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KINETICS OF ETHANE HYDROGENOLYSIS ON $Os_3(CO)_{12}/Al_2O_3$ CATALYST

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ABSTRACT. Kinetic data for hydrogenolysis of ethane on 1.59 wt % $Os_3(CO)_{12}/Al_2O_3$ catalyst are reported. The reaction was studied at 1 atm, total gas flow rate of 120 cm^3/min, temperature of 150 - 240°C and different partial pressures of hydrogen and ethane. The Arrhenius activation energy was found to be 128.4 kJ mol^{-1}. For ethane-excess and hydrogen-excess reactant feeds, reaction orders in hydrogen were found to be -1.2 and -0.7, and in ethane to be 1.1 and 0.7, respectively. The power law rate model and several steady state models were tested with the observed steady state rates. The steady state model which assumes competitive adsorption of ethane and hydrogen and a slow rate determining step (rds) involving adsorbed C_2H_4 and gaseous hydrogen gave the overall best fit to the observed rates.

INTRODUCTION

The catalytic hydrogenolysis of saturated hydrocarbons has been the focus of extensive research for many years [1-9], and several excellent reviews already exist in the literature [10-11]. These studies are geared towards understanding the kinetics and mechanisms of the processes as well as the structures and activities of the catalysts [4, 9, 12-14]. The proposed kinetic equations for describing the ethane hydrogenolysis reactions for instance have ranged from simple power law rate equations to very complicated ones in which the adsorption of the reactant gases are included [7, 15-16]. It is now generally accepted that the mechanism of ethane hydrogenolysis on supported transition metal catalysts involves three steps as follows:

i) fast dissociative chemisorption of hydrogen and ethane:

$$H_2 + 2* \rightleftarrows 2H(s) \tag{1a}$$

$$C_2H_6 + * \rightleftarrows C_2H_5(s) + H(s) \tag{1b}$$

$$C_2H_5 + H(s) \rightleftarrows C_2H_x(s) + aH_2 \tag{1c}$$

where a = (6 - x)/2, and x varies from o to 6, * = vacant site, and $C_2H_5(s)$ and H(s) are adsorbed species on the surface;

ii) slow decomposition of adsorbed ethane into monocarbon fragments:

$$C_2H_x(s) + A \rightleftarrows CHy(s) + CH_2(s) \tag{2}$$

where A = *, H(s), gaseous hydrogen or nothing at all, and

iii) fast hydrogenation of these monocarbon fragments to give methane:

$$CHy(s) + H_2 \rightleftarrows CH_4 \tag{3a}$$

$$CH_2(s) + H_2 \rightleftarrows CH_4 \tag{3b}$$

The existing rate equations which are based on the above reaction steps have so far failed to account for the observed rate for the entire range of the ratio of the partial pressures of hydrogen to ethane [1-9, 23]. Therefore the purpose of this study has been to collect kinetic data, over a wide range of partial pressures of hydrogen and ethane, for the hydrogenolysis of ethane on alumina-supported osmium catalyst derived from dodecarbonyl triosmium cluster compound, $Os_3(CO)_{12}$. Several theoretical rate equations will then be tested with the experimental data with a goal of providing better understanding of the reaction mechanism on osmium catalyst.

EXPERIMENTAL

Materials and catalyst preparation. The dodecarbonyl triosmium cluster compound, $Os_3(CO)_{12}$, was obtained from Strem Chemicals, USA, and the gamma Alumina (Al_2O_3) pellets and other chemicals and solvents were all of commercial grade and used without further purification. Ultra high purity hydrogen, helium, argon and ethane gases were obtained from British Gas, UK, and used without further purification. The alumina pellets were pretreated by heating in flowing oxygen at 673 K for several hours to remove hydrocarbon contaminants. This was followed by heating in vacuum for 10 h and cooling to room temperature. The 1.59 wt % $Os_3(CO)_{12}/Al_2O_3$ catalyst was made by heating a solution of the osmium carbonyl, $Os_3(CO)_{12}$, in n-octane with alumina pellets, under reflux in nitrogen atmosphere for three hours. The mixture was filtered and the brownish red catalyst precursor was washed with fresh solvent to remove physically adsorbed material. The pellets were then dried in vacuum at 110 °C for about six hours [17-19]. The light brown catalyst was kept in a sealed vial and reduced *in situ* before use.

Catalytic reaction rate measurements. The catalytic hydrogenolysis reaction was studied in a flow system employing a stainless steel reactor with external recycle effected by a bellows pump [20]. The carefully weighed catalyst pellets were loaded into the reactor, surrounded by layers of inert glass spheres. The catalyst pretreatment consisted of flushing with helium gas thoroughly, heating in flowing hydrogen at 350° for overnight (over 10 h) and then cooling the catalyst in hydrogen to the temperature required for the reaction. The experiments were carried out in the range of 150-240°, total gas flow rate of 120 cm^3/min, hydrogen partial pressure of 0.017 to 0.083 atm and ethane partial pressure of 0.009 to 0.067 atm, using argon as the diluent to have the reactor total pressure of 1 atm for each run. The reactor effluent was quantitatively analysed with flame ionization detector of a Pye Unicam series 104 Gas Chromatograph using ultra high purity helium flowing at 100 cm^3/min as the carrier gas. Other details of the experimental procedure are as described previously [21, 22].

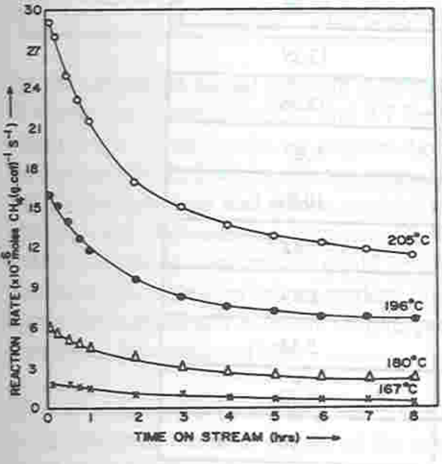
RESULTS AND DISCUSSION

The reactor was operated essentially under low conversion regime and the rate of methane production was calculated using the equation:

$$r_p = \frac{qC_p}{m} \qquad (4)$$

where C_p = concentration of methane produced, q = reactant feed flow rate, and m = mass of the catalyst.

The result in Figure 1 show that the 1.59 wt % $Os_3(CO)_{12}/Al_2O_3$ catalyst was active for the hydrogenolysis of ethane, showing initially high activity which decreased with time on stream before becoming stable. The behaviour is similar to that observed for Os/SiO_2 [22] and that reported by Jackson and co-workers [4].



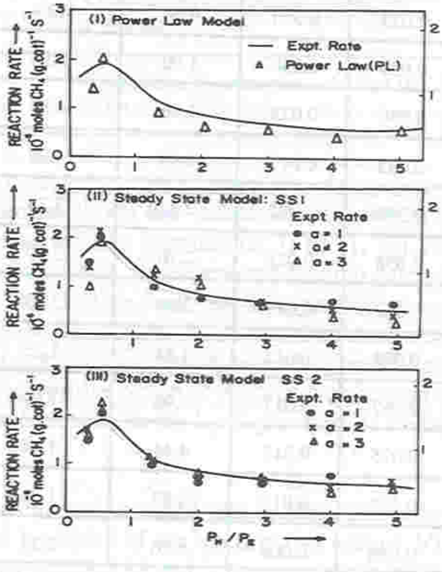


Figure 1. Activity of $Os_3(CO)_{12}/A_2lO_3$ catalyst for ethane hydrogenolyis.

Figure 2. Ethane hydrogenolyis on $Os_3(CO)_{12}/A_2lO_3$; model fitting experimental data.

Effect of reactant gas partial pressures on reactions rate. The variation of the observed rate of ethane hydrogenolysis with the partial pressures of hydrogen and ethane is presented in Table 1. For both hydrogen-excess and ethane-excess reactant feeds, the rate of hydrogenolysis increases with increase in ethane partial pressure at constant hydrogen partial pressure (P_H = 0.017 and 0.058 atm.). However, the hydrogenolysis rate decreases with increase in hydrogen partial pressure for reaction at constant partial pressure of ethane (P_E = 0.017 and 0.050 atm). Furthermore for both hydrogen-excess and ethane-excess reactant gas feed mixtures the rate of ethane hydrogenolysis first increases and then decreases steadily as the ratio of partial pressures of hydrogen to ethane increases from 0.17 to 6.8. A similar trend was observed for the same

Table 1. Observed rate of ethane hydrogenolysis on $Os_3(CO)_{12}/Al_2O_3$ catalyst at 181°.

Reactant gas partial pressure[a]			Methane produced ppm (x104)	Experimental rate[b] x 10^{-6} mol CH_4 (g. cat)$^{-1}$. s^{-1}
P_H atm	P_E atm	P_H/P_E		
0.008	0.050	0.17	14.5	47.96
0.017	0.084	0.20	26.3	86.98
0.017	0.067	0.25	24.7	81.69
0.017	0.050	0.33	19.7	65.15
0.017	0.034	0.49	15.3	50.60
0.033	0.050	0.66	12.4	41.01
0.050	0.050	1.00	8.94	29.57
0.058	0.033	1.76	4.83	15.98
0.033	0.017	1.94	4.02	13.29
0.058	0.025	2.32	3.74	12.36
0.058	0.021	2.76	2.99	9.87
0.050	0.017	2.94	3.03	10.03
0.058	0.017	3.44	2.25	7.44
0.067	0.017	3.96	1.94	6.43
0.075	0.017	4.44	1.64	5.44
0.083	0.017	4.92	1.31	4.32
0.058	0.009	6.76	1.14	3.76

[a] Argon gas was used as diluent to make total pressure of reactor 1 atm, P_H & P_E = hydrogen gas and ethane gas partial pressures, respectively.

[b] Reaction rate was calculated using equation (4) in the text.

reaction on Os/SiO_2 catalysts [22]. These results agree with literature reports on ethane hydrogenolysis by different supported transition metal catalysts [5-9, 23-25]. Sinfelt observed an increase in rate of platinum-catalysed ethane hydrogenolysis with increase in ethane partial pressure and a decrease in rate with increase in hydrogen partial pressure [5]. He interpreted the result with a mechanism in which extensive dehydrogenation occurs on the surface prior to a slow step in which carbon-carbon bonds are broken.

The order of reaction in hydrogen was determined by measuring the rate of hydrogenolysis as a function of hydrogen partial pressure at constant ethane partial pressure. The order of reaction in hydrogen was found to be -1.2 and -0.7 for hydrogen-excess and ethane-excess reactant feeds, respectively. In another set of experiments in which the hydrogenolysis rate was measured as a

Table 2. Steady state kinetic models for ethane hydrogenolysis.

Mode	Rate =	Comments
PL	$kP_E^{x}p^{y}_H$	Power law rate
SS1	$kKP_E/P_H^{(a-1)}$ $1 + K_EP_E/p_H^{a+1}$	C_2H_6 adsorption equilibrium; rds involves H_2 gas
SS2	K_1P_E $1 + bP_H^{(a-1)}$	C_2H_6 adsorption nonequilibrium; rds involves H_2 gas
SS3	$kK_EP_EP_H$ $[P_H^{a}K_HP_H)^{1/2} + K_EP_E + P_H^{a}]$	Competitive H_2 adsorption: H_2 gas in rds
SS4	$kK_EK_H^{1/2}P_E/P_H^{(a-1/2)}$ $[(K_HP_H)^{1/2} + K_EP_E + 1]^2$	Competitive H_2 adsorption vacant site (*) in rds
SS5	$kK_H^{1/2}P_E/P_H^{(a-1/2)}$ $[(K_HP_H)^{1/2} + K_EP_E/(P_H^{a}+1)]^2$	Competitive H_2 adsorption adsorbed H in rds

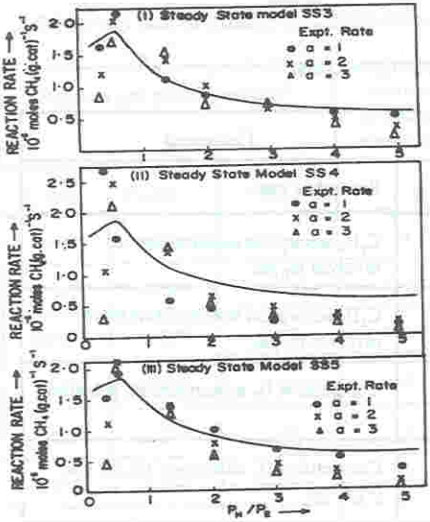
function of ethane partial pressure at constant hydrogen partial pressure, the order of reaction in ethane was found to be 1.1. and 0.7 for hydrogen-excess and ethane-excess reactant feeds respectively. These results are in good agreement with the literature [5, 7, 10-11, 16]. For the hydrogenolysis of ethane by silica-supported osmium metal, Sinfelt reported reaction order of -1.2 and 0.6 for hydrogen and ethane, respectively [11]. For the same reactions on silica-supported platinum and platinum-iron catalysts, Gudkov and co-workers found that the formal reaction orders in hydrogen and ethane could be either positive or negative depending on the reaction conditions [7]. Galvagno and co-workers obtained positive orders of reaction with respect to the hydrocarbon and negative orders with respect to hydrogen for the hydrogenolysis of ethane and propane on Ru catalysts [16].

Effect of temperature on reaction rate. The reaction rate increased with increase in temperature in the Arrhenius fashion. A plot of the natural logarithm of the reaction rate against 1/T was found to be linear, yielding an activation energy of 128.4 kJ mol^{-1}. This result falls within the range published for osmium catalysts. [4, 11, 22, 25].

Kinetic modelling. Table 2 contains the rate expression of the different theoretical models tested with our experimental data. The equations can be conveniently divided into three groups as follows:

1) *The power law model (PL)* is a three parameter model which does not consider the adsorption of reactants as essential for reaction [1, 5, 12, 16]. The steady state models SS1 to SS5 are based on equations 1-3, and they all assume single site ethane adsorption and that the rate determining step is equation 2 (i.e. the rupture of the C-C bond).

2) *Non-competitive hydrogen adsorption steady state models* SS1 and SS2 are two parameter models which assume that A in equation 2 is gaseous hydrogen. Model SS1 assumes that ethane



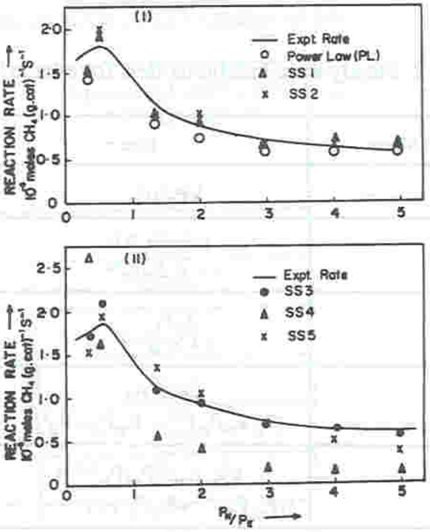


Figure 3. Ethane hydrogenolyis on $Os_3(CO)_{12}/A_2lO_3$; model fitting experimental rate.
Figure 4. Comparison of different kinetic models with experimental rate at 181 °.

adsorption is an equilibrium process whereas model SS2 assumes that ethane adsorption is a non-equilibrium process [5, 8, 15].

3) *The competitive hydrogen adsorption steady state models* SS3, SS4 and SS5 assume that ethane and hydrogen compete for adsorption on the catalyst. They are all three parameter models. In the slow rate-determining step (equation 2) the reactant A is gaseous hydrogen, a vacant site and adsorbed hydrogen for steady state model SS3, SS4 and SS5, respectively [7, 20].

The steady modelling was done by minimising the squares of the relative errors:

$$F = \sum_{i=1}^{n} [\frac{r_{(obs)_i} - r_{(cal)_i}}{r_{(obs)_i}}]^2 \qquad (5)$$

where $r_{(obs)i}$ = experimental rate calculated from equation (4), and $r_{(cal)i}$ = reaction rate calculated from model equations in Table 2.

The results of the kinetic modelling are given in Figure 2 to 4 which compare the experimental rate as a solid line (as a function of the ratio of the partial pressures of hydrogen to ethane) with rates calculated using the different kinetic models for three different values of the adjustable parameter. All the kinetic models predicted correctly the shape of the reaction rate versus P_H/P_E curve. For all the steady state models best fit with experimental rate was obtained when the adjustable parameter, a = 1. The power law model (Figure 2 (I)) consistently predicts lower reaction rate than the observed rate except at the maximum point on the curve where it predicts a higher value than the experimental rate. Thus the PL model gives a poor fit to the experimental rate. The steady state models SS1, SS2, SS4 and SS5 (Figure 2 and 3) predict reaction rates that are either higher or lower than the observed rates. However, the steady state model SS1 and SS2 which assume noncompetitive hydrogen adsorption have performed better than the models SS4

Table 3. Ethane hydrogenolysis on 1.59 wt % $Os_3(CO)_{12}/Al_2O_3$ summary of kinetic parameters at 181°.

Kinetic model	Adjustable parameter	Calculated kinetic parameters			RMS deviation %
SS1			K	k	
	1		$1.25\text{x}10^{-4}$	$3.32\text{x}10^{-1}$	11.4
	2		$1.31\text{x}10^{-2}$	$1.72\text{x}10^{-4}$	18.2
	3		$1.08\text{x}10^{-3}$	$1.05\text{x}10^{-4}$	35.3

SS2			b	k_1	
	1		1.08	2.61×10^{-4}	11.4
	2		3.84	4.80×10^{-5}	7.5
	3		3.64	4.50×10^{-5}	7.6

SS3		K_E	K_H	k	
	1	2.32×10^{-2}	5.00×10^{-7}	2.95×10^{-4}	8.4
	2	2.75×10^{-1}	5.0×10^{-7}	1.30×10^{-4}	27.6
	3	2.30	5.0×10^{-7}	8.39×10^{-5}	41.3

SS4		K_E	K_H	k	
	1	2.67×10^{-3}	1.00×10^{-7}	6.77×10^{-4}	24.5
	2	1.47×10^{-1}	1.59×10^{-4}	8.84×10^{-3}	47.0
	3	3.27×10^{-1}	4.65×10^{-7}	3.89×10^{-1}	60.0

SS5		K_E	K_H	k	
	1	4.23×10^{-2}	3.30×10^{-7}	7.68×10^{-6}	22.5
	2	1.22×10^{-1}	5.0×10^{-7}	9.21×10^{-6}	45.4
	3	2.83×10^{-1}	3.17×10^{-7}	9.29×10^{-6}	61.2

For PL model, $k = 6.11 \times 10^{-5}$; $x = 1.1$; $Y = 0.0$.

and SS5. The steady model SS3 (Figure 3 (I)) which assumes competitive hydrogen adsorption and a slow step involving gaseous hydrogen and adsorbed C_2H_x gave the overall best fit for the different values of the adjustable parameter and at all temperature and reactant composition of this study. The results in Figure 4 for the adjustable parameter a = 1 confirm this point. This meant that ethane hydrogenolysis on Os/Al_2O_3 catalyst proceeds according to equations 1-3, and that the predominant slow step is the reaction between gaseous hydrogen and adsorbed C_2H_4. This was the same conclusion on the Os/SiO_2 catalyst [22]. This conclusion does not however preclude the existence of other dehydrogenated ethane species on the catalyst surface such as C_2H_5(s), C_2H_3(s), C_2H_2(s), or even completely dehydrogenated C_2(s)(Table 3). The values of the kinetic parameters are presented in Table 3 along with the RMS deviation calculated using equation 5.

Gudkov and co-workers [7] found that the reaction rate could not be described by a single equation in the whole P_H/P_E range. They proposed different slow steps and consequently different rate equations for hydrogen-excess and ethane-excess reactant feedstocks. Our present results show that a single equation (SS3) accounts for both hydrogen-excess and ethane-excess feedstocks. Furthermore ethane adsorption on Os/Al_2O_3 catalysts does not require multiple sites contrary to the proposal by Kristyan and co-workers for ethane hydrogenolysis on nickel wire catalyst [9, 23].

Therefore, we can conclude that on alumina-supported osmium catalysts ethane hydrogenolysis proceeds by competitive adsorption of hydrogen and ethane to give adsorbed hydrogen and C_2H_4 species. The C_2H_4(s) reacts with gaseous hydrogen in a slow step to produce surface monocarbon fragments which in turn react with hydrogen gas to give methane [22]. This reaction scheme is independent of the composition of the reactants.

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