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Kinetics of Selective Hydrogenation of Dimethyl Maleate to Dimethyl Succinate in Liquid Phase

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In this paper, the dimethyl succinate produced by hydrogenation of dimethyl maleate and the kinetics of liquid phase hydrogenation of dimethyl maleate to dimethyl succinate was primary studied over ruthenium catalyst in a methanol solution in the temperature range of 323 to 343 K and hydrogen partial pressure from 0.4 to 1.2 MPa. The catalyst was found to be effective for the selective hydrogenation of dimethyl maleate and the dimethyl succinate was the only product. The reaction exhibited an apparent zero-order dependence on dimethyl maleate concentration at higher than *ca.* 0.26 mol/L, while a reaction order of 0.70 ± 0.03 with respect to dimethyl maleate was obtained in the range of 0.015-0.180 mol/L. However, the reaction order with respect to hydrogen partial pressure was 0.82 ± 0.05 in the tested dimethyl maleate concentration range. The activation energy had been found to be 58.926 ± 2 kJ/mol. The obtained rate laws fitted well the experimental data.

Key Words: Dimethyl maleate, Dimethyl succinate, Hydrogenation, Kinetics.

INTRODUCTION

The catalytic hydrogenation of maleic anhydride and its derivatives both in the liquid and in the gas phase are of scientific and industrial importance, where they have been the subject of many studies in the last decades[1-7]. Hydrogenation of maleic acid and its derivatives are industrially important processes for the manufacture of γ-butyrolactone (GBL), 1,4-butanediol (BDO) and tetrahydrofuran (THF).

Catalytic hydrogenation of maleic acid and its derivatives give several products. Using dimethyl maleate as the raw material, the products consist of dimethyl succinate, γ-butyrolactone, 1,4-butanediol and tetrahydrofuran as shown in Fig. 1.

Recently, much attention has been paid to the selective hydrogenation to succinic acid or ester, which is used to synthesize biodegradable poly butadiol succinate (PBS) polymer and dimethyl succinyl succinate (DMSS).

The kinetics of catalytic hydrogenation towards various products has been reported[8-13]. However, there has been no published literature on the kinetics of hydrogenation of dimethyl maleate (DMM) to dimethyl succinate (DMS) in methanol solution. The present study was conducted on catalytic hydrogenation of dimethyl maleate to dimethyl succinate in presence ruthenium in methanol phase. The effects of the mass transfer, temperature, hydrogen partial pressure as well as catalyst loading on the rates of the reaction were investigated and the obtained data were used to formulate the hydrogenation kinetic parameters.

EXPERIMENTAL

Dimethyl maleate (> 99.5 % purity) was prepared by esterification of maleic anhydride of analytical reagent grade followed by distillation. Ruthenium trichloride, used as a catalyst precursor, was obtained from Sino-Platinum Metals Co.,

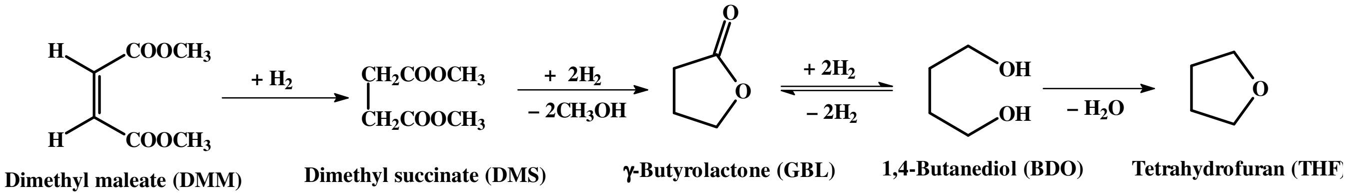


Fig. 1. Reaction scheme for the hydrogenation of DMM

Ltd., China. Methanol, used as solvent and esterification reagent, was of analytical reagent grade. Silver nitrate, used as a reagent to ascertain the absence of Cl^-, was of analytical reagent grade. Sodium hydroxide, used as a precipitant in catalyst preparation, was of analytical reagent grade. Hydrogen from a cylinder with a minimum purity of 99.999 % was used for hydrogenation as well as catalyst reduction. Nitrogen from a cylinder with stated purity of 99.999 % was used to flush reactor system.

The high pressure reactor made of stainless steel by Haian Oil Scientific Research Apparatus Co. Ltd., China, had a net volume of 0.2 dm^3 and had a maximum operating pressure of 16.0 MPa. The reactor was placed in an oil bath equipped with magnetic mixer for mixing the reactor contents. The reactor pressure was controlled using a JY model pressure regulator obtained from Beijing Yantang, Petrochemical Equipment Technical Co. Ltd., China. A DSN-2000 B model mass flow meter, obtained from Dongguan Design Electronics SCI. and Tech. Co. Ltd., China, was installed between pressure regulator and reactor in order to record both the consumption rate and cumulative amount of hydrogen.

Catalyst preparation: To prepare the catalyst, an aqueous solution of ruthenium trichloride trihydrate in deionized water was contacted with an aqueous sodium hydroxide solution and adjusted to a pH of about 10-11 and stirred for 1 h. Then the hydroxide precipitates were separated from the mother liquor by centrifugation, followed by washing several times with deionized water until free of Cl^- ions. The washed precipitate was air dried at room temperature naturally. The resulting powder was crushed and sieved to obtain particles of less than 300 μm. The obtained sample was pretreated under a hydrogen pressure of 0.5 MPa at 343 K for 2 h in methanol solution prior to hydrogenation reaction.

The hydrogenation reactions were conducted at 323-343 K and hydrogen partial pressure range of 0.4-2.5 MPa. Methanol solution of dimethyl maleate and catalyst were placed into reactor. The reactor was then purged three times with nitrogen gas to remove air and to ensure an inert atmosphere and checked for leaks under nitrogen pressure. Subsequently, hydrogen was used to purge out the nitrogen.

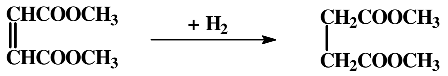
The reactor was heated under static condition and it took about 15-20 min for the temperature to reach the desired value. After the temperature was stabilized, the reactor was charged with H_2 from a cylinder and pressurized to a constant value by the pressure regulator. During this period, little hydrogen consumption was noticed.

By initiating the magnetic mixer, the hydrogenation reaction started as indicated by the mass flow meter. The speed of agitation was adjusted to 675 rpm, a value determined to be high enough to avoid external mass transport limitation. During the hydrogenation process, the rates of hydrogen consumption as well as the cumulative consumed hydrogen shown on the mass flow meter were recorded periodically as a function of time.

When consumption of hydrogen finished, the reactor was cooled to room temperature and vented to atmospheric pressure. The reactor content was collected, the liquid phase was separated and the solvent was removed at reduced pressure. Products were weighed to determine the mass balances.

RESULTS AND DISCUSSION

Selectivity of the catalytic hydrogenation: The hydrogenation of dimethyl maleate to dimethyl succinate is indicated as follows:



$$\begin{matrix} CHCOOCH_3 \\ \| \\ CHCOOCH_3 \end{matrix} \xrightarrow{+\ H_2} \begin{matrix} CH_2COOCH_3 \\ | \\ CH_2COOCH_3 \end{matrix}$$

The above reaction takes place in the presence of a catalyst such as noble metal or supported ones. Using ruthenium as catalyst, the hydrogenation went smoothly at moderate conditions. It was generally observed that dimethyl succinate was the only product formed as suggested by elemental analysis and GC-MS. The elemental analysis with Vario MICRO cube elemental analyzer gave 49.015 % C and 6.886 % H (theoretically 49.315 % C and 6.849 % H). The GC-MS data showed identical spectra with that of standard sample (spectra not shown). In Fig. 2 the GC-MS spectra of the reaction product after removing the methanol solvent is presented.

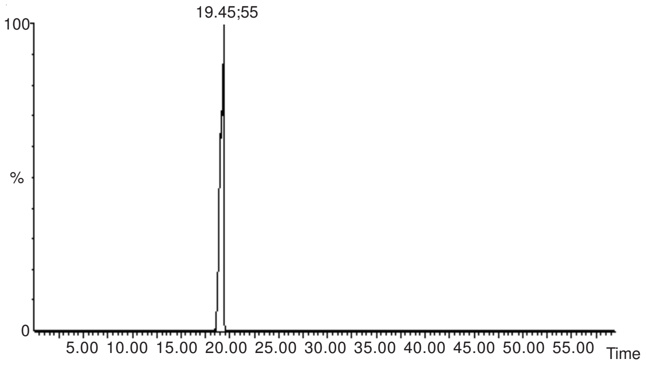


Fig. 2a. GC chart of dimethyl succinate product

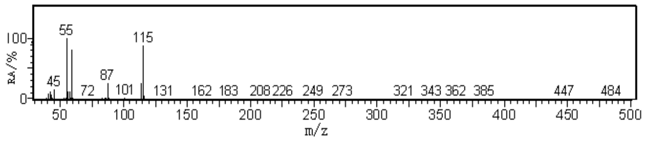


Fig. 2b. MS chart of dimethyl succinate product

Thus it can be said that dimethyl maleate can be completely converted and the catalytic hydrogenation selectivity was almost 100 %. In fact, hydrogenation of dimethyl maleate produced only dimethyl succinate and further reactions to subsequent products were not observed even at hydrogen partial pressure up to 2.5 MPa, which shows that the ruthenium catalyst gave much higher selectivity towards dimethyl succinate.

Mass transfer considerations: For heterogeneous gas-liquid-solid reaction system, the mass transfer effects, including gas-liquid, liquid-solid and intraparticle diffusional resistances, may influence the rate and selectivity of the chemical reaction[14,15]. Thus, it is essential that all mass transfer effects be eliminated. Therefore, the influences of agitation speed and the catalyst particle size on hydrogenation reaction had been done.

The influences of agitation rate were analyzed at 343 K, hydrogen partial pressure 0.48 MPa and dimethyl maleate concentration of 0.45 mol/L and the results are shown in Fig. 3.

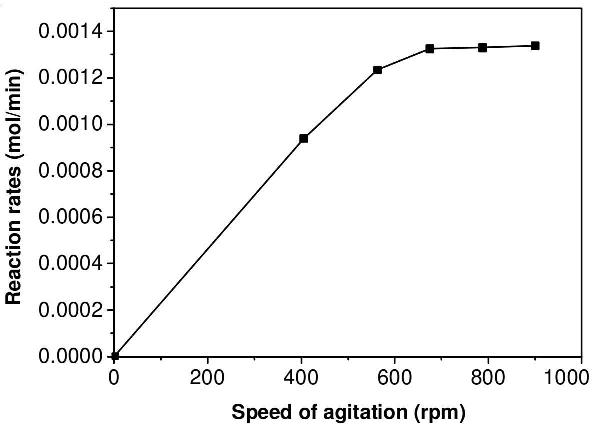


Fig.3. Effect of stirring rates on reaction rates

Fig. 3. shows that the reaction rates increased with agitation speed and leveled off at agitation speed above 600 rpm. Thus, in order to eliminate the influence of agitation speed, all further hydrogenation studies were carried out at a constant agitation speed of 675 rpm.

The impacts of catalyst particle size on hydrogenation rate were also investigated by using 80 mesh and 100 mesh catalyst samples. Nearly the same hydrogenation rate was observed with the two samples. In the following experiments, the catalyst was sieved to 100 mesh prior to hydrogenation reaction.

In summary, all diffusional resistance could be eliminated by using predetermined experimental conditions; hence it was possible to discern the true kinetics from experimental observations.

Effect of temperature: At a hydrogen partial pressure 0.72 MPa, catalyst loading of 0.25 g/L and the initial dimethyl maleate concentration of 0.6 mol/L, the effect of temperature on the hydrogenation of dimethyl maleate to dimethyl succinate was studied by varying reaction temperature. It was found that temperature has a large impact on hydrogenation rate, but negligible effect on the selectivity. In previous section, the 100 % selectivity of dimethyl succinate in this hydrogenation had been proven, so the reaction rate can be indicated by the rate of consumed hydrogen. In Fig. 4, the profiles of dimethyl maleate conversion *versus* time are shown. The conversion of dimethyl maleate had been calculated using the cumulative consumed hydrogen.

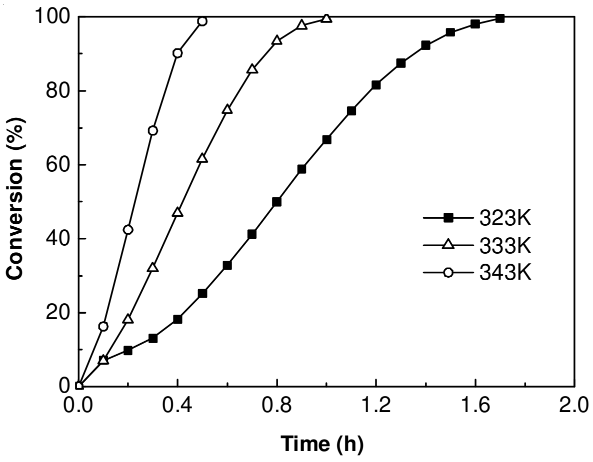


Fig. 4. Effect of temperature on reaction rates

It can be seen that the conversion of dimethyl maleate increased with time until complete transformation of dimethyl maleate. It can also be seen that as temperature increased, the conversion rate also increased.

Effect of concentration of dimethyl maleate reactant: During the hydrogenation process, the concentration of dimethyl maleate decreased, so the impact of dimethyl maleate concentration could only be obtained if the hydrogenation product dimethyl succinate has little influence on the reaction rate. Additional investigation revealed that adding the same amount of dimethyl maleate to a completely hydrogenated system, nearly the same time was observed for the second complete hydrogenation. This strongly suggested that the hydrogenation rate is almost the same in the presence of dimethyl succinate product, thus making it possible to investigate the dimethyl maleate concentration effects just by performing a hydrogenation test at constant temperature and hydrogen partial pressure.

It was found that the hydrogenation rate has a complicated relationship with dimethyl maleate concentration. In the range of 0.015-0.18mol/L, an approximately linear increase with concentration was observed, while a constant rate was obtained with concentrations higher than about 0.26 mol/L. The results shown in Fig. 5 were obtained at a temperature of 333 K and hydrogen partial pressure of 0.72 MPa.

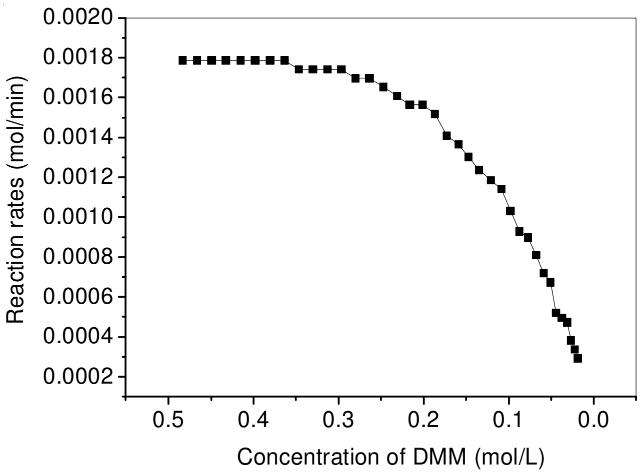


Fig. 5. Effect of concentration of dimethyl maleate (DMM) on reaction rates

Effect of hydrogen partial pressure: The effect of hydrogen partial pressure was studied by changing pressure from 0.4 MPa to 1.2 MPa at a constant dimethyl maleate concentration of 0.175 mol/L, 333 K and a catalyst loading of 0.25g/L. The results are shown in Fig. 6. It is clear that the hydrogenation rate increased with hydrogen partial pressure under the conditions employed. This could be explained by the fact that the solubility of hydrogen in methanol increases with the hydrogen partial pressure[16].

Effect of catalyst loading: The impact of catalyst loading was studied at a temperature of 343 K and hydrogen partial pressure 0.72 MPa. The catalyst loading was varied from 0.05 to 0.35 g/L and the results are shown in Fig. 7.

It can be seen that the rate of reaction increased with the catalyst loading under the conditions employed during hydrogenation.

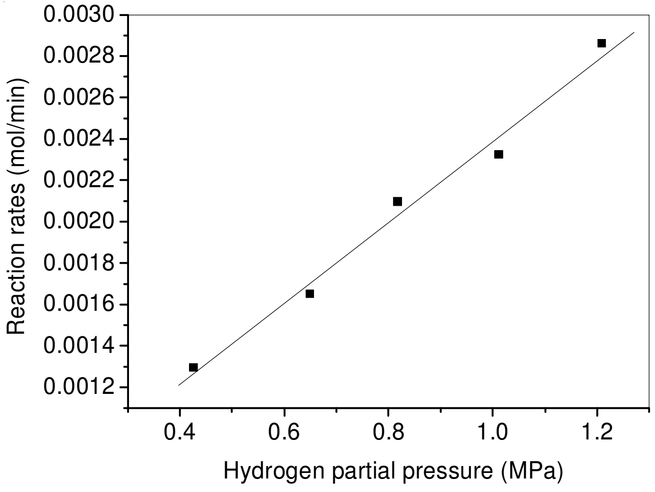


Fig. 6. Effect of hydrogen partial pressure on reaction rate

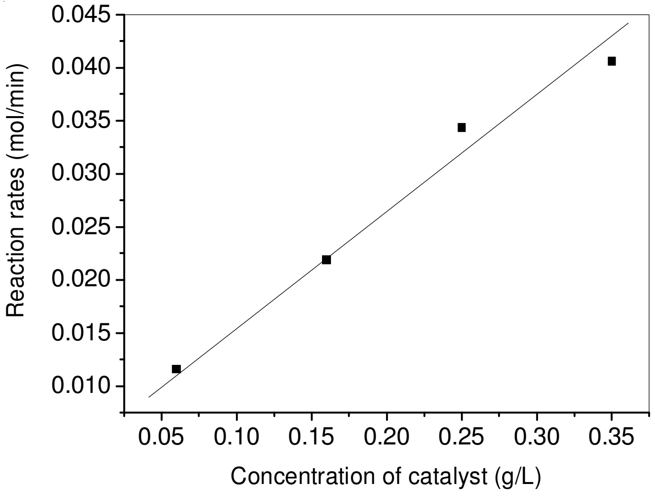


Fig. 7. Effect of catalyst loading on reaction rate

Determination of hydrogenation parameters: Based on the data obtained above, kinetic rate equations for this reaction were developed.

As shown in Fig. 5, the reaction rate shows an approximately linear increase with the concentration of dimethyl maleate in the range from 0.015 to 0.180 mol/L. However, nearly a constant rate was observed when the dimethyl maleate concentration was higher than about 0.26 mol/L. Therefore, two rate laws needed to be developed, one for each of the two dimethyl maleate concentration regions.

In the lower dimethyl maleate region, the reaction rate equation can be expressed as eqn. 1,

$$r = kP^{m}M^{n} \qquad (1)$$

where, P and M denote hydrogen partial pressure and dimethyl maleate concentration, respectively and m and n are the reaction orders with respect to hydrogen and dimethyl maleate.

Equation 1 can be further simplified by keeping constant hydrogen partial pressure, leading to the following equation:

$$r = k^{/}M^{n} \qquad (2)$$

By adopting a logarithm of (2), the rate equation can be expressed as:

$$\log r = \log k^{/} + n \log M \qquad (3)$$

The log-log plot gives a straight line and hence reaction order n can be obtained as shown in Fig. 8. Similarly, by keeping constant dimethyl maleate concentration, the reaction order with respect to hydrogen partial pressure could be obtained as shown in Fig. 9.

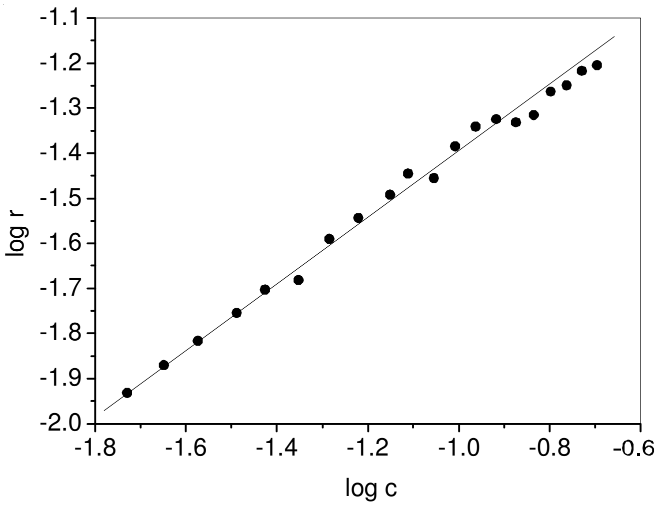


Fig. 8. log-log plots of r = f (M) (333 K, H_2 pressure 0.72 MPa, catalyst loading 0.25 g/L)

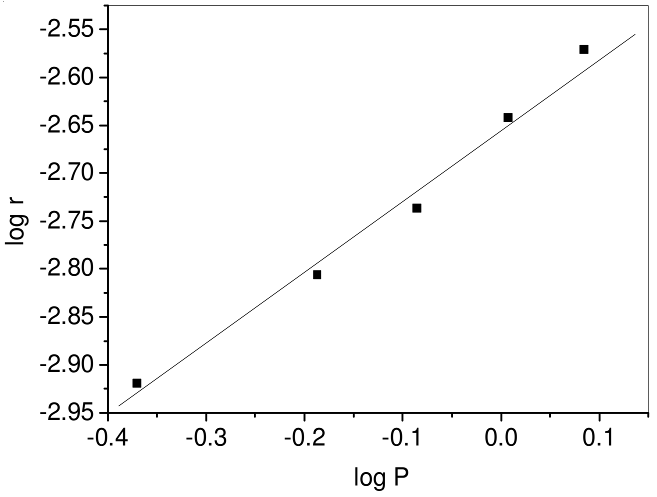


Fig. 9. log-log plots of r = f (P) (333 K, catalyst loading 0.25 g/L)

The calculated reaction orders m and n were 0.82 ± 0.05 and 0.70 ± 0.03, respectively. So the reaction rate equation can be expressed as:

$$r = k\,P^{0.82}\,M^{0.70} \qquad (4)$$

From the above equation, k values at different temperatures have been calculated as shown in Table-1.

TABLE-1
RATE PARAMETERS OBTAINED IN LOWER DMM CONCENTRATION REGION

Reaction order		Rate constant(k)		
m	n	323K	333K	343K
0.82 ± 0.05	0.70 ± 0.03	0.046780	0.092252	0.168293

Using Arrhenius equation k = A exp(-E/RT), the activation energy E and the pre-exponential factor A were calculated to be 58.926 ± 2 kJ mol^{-1} and $2.415 \times 10^{7}(mol/l)^{0.3}\cdot(MPa)^{-0.82}\cdot min^{-1}$, respectively. Thus, the rate eqn. 4 can further be expressed as:

$$r = 1.595 \times 10^{8}\,[\exp(-58926/RT)]\,P^{0.82}\,M^{0.70} \qquad (5)$$

In the higher dimethyl maleate concentration region (0.26-0.50 mol/L), the reaction order with respect to dimethyl maleate was zero, so the rate can be expressed as:

$$r = K''P^{m} \tag{6}$$

The reaction order m has been calculated to be 0.82 ± 0.05, which was the same as that in the lower dimethyl maleate concentration region. From the above eqn. 6, K"values at different temperatures have been calculated as shown in Table- 2.

TABLE-2
RATE PARAMETERS OBTAINED IN HIGHER DIMETHYL MALEATE CONCENTRATION REGION

Reaction order		Rate constant (K")		
M	n	323 K	333 K	343 K
0.82 ± 0.05	0	0.013924	0.0271764	0.049993

The activation energy and the pre-exponential factor A was calculated to be 58.851 ± 1kJ mol^{-1} and 4.603 × 10^{7} (MPa)$^{0.18}$·min^{-1}. Thus, the rate eqn. 6 can further be expressed as:

$$r = 4.603 \times 10^{7}\ [\exp(-58851/RT)]\ P^{0.82} \tag{7}$$

Comparison of experimental and calculated rates: Using equation 5 and 7, the hydrogenation rate can be calculated and the obtained values have been compared with experimental data. At the lower dimethyl maleate concentration ranges from 0.015 to 0.18 mol/L, the experimental data obtained at different temperatures and pressures have been plotted against the calculated value as shown in Fig. 10. The plot of experimental rates with calculated ones at dimethyl maleate concentrations ranging from 0.30 to 0.45 mol/L is presented (Fig. 11).

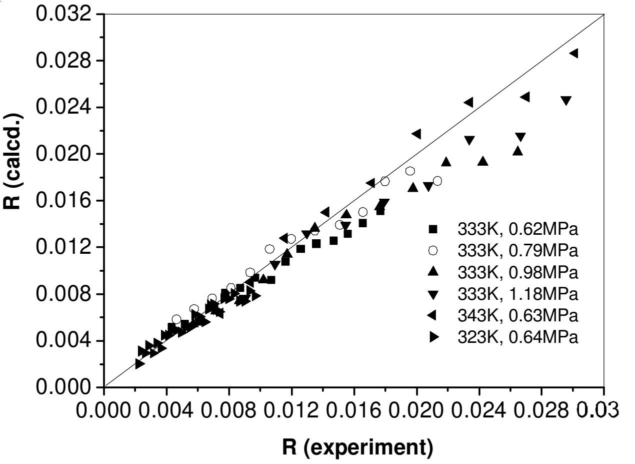


Fig. 10. Comparison of experimental and predicted rates at 0.015 to 0.180 mol/L

Conclusion

It was found that ruthenium catalyst was an efficient catalyst, which enables the selective hydrogenation of dimethyl maleate at low temperature and low hydrogen partial pressure, thus giving much higher selectivity for producing dimethyl succinate. After complete conversion of dimethyl maleate to dimethyl succinate, further hydrogenation to subsequent products was not observed, even with raising the hydrogen partial pressure to 2.5 MPa.

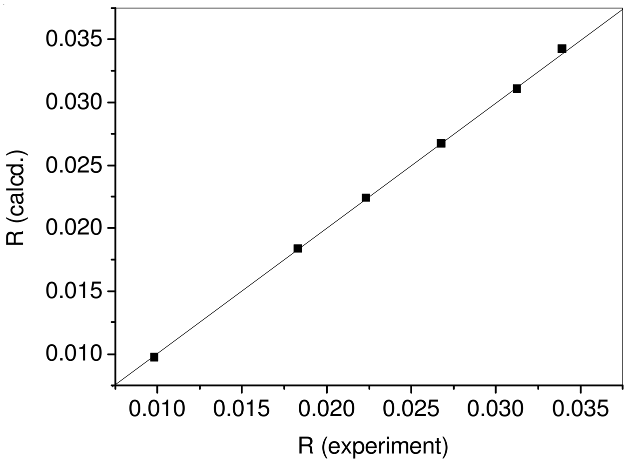


Fig. 11. Comparison of experimental and predicted rates at 0.30 to 0.45 mol/L

The kinetics of liquid phase catalytic hydrogenation of dimethyl maleate to dimethyl succinate in the presence of a ruthenium catalyst was studied in the temperature range of 323 K to 343 K with hydrogen partial pressure in the range of 0.4 MPa to 1.2 MPa.

The reaction exhibited an apparent zero-order dependence on dimethyl maleate concentration at higher than about 0.26 mol/L, while a reaction order of 0.70 ± 0.03 with respect to dimethyl maleate was obtained in the range of 0.015-0.180 mol/L. However, the reaction order with respect to hydrogen partial pressure was 0.82 ± 0.05 in the tested dimethyl maleate concentration range. The activation energy had been found to be 58.926 ± 2 kJ/mol. The obtained rate laws appear to accurately fit the experimental data, especially in the high concentration region.

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