Improved stability of a bimetallic Ni–Pt catalyst for hydrogenation of acetophenone and substituted derivatives

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The hydrogenation of acetophenone and its derivatives was studied using several supported Ni catalysts. Ni supported on zeolite Y catalyst offered the best hydrogenation activity. However, the activity of this catalyst decreases significantly on recycle and the extent of deactivation differs with respect to the substrate investigated. It is shown in this paper that a bimetallic Ni–Pt catalyst gives improved stability on recycle for hydrogenation of acetophenone and its derivatives. The role of zeolite Y support and a strong synergistic effect in a bimetallic Ni–Pt catalyst has been discussed.

Keywords: hydrogenation; bimetallic; recycle

1. Introduction

Liquid phase hydrogenation of organic compounds is used in a wide variety of chemical processes for the synthesis of fine chemicals and pharmaceuticals [1]. The hydrogenation of a carbonyl group containing organic compounds is usually carried out using supported metal catalysts and the desired product is most often a secondary alcohol derivative. The hydrogenation of *p*-isobutyl acetophenone to *p*-isobutyl phenyl ethyl alcohol is an important step in the new catalytic route developed for Ibuprofen, a non-steroidal anti-inflammatory drug, by Hoechst-Celanese and Boots [2]. The advent of microcrystalline, porous zeolite materials as supports has shown improved prospects [3–5] and zeolites have proven their potential as supports for many hydrogenation reactions [6]. Bimetallic catalysts or multimetallic catalysts are often used in order to achieve better performance in terms of activity and stability by making use of their geometric and electronic properties [7,8]. The aim of this paper is to demonstrate the high activity of zeolite Y supported Ni catalysts in hydrogenation of ketones and the role of bimetallic Ni–Pt catalyst in improving stability during recycle.

For hydrogenation of acetophenone and its derivatives both Ni and Pt are reported to be active along with Pd and Rh supported catalysts [9–12]. However, Ni catalysts are known to deactivate and hence, it is necessary to achieve catalysts of good stability. The hydrogenation of acetophenone, *p*-hydroxy acetophenone (*p*-HAP) and *p*-isobutyl acetophenone (*p*-IBAP) were investigated in this work. In this paper, we report results on hydrogenation of acetophenone to demonstrate that zeolite Y supported Ni catalyst offers several times higher activity when compared with other supported Ni catalysts. The role of bimetallic Ni–Pt, Ni–Pd, Ni–Fe catalysts was also investigated. Bimetallic Ni–Pt supported on zeolite Y catalyst showed improved stability and negligible deactivation during recycle unlike the monometallic Ni catalyst and this was found to be true for the three substrates under investigation. This has been attributed to a strong synergistic effect wherein Pt acts as a stabilizing agent and cooperates with Ni during the catalytic process as it was found that only Pt supported on zeolite Y catalyst offered a poor activity for the hydrogenation of acetophenone and also it deactivates substantially.

2. Experimental

All monometallic Ni supported catalysts (Ni content in % w/w) were prepared by the precipitation technique following the procedure described in literature [13]. The supports (United Catalysts India Ltd., India) were calcined at 773 K for 4 h prior to their use. Ammonium carbonate (Loba Chemie, India) was used for precipitating Ni from $Ni(NO_3)_2{\cdot}6H_2O$ (S.D. Fine, India). Bimetallic Ni–Pt (Pt precursor was $(PtC_8H_{12}Cl_2)$ [#1]), Ni–Pd (Pd precursor was $(Pd(PPh_3)_2Cl_2)$ [#1]) and Ni–Fe (Fe precursor was $Fe(NO_3)_2{\cdot}6H_2O$, S.D. Fine, India) catalysts were prepared by refluxing Ni supported catalyst (uncalcined) in toluene (for Ni–Fe it was doubly distilled water) for 4 h and toluene was removed using a rotavapor. The ratio of Ni to Pt, Pd and Fe was 10 : 1 (w/w). The catalysts were calcined in a static air furnace at 773 K for 10 h and reduced in an activation furnace using a silica-quartz tube at 773 K in H_2 flow of 50 cm^3/min for 10 h. The reduced catalysts were passivated under N_2

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[#1] Prepared in our laboratories by well established procedures.

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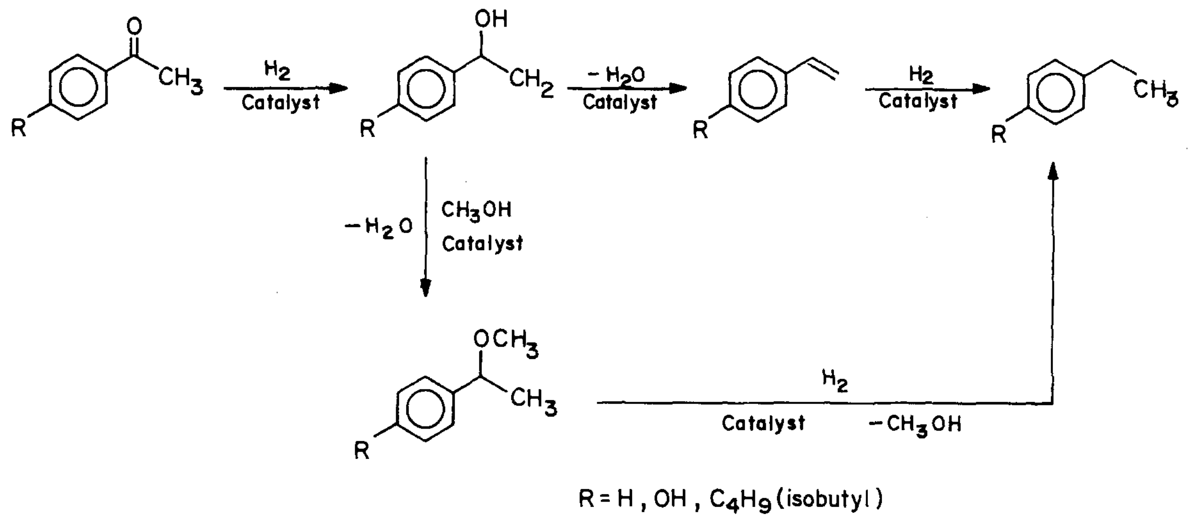

Fig. 1. Reaction scheme for hydrogenation of substituted acetophenone derivatives using Ni and bimetallic Ni–Pt supported on zeolite Y catalysts.

flow of 30 cm^3/min for 2 h. The hydrogenation experiments were carried out in a 300 cm^3, Parr autoclave which had provisions for automatic temperature control, safety rupture disc and dip tube for removing the liquid samples. A hydrogen gas reservoir vessel was connected to the reactor through a constant pressure regulator and H_2 consumption was monitored from the pressure drop in the reservoir. While performing the recycle experiments it was necessary to ensure that the catalysts were not exposed to air [#2]. In a typical experiment, 10 g of the substrate, 1 g of catalyst and solvent MeOH were added to make up the volume upto 100 cm^3. The contents of the reactor were flushed first with N_2 and then with H_2 at room temperature and the reactor was pressurized with H_2 after the desired temperature was attained. H_2 consumption as a function of time was noted and the analysis of liquid phase components was carried out using a 5840 HP gas chromatograph with a 10% OV 17 on Chromosorb W packed column and a Shimadzu GC-MS-QP-2000A instrument. The catalysts were characterized by a Phillips model No. 1730 using a Ni filtered Cu Kα radiation for XRD analysis, XPS spectra were recorded on ESCA-3-MK (VG Scientific, UK) and TEM analysis was done on model 1200 Jeol Japan TEM with a 120 keV electron source. The surface area of the support was determined by a CHEMBET 3000 apparatus by N_2 adsorption method at 77 K.

3. Results and discussion

The hydrogenation of substituted acetophenones is well represented by the reaction scheme shown in fig. 1. The reaction scheme has been proposed based on the products indentified and characterized by GC and GC-MS. The formation of these products and the catalytic aspects involved in hydrogenation of substituted acetophenone derivatives using Ni and bimetallic Ni–Pt supported on zeolite Y catalysts are discussed below. The results are expressed in terms of activity of the catalyst calculated based on the total moles of hydrogen consumed per unit weight of the catalyst present per unit time (kmol/(kg h)).

3.1. Hydrogenation of acetophenone

The results on hydrogenation of acetophenone using different supported Ni and bimetallic Ni–Pt, Ni–Pd and Ni–Fe catalysts are shown in table 1 and fig. 2 along with the recycle experiments. It is very clear that Ni supported on zeolite Y (Si/Al ratio 4.5) shows significantly improved activity compared to those with other supports. The XRD analysis revealed the existence of small metallic Ni particles of average crystallite size (as calculated from the Scherrer equation) of 12 nm on this support whereas on other supports like alumina, silica etc., lumps of around 30 nm were observed. XPS analysis revealed the existence of three Ni 2p core level peaks corresponding to Ni^0, Ni^{2+}, and Ni^{2+}_{sat}. The values agreed well with the values reported in the literature [5]. These analyses indicate that different types of crystallite sizes are formed which influence the degree of dispersion of metallic Ni. Also, the differences in XPS binding energy values indicate strong interaction of the support with the surface active metal. The high activity of zeolite Y supported Ni catalyst (see table 1 and fig. 1) could have been due to the formation of two different types of active sites, one where Ni gets exchanged with the protonic sites of the zeolite and forms small clusters of Ni on subsequent calcination/activation [3,4] and the other site being the

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[#2] In recycle experiments after the first experiment was over, the reactor was brought to room temperature and all H_2 was removed. The reactor was flushed with N_2 2–3 times and fresh amount of acetophenone was added through the dip tube of the reactor without opening the reactor.

Table 1
Hydrogenation of acetophenone using different catalysts[a]

Catalyst[b]	Temp. of activation	% conv.	$R_A \times 10^5$ [c] (kmol/(m^3 s))	Product distribution[d] % selectivity				XRD L[e]	XPS BE values (eV)		
				ALC	STY	ETH	EB	(nm)	Ni^0	Ni^{2+}	Ni$^{2+}_{sat}$
20% Ni/Al_2O_3	773	10	1.1	100	–	–	–	25	854.1	855.6	862.3
20% Ni/TiO_2	773	10	1.1	100	–	–	–	20	853.6	855.6	861
20% Ni/SiO_2	773	40	5.5	95	–	–	5	30	854.6	856.6	862.6
20% Ni/HZSM5	773	25	3	95	–	–	5	25	853.4	856.6	861.1
20% Ni/HY	773	75	10	75	5	5	15	15	853.0	855.6	861.6
10% Ni/HY	773	70	9.3	74	5	7	14	12[f]	852.6	855.6	861.5
10% Ni/HY	573	50	6.1	95	–	–	5	15	852.8	855.8	861.6
10% Ni/HY	673	61	7.8	80	5	4	11	15	852.6	855.6	861.5
10% Ni/HY	873	12	1.4	100	–	–	–	am	852.6	855.8	861.6
10% Ni 1% Pt/HY	773	95	14.4	65	–	5	30	10[g]	–	–	–
1% Pt/HY	773	5	0.5	100	–	–	–	–	–	–	–
10% Ni 1% Pd/HY	773	10	1.1	100	–	–	–	am	–	–	–
10% Ni 1% Fe/HY	773	48	6.1	90	–	–	10	am	–	–	–
10% Ni/HY + 2.5 mmol NaOH	773	65	7.6	99	–	–	–	12[f]	852.6	855.6	861.5
10% Ni 1% Pt/HY + 2.5 mmol NaOH	773	92	10.7	99	–	–	–	–	–	–	–

[a] Reaction conditions: conc. of acetophenone: 0.84 kmol/m^3; catalyst: 10 kg/m^3; solvent: MeOH; temp.: 373 K; P_{H_2}; 30 atm; agitation speed: 15 Hz; reaction volume: 1×10^{-4} m^3; reaction time: 2 h.

[b] Surface area of supports: Al_2O_3: 150 m^2/g; SiO_2: 50 m^2/g; TiO_2: 30 m^2/g; HZSM5: 250 m^2/g; HY: 500 m^2/g.

[c] R_A is the overall rate of hydrogenation calculated from the stoichiometry of the reaction.

[d] ALC: phenyl ethyl alcohol: STY: styrene; ETH: phenyl ethyl methyl ether; EB: ethyl benzene.

[e] Average crystallite size of metallic Ni calculated from XRD patterns using the Scherrer equation $L = k\lambda/\beta \cos\theta$, where $k = 0.9$ and $\lambda = 0.15403$ um for CuKα radiation. am: amorphous sample dimensions of the crystallite size of Ni below the detection limit of XRD.

[f] TEM analysis of the sample showed an average crystallite size of 10 um for 10% Ni/HY.

[g] TEM analysis of the sample showed an average crystallite size of 7 nm for 10% Ni 1% Pt/HY.

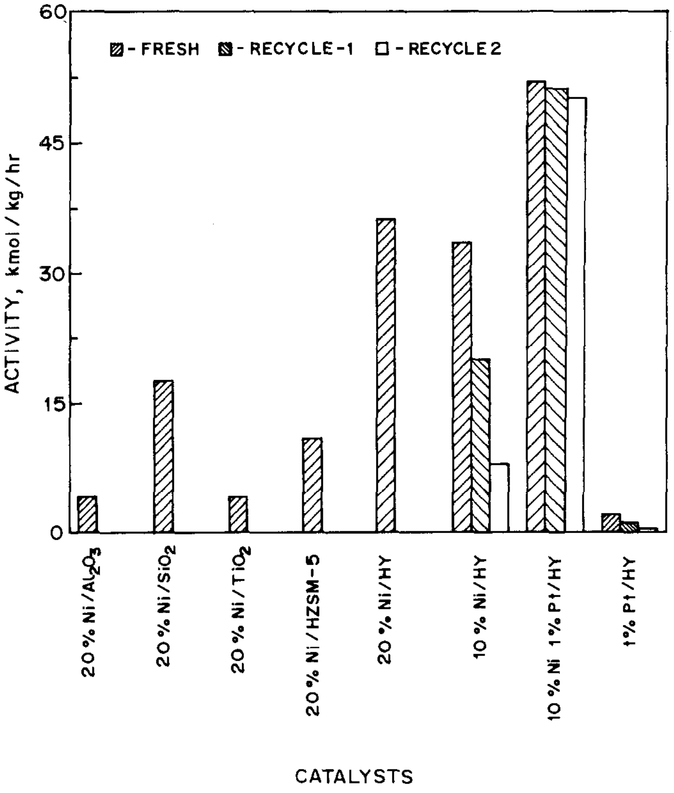

Fig. 2. Hydrogenation of acetophenone using different Ni and bimetallic Ni–Pt catalysts. Reaction conditions: conc. of acetophenone: 0.84 kmol/m^3; catalyst: 10 kg/m^3; solvent: MeOH; temp.: 373 K; P_{H_2}: 30 atm; agitation speed: 15 Hz; reaction volume: 1×10^{-4} m^3; reaction time: 2 h.

Ni present on the external surface of the zeolite. The influence of temperature of activation indicated that an optimum of 773 K was desired as decreasing it would have resulted in the formation of weakly interacting Ni agglomerates which would have reduced the exposed metal surface area.

The fact that we observe styrene and the ether derivative of phenyl ethyl alcohol indicates a strong participation of the acidic sites of the zeolite [10] in the course of reaction, dehydrating phenyl ethanol to form a resonance stabilized carbocation which would have either formed styrene or the ether derivative depending on the S_N1 type of reaction occurring with the carbocation and the solvent.

The synergistic role of Pt in bimetallic Ni–Pt catalysts in improving the activity and stability is shown in fig. 2. Ni–Fe bimetallic catalyst does not show this effect and addition of Pd deactivates Ni (table 1, runs 12 and 13). The most striking result is during the recycle study where the activity of 10% Ni supported on zeolite Y catalyst dropped significantly during recycle. For the bimetallic Ni–Pt catalyst the deactivation is insignificant indicating an improved stability. This result can be due to the cooperative effect of Pt which can stabilize the reduced state of Ni by forming an alloy of the type Ni–Pt or Ni_3Pt [14]. Also, it would have activated the CO bond favouring easy transfer of the adsorbed hydrogen. This is certainly due to a combined effect of Ni and Pt as only Pt supported on zeolite Y shows not only a poor activity but also is not stable on recycle (see table 1 and fig. 2). The PT supported on zeolite Y catalyst deactivated in the first recycle itself (~ 50% deactivation when compared with the fresh catalyst).

3.2. Hydrogenation of substituted acetophenone derivatives

The hydrogenation of *p*-hydroxy acetophenone (*p*-HAP) and *p*-isobutyl acetophenone (*p*-IBAP) was also studied using Ni and bimetallic Ni–Pt supported on zeolite Y catalysts. These experiments were carried out in order to confirm the synergistic effect of Ni–Pt bimetallic catalysts in terms of stability on recycle. The kinetics of hydrogenation of *p*-isobutyl acetophenone using a 10% Ni supported on zeolite Y catalyst has already been studied based on a similar reaction scheme as the one discussed here [15]. The results on hydrogenation of different substituted acetophenones using Ni and bimetallic Ni–Pt supported on zeolite Y catalysts are shown in fig. 3. The results are given in terms of relative activity of the catalysts calculated assuming the catalyst used in the first run as 100% active. After a reaction time of 2 h, the results indicate that monometallic Ni supported on zeolite Y catalyst deactivates significantly on recycle (nearly 50% drop in activity when compared with the fresh catalyst for both the substituted acetophenones) unlike the bimetallic Ni–Pt catalyst. However, for hydrogenation of *p*-IBAP using Ni–Pt bimetallic cat-

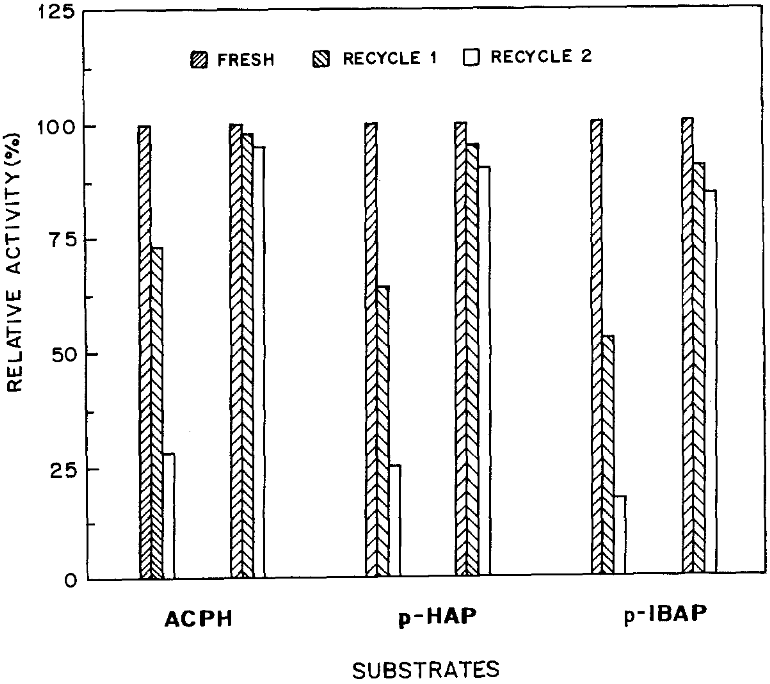

Fig. 3. Relative activity of Ni and bimetallic Ni–Pt catalysts for hydrogenation of substituted acetophenone derivatives. Reaction conditions: conc. of substrate: 0.5 kmol/m^3; catalyst: 10 kg/m^3; solvent: MeOH; temp.: 393 K; P_{H_2}: 30 atm; agitation speed: 15 Hz; reaction volume: 1×10^{-4} m^3. Acph: acetophenone; *p*-HAP: *p*-hydroxy acetophenone; *p*-IBAP: *p*-isobutyl acetophenone. * The first set of graphs represents relative activity for 10% Ni/HY catalyst and the second set for bimetallic 10% Ni 1% Pt/HY catalyst for each substrate.

alyst it was found that the activity of the catalyst dropped by about 12% after two recycles. This may be due to the difficulty in hydrogenating a bulkier organic molecule (*p*-IBAP) when compared with *p*-HAP or acetophenone. However, this small change in activity can also be due to experimental error. Typical concentration–time profiles for hydrogenation of *p*-HAP and *p*-IBAP using Ni–Pt bimetallic catalysts at 393 K are shown in figs. 4 and 5. It was observed that more amounts of the ether derivatives were formed due to the influence of the substituent group. The carbocation formed with different substituents (–OH and isobutyl group) on the aromatic ring would have been less stable and hence more reactive to form the ether derivatives due to the interactions with the intermediate secondary alcohol, solvent (MeOH) and the zeolitic protons. It was also observed that at a longer time of reaction, more amounts of *p*-isobutyl ethyl benzene were formed even after *p*-isobutyl phenyl ethanol was completely consumed [15]. This indicates that the methanolysis of the ether derivative took place leading to the formation of *p*-isobutyl ethyl benzene.

Even though there is no significant improvement in the activity due to the presence of the second metal, it was confirmed that there was a significant improvement in the stability due to the presence of Pt in a bimetallic Ni–Pt catalyst. This may be due to the presence of Pt which can stabilize the reduced state of Ni by forming well dispersed Ni–Pt alloy.

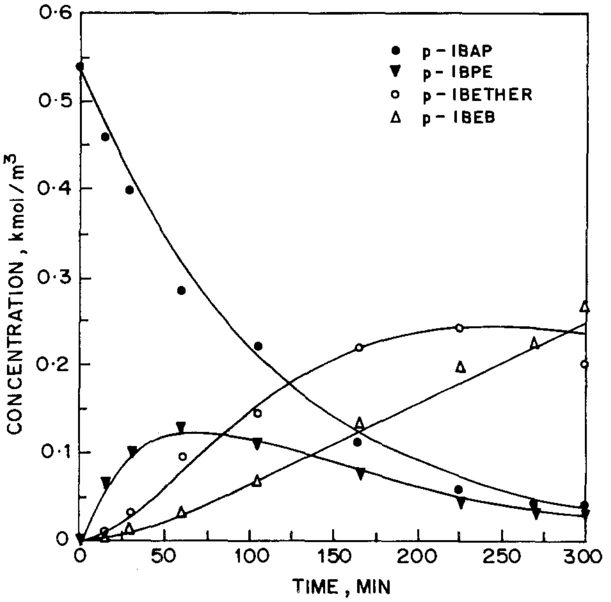

Fig. 4. Concentration–time profile for hydrogenation of *p*-isobutyl acetophenone at 393 K. Reaction conditions: conc. of *p*-IBAP: 0.54 kmol/m^3; catalyst: 10 kg/m^3; solvent: MeOH; temp.: 393 K; P_{H_2}: 30 atm; agitation speed: 15 Hz; reaction volume: 1×10^{-4} m^3. *p*-IBEB: *p*-isobutyl ethyl benzene; *p*-IBEther: *p*-isobutyl phenyl ethyl methyl ether; *p*-IBPE: *p*-isobutyl phenyl ethyl alcohol; *p*-IBAP: *p*-isobutyl acetophenone.

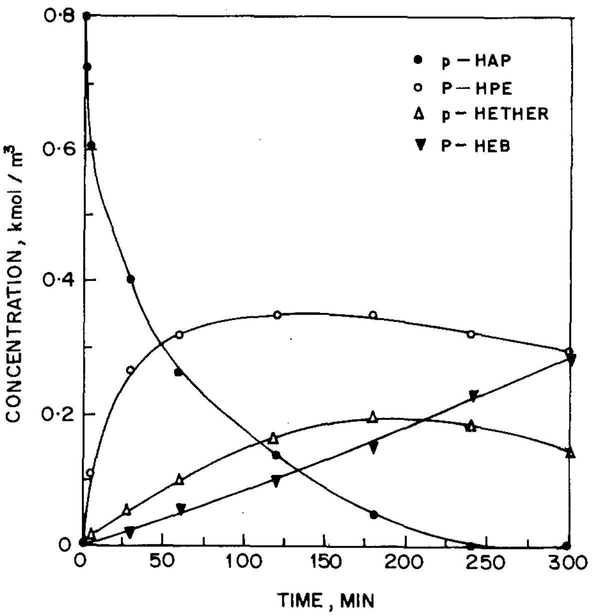

Fig. 5. Concentration–time profile for hydrogenation of *p*-hydroxy acetophenone at 393 K. Reaction conditions: conc. of *p*-HAP: 0.74 kmol/m^3; catalyst: 10 kg/m^3; solvent: MeOH; temp.: 393 K; P_{H_2}: 30 atm; agitation speed: 15 Hz; reaction volume: 1×10^{-4} m^3. *p*-HEB: *p*-hydroxy ethyl benzene; *p*-HEther: *p*-hydroxy phenyl methyl ethyl ether; *p*-HPE: *p*-hydroxy phenyl ethyl alcohol; *p*-HAP: *p*-hydroxy acetophenone.

Further it was noticed that addition of trace amount of a base like NaOH improved the selectivity significantly towards phenyl ethyl alcohol (> 99%) for both Ni and bimetallic Ni–Pt catalysts (see table 1 last two runs). This improved selectivity is due to the arrest of other reactions (see fig. 1) owing to the alkaline nature of the reaction medium.

4. Conclusions

A 10% Ni supported on zeolite Y catalyst showed improved activity for hydrogenation of acetophenone. However, this catalyst deactivated as a result of strong adsorption characteristics of acetophenone as well as the intermediate products formed during the course of hydrogenation. The deactivation of Ni supported on zeolite Y catalyst is prevented by the addition of Pt as the Ni–Pt bimetallic catalyst can be recycled several times without loss of significant activity. This synergistic effect in a bimetallic Ni–Pt catalyst has been demonstrated for hydrogenation of *p*-hydroxy acetophenone and *p*-isobutyl acetophenone also. A promoter base like NaOH can be used to improve the selectivity towards the secondary alcohol derivative, for both Ni and Ni–Pt catalysts.

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