SUPPORTING INFORMATION

Nickel-based perovskite-catalysed direct phenol-to-aniline liquid-phase transformations

Anna Adél Ádám,[‡a] Sándor Balázs Nagy,[‡a] Ákos Kukovecz,[b] Zoltán Kónya,[bc] Pál Sipos[a] and Gábor Varga*[b]

[a]Department of Molecular and Analytical Chemistry and Materials and Solution Structure Research Group, University of Szeged, Dóm tér 7, Szeged, H-6720 Hungary

[b]Department of Applied and Environmental Chemistry and Interdisciplinary Excellence Centre, Institute of Chemistry, University of Szeged, Rerrich Béla tér 1, Szeged, H-6720 Hungary

[c]HUN-REN-SZTE Reaction Kinetics and Surface Chemistry Research Group, Rerrich Béla tér 1, H-6720 Szeged, Hungary

‡These authors contributed equally. *Corresponding author: G. Varga (gabor.varga5@chem.u-szeged.hu)

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EXPERIMENTAL PART

1. Materials

All the applied compounds were the products of analytical grade from Sigma–Aldrich, and they were used as received.

2. The preparation route of the catalysts

$LaNiO_3$ perovskite-type and $La_{n+1}Ni_nO_{3n+1}$ (n= 1, 2, and 3) Ruddlesden-Popper-type (RP) structures were synthesized by using a standard sol-gel process involving ethylenediaminetetraacetic acid (EDTA) and sodium citrate complexing agents following Yu et al.'s procedure.[1] Briefly, stoichiometric amounts of $La(NO_3)_3 \times 6H_2O$ and $Ni(NO_3)_2 \times 6H_2O$ were first dissolved in deionized water while vigorously stirring followed by the addition of EDTA and sodium citrate to the solution as the complexing agents, setting up the molar ratio of EDTA/total metal ions/citric acid of *1:1:2*. The pH of the solution was adjusted to 6 with 25% NH_4OH solution. After evaporating the water, a gel was obtained which was dried at 250 °C in a furnace for 5 hours in air which resulted in a foam-like precursor. This precursor was further calcined at 800 °C for 8 hours for perovskite and at 1050 °C for 24 hours for RP structures in air, respectively.

The fcc Ni nanoparticles (NPs) were synthesized by chemical reduction, based on our previous study.[2] First, NiI_2 of 5 mmol was dissolved in 12.5 ml absolute ethanol. Then the potassium hydroxide (Ni^{2+}/KOH = 1/10) and the hydrazine monohydrate (Ni^{2+}/N_2H_4 = 1/10) were also mixed with 12.5 ml absolute ethanol in another vessel. The first solution was added into the second one and the mixture was stirred at 25 °C for 4 h. The obtained slurry was filtered and washed with 20–20 ml distilled water and absolute ethanol, then dried at 25 °C under a desiccator for 2 days.

For NiO particles, a direct precipitation method from $NiSO_4 \times 6H_2O$ solution was applied. In particular, a NaOH solution of 0.5 M was drop-by-drop added to 25 ml of $NiSO_4$ solution of 0.5 M. This dropping was kept until the solution pH obtained a value of 11 when $Ni(OH)_2$ precipitated. All products were collected by centrifugation (4750 rpm at room temperature for 15 min), washed several times with deionized water, and dried in an oven at 110 °C overnight. NiO nanoparticles were directly derived from $Ni(OH)_2$ by thermal decomposition at 350 °C for 2 hours in an air atmosphere.

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Pure Ni_2O_3 was prepared by a sustained oxidation of nickel precursor following Dey et al.'s procedure.[3] Briefly, 1.00 g of $Ni(NO_3)_2 \times 6H_2O$ was dissolved in deionized water of 20 ml under constant stirring. In another vessel, NaOH of 1.60 g was dissolved in 15 ml of sodium hypochlorite solution. This alkaline solution of hypochlorite was dropped into the nickel-containing solution and rigorously stirred. The stirring was continued for the formation of a black precipitate ($Ni_2O_3 \times 2\,H_2O$). The solid sample was then collected by centrifugation (4750 rpm at room temperature for 30 min), washed thoroughly with deionized water, and dried to form a greyish-black powder of nickel(III) oxide.

For the synthesis of Al_2O_3, La_2O_3 and MgO-supported $Ni/NiO/Ni_2O_3$ catalysts, a simple wet impregnation method was used. In the first step, the corresponding pre-prepared nickel specimen of 100 mg was completely suspended in an ethanol solution of 100 ml with the aid of ultrasonication. This was followed by the addition of the appropriate amount (500 mg) of the corresponding support materials purchased while rigorously stirring the ethanolic suspension. The obtained slurries were stirred at 50 °C for 24 hours before centrifuged (4750 rpm at room temperature for 15 min), washed with ethanol twice – and dispersed and centrifuged again – and dried at 150 °C overnight.

3. Structural characterization methods

The powder X-ray diffraction (XRD) patterns were recorded in the $\theta = 4 - 70^o$ range by a Rigaku Miniflex II instrument with 4°/min scan speed using CuKα (λ = 1.5418 Å) radiation. The identification of the characteristic reflections in the normalized diffractograms was done according to the JCPDS-ICDD (Joint Committee of Powder Diffraction Standards-International Centre for Diffraction Data) database.

Nitrogen sorption isotherms of the samples were obtained using a Quantachrome NOVA 3000e instrument at 77 K. The [Brunauer–Emmett–Teller (BET)] specific surface areas were calculated using adsorption data at a relative pressure range of p/p0 = 0.05–0.25. Before the measurements, the samples were degassed at 180 °C for 5 h in vacuum, to remove the surface adsorbents.

The amount of metal ions incorporated into the as-prepared, composite/mixed oxide catalysts as well as potential leaching during the catalytic reactions were monitored by inductively coupled plasma-mass spectrometry (ICP-MS) on an Agilent 7700× instrument. Before measurements, a few milligrams of the samples measured by analytical accuracy were digested in 1.0 ml of concentrated nitric acid, and then, they were diluted with distilled water to 50 ml and then filtered.

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The acidic sites of the perovskite catalysts were also characterized by using NH_3-temperature programmed desorption (TPD) technique. TPD measurements were carried out on a Hewlett-Packard 5890 GC system equipped with a TCD detector. Before the measurements, a quartz tube was loaded with a portion of the sample (100 mg) followed by an initial purge in a He stream (50 ml min^{-1}) at room temperature for 10 min to remove impurities. The temperature was then raised to 375 °C using the ramp rate of 10 °C min^{-1} and then held for 1 hour to remove water and other impurities. The temperature was then lowered to 100 °C. Finally, the gas was changed to 99.3% NH_3 in He (30 ml min^{-1} NH_3, 50 ml min^{-1} He) and circulated over the sample for 1 h. The gas was then removed from the sample by systematically increasing the temperature.

Temperature-programmed reduction (H_2-TPR) was performed in a BELCAT-A apparatus using a reactor (quartz tube with a 9 mm outer diameter) that was externally heated. Before the measurements, the catalyst samples were treated in argon at 300 °C for 90 min to remove impurities and surface adsorbed water. Thereafter, the samples were cooled in flowing Ar to room temperature and equilibrated for 15 min. The pre-treated samples were flushed with Ar containing 10% H_2 and then the reactor was heated linearly at a rate of 20 °C min^{-1} up to 700 °C and the H_2 consumption was detected by a thermal conductivity detector (TCD).

4. Optimized procedure for the catalytic reactions

The catalytic test reactions were carried out in a batch reactor of 5 ml equipped with a reflux condenser using hot plate for heating. In a typical experiment, 0.2 mmol of phenol (or its derivatives), 0.3 1.2 mmol of hydrazine monohydrate, 100 mg of the molecular sieves/0.3 mmol hydrazine monohydrate, catalyst of 10 mol% to phenol regarding Ni-centres as active ones and solvent of 4 ml were added to the reactor. In some cases, LiOH of 40 mol% to phenol was also added to the system as hydride source. The mixture was heated to reflux temperature and the reaction time was 24 h. After the reaction, the catalysts were removed by centrifugation (6000 rpm at room temperature for 15 min). Finally, the clear liquid was injected into the gas chromatograph (GC). The GC was a Hewlett-Packard 5890 Series II instrument equipped with 50-m-long-Agilent HP-1 column and flame ionization detector (FID). To quantify the obtained solutions, an internal standard method was used involving 1-octanol as standard. It is important to note, that the catalysts were activated at 130 °C for 3 h in an air atmosphere before each use. The products were identified by comparing them with authentic samples. Turnover frequency (TOF) values were determined by considering the linear part of the kinetic curve of the

perovskites-catalysed phenol-to-aniline transformations. For calculating TOF values, the catalyst loading was taken into account (mmol (aniline) g^{-1} (catalyst) h^{-1}).

To determine the heterogeneity of the catalytic reaction, a hot filtration test was also introduced. The amination was carried out under the optimized reaction conditions. The bulk catalyst was readily removed by simple centrifugation after 16 h (aniline yield: ~50 mol%). Then, in the absence of perovskite, the filtrate was further treated under the same optimized reaction conditions and the further progress of the reaction was also analysed. The filtrate was analysed by ICP-MS as well to study the possibility of the leaching of the cationic components.

To investigate the recyclability of the catalyst, after a phenol-to-aniline reaction carried out under the optimized reaction conditions, the catalyst was separated from the reaction mixture by centrifugation (6000 rpm at room temperature for 15 min), washed with water and DMSO, heat-treated at 130 °C for 3 hours, and reused under the optimized reaction conditions.

To support the proposed catalytic reaction mechanism, three different control experiments were performed when using $LaNiO_3$ perovskite as the actual catalyst.

1, Catalytic isomerisation of glucose to fructose was carried out at 100 °C under a nitrogen atmosphere. 5 ml of glucose solution of 10wt% was prepared for isomerisation reaction, into which 100 mg of perovskite catalyst was added. First, N_2 was introduced in the reactor, and then the temperature was increased up to the reaction temperature. The heating/stirring time was 60 minutes long. The resulting solution was collected after cooling down the reactor to room temperature and analysed with an NMR spectroscopy method previously published.[4]

2, To test the activity of the catalyst in transfer hydrogenation reaction, 1 mmol of nitro compound was added into a reactor with 20 mg of catalyst. 2 ml of water was added as solvent. The 60-minute-long reaction took place at 110 °C, and the yield was monitored by GC-FID using the internal standard method.

3, The catalytic capability of the perovskite structure was tested in a quinoxaline synthesis from o-phenylenediamine. For this test reaction, the perovskite catalyst of 20 mg, o-phenylenediamine (0.25 M), and ethylene-glycol of 2 ml were placed into a 2.5 ml round bottom flask. After vigorous stirring (500 rpm) for 5 minutes, the mixture was heated up to 110 °C and it was maintained at that temperature for 24 h stirring continuously. The reaction mixture was then cooled in an ice bath and the catalyst was removed by centrifugation (6000 rpm at room temperature for 15 min). The organic part was extracted with ethyl acetate (3 × 8 ml) and the solvent was evaporated under reduced pressure after drying over anhydrous Na_2SO_4. The conversion and selectivity were determined by GC-FID using the internal standard method.

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4, To understand the mechanism of the first, reduction step of the reaction pathway, the reaction studied was repeated under the same reaction conditions used/optimized. However, during these control experiments, either cyclohexanone or 2-cyclohex-1-one was use as reactant instead phenol.
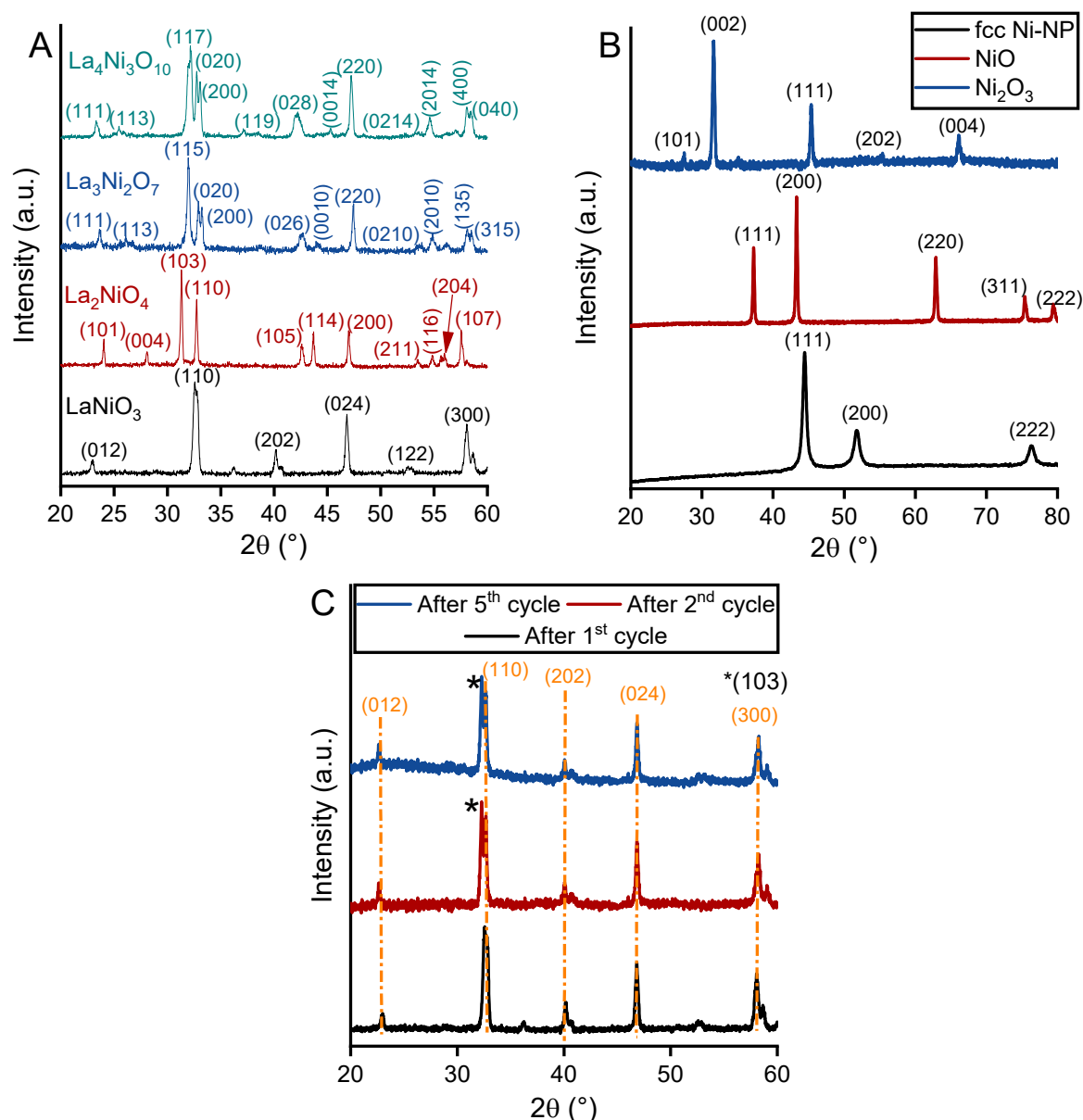
SUPPORTING RESULTS

Figure S1. XRD patterns of (A) the as-prepared La-Ni-perovskites, (B) the as-prepared nickel- and nickel-oxide specimens as well as (C) spent catalysts. (*new phase possibly related to the La_2NiO_4 structure)

Evaluation:

The different as-prepared structures were identified by the following JCPDS cards:

$LaNiO_3$: PDF#34–1028

La_2NiO_4: PDF#011–0557

$La_3Ni_2O_7$: PDF#50–0244

$La_4Ni_3O_{10}$: PDF#50–0243

fcc Ni NP: PDF#04–0850

NiO: PDF#01–1239

Ni_2O_3: PDF#14–0481

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Table S1. Characteristics of the as-prepared Ni-containing catalysts.

Entry	Composite	Actual Ni : M ratio[1]	Composition[2]	Specific surface area (m²/g)[3]
1	Ni/Al_2O_3	0.14	5.2 wt% Ni/Al_2O_3	188.0
2	Ni/La_2O_3	0.39	4.3 wt% Ni/La_2O_3	45.0
3	Ni/MgO	0.05	5.9 wt% Ni/MgO	32.0
4	NiO/Al_2O_3	0.03	5.1 wt% NiO/Al_2O_3	173.0
5	NiO/La_2O_3	0.25	5.7 wt% NiO/La_2O_3	35.3
6	NiO/MgO	0.03	5.6 wt% NiO/MgO	153.0
7	Ni_2O_3/Al_2O_3	0.03	5.7 wt% Ni_2O_3/Al_2O_3	144.1
8	Ni_2O_3/La_2O_3	0.14	6.3 wt% Ni_2O_3/La_2O_3	49.8
9	Ni_2O_3/MgO	0.01	5.4 wt% Ni_2O_3/MgO	111.9
10	*$LaNiO_3$*	*0.95*	*$Ni_{0.95}LaO_{2.85}$*	*7.5*
11	*La_2NiO_4*	*0.70*	*$La_2Ni_{1.4}O_{4.54}$*	*12.5*
12	*$La_3Ni_2O_7$*	*0.63*	*$La_3Ni_{1.89}O_{6.77}$*	*13.5*
13	*$La_4Ni_3O_{10}$*	*0.70*	*$La_4Ni_{2.8}O_{9.85}$*	*10.5*

[1] Determined by ICP-MS. [2] Calculated from the ICP-MS results considering the XRD results for perovskites (entries 10–13). [3] Determined by BET measurements.

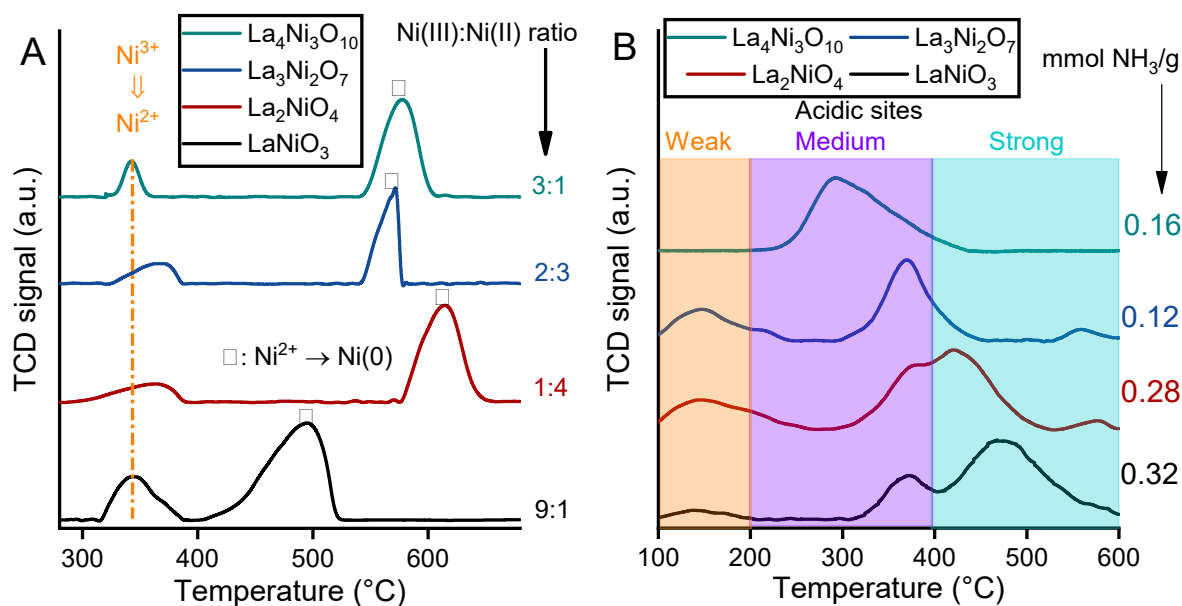**Figure S2.** H_2-TPR (A) and NH_3-TPD (B) profile of the perovskite-type catalysts.

Evaluation

(A) TPR profiles of Ni-containing perovskites can be seen in Fig. S2A. There are two reduction peaks in each profile in accordance with the literature data.[5] The first peak observed at about 350 °C can be assigned to the reduction of Ni^{3+} to Ni^{2+}. Besides, the peaks between 450 and 650 °C – depending on the host structure – are associated with the reduction of Ni^{2+} to $Ni(0)$. This suggests that all perovskite sample has Ni(III) centres without any exception. The actual Ni(II): Ni(III) ratio of the samples can be calculated from the ratio of the reduction peaks which are also depicted in Fig. S2A.

(B) NH_3-TPD profiles of the as-prepared catalyst candidates are exhibited in Fig S2B. From the view of both the acid strength and the number of the acidic sites (mmol NH_3/g(catalyst)), the same order of the samples, especially $LaNiO_3 > La_2NiO_4 > La_4Ni_3O_{10} > La_3Ni_2O_7$ can be determined. This is even so important since this trend matches that one describes the catalytic performance of the catalyst. This fact underpins our hypothesis that Lewis acidic centres play an important role in the catalytic cycle for phenol conversion.
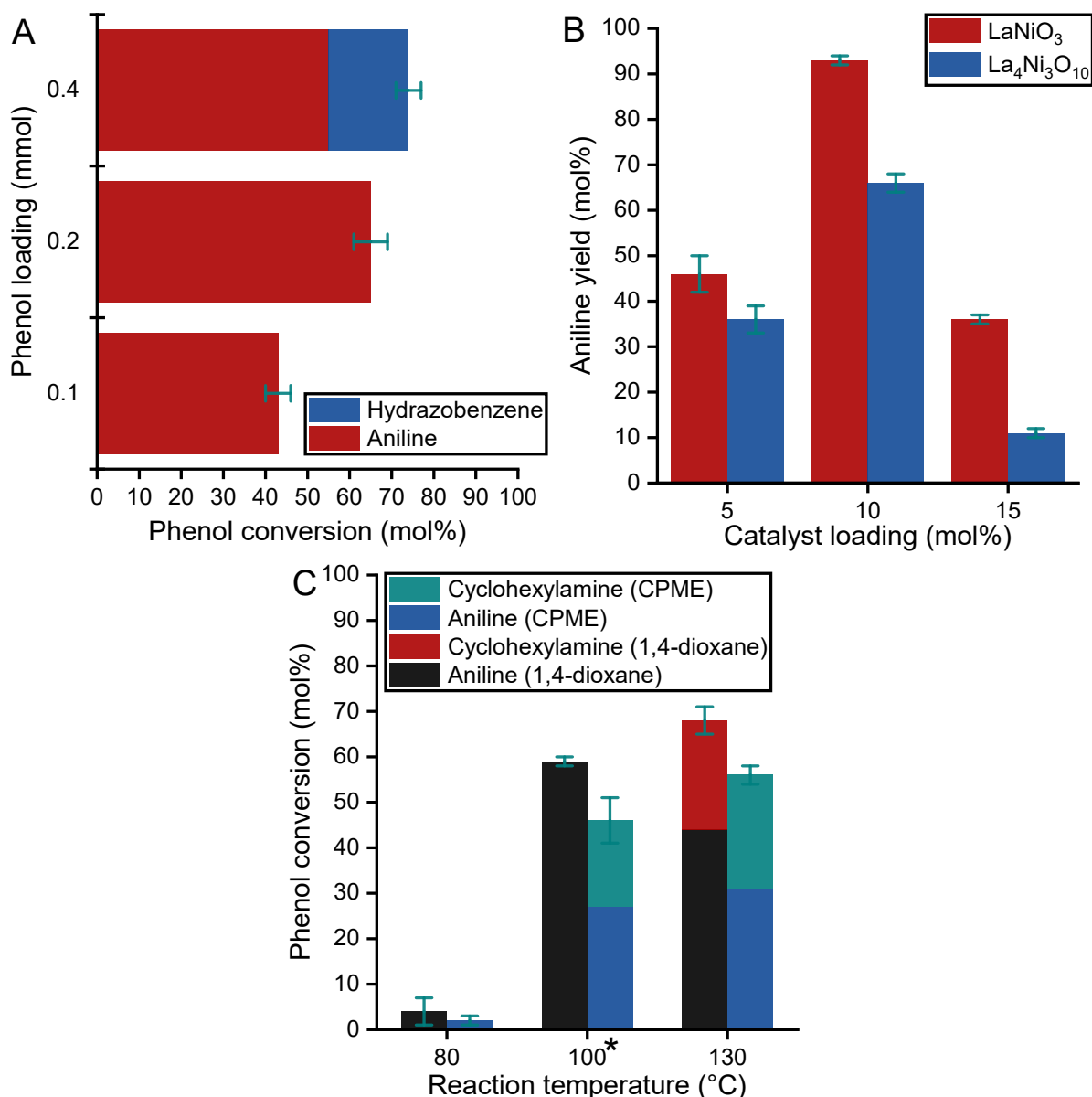
Figure S3. Optimization of reaction conditions. Evaluation of (A) reactant concentration; (B) catalyst loading and (C) reaction temperature. Reaction conditions: Phenol (0.1–0.4 mmol, optimum: 0.2 mmol), hydrazine (A and C: 0.6 mmol; B: 0.9 mmol), LaNiO$_3$ (or La$_4$Ni$_3$O$_{10}$) catalyst (10 mol%), 4A zeolite (A: 200 mg; B and C: 300 mg), LiOH (A: 40 mol%; B and C: —) in 1,4-dioxane (or CPME (C); 4 ml) at reflux temperature (or 80/130°C (C)) for 24 hours (A,B) or 16 hours (C). (*reflux temperature)

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Table S2. Screening of Ni-containing catalysts for the direct amination of phenol with hydrazine to aniline under the optimized reaction conditions. Reaction conditions: Phenol (0.2 mmol), hydrazine (0.9 mmol), catalyst (10 mol%), 4A zeolite (300 mg) in CPME (4 ml) at reflux temperature for 24 hours.

| Entry	Catalyst	Phenol conversion (mol%)	Aniline selectivity (mol%)	Aniline yield (mol%)
1	—	<1	—	—
2	Ni-NP	<1	—	—
3	Ni/Al_2O_3	3	—	—
4	NiO	—	—	—
5	NiO/Al_2O_3	—	—	—
6	Ni_2O_3	31	81	25
7	Ni_2O_3/Al_2O_3	39	91	35
8	Ni_2O_3/La_2O_3	43	86	37
9	*$LaNiO_3$*	*83*	*92*	*76*
10	*La_2NiO_4*	*74*	*94*	*70*
11	*$La_3Ni_2O_7$*	*48*	*91*	*44*
12	*$La_4Ni_3O_{10}$*	*60*	*94*	*56*

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Table S3. Recyclability tests of LaNiO$_3$ catalyst in phenol-to-aniline conversion. Reaction conditions: Phenol (0.2 mmol), hydrazine (0.9 mmol), LaNiO$_3$ catalyst (10 mol%), in 1,4-dioxane (4 ml) at reflux temperature for 24 hours.

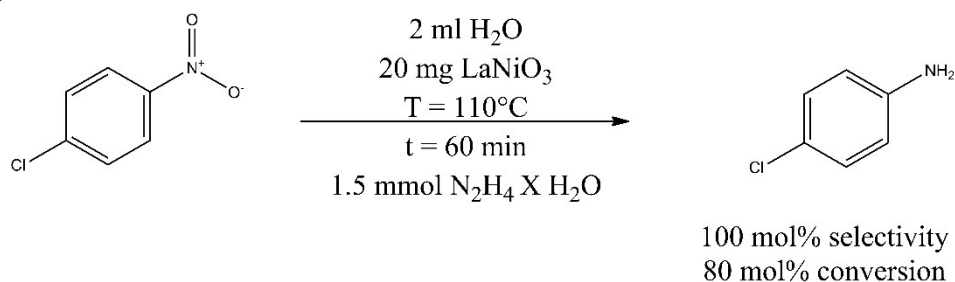| Catalytic cycles	Phenol conversion (mol%)	Aniline yield (mol%)	TOF (mmol g^{-1} h^{-1})
1st	47 ± 3	46 ± 4	1.5
2nd	37 ± 1	35 ± 3	1.7
3rd	36 ± 2	36 ± 3	1.7
4th	36 ± 2	34 ± 4	1.8
5th	35 ± 3	35 ± 3	1.6
6th	17 ± 4	17 ± 1	0.5
7th	9 ± 2	8 ± 2	0.4
After regeneration	41 ± 2	40 ± 2	1.4

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Scheme S1. Control experiments.

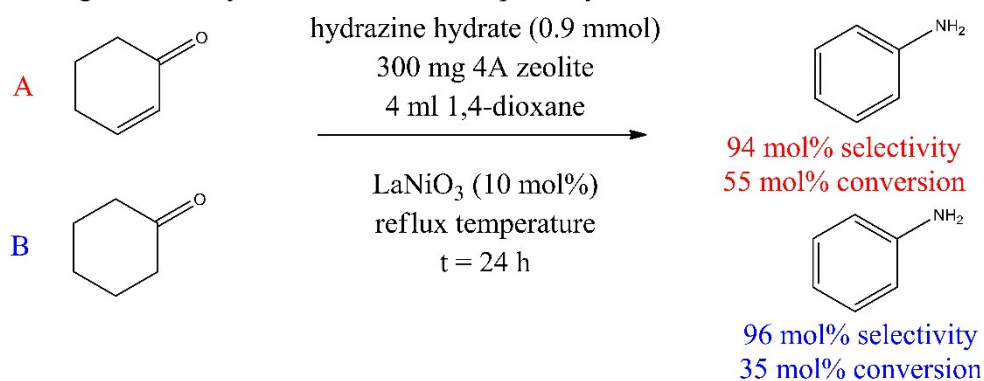1, Testing the catalytic ability of the perovskite to promote isomerisations

5 ml H_2O
100 mg $LaNiO_3$
T = 100°C
t = 60 min

82 mol% selectivity
18 mol% conversion
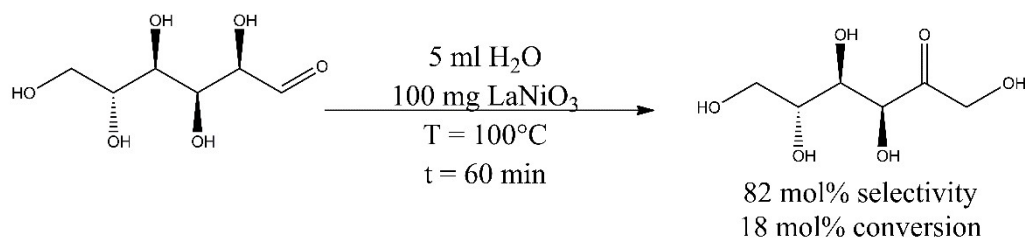
2, Testing the catalytic ability of the perovskite to promote transfer hydrogenation in the presence of hydrazine

2 ml H_2O
20 mg $LaNiO_3$
T = 110°C
t = 60 min
1.5 mmol N_2H_4 X H_2O

100 mol% selectivity
80 mol% conversion

3, Testing the catalytic ability of the perovskite to promote oxidative dehydrogenative coupling

2 ml ethylene glycol
20 mg $LaNiO_3$
T = 110°C
t = 24 h

100 mol% selectivity
71 mol% conversion
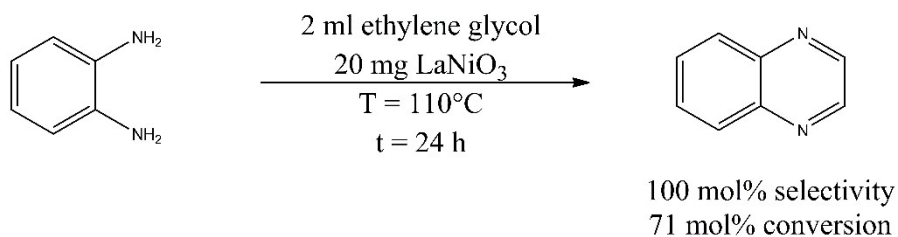
4, Testing the viability of different reaction pathways to undestand the mechanism

A

B

hydrazine hydrate (0.9 mmol)
300 mg 4A zeolite
4 ml 1,4-dioxane

$LaNiO_3$ (10 mol%)
reflux temperature
t = 24 h

94 mol% selectivity
55 mol% conversion

96 mol% selectivity
35 mol% conversion

Evaluation

With the aid of the control experiments which can be seen above (Scheme S1), the proposed reaction mechanism (Fig. 3) can be supported.

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(1) LaNiO$_3$ possesses the catalytic capability of promoting a glucose-fructose isomerisation reaction being competitive with other well-known catalysts.[6] Based on this fact, it is possible to assume that this structure will be suitable for catalysing a cyclohexenol-cyclohexanone isomerisation as well.

(2) In the proposed reaction mechanism, phenol assumably converts into cyclohexenol by undergoing transfer hydrogenation as hydrogen acceptor in which process hydrazine is the hydrogen donor. The 2nd control experiment exhibits that perovskite catalyst can enable efficient transfer hydrogenation when hydrazine is playing the donor role.

(3) This control experiment can present that this catalyst can catalyse dehydrogenative transformations efficiently. This means that the dehydrogenative conversion of intermediate (C) to (D) can occur through perovskite catalysis as we proposed (Fig. 3).

(4) Our last control experiment is able to show that both cyclohexanone or 2-cyclohexen-1-one would be the intermediate which is formed by the reduction of phenol possible followed by an isomerisation.

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