

A Highly Efficient and Selective Nickel/Clay Catalyst for Liquid Phase Hydrogenation of Maleic Anhydride to Succinic Anhydride

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Three Ni-based catalysts with different clay as support were prepared and tested in the hydrogenation of maleic anhydride, among which Ni/clay1 showed best activity and selectivity. Over Ni/clay1 catalyst prepared by impregnation method, 97.14% conversion of maleic anhydride and 99.55% selectivity to succinic anhydride were obtained at 180 °C under a pressure of 1 MPa. Catalytic activity was greatly influenced by the temperature and weighted hourly space velocity. Catalyst deactivation studies showed that this catalyst have a long life time, the yield of MA still higher than 90% even after a reaction time of 60 h. X-ray diffraction (XRD) and H₂ temperature programmed reduction (TPR) were use to investigate the properties of the catalyst. XRD and TPR studies showed that Ni was present as Ni²⁺ on the support, which indicated that there was no elemental nickel (Ni⁰) and Ni₂O₃ in the unreduced samples. The formation of Ni was strong impact on catalytic activity.

Key Words : Maleic anhydride, Ni, Clay, Hydrogenation, Succinic anhydride

Introduction

Hydrogenation of maleic anhydride (MA) is an important industrial chemical process, the products of which such as succinic anhydride (SA), γ -butyrolactone (GBL), 1,4-butanediol (BDO) and tetrahydrofuran (THF), are important intermediates or solvents in food, pharmaceuticals and textile industries.¹⁻⁵ The reaction pathway of the hydrogenation of MA to BDO and THF is illustrated in Figure 1.⁶⁻⁸ In this process, both hydrogenation and hydrogenolysis reactions are involved.

There are basically two processes for the production of SA-dehydration of succinic acid and hydrogenation of MA.⁹ Because of MA's availability and lower price which become possible by the construction of large fluid bed plants, according to Alusuisse-Lumnum and BP/UCB technologies, MA maybe considered as a good feedstock nowadays.^{2,3} The hydrogenation of MA is the most direct, environmentally benign, and economic way to produce SA compared with dehydration of succinic acid to SA.

Hydrogenation of MA over different noble metal and copper-based catalysts both in vapor and liquid phases have been reported.⁹⁻¹⁵ However, these catalysts are expensive and are susceptible to deactivation, as the coke deposition still must be resolved, so it is necessary to explore highly active catalysts which can work under much milder reaction pressure or, use less-expensive metals, if possible. Therefore, Ni-loaded clay-based catalyst was chosen to investigate MA hydrogenation for its low cost. We selected three different places of the clay as a support. They were named clay1, clay2 and clay3, respectively. The results show that the optimum catalyst for the hydrogenation of maleic anhydride was found to be Ni/clay1 impregnated catalyst. Furthermore, XRD and H₂-TPR were also used to charac-

terize these catalysts.

Experimental

The catalysts used in this study (with 5%wt Ni supported on clay1, clay2 and clay3) were prepared by kneading method, using clay1, clay2, clay3 and Ni₂O₃ (Aldrich). The monometallic nickel catalyst (5 wt % Ni supported on clay1) was prepared by impregnation of the support with an aqueous solution of nickel nitrate hexahydrate. All the catalysts were dried overnight at 120 °C, and then calcined in air at 550 °C for 3 h and then cooled to room temperature.

The catalysts were characterized by an array of techniques, including X-ray diffraction (XRD) and H₂ temperature-programmed reduction (TPR). *In situ* X-ray diffraction patterns during reduction of 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 2 θ range from 10° to 80°. Temperature-programmed reduction (TPR) of 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 reaction was performed in a fixed-bed reactor operated in a down flow mode. The temperature of the reactor was monitored and controlled using a PID controller. The reactant was a solution of MA in GBL (16.4 wt %) and then transported into the reactor with a micro-syringe pump. For each experiment, 1 g of unreduced catalyst (20-40 mesh) was loaded into the flow reactor. The catalyst was reduced *in situ* at 350 °C and a pressure of 1 MPa with H₂ (flow rate 32

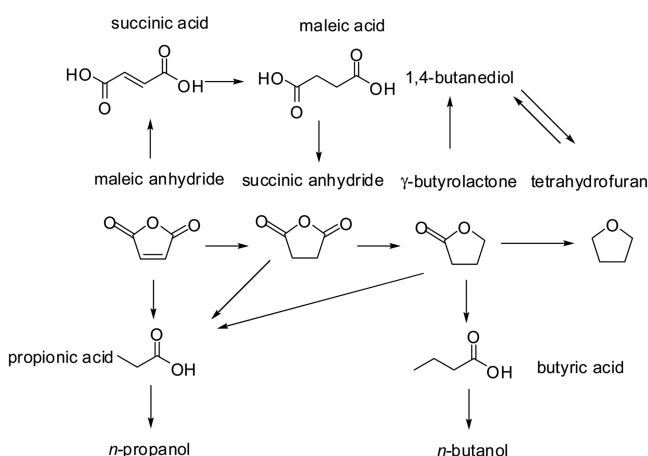


Figure 1. Reaction scheme of hydrogenation of maleic anhydride.

cm³/min) for 2 h. The products were analyzed using an Agilent 6890 N gas chromatograph (flame ionization detector, HP-5 column, 30 m × 5 mm × 0.25 μm) and confirmed by gas chromatography-mass spectroscopy (GC-MS).

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

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

$$S_i(\%) = \frac{Product_{i,out}}{MA_{in} - MA_{out}} \times 100 \quad (2)$$

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

Results and Discussion

XRD patterns (Figure 2) of all samples examined at the big angle showed the characteristic peaks for NiO species at

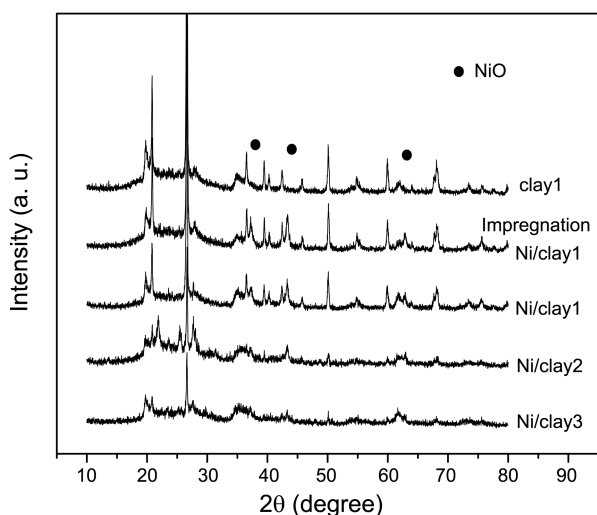


Figure 2. X-ray diffraction spectra of the Ni/kneading clay1, Ni/kneading clay2, Ni/kneading clay3, Ni/impregnation clay1 and clay1.

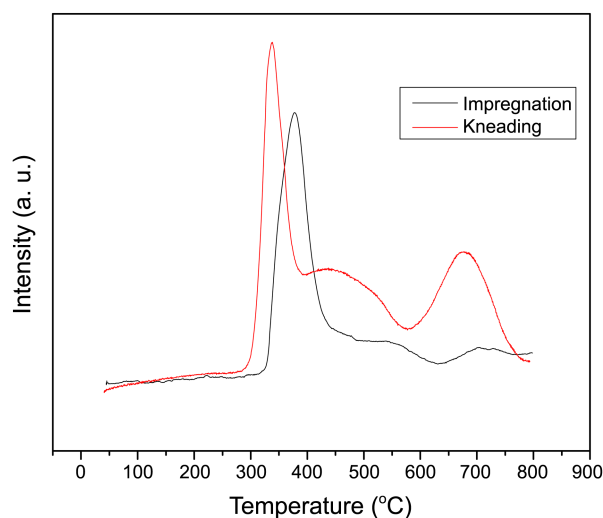


Figure 3. TPR profiles of the kneading and impregnation Ni/clay1 catalysts.

$2\theta = 37.24^\circ$, 43.34° and 64.48° corresponding to the planes (1 1 1), (2 0 0) and (2 2 0) of cubic NiO species, respectively.¹⁶ For peaks at $2\theta = 43.34^\circ$, the diffraction intensity visibly enhanced with Ni/kneading clay2. For peaks at $2\theta = 37.24^\circ$ and 64.48° the diffraction intensity visibly enhanced with Ni/kneading clay1. Comparison of these three catalysts prepared by kneading method, Ni/clay1 with the greatest diffraction peak intensity, followed by Ni/clay2, the smallest is Ni/clay3. But Ni/impregnation clay1 greater diffraction peak intensity relative to the Ni/kneading clay1.

XRD and TPR are complimentary techniques that when used in conjunction help identify the oxidation states of a reducible metal oxide and estimate the phase of the metal oxide in the catalysts. The TPR profiles for the two catalysts are shown in Figure 3. As shown in Figure 3, Ni/kneading clay1 catalyst could be reduced at a much lower temperature than the Ni/impregnation clay1 catalyst and the reduction temperature range became narrower. For example, the reduction temperature of the first step decreased from approximately 370 °C for 5 wt % Ni/impregnation clay1 to 340 °C for the 5 wt % Ni/kneading clay1 catalyst. For the 5 wt % Ni/kneading clay1, the first reduction peak and the second reduction peak are located very close, are very easy occurrence excessive reduction.

Three Ni catalysts with different support, Ni/clay1, Ni/clay2 and Ni/clay3, were prepared by the kneading method, tested during the hydrogenation of MA at a temperature of 200 °C under a pressure of 1 MPa. No significant amounts of over-hydrogenated or hydrogenolysis products like tetrahydrofuran, 1,4-butanediol and propionic acid were observed in this study. The major products consisted of SA and GBL. Figure 4 illustrates the obtained results over three kneading catalysts. The most active catalyst for the hydrogenation of MA was found to be Ni/clay1. Ni/clay2 showed a slightly lower activity than Ni/clay1. However, the conversion of MA of Ni/clay3 was only quarter compared with Ni/clay1. As mentioned early, Ni/clay1 with the greatest diff-

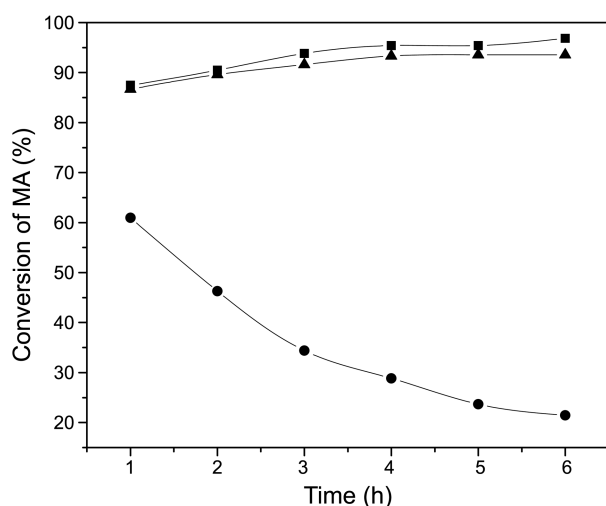


Figure 4. Conversion of MA according to the reaction time: Ni/kneading clay1 (■), Ni/kneading clay2 (▲) and Ni/kneading clay3 (●) catalysts. Reaction conditions: WHSV = 2 h⁻¹ MA, reaction temperature = 200 °C, reaction pressure = 1 MPa, H₂ flow = 50 mL/min.

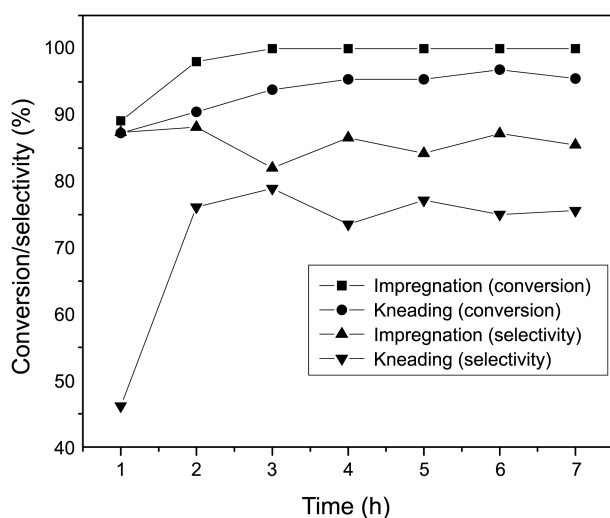


Figure 5. Hydrogenation of MA over 5 wt % Ni/clay1: effect of supporting method; WHSV = 2 h⁻¹ MA, reaction temperature = 200 °C, reaction pressure = 1 MPa, H₂ flow = 50 mL/min.

reaction peak intensity, followed by Ni/clay2, the smallest is Ni/clay3. The formation of Ni was strong impact on catalytic activity.

Two Ni/clay1 catalysts were prepared by kneading and impregnation method. The two catalysts tested during the hydrogenation of MA at 200 °C and a pressure of 1 MPa. Figure 5 illustrates the results over the two catalysts. The most active catalyst for the hydrogenation of MA was found to be Ni/impregnation clay1 because 100% conversion of MA and 85.88% selectivity of SA were achieved.

The effect of different reaction temperatures on the performance of catalyst were shown in Table 1. Reaction temperature was critical in obtaining the desired SA yield. As is seen in Table 1, MA conversion increased with increase in reaction temperature. The yield of SA as well as the selec-

Table 1. Effect of reaction temperature

T (°C)	Conversion of maleic anhydride (%)	Selectivity (%)		Yield (%) SA
		SA	GBL	
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: WHSV (weight hourly space velocity) = 4 h⁻¹ MA, reaction pressure = 1 MPa, H₂ flow = 50 mL/min. Catalyst: 5 wt % Ni/impregnation clay1.

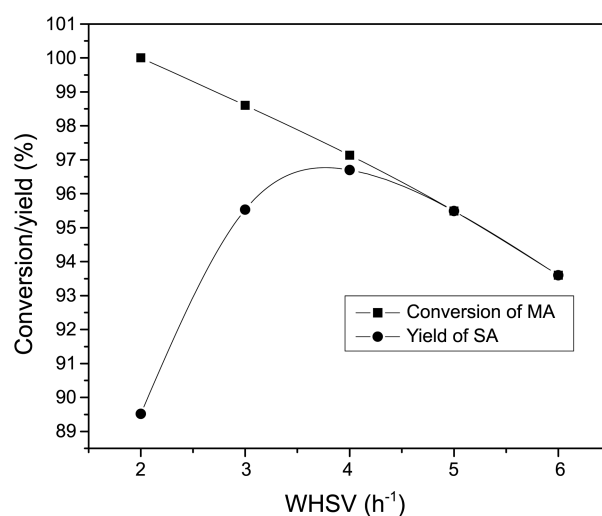


Figure 6. Hydrogenation of MA over 5 wt % Ni/impregnation clay1: effect of WHSV; reaction temperature = 180 °C, reaction pressure = 1 MPa, H₂ flow = 50 mL/min.

tivity of SA increased as the reaction temperature increase and achieve maximum yield at 180 °C, then decreased. It is obvious from the effect of reaction temperature that significantly changes the activity and selectivity for MA hydrogenation. So controlling of the reaction temperature could be used to regulate the desired product as well the product distribution such as the SA and GBL.

The hydrogenation of MA was carried out at 180 °C with weighted hourly space velocity (WHSV) varying from 2 to 6 h⁻¹ MA (Figure 6). It was observed that, as the WHSV increased, the conversion of MA decreased, in addition, as the WHSV increased, the yield of SA fell exponentially. The conversion decreased from 97.14% at 4 h⁻¹ to 93.60% at 6 h⁻¹, and the yield of SA decreases from 96.70% to 93.60% during this period. But the yield of SA was maintained more than 90%.

From the above preliminary studies, the following reaction parameters were chosen: reaction temperature, 180 °C; support, clay1; supporting method, impregnation; reaction pressure, 1 MPa; WHSV, 4 h⁻¹ MA. For the catalyst, 100% selectivity of MA was achieved when the timing is more than 3 h. Since GBL is formed via the hydrogenation of SA,¹⁷ it is understood that the yield of SA can indicate the activity of the catalyst. The yield of SA indicates the activity of the catalyst. Timing on stream studies showed that the

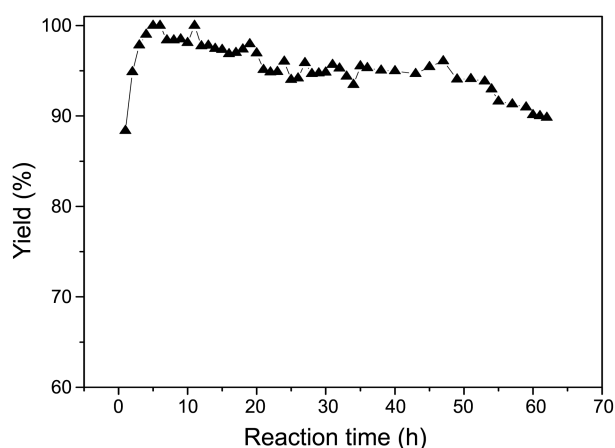


Figure 7. Hydrogenation of MA over 5 wt % Ni/impregnation clay1: time on stream study; WHSV = 4 h⁻¹ MA, reaction temperature = 180 °C, reaction pressure = 1 MPa, H₂ flow = 50 mL/min.

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 97.81% (Figure 7). The yield of MA declined slowly as the reaction going on, but still higher than 90% even after a reaction time of 60 h.

Conclusion

Ni supported on clay1, clay2 and clay3 catalysts have been evaluated using flow reactor for MA hydrogenation. The results showed that Ni/impregnation clay1 catalysts exhibited the highest activity among all as-prepared catalysts in MA hydrogenation. Catalytic activity was greatly influenced by the temperature and WHSV. The formation of Ni was strong impact on catalytic activity.

Ni/impregnation clay1 shows a remarkable activity and resistance to the deactivation regardless of reactants. Over

the 5 wt % Ni/impregnation clay1 catalyst, the MA conversion of 97.14% and SA selectivity of 99.55% was obtained under the optimized reaction conditions, with the main side product being GBL. Catalyst deactivation studies showed that this catalyst have a long life time, the yield of MA still higher than 90% even after a reaction time of 60 h.

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