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Innovative cyclohexanone synthesis *via* transfer hydrogenation of phenol and cyclohexanol

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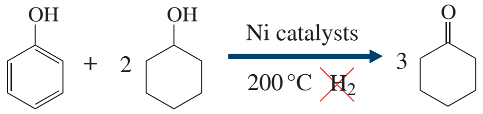
Novel and promising approach for cyclohexanone synthesis *via* the comproportionation reaction of cyclohexanol and phenol over conventional Raney nickel and Ni/Al$_2$O$_3$ was examined for the first time. Ni/Al$_2$O$_3$ catalyst was prepared by coprecipitation in supercritical CO$_2$.

Comproportionation of phenol and cyclohexanol



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Cyclohexanone is a platform molecule used as a precursor for polyamide synthesis. One of the primary methods to produce this ketone is the H$_2$ hydrogenation of phenol.[1] A notable drawback of this approach is the relatively low selectivity resulting from the hydrogenation of cyclohexanone to cyclohexanol. This limitation can be addressed by replacing H$_2$ with cyclohexanol, which acts as a hydrogen donor. In this scenario, transfer hydrogenation (TH) of cyclohexanol and phenol occurs yielding solely cyclohexanone. Earlier, cyclohexanol has been used in TH of carbonyl compounds over oxides,[2,3] and Cu-based catalysts.[4–7] At the same time, alcohols as hydrogen donors have exhibited remarkable efficacy in TH of a wide range of molecules, including phenolics,[8] asphaltenes,[9] levulinic acid,[10] 5-hydroxy-methylfurfural,[11] *etc*.[12,13] Pr^{i}OH is the most used lower aliphatic donor alcohol due to its excellent performance. However, acetone, formed from Pr^{i}OH, should be recycled or used for other purposes as it is not a high value product. Therefore, forming valuable products from hydrogen donor seems to be a promising approach to increase the economic viability of TH. This suggests that cyclohexanol is a perspective and green[14] candidate for use as a hydrogen donor.

The use of secondary alcohols in the TH of phenol results in the formation of cyclohexanol.[15–17] Consequently, the phenol hydrogenation and cyclohexanol dehydrogenation, which ultimately yields cyclohexanone, represents an optimal approach for the synthesis of the ketone *via* TH. The aforementioned process can be effectively catalyzed by Ni catalysts, which demonstrate excellent activity in TH of both phenolic compounds and secondary alcohols.

Here, we report for the first time the results of cyclohexanone synthesis *via* TH of phenol and cyclohexanol. In our comparative study, the TH was tested at different cyclohexanol to phenol ratios (see Table S2 in Online Supplementary Materials) over Raney nickel and Ni/Al$_2$O$_3$, which was prepared by coprecipitation in supercritical CO$_2$. The properties of both catalysts were ascertained through XRD, N$_2$ adsorption, XRF and HRTEM (for details, see Online Supplementary Materials). The catalysts have similar Ni content (87%) and BET surface area (79–81 m^2 g^{-1}), however, larger pore and particle size is typical for Ni/Al$_2$O$_3$ (see Table S1). The catalytic experiments below 200 °C were conducted in a 100 ml flask reactor and at 200–250 °C in a stainless steel 90 ml batch reactor.

The low thermal stability of Raney nickel significantly limits the temperature suitable for catalytic transformations.[18,19] Based on this, the first experiment was carried out at 100 °C using a molar ratio Raney nickel to phenol to cyclohexanol of approximately 1 : 10 : 100 (entry 2, hereinafter refers to Table 1), respectively. After 3 h at the target temperature, the conversion of phenol reached only 4%, and cyclohexanone was found as the only volatile product with a yield of 2.9 mmol. It is noteworthy that some amount of cyclohexanone can be formed *via* dehydrogenation of the alcohol, no phenol is required. Phenol displays high reactivity in TH over heterogeneous Ni-based catalysts, therefore, possible explanation for the observed low phenol conversion at 100 °C is the low donor activity of cyclohexanol. To test this, cyclohexanol was replaced with boiling Pr^{i}OH (entry 1). In this case, cyclohexanol was observed as the sole product. The use of Pr^{i}OH resulted in the 13% conversion of phenol, which was significantly higher than that observed for cyclohexanol. Thus, Pr^{i}OH demonstrated superior donor activity, however, no cyclohexanone was identified in the final reaction mixture.

After temperature increase to 150 °C (entry 3) the conversion remained low, reaching 11%, and the yield of cyclohexanone was 14 mmol. Increasing the reaction temperature to 200 °C has a significant impact on phenol conversion, reaching 86% over Raney nickel. This is accompanied by a cyclohexanone yield of 58 mmol (entry 9). The low phenol conversion and yield of cyclohexanone at temperatures below 200 °C can be attributed to strong adsorption of phenol on the catalyst surface.[20] After treatment at 200 °C Raney nickel underwent sintering that results in nickel crystallites aggregation, with the mean size increase from 3 to 10.0 nm (Table S1).

In order to demonstrate the effect of phenol concentration on the conversion, its quantity was reduced from 38 mmol to 6.3 mmol and 3.2 mmol (entries 4 and 5, respectively). This resulted in a higher conversion of phenol, which reached 47% and 79%, respectively.

To reduce competitive adsorption of the reactants on the catalyst surface, the load of both phenol and cyclohexanol was

Table 1 Phenol conversion and cyclohexanone yield in TH of phenol and cyclohexanol over Ni catalysts under different conditions. Time of each experiment is 3 h. Amount of PhOH is 38 mmol.

Entry	Catalyst	*T*/°C	PhOH to CyOH molar ratio	PhOH conversion (%)	Yield of cyclohexanone/ mmol
1	Raney nickel	82[a]	1 : 10	13	0
2		100	1 : 10	4	2.9
3		150	1 : 10	11	14
4		150	6 : 100[b]	47	12
5		150	3 : 100[c]	79	9.1
6		137	1 : 10[b]	49	4.1
7		200	1 : 2	56	40
8		200	1 : 5	71	51
9		200	1 :10	86	58
10		200	–[d]	–	22
11		200	–[d]	–	4.5
12	Ni/Al_2O_3	150	1 : 10	2	0.31
13		200	1 : 2	55	32
14		200	1 : 5	69	47
15		200	1 : 10	81	59
16		250	1 : 10	81	71

[a] Pr^iOH was used as hydrogen donor. [b] Amount of PhOH is 6.4 mmol. [c] Amount of PhOH is 3.2 mmol. [d] Phenol-free experiment.

decreased 6-fold, and the mixture was diluted with inert pentadecane (entry 6). The formed mixture was boiled at 137 °C, and the conversion of phenol reached 49%, which is slightly higher than the similar pentadecane-free transformation. Conversely, the yield of cyclohexanone exhibited a notable decline from 12 mmol to 4.1 mmol.

Additionally, experiments were conducted utilizing pentadecane as an inert solvent at 200 °C (entries 7 and 8). The phenol to cyclohexanol ratios reached 1 : 2 and 1 : 5, respectively. The reduction in the alcohol content resulted in the decrease in the conversion of phenol to 71% and 56% transformed into products. The yield of cyclohexanone also decreased from 58 mmol in pentadecane-free TH (entry 9) to 51 mmol and 40 mmol when the phenol to cyclohexanol ratio was reduced to 5 : 1 and 2 : 1, respectively.

To assess the impact of cyclohexanol dehydrogenation, supplementary experiments (entries 10 and 11) were conducted under phenol-free conditions at 200 °C. It was demonstrated that 22 mmol of ketone was formed from cyclohexanol. The dilution of cyclohexanol with pentadecane caused a reduction in the yield of cyclohexanone reaching 4.5 mmol. This indicates that hydrogen acceptor-free transformations of cyclohexanol proceed, although they result in lower yields of cyclohexanone compared with those observed in the co-processing of phenol and cyclohexanol.

The treatment of Ni/Al_2O_3 in the TH of phenol and cyclohexanol was initiated at 150 °C (entry 12). The results were notably low, aligning with the outcomes observed with Raney nickel. The Ni/Al_2O_3 catalyst maintains high dispersion following activation in a H_2 flow at 450 °C, indicating that this catalyst can be utilized at elevated temperatures. Also, this is consistent with XRD data showing no nickel particles agglomeration of Ni/Al_2O_3 in TH (Figure 1). An increase in temperature to 200 °C (entry 15) resulted in a significant enhancement in phenol conversion, reaching 81%. The yield of cyclohexanone increases to 59 mmol, which complies with the data obtained in the experiment with Raney nickel.

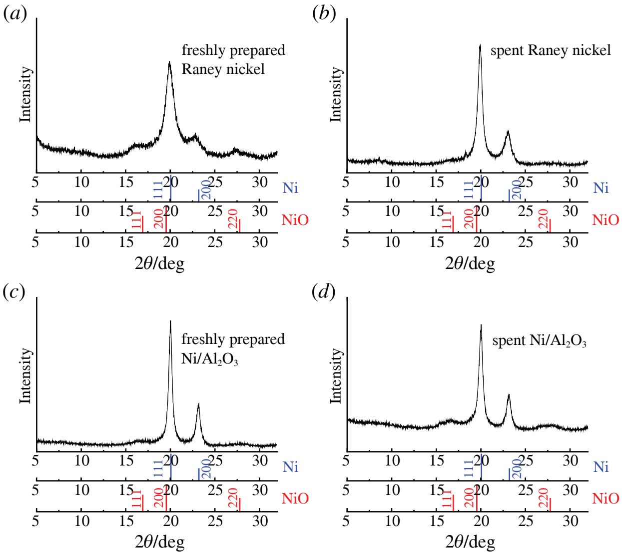

Figure 1 XRD data of (*a*) freshly prepared and (*b*) spent Raney nickel, (*c*) freshly prepared and (*d*) spent Ni/Al_2O_3 samples after 3 h at 200 °C.

The temperature increase to 250 °C did not affect the conversion of phenol (entry 16). This may be due to the competitive adsorption of numerous oxygen-containing compounds on the catalyst surface. At 250 °C, the highest yield of cyclohexanone (71 mmol) was observed (entry 16). In contrast to the previous experiments, cyclohexanone was not the sole volatile product, owing to deoxygenation, which resulted in the formation of cyclohexane (8.9 mmol) and benzene (6.0 mmol), and dehydration, which causes the generation of dicyclohexyl (2.3 mmol) and phenylcyclohexyl (2.5 mmol) ethers.

To optimize the conditions for the transformation TH, the amount of cyclohexanol was decreased to the mole ratios 5 : 1 and 2 : 1 to phenol (entries 14 and 13, respectively). This resulted in a decrease in conversion to 69% and 55% and yield to 47 mmol and 32 mmol at 200 °C, respectively. It can be postulated that a lower cyclohexanol concentration results in a smaller amount of H_2 formed, which in turn caused a lower catalyst surface concentration. This has negatively affected both phenol hydrogenation and the yield of cyclohexanol.

In conclusion, it was revealed that Raney nickel and Ni/Al_2O_3 have a limited activity in TH of cyclohexanol and phenol at low temperatures. However, at 200 °C high phenol conversion and cyclohexanone yield were achieved. The simple procedure of the Raney nickel synthesis and the high availability of this catalyst suggest promising prospects for its use in preparative synthesis, however, low thermal stability limits the scope of its applications. In contrast to Raney nickel, Ni/Al_2O_3 demonstrates high thermal stability, although the catalyst synthesis procedure is more complex.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7603.

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