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A novel liquid system of catalytic hydrogenation

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On the basis that endothermic aqueous-phase reforming of oxygenated hydrocarbons for H_2 production and exothermic liquid phase hydrogenation of organic compounds are carried out under extremely close conditions of temperature and pressure over the same type of catalyst, a novel liquid system of catalytic hydrogenation has been proposed, in which hydrogen produced from aqueous-phase reforming of oxygenated hydrocarbons is *in situ* used for liquid phase hydrogenation of organic compounds. The usage of active hydrogen generated from aqueous-phase reforming of oxygenated hydrocarbons for liquid catalytic hydrogenation of organic compounds could lead to increasing the selectivity to H_2 in the aqueous-phase reforming due to the prompt removal of hydrogen on the active centers of the catalyst. Meanwhile, this novel liquid system of catalytic hydrogenation might be a potential method to improve the selectivity to the desired product in liquid phase catalytic hydrogenation of organic compounds. On the other hand, for this novel liquid system of catalytic hydrogenation, some special facilities for H_2 generation, storage and transportation in traditional liquid phase hydrogenation industry process are yet not needed. Thus, it would simplify the working process of liquid phase hydrogenation and increase the energy usage and hydrogen productivity.

novel hydrogenation reaction, aqueous-phase reforming, liquid catalytic hydrogenation, coupling

Liquid phase catalytic hydrogenation is one of the most useful, broad-scoped reactions and has extensive applications in the synthesis of chemicals[1]. Currently, it is of two types, hydrogenations of organic compounds via hydrogen-transfer or with H_2 gas. For hydrogen-transfer hydrogenation, certain multi-atomic organic compounds containing hydrogen can serve as the hydrogen source in the presence of hydrogenation catalysts. Suitable donors include compounds, such as organic alcohols, hydrozines, organic acids and their salts. In general, apart from convenience, hydrogen-transfer reductions have no advantages over conventional hydrogenation. Oxidation of non-primary alcohols, the most commonly used hydrogen donors, to ketones is not an environmental-friendly procedure. In the view point of the mechanism of hydrogen-transfer reduction, the transference of hydrogen atoms takes place internally within the single molecule or between bi-molecules. Liquid phase catalytic hydrogenation using H_2 gas has been thought to be an environmentally benign method. In liquid phase catalytic hydrogenation procedure, organic reactants are reduced with H_2 gas into the products over Pt or Ni group metal catalyst in alcohol solvent. Therefore, an extra H_2 source is certainly needed.

Prof. Dumesic et al.[2−8] in the University of Wisconsin reported that H_2 could be produced from oxygenated hydrocarbons by aqueous-phase reforming (APR) under mild conditions (423−530 K) over catalyst of Pt, Raney Ni or Raney-Ni modified with Sn. Another study on H_2 production from aqueous-phase reforming of ethylene glycol deduced the same results[9]. Aqueous-phase reforming of oxygenated hydrocarbons, such as methanol, for H_2 production takes place according to the fol-

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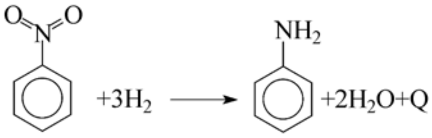
lowing stoichiometric reaction:

$$CH_3OH+H_2O \longrightarrow CO_2+3H_2-Q \qquad (1)$$

These reactions may take place via formation of CO as an intermediate product, which is subsequently converted to CO_2 by water-gas-shift reaction. Generations of H_2 and CO_2 by aqueous-phase reforming at low temperature, however, is accompanied by selectivity challenges, since the reaction of H_2 with CO or CO_2 to form alkanes (C_nH_{2n+2}) is highly favorable at these low temperatures by methanation and Fischer-Tropsch reactions[10−13]. Obviously, the reactions of alkanes formation should be effectively suppressed, if H_2 generated from the aqueous-phase reforming on the surface of catalyst could be promptly removed, or consumed by a combination with a reduction reaction of hydrogenation of organic compounds.

Comparison of the stoichiometric reaction of aqueous-phase reforming of oxygenated hydrocarbons with the chemical reaction (eq. (2)) of liquid phase hydrogenation of organic compounds, such as hydrogenation of nitrobenzene to aniline, in alcoholic solvent indicated that both procedures of H_2 production by endothermic aqueous-phase reforming of alcoholic oxygenated hydrocarbons and exothermic liquid phase hydrogenation of organic compounds are of good coincidence conditions. These two procedures are usually performed in liquid phase over an identical type of catalyst, such as Raney-Ni, Sn-Raney-Ni, Pt/Al_2O_3, Pd/Al_2O_3, etc., under the close conditions of temperature and pressure. Furthermore, “alcoholic oxygenated hydrocarbons”, “H_2O” and “H_2”, are two starting materials and one product, respectively, in aqueous-phase reforming for H_2 production, and they are “solvent”, “by product” and “starting material” correspondingly in the liquid phase hydrogenation of organic compounds. Therefore, in the present work, a novel liquid system of catalytic hydrogenation has been proposed on the basis of the coincidence of aqueous-phase reforming of alcoholic oxygenated hydrocarbons and liquid phase hydrogenation of organic compounds over an identical catalyst under the same conditions of temperature and pressure in a single reactor.



(2)

This novel liquid system of catalytic hydrogenation by the coincidence of two reactions realizes that active hydrogen on the surface of a catalyst generated from the aqueous phase reforming of oxygenated hydrocarbons is *in situ* used to the liquid phase catalytic hydrogenation of organic compound, which leads to the increase of selectivity to H_2 due to the prompt removal of H_2 from active centers of the catalyst, and also offers a potential routine to increase the selectivity to desired products of hydrogenation of organic compounds due to the fact that the activity of hydrogen *in situ* generated from the aqueous-phase reforming should be different from that of hydrogen adsorbed H_2 gas. The mechanism and stoichiometric reaction equation of novel liquid system of catalytic hydrogenation of organic compounds, such as “nitrobenzene + methanol + water”, are showed in Figure 1 and eq. (3), respectively.

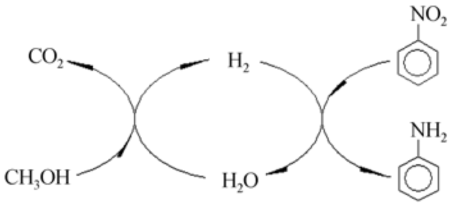
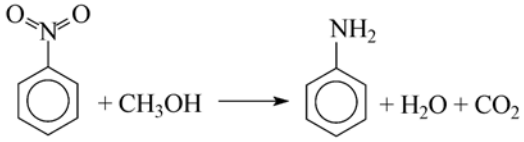
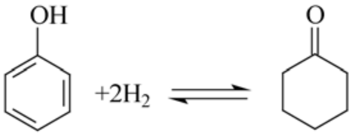


Figure 1 Sketch of mechanism for novel liquid system of catalytic hydrogenation.



(3)

This series of reaction system also includes the hydrogenation of phenol for cyclohexanone and cyclohexanol, the hydrogenation of halogenated nitrobenzene for halogenated aniline, etc. The hydrogenation reactions of phenol to cyclohexanone and cyclohexanol using H_2 gas are according to the following eqs. (4) and (5).



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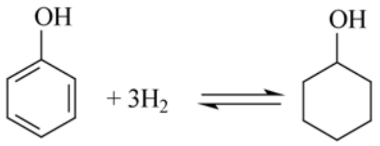
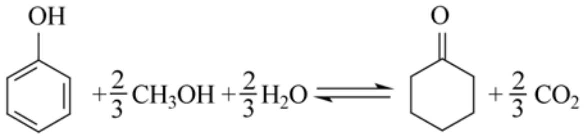


(5)

Meanwhile, the novel liquid system of catalytic hydrogenation of phenol to cyclohexanone and cyclohexanol in “phenol + methanol + water” could be expressed as the following eqs. (6) and (7).



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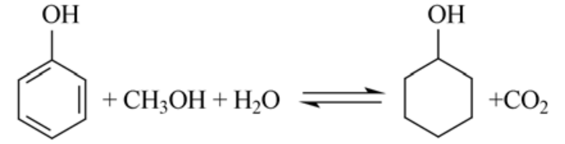


(7)

1 Experimental

1.1 Preparation and characterization of catalyst

Raney Ni catalyst was prepared from metallic alloy powders of Ni and Al with mass ratio of 9∶11. The detail was as follows: Ni-Al metallic alloy powders was slowly impregnated with 20% NaOH aqueous solution, while temperature was elevated to 353 K from room temperature, and then held at that temperature for 2—3 h to leach Al until the content of Al was less than 6wt% in the sample. The sample was subsequently washed with distilled water at 343—353 K until pH value reached about 7—8. Physical structure properties and chemical composition of Raney Ni catalyst and Ni-Al metallic alloy powders are listed in Table 1 and Figure 2, respectively.

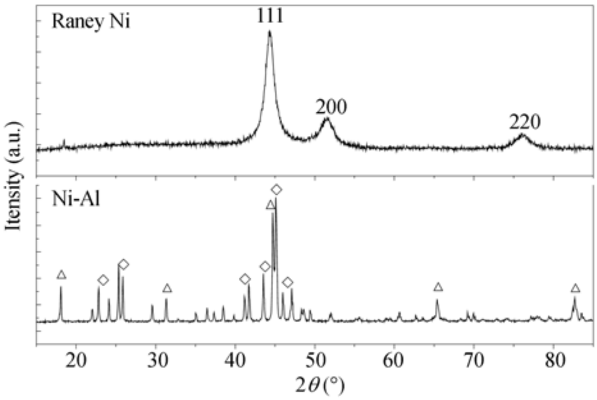


Figure 2 X-ray diffraction patterns of Raney Ni catalyst and Ni-Al alloy. ◇, Ni_3Al; △, Ni_3Al_2.

1.2 Evaluation of novel liquid system of catalytic hydrogenation

Novel liquid catalytic hydrogenation reactions of “nitrobenzene + methanol + water” or “phenol + methanol + water” were carried out in a fixed-bed reactor with a stainless-steel tube diameter of 8 mm. Raney Ni catalyst (wet mass 2.0 g) was loaded in the isothermal region of the reactor. A mixture solution of nitrobenzene : methanol∶water or phenol∶methanol∶water with a molar ratio of 1∶2.5—20∶20—80 was introduced into the reactor with an upflow configuration at LHSV of 0.706—5.3 h^{-1} with an HPLC pump. The reaction temperature is at 393—513 K, and corresponding pressure is at 0.6—4.2 MPa in Ar atmosphere. The gaseous products were analyzed using gas chromatographs (GCs) equipped with thermal conductivity detector (TCD), while the liquid products were analyzed with GC-MS (Agilent-6890GC-5973MS).

2 Results and discussion

2.1 *In situ* catalytic hydrogenation of nitrobenzene

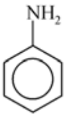
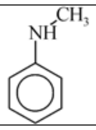
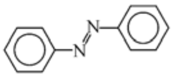
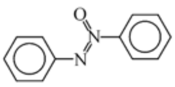
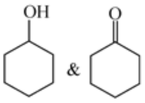
In the novel catalytic hydrogenation system of “nitrobenzene+methanol+water”, the aqueous reforming of methanol for H_2 production and liquid phase hydrogenation of nitrobenzene for aniline were synchronally performed in single reactor. Hydrogen generated from aqueous-phase reforming of methanol is *in situ* used for the hydrogenation of nitrobenzene to aniline, which is quite different from the classical liquid phase catalytic hydrogenation system. Raney Ni is used as the catalyst for hydrogenation of nitrobenzene to aniline, but also for the aqueous-phase reforming of methanol for H_2 production. Furthermore, methanol is still a solvent in this novel hydrogenation system, besides a starting material for H_2 production.

Table 2 summarizes the experimental results of novel liquid system of catalytic hydrogenation of nitrobenzene to aniline using hydrogen produced from the aqueous-phase reforming of methanol over Raney Ni catalyst. These experimental results indicated that the conversion rate of nitrobenzene was 0.73 mmol/g_{cat}/min with aniline selectivity of 96% under the conditions of temperature 403 K, pressure of 0.75 MPa and LHSV of 0.706 h^{-1}. However, the conversion rate of nitrobenzene was increased to 1.0 mmol/g_{cat}/min, the selectivity to aniline was decreased to 69.3%, and the selectivity to N-methylaniline reached to 27.6% when H_2 gas was used for catalytic hydrogenation of nitrobenzene to aniline at the same conditions in methanol solvent (nitrobenzene content is 0.75 mol/L). The difference of conversion rates of nitrobenzene and selectivities to aniline between the above two procedures could be attributed to the fact that the activity of hydrogen *in situ* generated from the aqueous-phase reforming of methanol is

Table 1 Physical structure properties and chemical composition of Raney Ni catalyst and Ni-Al alloy

Sample	Molar content (%)		Mass content (%)		Particle size (nm)	Surface area (m^2/g)	Pore volume (mL/g)
	Al	Ni	Al	Ni			
Raney Ni	12.0	88.0	5.9	94.1	22.1	131	0.204
Ni-Al alloy	64.0	36.0	45.0	55.0	41.2	15.3	0

Table 2 Experimental results of *in situ* catalytic hydrogenation of nitrobenzene[a)]

No.	Reaction conditions			Rate[b)]	Selectivity (%)					
	T (K)	p (MPa)	LHSV (h^{-1})							Other
1	393	0.60	0.706	0.36	98.4	0.48	0.30	0.82	0	0
2	403	0.75	0.706	0.73	96.0	4.00	0	0	0	0
3[c)]	403	0.75	0.706	1.00	69.3	27.6	0	1.2	1.9	0
4[d)]	403	0.75	0.706	0.77	45.0	51.3	0	0	2.7	1.00[e)]
5	423	1.2	1.76	1.09	48.7	1.80	19.5	30.0	0	0
6	433	1.6	1.76	2.21	52.1	43.8	0.69	1.4	2.01	0
7	443	1.9	3.53	2.68	70.7	29.3	0	0	0	0
8	453	2.3	1.76	3.50	23.3	46.1	0	0	5.1	25.5[f)]
9	473	3.5	7.06	6.72	38.0	55.0	0.21	0.39	4.4	2.00[f)]

a) Molar ratio of water: methanol : nitrobenzene equals 10 : 20∶1; b) mmol/g_{cat}/min; c) catalytic hydrogenation with H_2 gas; d) hydrogenation of nitrobenzene with hydrogen *in situ* generated from cracking of anhydrous methanol; e) toluene; f) *N*, *N*-dimethylaniline.

different from that of hydrogen *via* H_2 gas, besides to that the hydrogen pressures are different in these two systems. Of course, alkylation reaction between the intermediate from methanol cracking and aniline following the hydrogenation of nitrobenzene results in the decrease of selectivity to aniline greatly. Therefore, this novel liquid system of catalytic hydrogenation might be a potential way to increase the selectivity to desired product in the liquid phase catalytic hydrogenation of organic compounds.

Reaction conditions influence the product distribution of a novel liquid system of catalytic hydrogenation of organic compounds significantly. With the increase of temperature, the conversion rate of nitrobenzene will be increased, while the selectivity to aniline will be decreased. The conversion rates of nitrobenzene and the selectivities to aniline at 393, 423 and 453 K are 0.36, 1.09, 3.5 mmol/g_{cat}/min and 98.4, 48.7, 23.3%, respectively. Apart from the desired product aniline, azobenzol with 19.5% selectivity and oxygenated azobenzol with 30% selectivity were formed at 423 K; and *N*-methylaniline with 46.1% selectivity, *N*, *N*-dimethylaniline with 25.5% selectivity and cyclohexanol, cyclohexanone with 5.1% selectivity were formed at 453 K. The formations of *N*-methylaniline, *N*, *N*-dimethylaniline, azobenzol, cyclohexanol, cyclohexanone and cyclohexylamine might be attributed to the fact that the requirement of higher temperature for aqueous phase reforming of methanol would promote the occurrence of N-alkylation of aniline further with methanol[14], and the gap between H_2 production rate from aqueous reforming of methanol and H_2 consumption rate by hydrogenation of nitrobenzene changes with the temperature; which would result in the production of azobenzol and cyclohexylamine. Also, the occurrence of alcoholysis or hydrolyze of cyclohexylamine with methanol[15,16] would lead to the formation of cyclohexanol and cyclohexanone. Figure 3 shows the reaction pathways for novel liquid system of catalytic hydrogenation of nitrobenzene. In the procedure of *in situ* hydrogenation of nitrobenzene, the reactions include the portion hydrogenation of nitrobenzene to form the intermediates hydroxylamine and azobenzene, then the hydrogenation of azobenzene to produce aniline, also the hydrolysis of azobenzene and hydroxylamine to form oxygenated azobenzene, subsequently the hydrogenation of oxygenated azobenzene to produce azobenzene, and finally the hydrogenation of azobenzene to form the desired product aniline. However, the further hydrogenation of aniline will produce cyclohexylamine, and C-alkylation and N-alkylation of aniline with alcoholic oxygenated hydrocarbons will produce methyaniline and *N*-methylaniline. Therefore, more studies on the optimization of catalyst and reaction conditions are required because of the coincidence complexity of series and parallel reactions in this novel liquid system of hydrogenation of organic compounds.

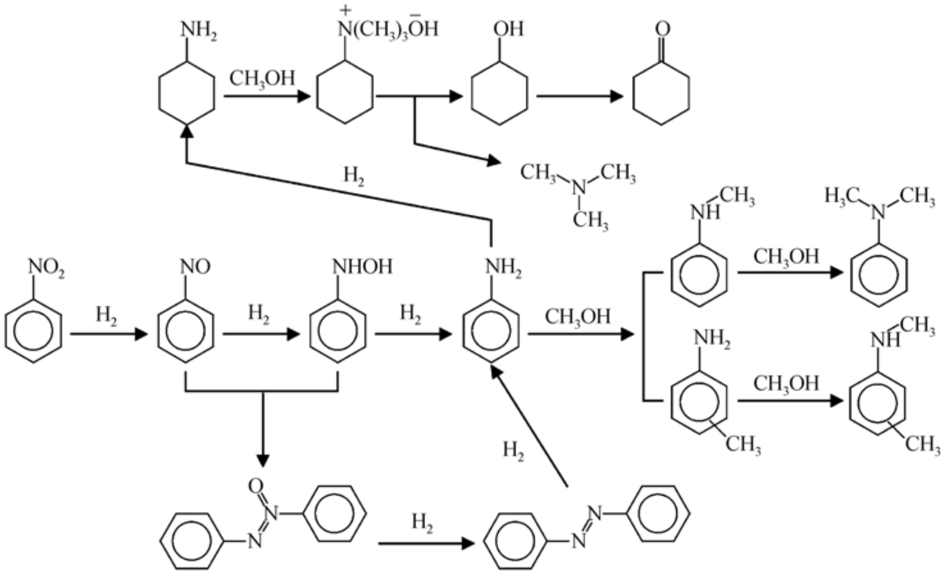


Figure 3 Reaction pathway for novel liquid system of catalytic hydrogenation of nitrobenzene.

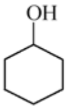
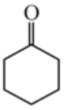
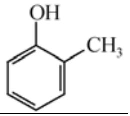
The hydrogenation of nitrobenzene to aniline in the system of "nitrobenzene + methanol" has been explored under the conditions of temperature 403 K, pressure 0.75 MPa and LHSV of 0.706 h^{-1}. In this case, the conversion rate of nitrobenzene is 0.77 mmol/g_{cat}/min, the selectivities of aniline, and *N*-methylaniline are 45 and 51.3%, respectively. A small amount of toluene has also been detected, while no toluene has been formed in the system of "nitrobenzene + methanol + water". This experimental result indicated that the hydrogenation of nitrobenzene with hydrogen *in situ* generated from the cracking of methanol is of significant difference from that with hydrogen *in situ* generated from the aqueous-phase reforming of methanol. The absence of CO in the gas products showed that CO generated from the cracking of methanol would quickly converted into CO_2 (yield 0.559 μmol/g_{cat}/min) and H_2 with H_2O formed from hydrogenation of nitrobenzene through water-gas shift reaction[17,18].

2.2 *In situ* catalytic hydrogenation of phenol

In the novel liquid system of catalytic hydrogenation of "phenol + methanol +water", the experimental results of hydrogenation of phenol for cyclohexanone and cyclohexanol using hydrogen *in situ* generated from aqueous-phase reforming of methanol over Raney Ni catalyst are listed in Table 3. The total selectivity to cyclohexanone and cyclohexanol maintains at over 99% under extensive conditions of temperature, pressure, and LHSV. Only a small amount of by-products (<1%), such as benzene and cresol, are formed. However, reaction conditions (temperature, pressure, LHSV, and molar ratio of starting materials) highly influence the ratio of cyclohexanone to cyclohexanol, thus further study on how to increase the selectivity to cyclohexanone is necessary. Figure 4 shows the reaction pathways of a novel liquid system of catalytic hydrogenation of phenol for cyclohexanone and cyclohexanol. As the same as the novel liquid catalytic hydrogenation system of "nitrobenzene + methanol + water", the aqueous-phase reforming of methanol for H_2 production and liquid phase hydrogenation of phenol were performed synchronally in a single reactor in the novel liquid hydrogenation system of "phenol+methanol+water". The hydrogen generated from aqueous-phase reforming of methanol is used for the catalytic hydrogenation of phenol, so an extra source of H_2 is not needed. Raney Ni is used as the catalyst for the liquid phase hydrogenation of phenol to cyclohexanone and cyclohexanol, but also for the aqueous-phase reforming of methanol for H_2 production. Furthermore, methanol is still a solvent in this novel hydrogenation system, besides a starting material for H_2 production.

The hydrogenation of phenol for cyclohexanone and cyclohexanol using hydrogen *in situ* generating from the cracking of methanol is also further explored. Under the conditions of temperature 493 K, pressure 3.5 MPa and LHSV of 3.53 h^{-1} with the mixture solution of phenol∶methanol at molar ratio of 1∶100, the conversion

Table 3 Experimental data for novel catalytic hydrogenation of phenol to cyclohexanone and cyclohexanol

No.	Reaction condition				Conversion (%)	Selectivity (%)			
	H_2O∶methanol∶ phenol (molar ratio)	T (K)	p (MPa)	LHSV (h^{-1})					
1	80∶20∶1	493	3.5	3.53	53.1	0.22	79.15	20.53	0.1
2	80∶20∶1	473	2.4	3.53	10.4	0	58.23	41.77	0
3[a)]	0∶100∶1	493	3.5	3.53	82.27	0	54.1	32.6	13.3
4	40∶20∶1	433	0.9	3.53	4.41	4.2	59.54	36.26	0
5	40∶20∶1	513	5.0	3.53	78.55	0	78.69	20.69	0.61
6	40∶20∶1	493	3.5	0.706	80.40	0	85.49	14.51	0
7	40∶20∶1	493	3.5	5.29	8.29	4.28	38.83	56.92	0
8	20∶5∶1	493	3.5	1.76	31.66	0.65	69.84	29.52	0
9	40∶10∶1	493	3.5	3.53	49.40	0.22	72.54	26.50	0.73
10	80∶10∶1	493	3.5	3.53	63.72	0.225	83.33	16.36	0.075
11	40∶5∶2	493	3.5	3.53	83.32	1.97	81.62	16.4	0
12	80∶5∶0.5	493	3.5	3.53	57.84	0.379	79.95	19.67	0
13	40∶10∶0.5	493	3.5	3.53	54.60	0.24	85.32	14.44	0
14	20∶10∶2	493	3.5	3.53	28.25	4.61	61.42	31.4	2.56
15	20∶20∶0.5	493	3.5	3.53	58.73	0.355	80.68	18.23	0.736
16	20∶5∶1	493	3.5	3.53	31.66	0.65	69.84	29.52	0

a) Catalytic hydrogenation with H_2 gas.

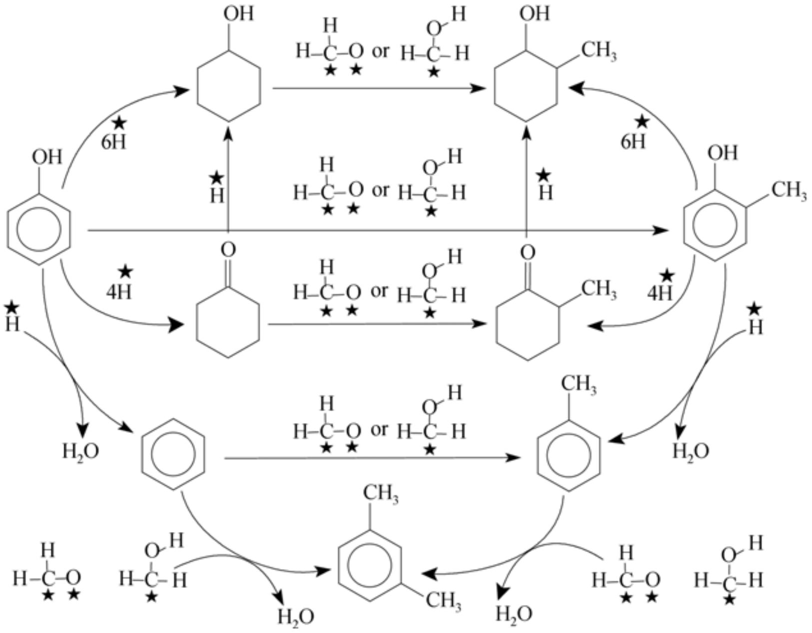


Figure 4 Reaction pathway for liquid phase *in situ* hydrogenation of phenol (asterisk represents a surface metal site).

rate of phenol is 2.44 μmol/g_{cat}/min (conversion percentage 15.12%), and the selectivities of cyclohexanone, cyclohexanol, toluene, *p*-xylene, and cresol are 17.91, 42.54, 14.98, 12.07 and 12.50%, respectively. The experimental result indicated that the intermediate from the cracking of methanol for H_2 production is favorable to the occurrence of C-alkylation with phenol in anhydrous condition, which results in the formation of toluene, *p*-xylene and cresol. Under the same conditions of temperature, pressure and LHSV, the conversion rate of phenol has been increased significantly and the total selectivity of cyclohexanone and cyclohexanol reaches to exceeding 99% in the system of “phenol + methanol + water” with molar ratio of 1∶20∶80 (seeing in Table 3). In the case of anhydrous state, the gaseous yeilds of H_2, CH_4 and CO are 53, 11.5 and 41.8 μmol/g_{cat}/min, respectively, but no CO_2 has been detected in the gas products. This experimental result further indicated that

Table 4 Experimental data for gaseous products in novel catalytic hydrogenation and aqueous phase reforming

Reaction conditions			Total carbon in gas ($\mu mol \cdot g_{cat}^{-1} \cdot min^{-1}$)		Hydrogen selectivity (%)	
T (K)	*p* (MPa)	LHSV (h^{-1})	Novel system 1[a)]	APR of methanol[b)]	Novel system 1[a)]	APR of methanol[b)]
453	1.8	3.53	6.12	5.52	59.5	51.9
473	2.4	3.53	23.19	22.5	56.0	36.5
493	3.5	3.53	69.2	67.4	49.3	45.4
513	5.0	3.53	179.8	135.8	65.3	43.8
			Novel system 1[c)]	APR of methanol[d)]	Novel system 1[c)]	APR of methanol[d)]
403	0.75	0.706	0.56	–	100	–
433	1.6	1.76	18.37	1.63	93.7	26.7
443	1.85	3.53	22.49	3.72	95.9	25.6
473	3.5	7.06	98.60	19.24	81.6	20.5

a) Molar ratio of water: methanol : phenol equals 80∶20∶1; b) molar ratio of water: methanol equals 80∶201; c) molar ratio of water∶methanol ∶nitrobenzene equals 80∶20∶1; d) molar ratio of water∶methanol equals 10∶20.

the water-gas-shift reaction between CO and H_2O takes place easily to produce CO_2 and H_2 in the presence of H_2O; while H_2 is only from the cracking of methanol in the absence of H_2O. In comparison of the experimental results of the coincidence system of the aqueous reforming of alcoholic oxygenated hydrocarbons and catalytic hydrogenation of organic compounds with the coupling system of the cracking of alcoholic oxygenated hydrocarbons and catalytic hydrogenation of organic compounds, their selectivities to the desired products are highly different.

2.3 Novel liquid system of catalytic hydrogenation and aqueous-phase reforming

The usage of hydrogen generated from aqueous-phase reforming of alcoholic oxygenated hydrocarbons *in situ* for catalytic hydrogenation of organic compounds leads to the prompt transference of adsorbed active hydrogen from the surface of the catalyst into the organic compound, it suppresses the alkylation occurrence of CO and/or CO_2 with H_2 by methanation and Fischer-Tropsch reactions, and it increases the selectivity to H_2 in the aqueous-phase reforming of alcoholic oxygenated hydrocarbons. The composition of gaseous products in the aqueous-phase reforming of methanol for the systems of “methanol+water”, “nitrobenzene+methanol+water” and “phenol+methanol+water” are listed in Table 4, respectively. The experimental results listed in Table 4 indicate that the selectivity to H_2 and the conversion rate of methanol are highly increased in the aqueous-phase reforming of methanol as a coincidence of the aqueous-phase reforming of methanol with the catalytic hydrogenation of nitrobenzene or phenol. Meanwhile, no CO has been detected. Therefore, both the activity and selectivity for aqueous-phase reforming for H_2 production are highly improved through the coincidence of these two reactions.

3 Conclusion

A novel liquid system of catalytic hydrogenation has been proposed, where the coincidence of endothermic aqueous-phase reforming for H_2 production and exothermic liquid phase catalytic hydrogenation realized that H_2 production and hydrogenation reactions were carried out in single reactor. In this novel reaction system, the usage of hydrogen generated from the aqueous-phase reforming of alcoholic oxygenated hydrocarbons *in situ* for the reduction of organic compounds could promptly remove the hydrogen on the active centers of catalyst from the aqueous-phase reforming, which increases the selectivity to H_2 in the aqueous-phase reforming. Meanwhile, it might be a potential method to increase the selectivity to the desired product of liquid phase hydrogenation of organic compounds. Compared with conventional hydrogenation method, this novel liquid system of catalytic hydrogenation does not need an extra H_2 source. The active hydrogen atom directly generated from reaction solvent, such as alcoholic oxygenated hydrocarbons like methanol, by the aqueous-phase reforming was used for the hydrogenation of organic compounds. On the other hand, some special facilities for H_2 generation, storage and transportation in traditional liquid phase hydrogenation industrial process are not yet needed. Thus, it would simplify the working process. In the novel liquid systems of catalytic hydrogenation of “nitrobenzene + methanol + water” or “phenol + methanol + water”, a high conversion and selectivity could be achieved. However, more studies on the optimization of catalyst and reaction conditions are important to realize the balance between H_2 production from aqueous-phase reforming and its consumption by catalytic hydrogenation in this novel liquid system of catalytic hydrogenation.

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