hexene, propionic acid, propanaldehyde, benzene, toluene, ethylbenzene, and carbon monoxide were hydrogenated in vapor phase under the pressure, temperature, and flow rate conditions at which CO is hydrogenated to methanol. The results are summarized in Table 1, which shows that the hydrogenation rates were substrate dependent in the order: olefin > aldehyde > CO → CH₃OH > carboxylic acid > ethylbenzene ~ toluene > benzene.

It is noteworthy that carbon monoxide is hydrogenated faster than the aromatic ring over the Cu/ZnO catalyst. The order of hydrogenation rates of CO and aromatics is just the opposite over nickel: while Vannice reports a turnover rate of $3.2 \times 10^{-2} \text{ s}^{-1}$ at 275°C for hydrogenation of CO to methane

over nickel catalysts (2), those for benzene hydrogenation can be estimated as $4.6 \times 10^{-1} \text{ s}^{-1}$ at 275°C and $3.4 \times 10^{-1} \text{ s}^{-1}$ at 250°C from the report by Danes *et al.* (3)¹ and these compare well with the values estimated from Richardson (4) and Taylor and Staffin (5). The above comparison suggests that *on those catalysts on which carbon monoxide is hydrogenated to methanol, this reaction proceeds faster than the hydrogenation of aromatics, while on catalysts which steer the CO hydrogenation to hydrocarbons, the hydrogenation of aromatics is the faster of the two reactions.* The latter pattern may result from the requirement that the CO molecule dissociates in the course of methanation. This is supported by the observation of higher activation energy of methanation than of methanol synthesis on those catalysts which guide CO hydrogenation to both methane and methanol (6).

A further point of difference between the Cu/ZnO and transition metal catalysts is the relative rate of hydrogenation of substituted aromatics. Völter *et al.* (7) have found that over nickel, cobalt, and rhodium catalysts, the rate of hydrogenation of substituted benzenes *decreases* with increasing electron density on the aromatic ring [although activation energies varied in a man-

¹ The turnover rate for benzene hydrogenation on nickel was calculated using the data in Ref. (3): 92.2% conversion at 66°C over 1.49 g Ni of surface area ca. 10 m²/g, flow rate 21 cm³/min of H₂/benzene = 7/1 feed gas. A surface density of 1×10^{15} sites/cm² was assumed. The minimum turnover rate at 275°C was estimated using the minimum activation energy of 7.3 kcal/mol derived from data in Table II of the given reference.

TABLE 1

Relative Hydrogenation Rates of Carbon Monoxide, Hydrocarbons, and Oxygenates over the Cu/ZnO Catalyst^a

Substrate	Percentage conversion ^b	Turnover rate ^c (s ⁻¹)	Substrate feed rate (mol/hr)	Ionization potential (eV)
Benzene	16.6	4.95×10^{-3}	0.0068	9.24
Toluene	25	6.27×10^{-3}	0.0057	8.82
Ethylbenzene	29	6.24×10^{-3}	0.0049	8.76
Propionic acid	63	1.48×10^{-2}	0.0080	
Propanaldehyde	99	4.23×10^{-1}	0.2922	
1-Hexene	100	4.33×10^{-1}	0.2957	
Carbon monoxide	55	2.96×10^{-1}	0.147	

^a Cu/ZnO = 30/70 catalyst and testing conditions are described in Ref. (1). The hydrogenation products were cycloparaffins from aromatics, paraffins from olefins, primary alcohols from oxygenates, and methanol from CO.

^b Conversion was measured at 250°C, 75 atm, over 2.45 g catalyst using a feed of 10.5 liters (STP) of hydrogen per hour (0.43 mol H₂/hr) and that of the substrate indicated in the fourth column of this table.

^c The turnover rate was calculated from the measured conversion rates assuming 2×10^{18} sites/m² of ZnO on the Cu/ZnO catalyst having 23.3 m² ZnO surface per gram of catalyst (8). The turnover rate is defined as the number of conversions per site per second per hydrogen molecule consumed. Hence the substrate turnover is two (three) times smaller in the case where the substrate is hydrogenated by two (three) hydrogen molecules.

ner that differed from one metal to another]. The Cu/ZnO catalyst behaves, once again, in an opposite fashion: ethylbenzene and toluene are hydrogenated faster than benzene showing that the aromatic ring hydrogenation rate *increases* with increasing

electron density. Such behavior is strong evidence in favor of π -bonded intermediates, the surface concentration of which increases with increasing electron-donating ability of the π -electron system, and indicates that hydrogenation might involve an

TABLE 2

Hydrogenation Rates of Carbon Monoxide, Hydrocarbons, and Oxygenates when CO plus an Additional Substrate and Hydrogen Were Admitted to the Cu/ZnO Catalyst^a

Reaction mixture	Molar ratio	Percentage MeOH from the hydrogenation of CO	Percentage hydrogenation of the hydrogenable substrate other than CO or CO ₂
CO/CO ₂ /H ₂	24/6/70	55	—
1-Hexene/CO/CO ₂ /H ₂	4.4/22.9/5.8/66.8	25–42 ^b	100% to <i>n</i> -hexane
Propanaldehyde/CO/CO ₂ /H ₂	3.9/23/5.8/67.2	32–51 ^b	99% to <i>n</i> -propanol
Acrolein/CO/CO ₂ /H ₂	1.5/23.6/5.9/69.0	13.6 ^b	99% to <i>n</i> -propanol
Propionic acid/CO/CO ₂ /H ₂	1.3/23.7/6.0/69.0	0.6 ^b	63% to <i>n</i> -propanol
Ethylbenzene/CO/CO ₂ /H ₂	0.8/23.8/6.0/69.4	31.5 ^b	0% to ethylcyclohexane (traces of toluene)
Toluene/CO/CO ₂ /H ₂	0.9/23.8/6.0/69.3	34.0 ^b	0% to methylcyclohexane
Benzene/CO/CO ₂ /H ₂	1.1/23.7/6.0/69.2	30.5 ^b	0% to cyclohexane

^{a,b} See footnotes of Table 1. The CO/CO₂/H₂ = 24/6/70 mixture was used at 250°C, 75 atm, and total flow rate of 15 liters/hr over 2.45 g of the Cu/ZnO = 30/70 catalyst. The substrate was admitted from a liquid feed valve to produce concentrations indicated in the second column.

electrophilic attack of the surface intermediate. A simple explanation of the observed pattern is provided by a model wherein the aromatics are π -bonded to the surface cations of the Cu/ZnO catalyst followed by a facile stepwise addition of hydrogen. Because the hydrogenation rates are proportional to the stability of the π -donor complexes, no σ -bonded intermediates need to be invoked for the Cu/ZnO catalyst as it was deemed necessary to explain the inverse proportionality between the hydrogenation rates and the stability of π -donor complexes on Ni, Co, and Rh (7). Additional evidence which supports the proposed model is the observed increase in the rate of hydrogenation with decreasing ionization potential. The ionization potentials and the turnover rates of ethylbenzene and toluene are nearly equal, 8.76 and 8.82 eV, but there is a significant increase of ionization potential and decrease of hydrogenation rate between these two substituted aromatics and benzene (ionization potential, 9.24 eV). The criterion for a π -complex is its increasing stability with decreasing ionization potential, and it is suggested that the hydrogenation rate increases where increased stability of the π -complex increases its surface coverage. However, this argument can only be used to compare hydrogenation rates within one class of compounds such as aromatics, since other variables such as steric influence, resonance energy, dipole moments, etc., would differ significantly from one class of substrates to another and offset simple correlations that may exist in one homolog series.

Further experiments, in which a hydrogenable substrate and carbon monoxide were simultaneously admitted to the cata-

lyst, showed that aromatics, carbon monoxide, carboxylic acids, aldehydes, and olefins compete for the same active sites. The results, summarized in Table 2, demonstrate clearly that the addition of a small percentage of the substrate results in a suppression of the methanol yield, while the hydrogenation of the benzene ring is completely inhibited by the presence of carbon monoxide. The results of Table 2 thus show that the same active sites are involved in activating aromatics, olefins, carboxylic acids, aldehydes, and carbon monoxide. The notion that these sites are surface cations is entirely consistent with our earlier suggestion that carbon monoxide is activated for methanol synthesis by copper ions in the zinc oxide surface (1).

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