Highly Active and Selective Nickel–Platinum Catalyst for the Low Temperature Hydrogenation of Maleic Anhydride to Succinic Anhydride and Synthesis of Succinic Acid at 40 °C

Jie Li · Wei-Ping Tian · Li Shi

Abstract PtNi bimetallic and Ni monometallic catalysts supported on HY–Al_2O_3, HX–Al_2O_3, ZSM-5–Al_2O_3, USY–Al_2O_3, Beta–Al_2O_3 and Al_2O_3 were prepared and evaluated for the hydrogenation of maleic anhydride in the temperature range of 40–150 °C. Results from flow reactor studies showed that supports strongly affected the catalytic properties of different bimetallic and monometallic catalysts. The results showed that the HY–Al_2O_3 support exhibited the highest activity and selectivity. Using NiPt/Al_2O_3–HY catalyst and performing the reaction, it was possible to carry out the lowest reaction temperature ever carried at 100% conversion. Adding a small amount of Pt (0.5) to the Ni (5%)/Al_2O_3–HY catalyst that is effective for increasing the selectivity and activity. We also found that PtNi is an efficient catalyst for the one-pot conversion of maleic acid into succinic acid with 100% conversion at 40 °C.

Keywords Al_2O_3–HY · Maleic anhydride · Pt–Ni · Hydrogenation · Succinic anhydride

1 Introduction

The reaction network for maleic anhydride (MA) hydrogenation is shown in Fig. 1. [1–3]. In this process, both hydrogenation and hydrogenolysis reactions are involved. Some of the reaction products, succinic anhydride (SA), γ-butyrolactone (GBL), tetrahydrofurane (THF), and 1,4-butanediol (BDO), are valuable products that find a wide market as solvents or as starting material for polymers like polyuretanes. In particular, SA is required as intermediate for the chemical, pharmaceutical and food industries [1].

These compounds are produced by mainly four processes: the Reppe process, the Arco process, the Mitsubishi Kasei process, and the Davy McKee [4]. However, these processes present some disadvantages. The Reppe process uses acetylene and formaldehyde as starting material, and severe reaction conditions (140–280 bar, 250–350 °C) [5]. The Davy McKee process needs two different reactors, catalysts and reaction conditions [6].

Compared to the other processes, hydrogenation of maleic anhydride is the most direct, environmentally benign, and economic way to produce succinic anhydride. The reactions were carried out over several types of noble metal-based catalysts, such as Pd [7], Ru [8], Cu [9], both in liquid phase and gas phase. The analysis of literatures on hydrogenation of MA shows that the most papers refer to catalytic studies at temperature over 200 °C by batch process, while limited attention has been devoted to flow condition at temperature under 100 °C conditions [5, 10–12]. Moreover, many questions concerning catalyst stability, reaction and deactivation are still open questions.

It is well known that bimetallic catalysts often show properties that are distinctly different from those of the corresponding monometallic catalysts. However, relatively few articles on the hydrogenation of MA to SA, in general, and by bimetallic catalysts, in particular, have been published. In a recently published work by the authors [13], hydrogenation of maleic anhydride was investigated over Ni-loaded zeolites catalysts. The results indicated that zeolites were excellent supports for SA production from MA hydrogenation.

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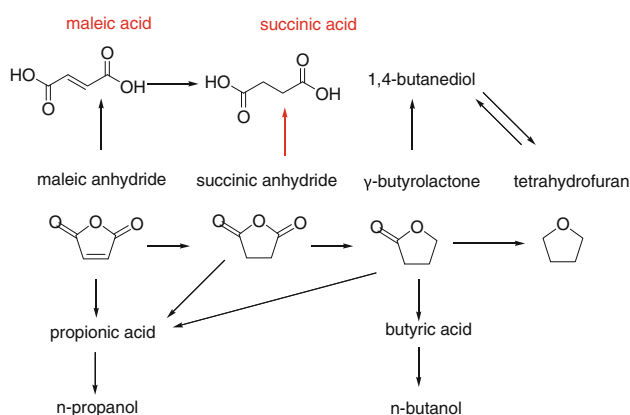e-mail: yyshi@ecust.edu.cn

Fig. 1 Reaction scheme of hydrogenation of maleic anhydride

The objective of the present study was to develop a highly efficient, more stable catalyst for hydrogenation of maleic anhydride at relatively low temperature to produce SA with high selectivity. A series of supported Ni and NiPt catalysts have been studied. The effects of the support (HY, HX, ZSM-5, Beta, USY, Al_2O_3) and the reaction conditions (temperature, pressure, WHSV) on the catalyst activity, selectivity and stability have been investigated and the best catalyst formulation with respect to selectivity and activity have been identified. Moreover, the results of the investigation of hydrogenation of MA on the selected NiPt/HY–Al_2O_3 catalyst at 40 °C and the deactivation of a reason were reported. Owning to the high activity of PtNi for MA hydrogenation and the fact that MA is the main precursor for the production of succinic acid, we have also carried out the catalytic synthesis of succinic acid starting from maleic acid at 40 °C, this help the viability and economics of the process.

2 Experimental

2.1 Catalyst Preparation

The catalysts used in this study, 5%Ni/Al_2O_3–HY (Al_2O_3/HY mass ratio ∼0.4), were prepared by the kneading method using γ-Al_2O_3, HY zeolites, and Ni_2O_3 (Aldrich). The 0.5 wt%Pt–5 wt%Ni/Al_2O_3–HY bimetallic catalyst was prepared using $H_2PtCl_6 \cdot 6H_2O$ (Aldrich, 99%) and Ni_2O_3. All the catalysts were dried overnight at 120 °C in an oven, and then calcined in air at 550 °C for 3h. The 5 wt%Ni/Al_2O_3–HY (HX, ZSM-5, Beta, USY and Al_2O_3) and 0.5 wt%Pt–5 wt%Ni/Al_2O_3–HY (HX, ZSM-5, Beta, USY and Al_2O_3) catalysts were also prepared using the same method. More details can be found in a previous study [13].

2.2 Catalyst Characterization

X-ray diffraction 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 and using CuKα 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) of H_2 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.% H_2 in Ar with a temperature ramp from ambient temperature to 800 °C at a heating rate of 10 °C/min.

2.3 Catalytic Test

The reaction was performed in a fixed-bed reactor operated in the down flow mode. The reaction temperature was measured with a thermocouple in contact with the catalyst bed. The organic feed consisted of a solution of maleic anhydride in γ-butyrolactone (22 wt%) and was fed into the reactor by 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 atmospheric pressure with H_2 (flow rate 32 cm^3/min) for 3 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).

Maleic anhydride (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.

3 Results and Discussion

3.1 Catalyst Characterization

3.1.1 XRD Analysis of Optimizing Catalysts

XRD patterns of two optimizing catalysts are shown in Fig. 2. The characteristic peaks for NiO species at $2\theta = 37.24°$, $43.34°$ and $64.48°$ corresponding to the
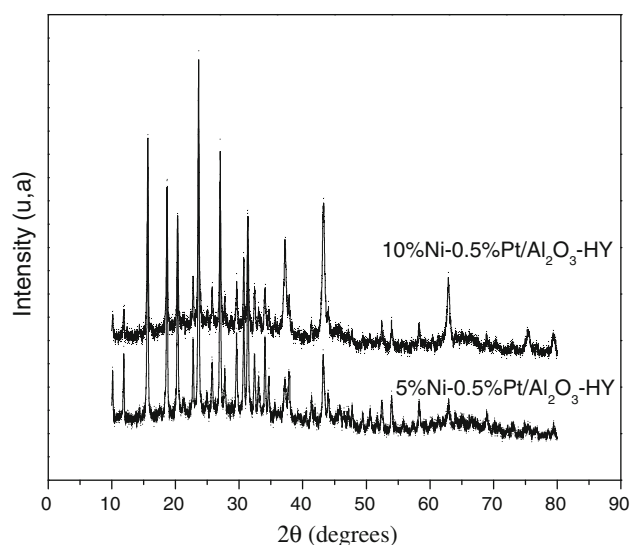
Fig. 2 X-ray diffraction pattern of calcined 5%Ni–0.5%Pt/Al₂O₃-HY and 10%Ni–0.5%Pt/Al₂O₃-HY

Fig. 3 Temperature-programmed reduction (TPR) profiles of the 5%Ni–0.5%Pt/Al₂O₃-HY catalyst

planes (1 1 1), (2 0 0) and (2 2 0) of cubic NiO species, respectively [14]. The XRD results also clearly show that the concentration of NiO increased with Ni loading. Peaks at $2\theta = 75.50°$ and $79.38°$ for Ni_2O_3 species were visible at Ni loading of around 10 wt%. The XRD characteristic peaks associated with Pt^0 or PtO phase were not observed in the two samples. This was probably due to the very low amount of Pt (0.5 wt%) present and/or a very good dispersion of Pt phase on the supports.

3.1.2 TPR of 5%Ni–0.5%Pt/Al₂O₃–HY Catalyst

In order to decide the reduction conditions, the TPR experiment was carry out. The TPR profiles of the samples are presented in Fig. 3. The presence of Ni^{3+} in the catalyst can be precluded by the absence of a reduction peak at 260 °C [9, 13]. The peak with T_{max} at 300 °C can be attributed to the reduction of NiO particles with no interaction with the support [15]. The interaction of NiO with the support decreases its reducibility. The peak with T_{max} at around 450 °C thus can be assigned to the Ni^{2+} of the NiO species interacting with the support and are not due to the Ni silicate/aluminate peak, because the reduction peak of Ni silicate/aluminate would appear at a much higher temperature. The peak with T_{max} around 600 °C may be due to the formation of amorphous Ni silicate/aluminate species [9].

3.2 Catalytic Activity

Preliminary investigations were carried out on the effect of various reaction parameters on the hydrogenation of MA to optimize the reaction conditions.
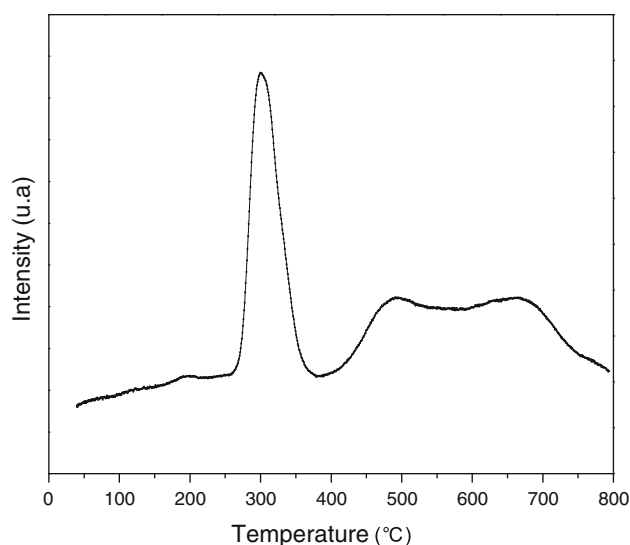
3.2.1 Comparison of Different Catalyst Supports

The bimetallic and the corresponding monometallic catalysts were evaluated for MA hydrogenation at 140 °C and 1MPa pressure. As shown in Table 1, the conversion of maleic anhydride was nearly 13% for 5%Ni/Beta–Al₂O₃, about 35% for 5%Ni/USY–Al₂O₃, about 70% for 5%Ni/ZSM-5–Al₂O₃ and 5%Ni/Al₂O₃, and nearly 90% for 5%Ni/HX–Al₂O₃ and 5%Ni/HY–Al₂O₃. In comparison, the supported PtNi bimetallic catalysts showed much higher conversion. Furthermore, the four supported PtNi bimetallic catalysts exhibited quite different catalytic activities and selectivities. As present in Tab.1, the conversion of maleic anhydride was about 100% over 5%Ni–0.5%Pt/HY–Al₂O₃ and 5%Ni–0.5%Pt/HX–Al₂O₃ catalysts, which were much higher than Beta–Al₂O₃, USY–Al₂O₃ or ZSM-5–Al₂O₃ supported PtNi bimetallic catalysts. In summary, HY–Al₂O₃ supported PtNi bimetallic catalysts exhibited much better performance. And the conversion of maleic anhydride over PtNi bimetallic catalysts followed the trend: HY–Al₂O₃ ∼ HX–Al₂O₃ > USY–Al₂O₃ ∼ ZSM-5–Al₂O₃ > Beta–Al₂O₃. However, the SA selectivity followed another trend: HY–Al₂O₃ > HX–Al₂O₃ > ZSM-5–Al₂O₃ > USY–Al₂O₃ > Beta–Al₂O₃ over the bimetallic catalysts. Additionally, all the PtNi bimetallic catalysts showed much higher activities than the Ni monometallic catalysts.

It has been reported that large and medium pore supports display higher activities compared to smaller pore size ones [16]. However, we found that using large pore Al₂O₃ as supports decreased the conversion of hydrogenation of MA. This may be due to the different reaction mechanism here, with the SA formed mainly by the MA hydrogenation over metal rather than the supports.

Table 1 Catalytic properties of studied catalysts

Samples	Conversion of maleic anhydride (%)	Selectivity (%) SA	Selectivity (%) GBL
5%Ni/HX–Al$_2$O$_3$	89.61	64.40	35.60
5%Ni/USY-Al$_2$O$_3$	34.62	56.16	43.84
5%Ni/ZSM-5-Al$_2$O$_3$	68.71	65.67	34.33
5%Ni/Beta-Al$_2$O$_3$	12.76	29.40	70.60
5%Ni/HY–Al$_2$O$_3$	90.24	82.87	17.13
5%Ni/Al$_2$O$_3$	65.37	64.19	35.81
5%Ni–0.5%Pt/HX–Al$_2$O$_3$	99.84	86.92	13.08
5%Ni–0.5%Pt/USY-Al$_2$O$_3$	95.48	67.60	32.40
5%Ni–0.5%Pt/ZSM-5-Al$_2$O$_3$	93.69	72.04	27.96
5%Ni–0.5%Pt/Beta-Al$_2$O$_3$	37.45	34.11	65.89
5%Ni–0.5%Pt/HY–Al$_2$O$_3$	99.89	91.93	8.07
5%Ni–0.5%Pt/Al$_2$O$_3$	85.56	75.61	34.39

Reaction conditions: WHSV = 2 h^{-1} maleic anhydride, reaction pressure = 1 MPa, reaction temperature = 140 °C, H$_2$/MA = 50 (molar ratio)

3.2.2 Effect of Reaction Temperature

Reactions were carried out at 120–150 °C (Fig. 4). As expected, the rate of conversion of MA increased as increased the reaction temperature. Temperature was critical in controlling the desired production selectivity. The conversion of maleic anhydride increased from 85 to 100% after 4 h reaction time on increasing the reaction temperature from 120 to 140 °C. This could be the result of NiPt being a good bimetallic hydrogenation catalyst. SA yield/selectivity decreased with increasing in the reaction temperature from 140 to 150 °C. A high SA yield could be obtained at 140 °C. In agreement with the results shown here, previous studies have reported that at higher temperature, over-hydrog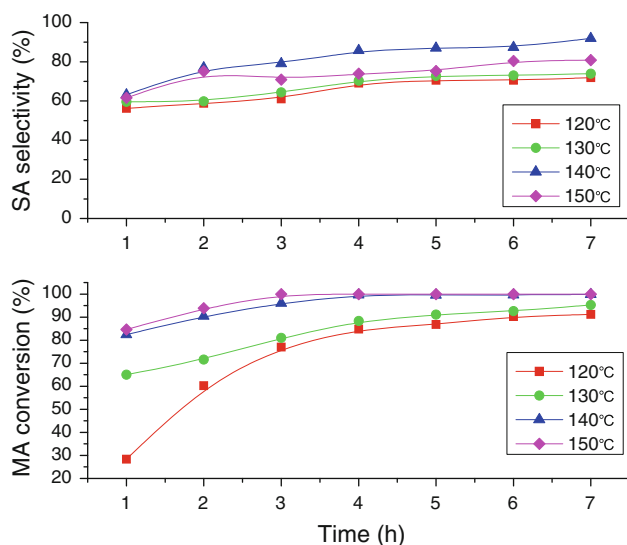enated reaction occurred, the production of the MA hydrogenation is formation of GBL rather than SA [10]. However, the rate of reaction was lower than for the composite system at 150 °C, and complete conversion could be reached after 4 h run time, instead of the 3 h on the stream needed for the latter. It is apparent from the results that the desired product selectivity can be obtained by controlling the temperature.

3.2.3 Effect of Reaction Pressure

The effect of H$_2$ pressure on the maleic anhydride hydrogenation (Fig. 5) shows that 100% MA conversion with more than 97% selectivity to SA could be obtained at 140 °C and at a pressure of 0.8 MPa H$_2$. Product conversion and selectivity, however, varies significantly with changes in pressure (Fig. 5). It is seen that SA selectivity
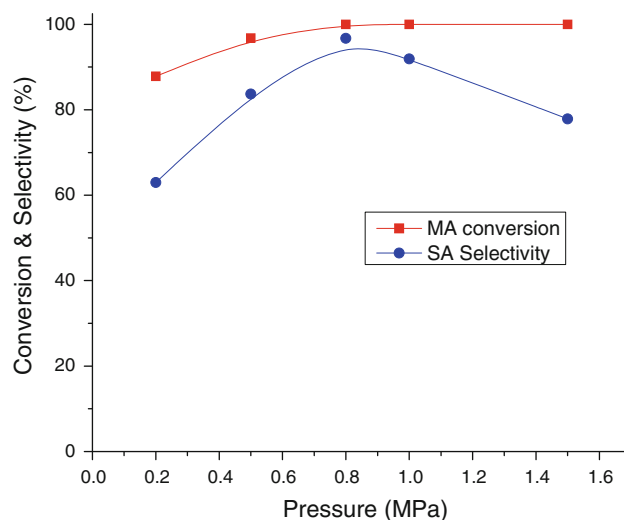
Fig. 4 Hydrogenation of maleic anhydride over 5%Ni–0.5%Pt/HY–Al$_2$O$_3$: effect of reaction temperature; reaction conditions: WHSV = 2 h^{-1} maleic anhydride, reaction pressure = 1 MPa, H$_2$/MA = 50 (molar ratio)

Fig. 5 Hydrogenation of maleic anhydride over 5%Ni–0.5%Pt/HY–Al$_2$O$_3$: effect of reaction pressure; reaction conditions: WHSV = 2 h^{-1} maleic anhydride, reaction temperature = 140 °C, H$_2$/MA = 50 (molar ratio)

decreased with increase in H_2 pressure from 0.8 to 1.5 MPa. This is because that over hydrogenated reaction occurred, as proposed by Pillai and Wang [4, 8]. This explains the observed increase in GBL selectivity at the expense of SA due to the formation of more GBL. The gas phase reaction under 0.2 and 0.5 MPa at 140 °C yielded much lower MA conversion than that obtained under 0.8 MPa at the same temperature. As a result, the selectivity in this system can be affected not only by manipulating the reaction temperature, but also varying the hydrogen pressure, as well.

3.2.4 Effect of Weighted Hourly Space Velocity (WHSV)

The hydrogenation of maleic anhydride was carried out at 140 °C with WHSV varying from 0.2 to 3 h^{-1} (Fig. 6). It was seen that as the WHSV increased, the conversion of maleic anhydride decreased. And as the WHSV increased, the yield of SA fell exponentially. The conversion decreased from 100% at 2 h^{-1} to 81% at 3h^{-1}, and the selectivity of SA fell from 97 to 62% during this period. A high SA selectivity and MA conversion could be obtained at WHSV of 2 h^{-1}.

3.2.5 Hydrogenation of Maleic Anhydride to Succinic Anhydride at 40 °C

In our previous work, we have found that the catalyst activity increased as increased Ni content [13]. On basis of these results, we were hoping that the MA hydrogenation reaction could be happened at lower temperature over the high Ni content catalysts. It must be remarked that, from an industrial point of view, this will be mostly energetically
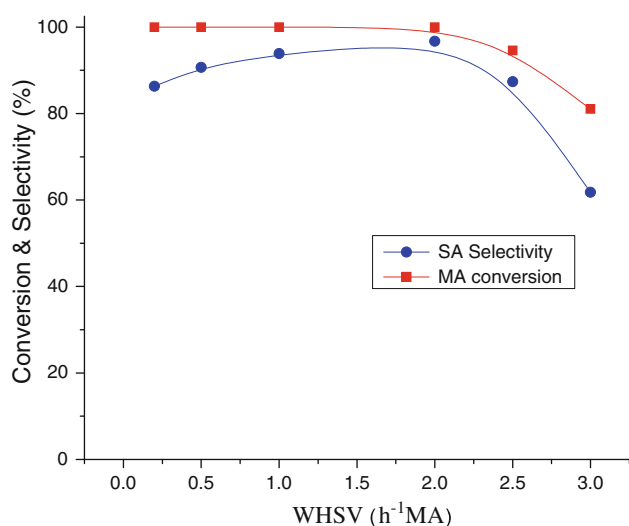
Fig. 6 Hydrogenation of MA over 5%Ni–0.5%Pt/HY–Al_2O_3: effect of WHSV; reaction conditions: reaction temperature = 140 °C, reaction pressure = 0.8 MPa, H_2/MA = 50 (molar ratio)
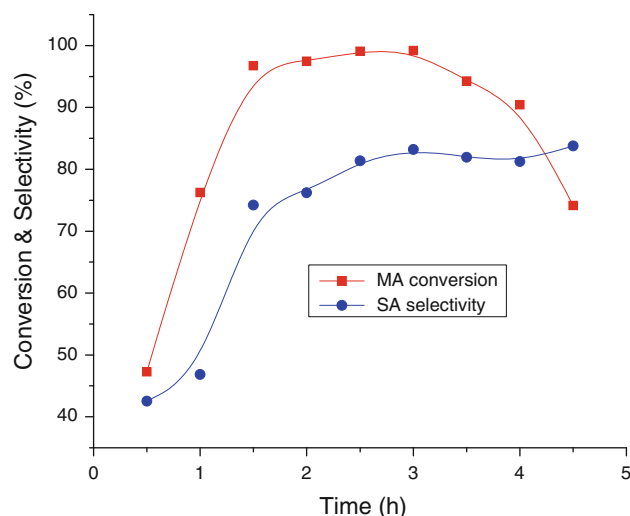
Fig. 7 Reaction conditions: WHSV = 2 h^{-1} maleic anhydride, reaction pressure = 0.8 MPa, reaction temperature = 40 °C, H_2/MA = 50 (molar ratio), catalyst: 10 wt%Ni–0.5 wt%Pt/Al_2O_3-HY

less demanding. For this purpose, the 10 wt%Ni–0.5 wt%Pt/Al_2O_3–HY was prepared by the above mentioned method. The following operating conditions were chosen: reaction temperature, 40 °C; WHSV, 0.2 h^{-1}. Figure 7 showed the catalyst is not very active at the beginning of the test, but after an induction period of about 5 h the conversion raises steeply to 100% (Fig. 7). As can be seen the selectivity to SA parallels the increase of conversion, starting from an initial value of 42% and reaching 83%. The conversion of maleic anhydride was stable up to around 2 h of reaction, after which considerable loss of catalytic activity occurred. Thus, the PtNi bimetallic catalyst has the advantage over the conventional heterogeneous catalyst at low temperature operating for MA hydrogenation but has some drawbacks with respect to rapid deactivation. For Cu/SiO_2, it has been reported that the rapid deactivation was initially attributed to carbonaceous compounds deposited on the metal surface (1). In our case, the formation of coke sites at the metal-support interface seems unlikely, because reaction was carried out at only 40 °C. The most possible deactivation is due to the formation of H_2O during reaction. In the hydrogenation of MA to SA, an equivalent amount of H_2O is always formed as a by-product which prevents the adsorption of malefic anhydride or decreases the concentration acid sites [17]. A relatively large amount of acid sites is helpful for hydrogenation reactions. Thus, the reaction must operate at temperature over 100 °C in order to remove the H_2O formed in the reaction mixture.

To test this idea, the hydrogenation reaction was carried out at 110 °C. The result is shown in Fig. 8, no traces of deactivation are observed after 10 h run time. The results indicate unquestionably that the presence of H_2O increases
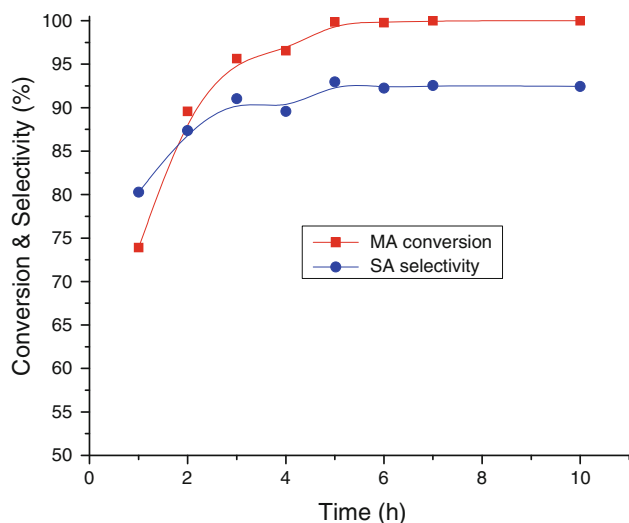
Fig. 8 Reaction conditions: WHSV = 0.2 h^{-1} maleic anhydride, reaction pressure = 1 MPa, reaction temperature = 110 °C, H$_2$/MA = 50 (molar ratio), catalyst: 10 wt%Ni–0.5 wt%Pt/Al$_2$O$_3$-HY
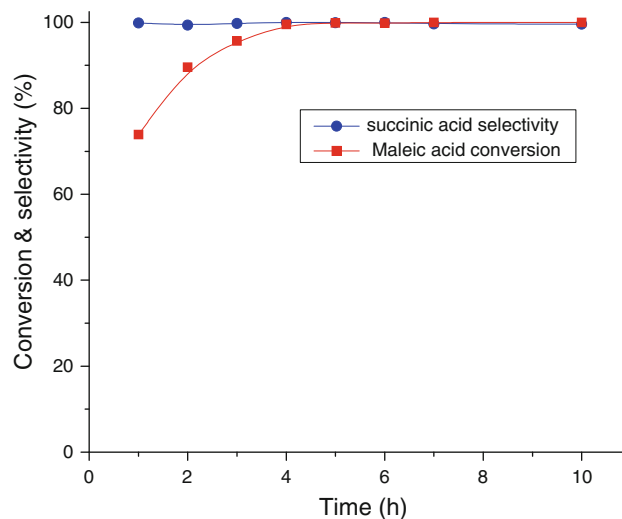

Fig. 10 Reaction conditions: WHSV = 0.2 h^{-1} maleic anhydride, reaction pressure = 1 MPa, reaction temperature = 40 °C, H$_2$/maleic acid = 50 (molar ratio)

be 270 kt/year [18]. The main problems are being carefully studied in order to make succinic acid economically competitive. The major feedstock that can be replaced by succinic acid is maleic acid; Since PtNi catalyst is highly activity for the hydrogenation of MA to SA, it was considered the possibility to obtain succinic acid derivates directly from maleic acid. If the proposed process would take place with high efficiency and selectivity at lower temperature, it would be an interesting general catalytic process for the formation of succinic acid. Moreover, unlike the hydrogenation of maleic anhydride, the reaction is to hydrogenate the C=C bond of maleic acid, accordingly H$_2$O is not formed. The result is shown in Fig. 10.

Time on stream (TOS) studies showed the PtNi catalyst is not very active at the beginning of the test, but after an induction period of about 4 h the conversion raises steeply to 100% (Fig. 10). And the selectivity of the malefic acid hydrogenation to succinic acid is very high (~100%). The PtNi catalyst showed high activity and stability at 40 °C; No deactivation or change in product distribution was observed over 10 h TOS. In the Au–Pt bimetallic catalytic system, Budroni et al. [19] found that the small amount of Pt doped into Au further improved the catalyst activity and selectivity, due to formation of mixed Au–Pt ensembles that led to enhanced overall activity and selectivity for partial hydrogenation.
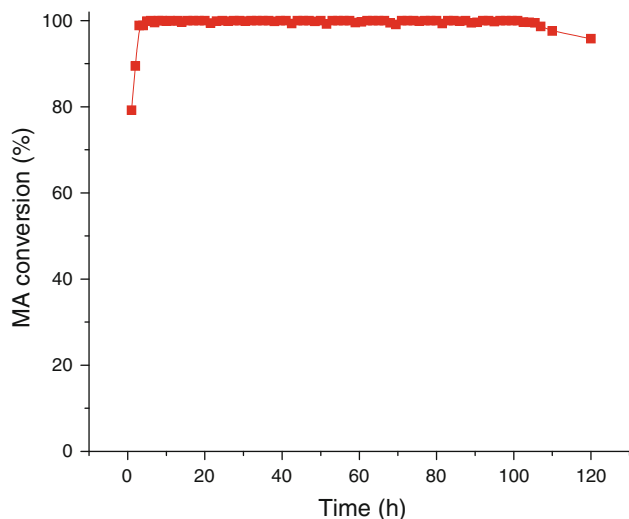

Fig. 9 Reaction conditions: WHSV = 3 h^{-1} maleic anhydride, reaction pressure = 0.8 MPa, reaction temperature = 220 °C, H$_2$/MA = 50 (molar ratio)

a deactivation rate of the PtNi catalyst on the hydrogenation of maleic anhydride. As mentioned above, a process of deactivation in the hydrogenation of maleic anhydride in the presence of PtNi metal catalysts is caused by the formation of H$_2$O that would cover the active surface and prevent the adsorption of maleic anhydride. In our case (see Fig. 9) more than 120 h of fast ageing (increased reaction temperature and higher WHSV) was carried out to observe only a 4% loss of activity.

3.2.6 From Maleic Acid to Succinic Acid at 40 °C

Succinic acid is an important building block and the world market of its derivatives has a potential that is estimated to

4 Conclusion

HY–Al$_2$O$_3$, HX–Al$_2$O$_3$, ZSM-5–Al$_2$O$_3$, USY–Al$_2$O$_3$, Beta–Al$_2$O$_3$ and Al$_2$O$_3$ supported PtNi bimetallic and Ni monometallic catalysts have been prepared by kneading

method and evaluated using a flow reactor for maleic anhydride hydrogenation at low temperatures. Overall, catalyst supports strongly affect the catalytic activities of both monometallic and bimetallic catalysts. The results show that HY–Al_2O_3 supported PtNi bimetallic catalysts exhibit the best performance among all as-prepared bimetallic and monometallic catalysts, which is mainly due to the Pt–Ni bimetallic formation. Furthermore, for all the supports, PtNi bimetallic catalysts show higher hydrogenation activities than the corresponding monometallic catalysts. Finally, we have shown that PtNi is able to catalyze the reaction for the production of succinic acid at 40 °C with 100% conversion.

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