Research Article

A Simulation Study for Trimetallic Nanosized Alloy (Ni, Cu, and Ag) in Hydrogenation of Organic Compounds: A Case Study of “Nitrophenols”

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Trimetallic system (Ni, Cu, and Ag) supported on alumina was utilized for hydrogenation of nitrophenols. The catalytic active centers for hydrogenation were attributed only to the presence of Ni. However, the presence of bi- or trimetallic systems improves the catalytic activity via extra synergism. The catalytic activity was measured as the time for reaching 100% conversion. The function of synergism was fitted for both bimetallic systems (Ni:Ag; Ni:Cu) individually. Subsequently, three-dimensional function was fitted for trimetallic system (Ni:Cu:Ag) based on the linear combination of data for individual bimetallic system. After a complex calculation areal function was evaluated. An Excel program was written to simply evaluate the catalytic activity of trimetallic system with high accuracy. Characterization of catalysts was performed using EPR and pulsed chemisorption by hydrogen. These characterizations of samples enable us to evaluate particle size, metallic surface area, and degree of dispersion. These values were successfully correlated with the synergism function. The program written then could be capable of predicting these values for any trimetallic system.

1. Introduction

Hydrogenation reactions are one of the most important reactions for preparation of many fine chemicals and important intermediates [1–5]. The selectivity and activity of such reactions are an issue of most recent researches [1, 2]. Most of catalysts used in such important reactions are metal catalysts [6, 7]. The basic idea of hydrogenation reactions is to adsorb both metal and target organic moiety subject to hydrogenation. The challenge in this subject is to find that metal has high activity and selectivity towards the desired compound. In order to attain both activity and selectivity researches tend to use bimetallic system. Thus, a combination of Ni-Ag, Ni-Cu, and Ni-Au was used in [1] for active and selective hydrogenation of cinnamaldehyde. In addition, Ni-Pd bimetallic system was used in hydrogenation of nitrobenzyl ethers to amino benzyl [2]. Moreover, Ni-Ag bimetallic system was used in hydrogenation of dimethyl oxalate [3].

Many others researches also used many combinations of bimetallic systems in order to enhance the selectivity and activity [4–8]. Searching the literature data, only few papers deal with the trimetallic system. Thus, in [9] homogenous catalyst containing trimetallic system of Sn, Ru, Pt in selective reduction of cyclodecatene. However heterogeneous catalyst containing clusters of PtRu₅Sn was evaluated as hydrogenation catalyst [10, 11]. Just as rare sole example we found a paper that deals with hetero quarter metallic nanoparticle hydrogenation catalyst of Ni/Ru/Pt/Au [12]. In all above examples of hydrogenation catalysts containing bi- or tri- or even quaternary metallic systems a simple evaluation of one sample or more is performed just to bring the selectivity and compare it to bi- or monometallic catalyst. In this paper we aim to investigate and write a mathematical simulation program containing trimetallic heterogeneous catalyst containing Ni, Ag, and Cu.

In order to fulfill this purpose, we choose a simple effective hydrogenation reaction. Thus hydrogenation of nitrophenol into amino phenol using supported metal and using hydrazine hydrate as a hydrogen source was proven to be 100% selective and finishes with 100% conversion in only few minutes [13, 14]. The program will evaluate the effect of this trimetallic system and will build three-dimensional model for the activity function of these catalysts and also will be capable of evaluating some physical properties of these metals.

2. Experimental

2.1. Materials Used. NaOH (Merck), copper nitrate (Merck), nickel nitrate (Merck), silver(I) nitrate (Merck), hydrazine hydrate (99.999% Merck), alumina (FLUKA Typ 507c), P-nitrophenol (PNP) (Merck), o-nitrophenol (oNP) (Merck), m-nitrophenol (mNP) (Merck), P-aminophenol (PAP) (Merck), m-aminophenol (mAP) (Merck), and o-aminophenol (oAP) (Merck) were used as a standard materials.

2.2. Preparation of the Catalyst. Typically 10 g of alumina was impregnated with 5 wt% metals. Different mole ratios of mono-, di-, and trimetal are varied keeping 5 wt% constant. After drying at 100°C the catalyst is subjected to chemical reduction using hydrazine hydrate in alkaline solution of NaOH. After completion of reduction, the catalyst was rapidly filtered and dried and kept in a closed bottle.

2.3. Catalytic Reaction. Typically, a solution containing 0.125 g of nitrophenols with 20 mL of hydrazine hydrate was heated to 80–100°C in a three-necked flask connected to a condenser.

0.5 g of the catalyst was added to the above solution. The time was recorded just upon the addition. After reaction completion the color of the system is changed to grayish white indicating 100% conversion [14]. The filtrate was then evaporated under reduced pressure. The residual solids were recrystallized from hot water to give the pure product of corresponding amino phenols in almost 100% yield.

2.4. Characterization Techniques

2.4.1. XRD (X-Ray Diffraction Analysis). X-Ray diffractograms of various solids were collected using a Bruker D8 advance instrument with CuK α 1 target with second monochromator 40 kV, 40 mA.

2.4.2. EPR (Electron Paramagnetic Resonance). The EPR spectra were recorded on EMX Bruker instrument operated at X-band frequency. The following parameters are generalized to all samples otherwise mentioned in the text. Microwave frequency is 9.79 GHz. Receiver gain is 20. Sweep width is 6000, center at 3480 Gs. Microwave power is 0.202637 W.

2.4.3. Pulsed Chemisorption. The H₂ chemisorption experiments were carried out at 373 K using a pulse reactor to determine the Ni metal area and Ni metal particle size. In a typical experiment, approximately 150 mg of the catalyst sample was

FIGURE 1: XRD patterns of pure Ni, some trimetallic systems, and bare alumina.

loaded in a micro quartz reactor (8 mm i.d., and 250 mm long) and the catalyst sample was first subject to hydrogen flow at 420 K for 1 h and kept at the same temperature for 1 h under He flow and then the reactor was cooled to 373 K under helium gas flow. The outlet of the reactor was connected to a microthermal conductivity detector (TCD) of GC-17A (Quantachrome ChemBET 3000, USA) through an automatic six-port valve after cooling of the sample to 303 K, pulses of gas (5% H₂ balance He) (500 mL), until there is no further change in the intensity of TCD peak due to gas pulse.

3. Results and Discussion

3.1. X-Ray Diffraction (XRD). Figure 1 represents the XRD patterns of bare alumina, 5% Ni, and some trimetallic systems. From these figures it could be shown that Ni metal phase was observed only in pure 5% wt Ni. While in the rest of the samples there was no observation of such phase. This could be explained by the lower amount of metal which could not be detected by XRD techniques. Another reason is that the metal phases could be existing in amorphous nanoscale with bi- or trimetallic system. This will be declared further in EPR section.

3.2. Electron Spin Resonance (EPR). EPR spectra of all samples are given in Figure 2. In this figure we can observe an EPR signal characterized for the nanosized nickel [13].

3.3. Program for Trimetallic System. In this research we aimed to study and evaluate trimetallic system of Ni, Cu, and Ag as an effective catalyst for hydrogenation of nitrophenols.

TABLE 1: Examples of some measured bimetallic and trimetallic systems.

Catalyst (5 wt% loading on alumina)	Time to reach 100% conversion (sec)		
	PNP	MNP	ONP
Ni	505	149	80
1Ni:1Cu	426	67	125
2Ni:1Cu	145	23	43
1Ni:2Cu	669	106	197
1Ni:1Ag	403	64	119
1Ni:2Ag	603	96	178
2Ni:1Ag	136	22	40
1Ni:1Cu:1Ag	275	44	81
1Ni:2Cu:1Ag	300	47	89
1Ni:1Cu:2Ag	327	52	96
2Ni:1Cu:1Ag	138	22	41
2Ni:1Cu:2Ag	320	52	95
2Ni:2Cu:1Ag	179	29	53

FIGURE 2: EPR spectra of different investigated samples.

In order to study this system we make a series of bimetallic systems Ni:Cu and Ni:Ag with different molar ratios (Table 1). The catalytic activity was taken as time to reach 100% conversion [13]. However we added a term “catalytic activity response” as a reciprocal of this time. This was taken as real measure of catalytic activity and thus as time decreases catalytic activity response increases.

From experimental test it was found that neither Cu nor Ag alone gives any catalytic activity in these reactions;

FIGURE 3: Fitted function of synergism of Ag.

FIGURE 4: Fitted function of synergism of Cu.

however in presence of Ni as a bimetallic system they could enhance the catalytic activity.

In order to study the effect of these metals on the activity of Ni, we first determined what is called the linear catalytic activity which is the catalytic activity of catalyst based on its % nickel theoretically calculated from the pure nickel catalyst. Based on these values we can check any presence of synergism occurring due to addition of either Cu or Ag as bimetallic system with nickel. A function of synergism was evaluated for bimetallic system individually (Ni:Cu and Ni:Ag), was given below, and was fitted with regression with R^2 more than 0.99 as indicated below (Figures 3 and 4).

Fitted Function of Ag

$$R^2 = 0.99999.$$

$$y = (a + cx + ex^2 + gx^3 + ix^4 + kx^5 + mx^6 + ox^7 + qx^8 + sx^9) / (1 + bx + dx^2 + fx^3 + hx^4 + jx^5 + lx^6 + nx^7 + px^8 + rx^9)$$

$$a = 8.38079978776094534e - 12.$$

$$b = -0.13125008769893421.$$

$$c = 0.00875045445894009892.$$

$$d = 0.00879799437475077272.$$

$$e = -0.000542659485512226170037.$$

$$f = -0.000369150693507672097.$$

$$g = 0.000130160541802780922.$$

$$h = 1.04721425663883469e - 05.$$

$$i = -2.37748383168755742e - 06.$$

$$j = -2.04370666255700862e - 07.$$

$$k = -1.04465938816921968e - 07.$$

$$l = 2.7069883330420037e - 09.$$

$$m = 4.38513923648865887e - 09.$$

$$n = -2.30678157052159122e - 11.$$

$$o = -6.44850744978172715e - 11.$$

$$p = 1.12348816431769573e - 13.$$

$$q = 4.3709878480847383e - 13.$$

$$r = -2.33307317855799149e - 16.$$

$$s = -1.15082085584729222e - 15.$$

where x is wt% of Ag in the sample and y is % syn/Ni.

Simulated Function of Cu Synergism

$$R^2 = 0.9997.$$

$$y = (a + cx^{(0.5)} + ex + gx^{(1.5)} + ix^{(2)}) / (1 + bx^{(0.5)} + dx + fx^{(1.5)} + hx^{(2)}) [NL]$$

$$a = -0.0426081493584968437.$$

$$b = -0.54328913086813246.$$

$$c = 0.0447085498764833328.$$

$$d = 0.108691551874143843.$$

$$e = 0.000882635994217492438.$$

$$f = -0.00934404638076721272.$$

$$g = -0.00135640497689789237.$$

$$h = 0.000291267840703249792.$$

$$i = 8.63726742343394856e - 05.$$

where x is wt% of Cu in the sample and y is % syn/Ni.

From Figures 3 and 4 curves it was found that the synergism function is increased as the % added metal (Cu or Ag) increases reaching maximum and then decreases again.

In order to study the trimetallic system we make a linear addition of both functions of individual synergism. Figure 5 represents the 3D graph of raw data given.

FIGURE 5: 3D presentation of trimetallic system Ni:Cu:Ag. Cu:Ag against synergism per % Ni.

The above data was simulated as 3D function as given below:

$$z = a + b \exp(-\exp(-(x - c)/d) - (x - c)/d + 1) + e \exp(-\exp(-(y - f)/g) - (y - f)/g + 1) + h \exp(-\exp(-(x - c)/d) - (x - c)/d + 1) * \exp(-\exp(-(y - f)/g) - (y - f)/g + 1).$$

$$a = 1.06593487136815043.$$

$$b = 6.21497398634458147.$$

$$c = 30.766242892928571.$$

$$d = 10.6485929178985698.$$

$$e = 14.6057695738211414.$$

$$f = 36.2251355611607967.$$

$$g = 12.5973938666555902.$$

$$h = 0.371621313243641629.$$

$$R^2 = 0.99606799,$$

where x is % copper, y is the % Ag, and z is the % syn/Ni.

Figure 6 represents the 3D model of simulated function which gives us high accuracy.

Figures 5 and 6 showed clearly that the 3D model of the linear synergism functions showed more than 3D peaks varied according to the composition of the system. The maximum synergism was found to be of value about 22% syn/Ni.

This 3D figure could give us the ability to evaluate the four parameters in one time (% syn, % Ni, % Cu, and % Ag). However, subsequently, analysis of the real system should be compared which will be performed in the next section.

After applying the previous function on real trimetallic systems we observed that extra synergism occurs due to

FIGURE 6: 3D model for the trimetallic system of Ni:Cu:Ag.

FIGURE 8: 3D representation of calculated real synergism function.

FIGURE 7: Difference between real and linear synergism against % Ni.

presence of both Cu and Ag together. In order to evaluate this extra synergism we correlate the difference in synergism with the % Ni (Figure 7).

Thus, it was found that extra synergism is observed only in % Ni between 5 and 40%. In order to calculate it automatically we simulate this function as follows:

$$y = (a + c \ln x + e(\ln x)^2 + g(\ln x)^3) / (1 + b \ln x + d(\ln x)^2 + f(\ln x)^3 + h(\ln x)^4)$$

$$R^2 = 0.998.$$

$$a = 0.0635566682938822554.$$

$$b = -1.45700051352569521.$$

$$c = 0.0405819231287318062.$$

$$d = 0.798911010088653167.$$

$$e = -0.052037125263925555.$$

$$f = -0.195314109600566023.$$

$$g = 0.0106381602099602297.$$

$$h = 0.0179571310856602618.$$

where y is difference between simulated linear synergism and real trimetallic synergism and x is % Ni.

FIGURE 9: Correlation between particle size and function of synergism over % Ni.

After applying the above function on the three-dimensional linear synergism function we could obtain the real function of synergism (Figure 8).

Obtaining the previous function enables us to deduce the catalytic activity and consequently the time to reach 100% for trimetallic system simply by input of the mole ratio of Ni:Cu:Ag.

Particle Size Simulation. Particle size was evaluated by Kawabata equation correlating the peak-to-peak width of EPR spectra of nanoparticles with corresponding particle size:

$$d = a * \sqrt{\Delta H_{pp}},$$

where a is proportionality constant and ΔH_{pp} is the peak width. Knowing that " a " for Ni is 1.6 [13] we can evaluate the particle size of each catalyst.

We correlate the particle size of different ratio of trimetallic catalysts with the function of real synergism Figure 9.

TABLE 2: Experimental data for some selected samples for dispersion and metallic surface area.

Catalyst	% Ni	Dispersion	Metal surface area
1Ni:1Ag:1Cu	25.65	30.41	10.13
2Ni:1Cu	64.9	55.27	18.42
1Ni:1Ag	35.43	32.51	10.83
Ni	100	4.12	1.37
2Ni:1Ag	52.32	3.63	1.21
1Ni:1Cu	48.04	2.71	0.9

The function correlating the syn/Ni with particle size is as follows:

$$\text{Eqn} = \text{Decay } 1 + 2(a, b, c, d, e).$$

$$y = a + b \exp(-cx) + d/(1 + dex).$$

$$y = \frac{-34.6564331294717461 + 6.41868775476660539 * \exp(-2.1574343708473217 * x) + 50.9940759663696104}{(1 + 50.9940759663696104 * 4.04301775665067334e - 05 * x)}$$

$$a = -34.6564331294717461.$$

$$b = 6.41868775476660539.$$

$$c = 2.1574343708473217.$$

$$d = 50.9940759663696104.$$

$$e = 4.04301775665067334e - 05.$$

$$R^2 = 0.9952975.$$

where y is particle size by nm and x is the syn/Ni.

By the above function we can deduce the particle size of any trimetallic system by the syn/Ni function.

In order to evaluate the secret of catalytic activity we make pulsed chemisorption to measure the metallic surface area and degree of dispersion and average crystallite size of Ni. This pulsed chemisorption was performed at reaction temperature (Table 2).

Correlating surface area per unite % Ni with the synergism function we can obtain a good correlation as in Figure 10.

We can simulate the previous function as follows:

$$y = a + b * \exp(-\exp(-(x - d \ln(\ln(2)) - c)/d))).$$

$$r^2 = 0.999964110919114507.$$

$$a = 0.0132405008193570401.$$

$$b = 0.381497786254137327.$$

$$c = 5.72848339592924586.$$

$$d = 1.48550214791616277,$$

where y is the metallic surface area by % Ni and x is the synergism function per % Ni.

By the above correlation we can simulate the metallic surface area to the synergism function easily to fully simulate

FIGURE 10: Metallic surface area per % Ni against synergism per % Ni.

the trimetallic system. The program written in Excel could simulate easily with a good precision the whole system for the all isomers of nitrophenol (p-, m-, and o-).

Figure 11 is the image of this Excel program which is attached with this manuscript as Supplementary Material (available online at <https://doi.org/10.1155/2017/9464209>).

Evaluation of the Program. In order to evaluate the program the catalytic activities of some random samples were measured and compared with data given from the program, Table 3.

From Table 3 we could realize that the program could predict precisely the time to reach 100% with average % error not exceeding 1.83% and max error not increasing by 8%.

Mechanism of Reduction of Nitrophenols. Figure 12 represents the kinetic curve of the three nitrophenols which shows that all reduction processes follow first-order equation with respect to nitrophenols.

Durability Study of Some Samples Given. From Table 4 it was found that most of trimetallic system showed a good durability upon five times of successive use.

4. Conclusions

The trimetallic system (Ni, Cu, and Ag) was proved to be very effective for reduction of nitrophenols using hydrazine hydrate. Thus, nickel metal was found to be the only active center in this reaction. However, the presence of bimetallic and trimetallic alloy with nickel exhibits extra synergism. A program with high precision was successfully written to simulate the synergism function and the catalytic activity of the trimetallic system. The method of calculation used will open new aspect to deal with similar system in the

FIGURE 11: Image of Excel program.

TABLE 3: A comparison between real and calculated results of some random samples combined with % error.

Catalyst (5 wt% loading on alumina)	Time to reach 100% conversion (sec)								
	Real	PNP Calculated	% error	Real	MNP Calculated	% error	Real	ONP Calculated	% error
Ni	505	505.1	0.02	149	148.7	0.20	80	79.86	0.18
1Ni:1Cu	426	425.5	0.12	67	67.27	0.40	125	125.3	0.24
2Ni:1Cu	145	144.9	0.07	23	22.9	0.43	43	42.66	0.79
1Ni:2Cu	669	668.3	0.10	106	105.7	0.28	197	196.8	0.10
1Ni:1Ag	403	403.1	0.02	64	63.72	0.44	119	118.7	0.25
1Ni:2Ag	603	603.3	0.05	96	95.39	0.64	178	177.7	0.17
2Ni:1Ag	136	135.7	0.22	22	21.45	2.50	40	39.95	0.12
1Ni:1Cu:1Ag	275	274.7	0.11	44	43.42	1.32	81	80.88	0.15
1Ni:2Cu:1Ag	300	299.1	0.30	47	47.29	0.62	89	88.08	1.03
1Ni:1Cu:2Ag	327	327.2	0.06	52	51.73	0.52	96	96.35	0.36
2Ni:1Cu:1Ag	138	137.3	0.51	22	21.71	1.32	41	40.43	1.39
2Ni:1Cu:2Ag	320	319.6	0.12	52	50.53	2.83	95	94.11	0.94
2Ni:2Cu:1Ag	179	178.3	0.39	29	28.19	2.79	53	52.51	0.92
4Ni:1Cu:2Ag	140	138.2	1.29	23	21.84	5.04	42	40.68	3.14
1Ni:2Cu:3Ag	1128	1122	0.53	180	177.3	1.50	333	330.3	0.81
3Ni:1Cu:1Ni	104	105	0.96	18	16.6	7.78	32	30.92	3.37
1Ni:3Cu:2Ag	718	716.8	0.17	115	113.3	1.48	213	211.1	0.89
2Ni:1Cu:2Ag	322	319.6	0.75	52	50.53	2.83	96	94.11	1.97
Average error			0.32			1.83			0.94

TABLE 4: A durability study for some trimetallic samples for reduction of PNP.

Sample	Time to reach 100% for PNP (sec)				
	1st use	2nd use	3rd use	4th use	5th use
1Ni:1Cu:1Ag	275	280	290	300	330
1Ni:2Cu:1Ag	300	310	310	330	350
1Ni:1Cu:2Ag	327	328	330	335	340
2Ni:1Cu:1Ag	138	140	142	146	150
2Ni:1Cu:2Ag	320	322	324	330	340
2Ni:2Cu:1Ag	179	182	183	185	190

FIGURE 12: Kinetic curve of reaction of nitrophenols into aminophenol under our reaction conditions.

future. Some physical properties such as particle size and metallic surface area could be simulated successfully for whole trimetallic system.

Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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