Hydrogenation of maleic anhydride to succinic anhydride over nickel/clay catalysts

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Received: 9 July 2012/Accepted: 12 September 2012 © Springer Science+Business Media Dordrecht 2012

Abstract Hydrogenation of maleic anhydride (MA) to succinic anhydride (SA) over Ni/clay catalysts prepared by an impregnation method has been studied at different temperatures, Ni contents, pressures and weighted hourly space velocity (WHSV). The catalytic activity was greatly influenced by the temperature, Ni content, WHSV and pressure. A 97.1 % MA conversion with 99.6 % selectivity to SA was obtained over 5 %wt catalyst at 180 °C and at a pressure of 1 MPa H₂. The catalysts were characterized by an array of techniques, including X-ray diffraction (XRD), H₂ temperature-programmed reduction (TPR) and thermogravimetric analysis (TGA). XRD and TPR studies showed that nickel was present as Ni²⁺ species on the support. Increasing the calcination temperature up to 650 °C led to the destruction of the support structure, as observed by TGA, while a calcination temperature of 550 °C gave the best results. Catalyst deactivation studies showed that the catalyst has a long lifetime, the yield of SA remaining better than 90 % even after a reaction time of 60 h. Studies on the catalyst induction showed that the presence or absence of an induction period was determined by the type of hydrogenation catalyst.

Introduction

Hydrogenation of maleic anhydride (MA) is an important industrial chemical process, the products of which, such as

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The State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China e-mail: yyshi@ecust.edu.cn succinic anhydride (SA), γ -butyrolactone (GBL), 1,4butanediol (BDO) and tetrahydrofuran (THF), are important chemicals in the food, pharmaceuticals and textile industries [1–5]. The reaction pathway for the hydrogenation of MA to BDO and THF is illustrated in Fig. 1 [6–8]. In this process, both hydrogenation and hydrogenolysis reactions are involved.

These compounds are mainly produced by four industrial processes: (1) the Reppe process, based on acetylene– formaldehyde condensation; (2) the Arco process, based on isomerization of propylene oxide to allyl alcohol and subsequent hydroformylation; (3) the Mitsubishi Kasei process (MKC), based on 1,3-butadiene diacetoxylation; and (4) the Davy McKee process based on hydrogenation of diethyl or dimethyl maleates [3]. However, each of these processes has some disadvantages. The Reppe process uses acetylene and formaldehyde as starting materials, plus severe reaction conditions (140–280 bar, 250–350 °C) [9]. The Davy McKee process needs two different reactors, catalysts and reaction conditions [10].

In principle, hydrogenation of MA is the most direct, environmentally benign, and economic way to produce SA. Because of MA's ready availability and low price, which became possible by the construction of large fluid bed plants, according to Alusuisse–Lumnus and BP/UCB technologies, MA may be considered as a good feedstock [2, 3].

Hydrogenation of MA over different noble metal and copper-based catalysts in both vapor and liquid phases has been reported [11–17]. However, these catalysts are expensive and are susceptible to deactivation, as the coke deposition must still be resolved, so it is necessary to explore highly active catalysts which can work under much milder reaction pressures or use less expensive metals, if possible. We have studied Ni/HY-Al₂O₃ catalysts for



Fig. 1 Reaction scheme of hydrogenation of maleic anhydride (MA)

hydrogenation of MA to SA. Over 5 %wt of Ni/Al₂O₃-HY catalyst, a SA yield of 95 % was obtained under the optimized reaction conditions [reaction temperature = $190 \,^{\circ}$ C; reaction pressure = 1 MPa; weighted hourly space velocity $(WHSV) = 2 h^{-1} MA$ [18]. These results show that nickel-based systems are good alternatives to noble metal hydrogenation catalysts. Therefore, in this work, an inexpensive Ni-loaded clay-based catalyst was chosen to investigate MA hydrogenation. For the most active catalyst, a systematic study of the reaction system, including the influence of temperature, Ni content, pressure and WHSV, has been carried out. Moreover, catalyst deactivation and induction period have been investigated. Compared with the Ni/HY-Al₂O₃ catalyst for hydrogenation of MA, higher yield of SA and longer stream time were obtained for the Ni/clay catalyst at a greater WHSV and lower reaction temperature.

Experimental

Catalysts preparation

The support was prepared via the kneading method, using clay. The clay was obtained from Yongsheng catalyst plant (Linan China). The elemental analysis (mass %) showed the composition of the clay to be SiO₂: 67.8; Al₂O₃: 16.3; Fe₂O₃: 4.0; MgO: 1.7; CaO: 1.1; TiO₂: 0.4; Na₂O: 0.9; K₂O: 1.6 %. First, the clay was shaped with normal aqueous solutions of HNO₃ (10 %wt) and dried at 120 °C overnight and then calcined in air at 550 °C. After the calcination, the clay was cooled to room temperature and then crushed and sieved to a particle size between 0.38 and 0.83 mm.

The monometallic nickel catalysts (Ni supported on clay) were prepared by impregnation of the support with an aqueous solution of nickel nitrate hexahydrate. First, the support was impregnated in normal aqueous solutions of Ni(NO₃)₂·6H₂O (0.852 mol/L analytical grade) at room temperature and left to stand for 12 h. After the impregnation step, all the catalysts were dried at 120 °C overnight and then calcined in air at different temperatures (250, 350, 450, 550 or 650 °C) for 3 h and allowed to cool to room temperature. The amount of clay and Ni precursor was varied to obtain catalysts with different nickel contents. For example, 5 %wt Ni/clay requires 5 ml of the normal aqueous solution of Ni(NO₃)₂·6H₂O and 4.75 g of the support.

Catalyst characterization

In situ X-ray diffraction patterns during reduction of the catalysts were obtained with a Bruker D8 Advance X-ray diffractometer equipped with an atmosphere and temperature control stage using CuK α radiation operated at 40 kV and 100 mA. The powder diffraction patterns were recorded in the 2θ range from 10° to 80°.

Temperature-programmed reduction (TPR) with H₂ was carried out on Auto Chem 2910 (Micromeritics) instrument. In a typical experiment, 0.050 g of calcined catalyst was exposed to a reducing gas consisting of 5.0 vol % H₂ in argon with a temperature ramp from ambient to 800 °C at a heating rate of 10 °C/min.

The thermogravimetric analysis (TGA) was carried out in air using a Dupont thermo-balance. In these experiments, the sample temperature was increased from 40 to 700 °C with a heating rate of 10 °C/min.

Catalytic tests

The reaction was performed in a fixed-bed reactor operated in the down-flow mode. The temperature of the reactor was controlled using a PID controller. The temperature of the catalyst bed was measured using a Ni-Cr-Ni thermocouple. Isothermal operating conditions were maintained by a cooling coil inside the reactor and an electrical heating jacket covering the outer side of the reactor wall. The pipings of the system were heated with three independent heating sets. The reactant was a solution of MA in γ -butyrolactone (22 wt%), which was transported into the reactor with a micro-syringe pump. For each experiment, 1 g of unreduced catalyst (20-40 mesh) was loaded into the reactor. The catalyst was reduced in situ at a pressure of 1 MPa with H_2 (flow rate 32 cm³/min) for 2 h. The products were analyzed using an Agilent 6,890 N gas chromatograph (flame ionization detector, HP-5 column, 30 m \times 5 mm \times 0.25 μ m) and confirmed by gas GC–MS.

MA conversion and selectivity to the product *i* was calculated according to the following equations:

$$X_{\rm MA}\,(\%) = \frac{\rm MA_{in} - \rm MA_{out}}{\rm MA_{in}} \times 100 \tag{1}$$

$$S_i (\%) = \frac{\text{Product}_{i,\text{out}}}{\text{MA}_{\text{in}} - \text{MA}_{\text{out}}} \times 100, \qquad (2)$$

where MA_{in} , MA_{out} and $Product_{i,out}$ represent the concentrations of reactant or products entering (in) or leaving (out) the reactor, respectively.

Results and discussion

XRD analysis

XRD patterns (Fig. 2) of all the catalyst samples examined at the big angle showed the characteristic peaks for NiO species at $2\theta = 37.25$, 43.28, 62.88, 75.41 and 79.41° corresponding to the planes (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) of cubic NiO species, respectively. For the peaks at $2\theta = 37.25$ and 62.88°, the diffraction intensity was clearly enhanced with Ni loading of around 7 %wt. With further increase in nickel content, the diffraction peak intensities increased without any other visible change. This suggests the presence of NiO when the loading of nickel is more than 7 %, but there are no other kinds of Ni oxides or elemental Ni present.

Temperature-programmed reduction of 5 %wt Ni/clay

The TPR profiles of the samples are presented in Fig. 3. The peak with T_{max} at 370°C can be attributed to the reduction of NiO particles with no interaction with the support [19]. The peak with T_{max} at around 550 °C can be



Fig. 2 X-ray diffraction pattern of calcined Ni/clay (calcined in air at 550 $^{\circ}$ C) samples with different Ni loadings



Fig. 3 TPR profiles of the 5 %wt Ni/clay (calcined in air at 550 °C) catalyst

assigned to the Ni²⁺ of the NiO species interacting with the support and other than Ni silicate/aluminate peak, since the reduction peak of Ni silicate/aluminate would appear at higher temperature [16]. The peak at $T_{\text{max}} = 730$ °C may be due to the formation of amorphous Ni silicate/aluminate species.

Thermogravimetric analysis

TGA of the dried sample was performed at a range of temperatures from 40 to 700 °C. The TGA curves are illustrated in Fig. 4. These curves show that the removal of physisorbed water was complete by 150 °C. The weight loss and the derived weight observed in the temperature range of 250–450 °C can be attributed to the decomposition of nitrates entrapped in the narrow pores of the Ni



Fig. 4 TGA analysis of the of 5 %wt Ni/clay catalyst

containing xero- and aerogels [20]. Consistent with Fig. 2, the Ni(NO₃)₂· $6H_2O$ should be decomposed to NiO in the temperature range of 250–450 °C. Finally, the weight loss observed at temperatures higher than 550 °C can be attributed to the removal of structural water from the support.

Effect of reduction and calcination temperatures

The catalysts were reduced for 2 h in H₂ flow at a range of temperatures from 250 to 450 °C. The effect of reduction temperature on the conversion of MA and selectivity for SA is shown in Fig. 5. Both the MA conversion and SA selectivity increased rapidly when the temperature was increased from 250 to 350 °C. Though higher temperatures gave a small further increase in conversion of the MA, the selectivity for SA was decreased.

Catalysts calcined at a temperatures ranging from 250 to 650 °C were used to investigate the effect of calcination temperature on the conversion of MA, and the results are shown in Fig. 6. The selectivity for SA was proximity 100 %in the catalyst activity tests, so it is understandable that the conversion of MA could be evidence for the activity of the catalyst. In Fig. 6, the conversion of MA increased as the calcination temperature increased, achieving maximum conversion at 550 °C, and then decreased rapidly. As mentioned above, Ni(NO₃)₂·6H₂O should be decomposed to NiO in the temperature range of 250-450 °C. With the calcination temperature increasing from 250 to 550 °C, more $Ni(NO_3)_2 \cdot 6H_2O$ would be decomposed to NiO; hence, more NiO could be reduced to Ni. Therefore, samples with high calcination temperature would be more active than samples with low calcination temperature. The conversion of MA



Fig. 5 Hydrogenation of MA over 5wt % Ni/clay: effect of reduction temperature. Reaction conditions: calcination temperature = 550 °C, WHSV = 4 h^{-1} MA, reaction temperature = 200 °C, reaction pressure = 1 MPa, H₂ flow = 50 ml/min



Fig. 6 Hydrogenation of maleic anhydride over 5 %wt Ni/clay: effect of calcined temperature. Reaction conditions: reduction temperature = 350 °C, WHSV = 4 h^{-1} MA, reaction temperature = 180 °C, reaction pressure = 1 MPa, H₂ flow = 50 ml/min

ranged from 96.1 to 97.1 % as the calcination temperature increased from 250 to 550 °C. When the calcination temperature reached 650 °C, the conversion of MA was drastically decreased, as a result of the removal of structural water from the support and the resulting collapse of the support structure. The TGA results showed clearly that loss of structural water from the support occurred at temperatures higher than 550 °C.

As the calcination temperature was increased from 250 to 550 °C, conversion of MA only increased by about 1 %. So, in view of its lower energy consumption, we concentrated on the catalyst calcined at 250 °C. Figure 7 shows that the catalyst was not very active at the beginning of the



Fig. 7 Hydrogenation of MA over 5 %wt Ni/clay calcined at 250 °C: time-on-stream study. Reaction conditions: reduction temperature = 350 °C, WHSV = 4 h⁻¹ MA, reaction temperature = 180 °C, reaction pressure = 1 MPa, H₂ flow = 50 ml/min. Catalyst calcined at 250 °C

test, but after 1.5 h, the conversion of MA increased to 96 %. However, the conversion rate was only stable up to 5.5 h, and the conversion decreased from 96 to 50 % for longer reaction times. Compared with Fig. 9 which shows the time-on-stream of the catalyst calcined at 550 °C, the catalyst calcined at 250 °C is less active.

In general, the calcination temperature has a strong influence on the catalytic activity and stability. Calcination at low temperature (250 °C) is not effective due to the lower concentration of NiO. Conversely, high calcination temperatures (650 °C) cause low MA conversion due to damage to the structure of the support.

Effect of Ni content

The conversion of MA increased with increasing Ni content (Table 1). No significant amounts of over-hydrogenated or hydrogenolysis products such as tetrahydrofuran, 1,4-butanediol or propionic acid were observed in this study. The major products were SA and GBL. Since GBL forms via the hydrogenation of SA [21], it is reasonable that the yield of SA can be used to estimate the activity of the catalyst. The conversion of MA was 93.2 % when the Ni content was 3 %, increasing to 99.2 % when the Ni content was increased to 20 %. However, the yield of SA as well as the selectivity for SA increased as the Ni increased, achieving maximum yield at 5 % wt Ni content, then decreasing. This decrease is due to over-hydrogenation. As mentioned above, Ni⁰ is the active species in the hydrogenation reaction. Therefore, samples with high nickel (after NiO reduction) content would be more active than samples with low nickel content, resulting in a decrease in the selectivity for SA. The XRD results clearly show that the relative concentration of free NiO increases with Ni loading.

Effect of pressure and temperature

Different reactions were carried out at a pressure of 0-1.5 MPa (Table 2). Pressure was critical in obtaining

Table 1 Effect of Ni content

Ni content (%wt)	Conversion of maleic anhydride (%)	Selectivity (%)		Yield (%)	
		SA	GBL	SA	
3	93.17	96.61	3.39	90.01	
5	97.14	99.55	0.45	96.70	
7	97.64	96.89	3.11	94.60	
10	98.13	95.25	4.75	93.46	
20	99.20	80.52	9.48	79.87	

Reaction conditions: reduction temperature = 350 °C, calcination temperature = 550 °C, WHSV = 4 h⁻¹ MA, reaction temperature = 180 °C, H₂ flow = 50 ml/min

P (MPa)	Conversion of maleic anhydride (%)	Selectivity (%)		Yield (%)	
		SA	GBL	SA	
0	11.70	100	0	11.70	
0.5	85.45	100	0	85.45	
1	97.14	99.55	0.45	96.70	
1.5	98.52	97.68	2.32	96.23	

Reaction conditions: reduction temperature = 350 °C, calcination temperature = 550 °C, WHSV = 4 h⁻¹ MA, reaction temperature = 180 °C, H₂ flow = 50 ml/min, catalyst: 5 %wt Ni/clay

good SA yields. The effect of H_2 pressure on the MA hydrogenation (Table 2) shows that 97.1 % MA conversion with 99.6 % selectivity to SA could be obtained at 180 °C and a pressure of 1 MPa H_2 . Product conversion, however, varied significantly with changes in pressure (Table 2). Thus, the conversion of MA increased from 11.7 to 98.5 % as the reaction pressure increased from 0 to 1.5 MPa, while the SA selectivity decreased with increasing H_2 pressure, because of over-hydrogenation. The yield of SA increased as the reaction pressure increased up to a maximum at 1 MPa, then decreased. Hence, control of the reaction pressure could be used to regulate the desired product as well the product distribution between SA and GBL.

The effects of different reaction temperatures on the performance of the catalyst are shown in Table 3. Reaction temperature proved to be critical in obtaining good SA yields. As is seen in Table 3, MA conversion increased with increasing temperature. Both the yield and the selectivity of SA increased as the reaction temperature increased, reaching a maximum at 180 °C, then decreased. Thus, the yield is affected not only by manipulating the temperature, but also by varying the hydrogen pressure and Ni content.

Effect of weighted hourly space velocity

The hydrogenation of MA was carried out at 180 °C with WHSV varying from 2 to 6 h^{-1} (Fig. 8). As the WHSV

Table 3 Effect of reaction temperature

<i>T</i> (°C)	Conversion	Selectivi	Selectivity (%)	
	of maleic anhydride (%)	SA	GBL	SA
150	93.83	83.51	16.49	78.36
180	97.14	99.55	0.45	96.70
190	97.26	99.29	0.71	96.57
200	97.46	98.91	1.09	96.40

Reaction conditions: reduction temperature = 350 °C, calcination temperature = 550 °C, WHSV = 4 h⁻¹ MA, reaction pressure = 1 MPa, H₂ flow = 50 ml/min. Catalyst: 5 %wt Ni/clay



Fig. 8 Hydrogenation of MA over 5 %wt Ni/clay: effect of WHSV. Reaction conditions: reduction temperature = 350 °C, calcination temperature = 550 °C, reaction temperature = 180 °C, reaction pressure = 1 MPa, H₂ flow = 50 ml/min

increased, the conversion of MA decreased; in addition, as the WHSV increased, the yield of SA fell exponentially. The conversion decreased from 97.1 % at 4 h⁻¹ to 93.6 % at 6 h⁻¹, while the yield of SA decreased from 96.7 to 93.6 % during this period.

Stability and reusability of the catalyst

To study the stability and reusability of the catalyst, three identical experiments were performed using of 5 %wt Ni/clay for 4 h. Table 4 shows that the conversion of MA was 97.1, 98.4 and 97.1 %, respectively. The results indicate that the catalyst has high stability and reusability for hydrogenation of MA to SA.

Time-on-stream study

From the above preliminary studies, the optimum reaction parameters were chosen as: reduction temperature, 350 °C; calcination temperature, 550 °C; reaction temperature, 180 °C; reaction pressure, 1 MPa; WHSV, 4 h^{-1} MA.

Table 4 Stability and reusability of 5 %wt Ni/clay

The number of reactions	Conversion of MA (%)	Selectivity of SA (%)	Yield of SA (%)
No. 1	97.14	99.55	96.70
No. 2	98.41	97.14	95.60
No. 3	97.06	99.67	96.74

Reaction conditions: reduction temperature = 350 °C, WHSV = 4 h^{-1} MA, calcination temperature = 550 °C, reaction temperature = 180 °C, reaction pressure = 1 MPa, H₂ flow = 50 ml/min



Fig. 9 Hydrogenation of MA over 5 %wt Ni/clay: time-on-stream study. Reaction conditions: reduction temperature = 350 °C, calcination temperature = 550 °C, WHSV = 4 h⁻¹ MA, reaction temperature = 180 °C, reaction pressure = 1 MPa, H₂ flow = 50 ml/min



Fig. 10 Hydrogenation of MA over 5 %wt Ni/clay and 0.5 %wt Pt/ clay. Reaction conditions: reduction temperature = 350 °C, calcination temperature = 550 °C, reaction temperature = 180 °C, reaction pressure = 1 MPa, H₂ flow = 50 ml/min. **a** Reduction time = 5 h, WHSV = 8 h⁻¹ MA. **b** Reduction time = 2 h, WHSV = 4 h⁻¹ MA

Time-on-stream studies showed that the catalyst is not very active at the beginning of the test, but after an induction period of about 3 h, the yield raises steeply to 97.8 % (Fig. 9). The yield of MA declined slowly as the reaction proceeded, but was still higher than 90 % even after a reaction time of 60 h.

Figure 8 reveals that the catalyst is not very active at the beginning of the test, but after an induction period of about 3 h, the yield raises steeply to 97.8 %. In order to find the reasons for this phenomenon, we increased the reduction time from 2 to 5 h to see whether inadequate reduction was responsible for the induction period. The results shown in Fig. 10a show that the induction period was not eliminated

in this case. Previous studies on nickel catalysts have also revealed an induction period in the hydrogenation of MA to SA [18]. The results also show that with increased reduction time, the catalytic activity decreases. This can be explained by the reduction of other metal oxides like Fe₂O₃ contained in the clay. We also observed the hydrogenation activity of 0.5 %wt Pt/clay [prepared by impregnation of clay pellets with platinum chloride (Aldrich) solution], as shown in Fig. 10b. This catalyst is active at the beginning of the test, but decreases with time. Consequently, the presence of an induction period is determined by the type of catalyst.

Conclusion

In summary, hydrogenation of MA to SA over Ni/clay impregnated catalysts has been studied under a range of conditions. Catalytic activity was greatly influenced by the temperature, Ni content, WHSV and pressure. Nickel was present in the +2 state, as NiO on the catalyst. There was no elemental nickel or Ni₂O₃ in the unreduced samples. The catalyst calcined at 550 °C gave the best catalytic performance, since most of the Ni(NO₃)₂·6H₂O was decomposed to NiO but the support structure remained intact. Catalyst deactivation studies showed that the catalyst has a long lifetime, the yield of MA remaining higher than 90 % even after a reaction time of 60 h.

Using 5 %wt Ni/clay, 97.1 % conversion for MA and 99.6 % selectivity for SA were obtained for MA hydrogenation at a reaction temperature of 180 °C and WHSV of 4 h^{-1} under 1 MPa pressure.

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