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Kinetic studies of gas-phase hydrogenolysis of methyl formate to methanol over copper-based catalyst

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Abstract

Hydrogenolysis of methyl formate was studied at atmospheric pressure over skeletal copper and copper chromite catalysts. Measurements of initial activity, made for the skeletal copper catalyst due to its fast deactivation by fouling, showed that the rates of hydrogenolysis were approximately zero order with respect to methyl formate and had positive order for hydrogen. The activation energy for the reaction was found to be around 54 kJ/mol for skeletal copper and 83 kJ/mol for the copper chromite catalyst. Methanol had negligible effect on the activity of the reaction in the absence of CO. The kinetics were interpreted using Langmuir–Hinshelwood empirical models and it appears that the rate-determining step involves formation of a surface hemiacetal species, which gives a surface methoxy group and formaldehyde, by reaction with atomic hydrogen adsorbed on adjacent sites.

Keywords: Kinetics; Hydrogenolysis; Methyl formate; Methanol; Skeletal copper; Copper chromite

1. Introduction

Copper-based catalysts have been identified as very effective for the hydrogenolysis of esters to the corresponding alcohols [1]. Among the copper catalysts, copper chromite is widely used [2] and skeletal copper catalysts have also been considered [3]. The hydrogenolysis of methyl formate has been proposed as part of an alternative route for methanol production [4,5], in which methanol itself is first reacted with CO to generate methyl formate. Hydrogenolysis of methyl formate (MF) then yields 2 mol of methanol. It has been claimed that substantial energy savings in methanol production can be achieved if this route proves to be feasible [6].

The following stoichiometric equations describe the reactions occurring in the process of hydrogenolysis of methyl formate:

$$CH_3OCHO + 2H_2 \rightarrow 2CH_3OH \qquad (1)$$

$$CH_3OCHO \rightarrow CO + CH_3OH \qquad (2)$$

The decarbonylation of methyl formate is a side reaction under moderate reaction temperatures. The optimal equilibrium conditions for good yields of methanol from MF and low selectivity to CO are in the temperature range 298–500 K at atmospheric pressure [7]. In this work we have studied the kinetics of methyl formate hydrogenolysis to methanol over copper-based catalysts under mild reaction conditions.

2. Experimental

2.1. Catalysts

The commercial copper chromite catalyst used was obtained from Harshaw Chemical Company and designated as type 0203. The skeletal copper catalyst was prepared by leaching 300–420 μm particles of a 50 wt.% Cu:50 wt.% Al alloy with 20 wt.% aqueous NaOH at 50 °C for 4 h as described previously [3,8]. Characterization using methods described in those publications gave the results shown in Table 1. The copper content was determined by atomic absorption spectroscopy and the BET surface areas by nitrogen adsorption at 77 K using a Micromeritics High Speed Surface Area Analyser. Copper metal areas were estimated by reaction with nitrous oxide following the pulse method of Evans et al. [9] and the approximate copper particle size by X-ray line broadening.

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Table 1
Properties of reduced catalyst samples

Catalyst	Source	Cu content (wt.%)	Surface area ($m^2 g^{-1}$)		Crystallite diameter (nm)
			S_{BET}	S_{Cu}	
Copper chromite, type 0203	Harshaw	59.4	16.3	10.8	10
Skeletal copper	Laboratory	99.3	18.6	18.1	10

2.2. Experimental procedure

The hydrogenolysis reaction was conducted in a conventional stainless steel micro-reactor system operated at atmospheric pressure. A schematic of the system is shown in Fig. 1. Methyl formate was introduced to the reactor by passing carrier gas through saturators connected in series. The gas flow rates were controlled by mass flow controllers (MFCs). The products were analyzed using two on-line gas chromatographs (GCs) equipped with thermal conductivity detectors (TCDs) and a Porapak Q column in GC-1 and a CTR-1 column in GC-2. An ice-bath between GC-1 and GC-2 was used to condense liquid products from the gas stream to improve the performance of the CTR-1 column.

When used continuously the skeletal copper catalyst was found to lose activity by fouling due to the build-up of polymeric material in the way similar to that observed previously during methanol decomposition [8]. This deactivation was minimized in the present work by confining passage of the reactant mixture to short periods of 2 min at one time with hydrogen alone then passed to remove foulant before the next exposure to the reactant mixture. The kinetic behaviour was then reproducible with no loss of activity after repeated exposures. The copper chromite catalyst did not undergo deactivation during continuous use and the kinetics could be investigated without need for periodic hydrogen treatment.

Around 0.5 g of skeletal copper and 0.15 g of copper chromite catalyst were used. The copper chromite catalysts were reduced using pure hydrogen at 513 K for 4 h prior to use. For the skeletal copper samples, the activation process involved drying in a flowing hydrogen stream (30–45 min) at approximately 373 K followed by reduction at 483 K for 1–2 h. The experimental conditions for skeletal copper were: 393–413 K, methyl formate partial pressure of 2–22 kPa, hydrogen partial pressure of 12–96 kPa, space velocity of 60 000 h^{-1} and for copper chromite 0203: 433–453 K, methyl formate partial pressure of 4–16 kPa, hydrogen partial pressure of 20–90 kPa, space velocity of 120 000 h^{-1}, methanol partial pressure (when added) of 0–6 kPa.

2.3. Reaction rate for hydrogenolysis

In all cases a stoichiometric or excess ratio of hydrogen to methyl formate ($H/C \geq 2$) was maintained and helium was used as a diluent. Initial rates for skeletal copper and steady-state rates for copper chromite were obtained by using conditions that provided differential conversions (<15%). Since conversions and temperatures were kept low, formation of by-product carbon monoxide was always very small, and thus inhibition due to its presence was assumed to be negligible. The rates were calculated using the differential reactor approximation

$$-r = \frac{F_{in} X}{W} \qquad (3)$$

where $-r$ is the reaction rate for hydrogenolysis (mol/h g_{cat}), F_{in} the flow rate of methyl formate entering the reactor

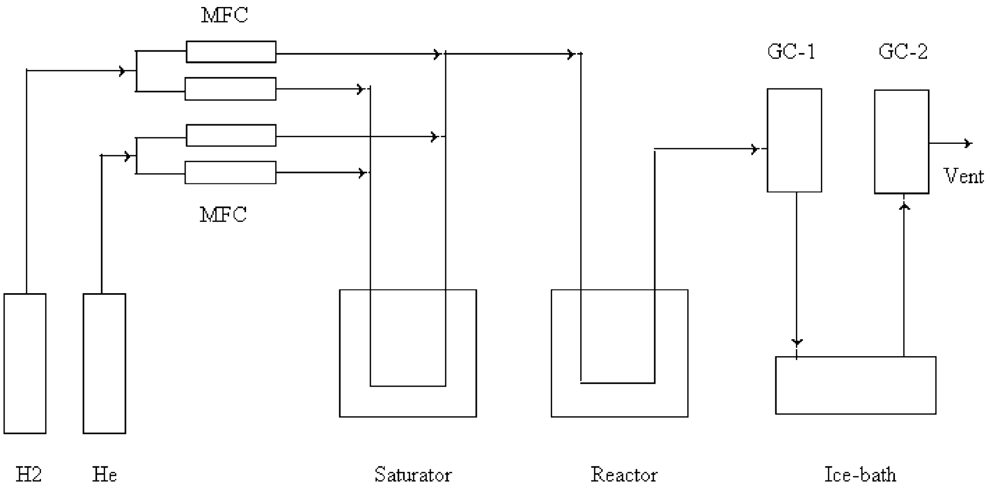

Fig. 1. Schematic representation of the apparatus used for catalyst activity testing.

(mol/h), X the fractional conversion of methyl formate and W the mass of catalyst (g).

Under the low conversion conditions used, the selectivity for methanol formation was always >95%, with CO_2 the only significant by-product. CO_2 is probably formed by steam reforming of methanol with trace amounts of water in the feed. In experiments without added products, the conversion was calculated from the composition of the outlet stream in mol% (Y), i.e.

$$X = \frac{Y_{CH_3OH} + Y_{CO_2}}{Y_{CH_3OH} + 2Y_{CH_3OCHO} + Y_{CO_2}} \quad (4)$$

If methanol was added to the feed, the rate was calculated directly from the net values of Y_{CH_3OH} excluding the mole percentage of methanol in the feed.

3. Results and discussions

3.1. Thermodynamic analysis

The main reaction (1) is highly exothermic and is unfavorable at high temperatures. Thermodynamic evaluation by Kim et al. [7] showed that below 500 K each mole fraction is constant since the chemical equilibrium is affected by reaction (1) only. The conversion of MF is similarly dependent on the equilibrium mole fraction, which remains constant at lower temperatures and then abruptly changes at the transition region of about 500 K. Above 500 K the dominant reaction shifts from the hydrogenolysis reaction (1) to the decarbonylation reaction (2).

In this study, equilibrium conversions X_e were calculated for different H_2/MF ratios where the side reaction could be ignored. Table 2 summarizes the extremes of the conditions used here. The equilibrium constant was calculated using standard methods for ideal gases. The value for ΔH_f^0 (CH_3OCHO) was taken from the measurements of Hall and Baldt [10], the remaining data for methyl formate and that for methanol from Chao et al. [11] and that for hydrogen from the tabulations of Barin [12]. The equilibrium conversion was then obtained by solution of the cubic expression for the equilibrium constant.

The values for X_{max} are the maximum conversions reached in the present work for the conditions shown. As may be seen, X_e is in the range 72–97% under the conditions we used. Thus the experimental conversions did not exceed 18% of the equilibrium values, with most values much less and so the kinetic measurements were carried out far from equilibrium.

3.2. Kinetic studies

An empirical power law equation (5), which incorporated the normal Arrhenius temperature dependence, was used to model the kinetic data obtained from the fixed-bed flow reactor:

$$-r = A\,e^{-E_a/RT} P_{MF}{}^{\alpha} P_{H_2}^{\beta} \quad (5)$$

where $-r$ is the rate of methyl formate consumption (mol/h g_{cat}), A the pre-exponential factor (mol/h g_{cat} $kPa^{-(\alpha+\beta)}$), E_a the activation energy (kJ mol^{-1}), R the gas constant (8.314 J K^{-1} mol^{-1}), T the reaction temperature (K), P_i the partial pressure for species i (kPa), α and β are the reaction orders.

The influence of the partial pressure of reactants was investigated and the plots used to determine reaction orders are shown in Figs. 2 and 3 for the skeletal copper and copper chromite catalysts, respectively. For skeletal copper catalysts, the rate decreased by ca. 5–10% when the pressure of methyl formate was raised from 2 to 22 kPa, as shown in Fig. 2b. By contrast, as shown in Fig. 2a, hydrogen had a significant positive effect on the reaction. This is to be expected since skeletal copper is known to be a poor chemisorber of hydrogen [13].

As shown in Fig. 3a and b, slightly positive orders were found for both methyl formate and hydrogen for hy-

Table 2
Equilibrium conversions calculated for hydrogenolysis of methyl formate to methanol

T (K)	K[a]	Input partial pressure (kPa)			Conversions (%)		X_e/X_{max}
		CH_3OCHO	H_2	CH_3OH	X_e	X_{max}[b]	
393	464.1	4.0	12	0.0	88.7	4.58	0.05
403	313.4	4.0	12	0.0	85.8	6.21	0.07
413	215.7	4.0	12	0.0	71.8	9.85	0.14
433	107.6	7.0	20	0.0	79.3	3.47	0.04
433	107.6	7.0	40	0.0	96.5	4.85	0.05
433	107.6	7.0	40	4.0	94.5	4.12	0.04
443	77.8	7.0	20	0.0	76.1	5.23	0.07
443	77.8	7.0	40	0.0	95.4	8.24	0.09
443	77.8	7.0	40	5.0	92.0	7.39	0.08
453	57.1	7.0	20	0.0	72.9	10.89	0.15
453	57.1	7.0	40	0.0	94.0	16.78	0.18
453	57.1	7.0	40	6.0	88.8	15.24	0.17

[a] The equilibrium constants are for reaction (1) as written.

[b] Maximum conversions used in the present experiments.

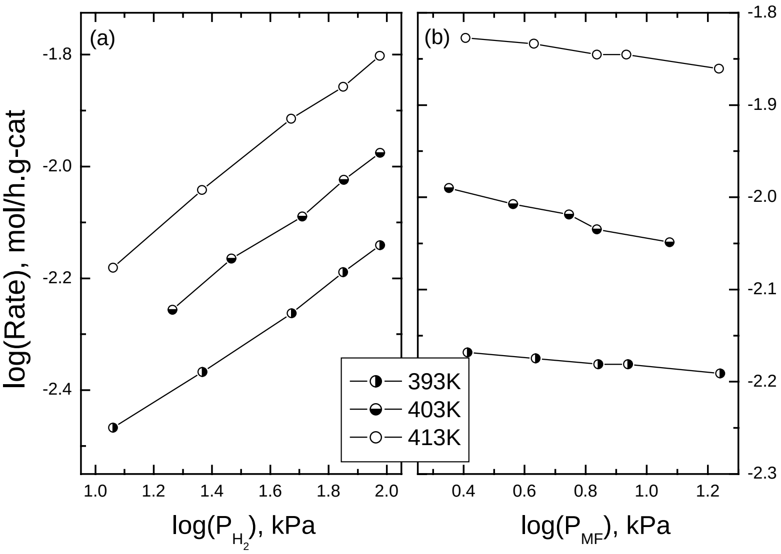

Fig. 2. log–log plots of the rates of methyl formate consumption vs. hydrogen partial pressure with P_{MF} fixed at 3.5 kPa (a) and methyl formate partial pressure with H_2 held at 75 kPa (b) over the skeletal copper catalyst.

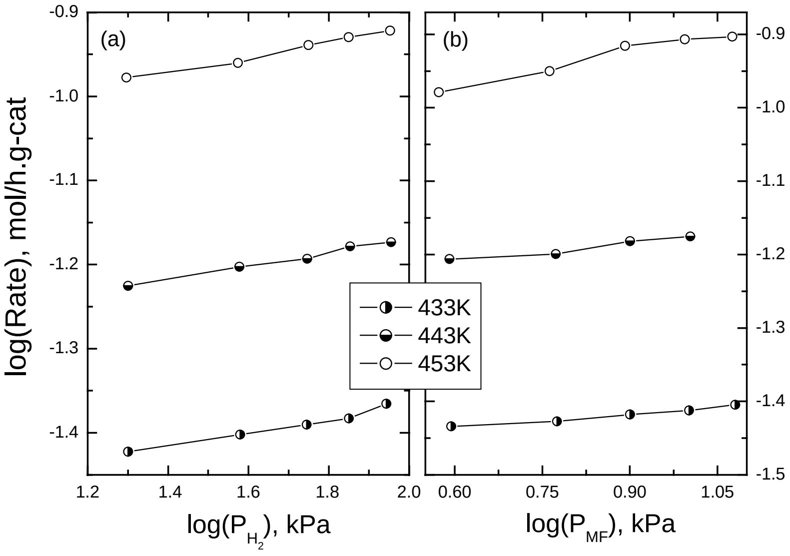

Fig. 3. log–log plots of the rates of methyl formate consumption vs. hydrogen partial pressure with P_{MF} fixed at 8.9 kPa (a) and methyl formate partial pressure with H_2 held at 53 kPa (b) over the copper chromite catalyst.

Table 3
Power-law kinetic parameters for gas-phase hydrogenolysis of methyl formate to methanol

Catalyst	T (K)	$k \times 100$ (mol/h g_{cat} kPa$^{-\alpha+\beta}$)	A (mol/h g_{cat} kPa$^{-(\alpha+\beta)}$)	α	β	E_a (kJ/mol)
Skeletal copper	393	0.70				
	403	1.09	9.65×10^6	-0.05 ± 0.03	0.39 ± 0.02	53.6 ± 3
	413	1.55				
Copper chromite	443	3.13				
	453	5.10	1.93×10^{10}	0.1 ± 0.04	0.1 ± 0.01	83.0 ± 1
	463	8.29				

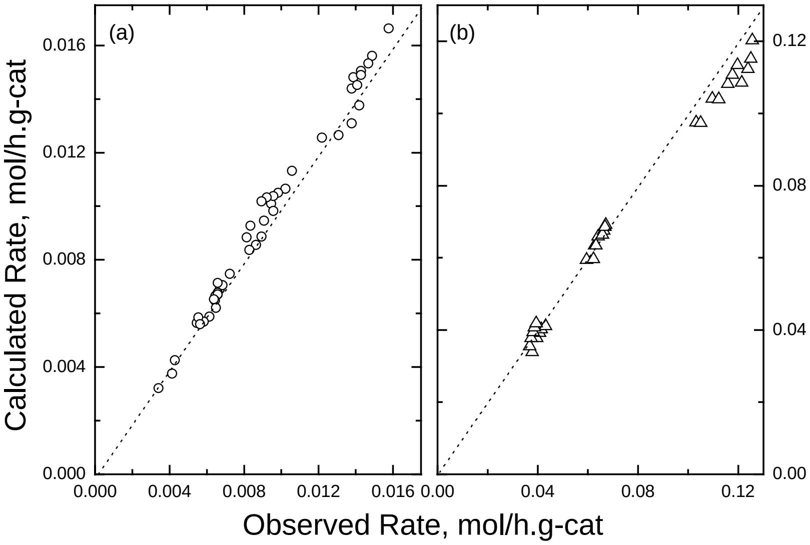

Fig. 4. Plots of observed rate and calculated rates using the power-law equation (4) for hydrogenolysis of methyl formate to methanol over skeletal copper (a) and copper chromite (b) catalysts.

drogenolysis over the copper chromite catalyst. Monti et al. [14], in a study of methyl formate hydrogenolysis over an ion-exchanged copper on silica catalyst containing 5 wt.% Cu with Cu area of 6.5 $m^2 g^{-1}$, found zero-order dependency with respect to hydrogen. The rate was found to depend on the concentration of methyl formate alone (0.4 order).

The kinetic parameters for both skeletal copper and copper chromite are listed in Table 3. Plots of the calculated values using the power law equation (4) versus those observed experimentally in Fig. 4a and b show that the power law expression fits the experimental data well for both catalysts.

3.3. *Effect of the product*

The effect of the principal product (methanol) on the reaction rate was not investigated for the skeletal copper catalyst due to deactivation. The effect of added methanol over the copper chromite catalyst (Fig. 5) was insignificant within the limits of the accuracy of the measurements implying that methyl formate is adsorbed more strongly on copper than methanol. This agrees with a recent DFT study of methanol decomposition on Cu (1 1 1), which showed methanol is weakly bound to the surface of copper [15].

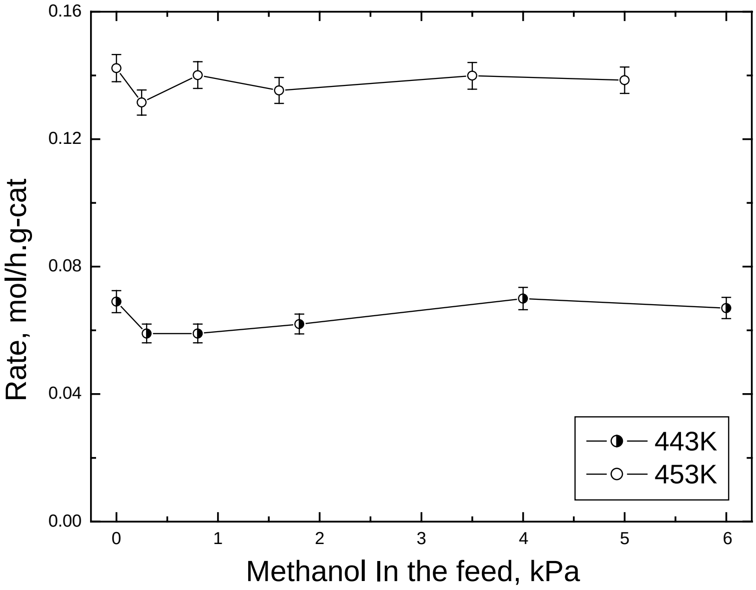

Fig. 5. Effects of methanol in the feed on the rate of hydrogenolysis of methyl formate with P_{MF} fixed at 6.7 kPa and H_2 held at 40 kPa over the copper chromite catalyst.

Table 4
Kinetic parameters for methyl formate hydrogenolysis over copper-based catalysts

Catalyst	Rate expression[a]	T (K)	Kinetic parameters[a]			E_a (kJ/mol)	R^2
			k	K_A	K_B		
Skeletal copper	$\text{rate} = kK_A P_A P_B/[1 + K_A P_A + (2K_B P_B)^{1/2}]^3$	393	0.48	0.18	0.014	61.7	0.97
		403	0.66	0.22	0.015		
		413	1.20	0.16	0.010		
Copper chromite	$\text{rate} = kK_A P_A K_B P_B/[1 + K_A P_A + (K_B P_B)^{1/2}]^2$	433	0.18	1.06	0.99	108.0	0.99
		443	0.29	1.33	1.47		
		453	0.66	0.39	0.15		

[a] k is the specific rate constant and has units of mol g^{-1} h^{-1}; K_A and K_B are the equilibrium adsorption constants for methyl formate (with units of Pa^{-1}) and hydrogen (units Pa$^{-1/2}$); R is the regression coefficient for the fit to the linearized rate expression.

3.4. Mechanistic considerations

The kinetic data for both skeletal copper and copper chromite catalysts were modeled against a large set of Langmuir–Hinshelwood empirical models for ester hydrogenolysis [16]. Each model assumed that all steps after the rate-determining one were fast and that coverage of the surface by all species resulting from these steps (including the product methanol) was negligible. The models differed according to the modes of adsorption of methyl formate and hydrogen (molecular or dissociative), the rate-determining step (RDS) and the surface intermediates involved in the subsequent steps leading to methanol.

Testing was carried out with linearized versions of each rate expression using the Excel function Linest. Most models could be excluded immediately because they gave one or more negative adsorption coefficients, sometimes in combination with a negative rate constant, both of which are physically unreasonable. The Langmuir–Hinshelwood schemes giving the best fit to the experimental data have the following reaction steps:

$$CH_3OCHO(g) + * \overset{K_A}{\leftrightarrow} + CH_3OCHO* \tag{6a}$$

$$H_2(g) + 2* \overset{K_B}{\leftrightarrow} 2H* \tag{6b}$$

$$CH_3OCHO * + H * \text{ or } 2H * \xrightarrow{k} \text{surface intermediate(s)} \ldots \text{the RDS} \tag{6c}$$

$$-r = k\theta_{MF}\theta_H^2 \text{ (skeletal copper)} \tag{6d}$$

$$-r = k\theta_{MF}\theta_H \text{ (copper chromite)} \tag{6e}$$

These models are consistent with the conclusions of Monti et al. [17], from studies using labeled compounds over Cu/SiO_2, that hydrogenolysis of methyl formate involves addition of hydrogen atoms to molecularly adsorbed methyl formate molecules to form a hemiacetal species which, on cleavage of the C–O bond, gives methoxy groups and formaldehyde. However, it was unclear if the slow step was bond cleavage or the addition step that formed the intermediate. On the basis of the present modeling, it appears that the formation of a surface hemiacetal-like species (CH_3OCH_2O–) could be the rate-determining step for copper chromite, while formation of the hemiacetal itself (CH_3OCH_2OH), through the addition of two atomic hydrogen, is more likely for skeletal copper.

The parameters of the rate expressions best-fitting the data for the two catalysts are presented in Table 4, from which it can be there is a good fit to the Arrhenius plots and that the activation energies obtained are close to the values for power law equation (Table 3).

4. Conclusions

Kinetic studies of the hydrogenolysis of methyl formate to methanol over copper-based catalysts showed that a near-zero-order dependence on methyl formate and a positive order in hydrogen under the conditions investigated. Methanol was found not to influence the activity of the reaction indicating weak adsorption. The reaction kinetics were interpreted using Langmuir–Hinshelwood models, which indicated that the rate-determining step involves the reaction between adsorbed methyl formate and atomic hydrogen adsorbed on adjacent active sites.

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