Catalytic Reaction Coupling of Propane Dehydrogenation with Nitrobenzene Hydrogenation over Pt/Al_2O_3

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Abstract

Reaction coupling between propane dehydrogenation and nitrobenzene hydrogenation over a commercial Pt/Al_2O_3 catalyst is presented. The effects of coupling, use of the catalyst, and reaction temperature were studied using a fixed-bed reactor. The coupling of the two reactions drastically increased propane and nitrobenzene conversions regardless the presence of the catalyst. The use of Pt/Al_2O_3 further increased the conversions and the selectivity towards propylene and nitrobenzene hydrogenation products. Higher reaction temperatures favored the selectivity towards pyrolysis products. Reaction pathways are sketched to explain our experimental findings.

Keywords: Reaction coupling; propane dehydrogenation; nitrobenzene hydrogenation; shale gas

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1. Introduction

Propylene is one of the most important building blocks in the petrochemical industry, used extensively in the production of polypropylene, propylene oxide, and acrylic acid [1]. Currently, propylene is a byproduct in steam or catalytic cracking of petroleum naphtha for ethylene production. Recent advances in hydraulic fracturing and precision drilling allow the United States to gain access to previously unattainable shale gas such as methane, ethane, and propane [2-4]. Due to this development, the chemical industry is in the process of shifting from using petroleum–based naphtha to shale–derived alkanes as feedstocks to produce ethylene [5]. Since shale gas cracking aiming for ethylene production is not optimized for forming propylene, this shift has resulted in decreased production of propylene, causing a gap of propylene supply [6]. To overcome this challenge, several on-purpose propylene (OPP) production technologies have been developed, including propane dehydrogenation (PDH), olefin metatheses, methanol-to-olefins, and olefin cracking [7]. Among these technologies, catalytic PDH provides the highest yields [8-12]. Furthermore, propane price has fallen far enough that it has become economically attractive to directly use it to produce high-demand propylene.

PDH is highly endothermic and is thermodynamically limited [13]. Most research efforts on PDH have focused on optimizing catalyst performance to achieve higher propylene yields and to suppress side reactions. Two families of catalysts are typically used for catalytic PDH: supported noble metal catalysts and metal oxide catalysts. Among the supported noble metal catalysts, platinum-based catalysts are the most used due to its high activity toward C–H bond cleavage and low activity toward C–C bond cleavage [14-17]. However, its selectivity towards propylene is not satisfactory due to side reactions such as hydrogenolysis, isomerization, and coking. Consequently, tin (Sn) is typically added as a promoter to suppresses these side reactions, to neutralize the acidity of support, and to prevent the formation of coke precursors [18, 19]. In terms of metal oxides, chromium oxide catalysts are the most commonly used for large scale PDH operations [20, 21]. Regardless of the types of catalysts used, the role of active sites and supports and the mechanisms of PDH have been extensively investigated. Promising results have also been obtained by doping the catalysts with other transition metals, including gallium [22, 23], indium [24], vanadium [25, 26], and molybdenum [27].

Although significant advances have been made for PDH catalysts, its low equilibrium conversion remains to be the main limitation. Based on the Le Chatelier's principle, equilibrium conversion can be shifted higher by removing hydrogen from the product stream. One approach of removing hydrogen is to couple PDH with another hydrogen consuming reaction. Nitrobenzene hydrogenation (NBH), a common petrochemical process to produce aniline as a precursor of many chemicals and consumer products, including polyurethane, dyes, and amine-based medications, is a promising candidate for reaction coupling with PDH [28-30]. Most transition metals are capable of catalyzing NBH under mild conditions (< 350 °C), with nickel and copper-based catalysts the most used in the industry. At higher temperatures (400–600 °C), nitrobenzene undergoes pyrolysis, leading to the formation of benzene, phenol, biphenyl, and dibenzofuran [31].

There are three major advantages to couple NBH with PDH. First, PDH is hydrogen-producing, while NBH is hydrogen-consuming. Coupling these two reactions in one stream has the benefit of utilizing the hydrogen produced from one reaction for the other, bypassing the cost and energy of acquiring hydrogen from methane steam reforming. Second, equilibrium of PDH can be shifted to achieve higher conversion and propylene yields. Finally, PDH is endothermic and NBH is exothermic. The energy released from NBH can be readily utilized in PDH. Sun et al. [32] investigated ethylbenzene dehydrogenation in the presence of nitrobenzene over γ–Al_2O_3, ZSM-5, activated carbon (AC), and Pt/AC at 400 °C. They observed that ethylbenzene conversion was greatly improved via reaction coupling over Pt (0.02 wt%)/AC. The highest ethylbenzene conversion reached 33.8%, as opposed to 2.4% without reaction coupling. Harikrishna et al. [33] studied the functionalities of Pd catalysts supported on spinel $MgAl_2O_4$ for the coupling of ethylbenzene dehydrogenation with NBH. It was concluded that a Pd loading of 0.5 wt% is optimal to achieve maximum conversions of ethylbenzene and nitrobenzene at 51.8% and 47.3%, respectively.

Despite potential promise that reaction coupling between a dehydrogenation reaction and a hydrogenation reaction can offer, the coupling between PDH and NBH is rarely explored. In our previous work, co-pyrolysis of propane and nitrobenzene without the use of catalysts was studied [31]. Propane conversion increased from 15% to 35% at 650 ^{o}C with the addition of nitrobenzene. In this work, reaction coupling between PDH and NBH over a commercial Pt/Al_2O_3 catalyst is studied. The effects of coupling, the presence of the catalyst, and reaction temperature was systematically investigated using a laboratory-scale fixed bed reactor. Possible reaction pathways in the gas phase and on the catalytic surfaces are hypothesized based on our experimental findings.

2. Experimental

2.1. Catalyst characterization

The Pt/Al_2O_3 catalyst used in our experiments was acquired from Alfa Aesar (5 wt% Pt). The surface area of the catalyst was determined by a Quantachrome Autosorb 3b Automatic Surface Area and Pore Size Analyzer to be 92 m^2/g, based on the nitrogen adsorption–desorption isotherm at 77 K using the Brunauer–Emmett–Teller (BET) theory [34]. The morphology of the catalyst powder was characterized with a JEOL JSM 7401F scanning electron microscope (SEM), with accelerating voltage ranged between 10 and 15 kV. The backscattered mode in SEM was used to visualize the highly dispersed Pt spots on the catalyst surfaces. Energy dispersive X-ray spectroscopy (EDS) was used to quantify the composition of Pt, Al, and O contents of the catalyst. To prepare for the SEM analysis, the catalyst powder was directly dispersed in ethanol and transferred onto the surface of a piece of a silicon wafer attached to the aluminum stub via carbon tapes.

Crystal structure of the Pt/Al_2O_3 catalyst was determined by x-ray diffraction (XRD). The catalyst powder was directly scanned as purchased. Each sample was analyzed using the AXRD Benchtop Powder X-ray Diffractometer (Proto Mfg.) with a copper anode. The 2θ range was from 20° to 90° (0.02° step) with a dwell time of 2 s. The identification of peaks and patterns was based on American Mineralogist Crystal Structure Database.

2.2. Catalyst activity measurements

The coupled PDH/NBH reaction was carried out in a fixed-bed reactor at a temperature range between 450 and 550 °C at atmospheric pressure. Approximately 105 mg of the Pt/Al_2O_3 catalyst, supported by quartz wool, was loaded in a quartz tube with a diameter of 0.5 in for all reactions. The total length of the catalyst bed was 1.5 in. A type-K thermocouple (OMEGA, KMQSS-062U-12) was positioned inside the catalyst bed to measure the reaction temperature. The catalyst was reduced under H_2 flow of 30 ml/min for 1 h at 550 °C before being cooled to the target reaction temperature for the activity experiments. Liquid-phase nitrobenzene was delivered by a syringe pump (KD Scientific) at a fixed feed rate of 9.5 μL/min at room temperature. The propane feed was controlled by a flowmeter (Porter VCD–1000) at a constant flow rate of 7 ml/min at room temperature. Nitrogen was used as a carrier gas at flow rates of 1.2, 3.6, and 8.2 ml/min for reaction coupling, PDH, and NBH experiments, respectively. These flow rates were used to ensure that the total vapor flow rate entering the reactor was the same for all three sets of experiments. The gas and liquid feed lines were both heated to 250 °C to vaporize nitrobenzene and to prevent reactant condensation. The propane to nitrobenzene molar ratio in the feed prior to entering the reactor was approximately stoichiometrically at 3:1. Two ice-water traps were used downstream of the reactor to collect condensed products at regular intervals of 30 mins. Non-condensable gaseous products were then collected in a 0.6-L Tedlar bag (Supel™-Inert) downstream of the ice-water traps, also at regular intervals of 30 min. Both condensed and gaseous products were analyzed by gas chromatography (GC).

2.3. Products analysis

Identification of the reaction products was achieved using a Shimadzu GC2010 Plus GC equipped with a mass spectrometer (MS). 1 µL of sample was injected into the GC/MS system equipped with a Shimadzu SH-RXi-5Sil MS column (30 m), with a split ratio of 20. Ultra-high purity helium (99.999%, Airgas) was used as a carrier gas in the column with a constant flow rate of 88.8 mL/min. The inlet temperature was set at 285 °C. The programmed temperature regime for the GC oven was: start at 35 °C, hold for 7 minutes, ramp up to 185 °C at 7.5 °C/min, and ramp up to 285 °C at 20 °C/min. The temperature of the MS detector was set at 285 °C.

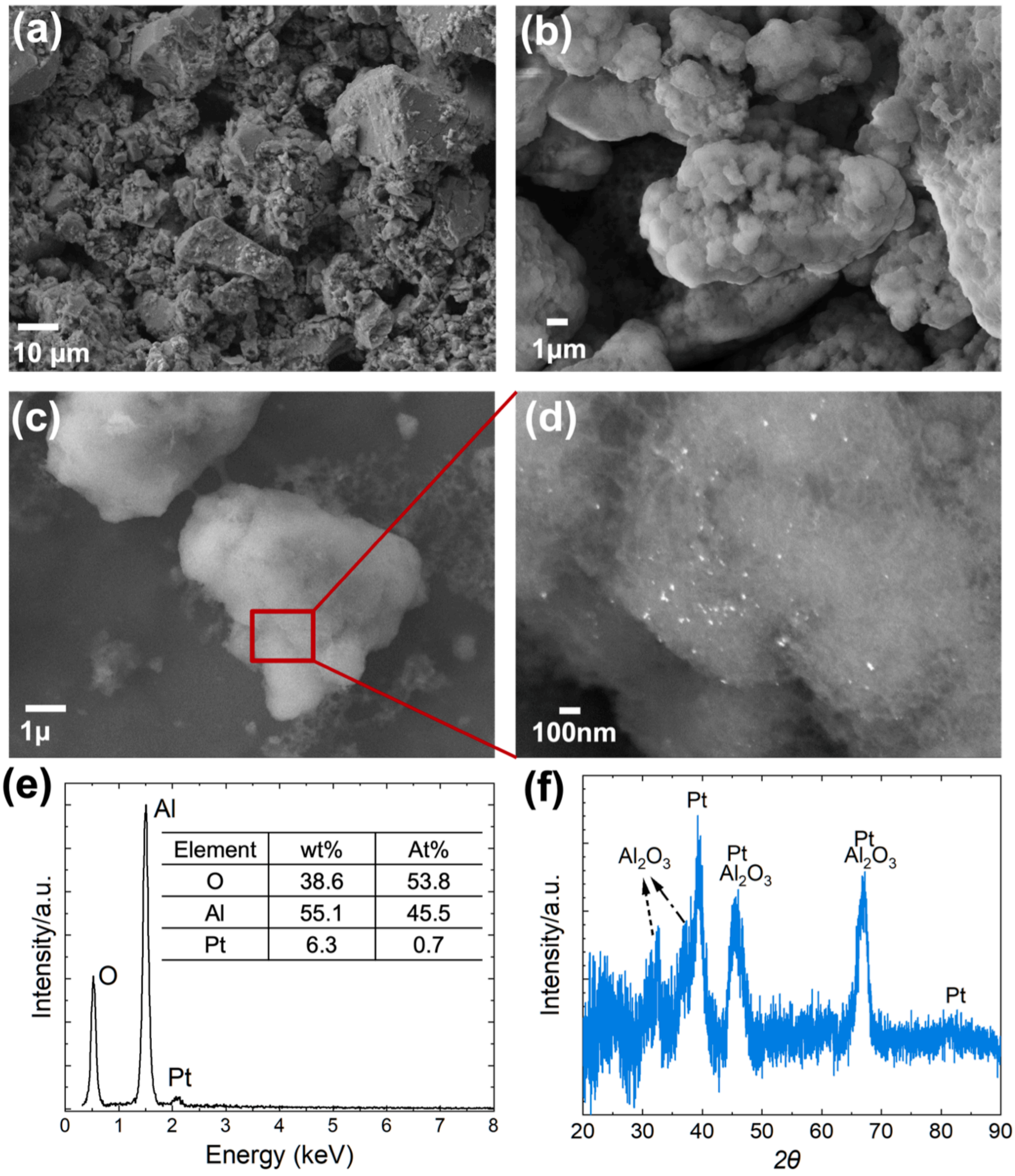
Quantification of the reaction products was achieved using a Shimadzu GC2010 Plus GC with a flame ionization detector (FID). 1 µL of the sample was injected into the GC/FID system equipped with a Shimadzu Rxi-5ms column (15 m). The GC was programmed with the following inlet operating parameters: ultra-high purity helium carrier gas set at a constant flow pressure of 22.1 kPa, inlet temperature set at 285 °C, and a split injection mode with split ratio of 150. The detector temperature was set at 285 °C, with an air flow rate of 400 mL/min, a hydrogen gas flow rate of 40 mL/min, and a makeup gas flow rate of 30 ml/min. The GC oven was programmed with the following temperature regime: start at 35 °C, hold for 7 minutes, ramp up to 87.5 °C at 7.5 °C/min and hold for 2 minutes, ramp to 185 °C at 7.5 °C/min, and ramp to 285 °C at 20 °C/min.

In this work, propane conversion was defined as the fraction of the carbon atoms in the propane feed that ended up in the propane-derived products. Likewise, the yield of a propane-derived product was defined as the fraction of the carbon atoms in the propane feed that ended up in that product. For NBH, it was challenging to quantify vapor-phase products, such as NO, NO_2, and H_2O. As a result, nitrobenzene conversion was defined as the mass fraction of the aromatic portion of the nitrobenzene feed that ended up in the nitrobenzene-derived products. Likewise, the yield of a nitrobenzene-derived product was defined as the mass fraction of the aromatic portion of the nitrobenzene feed that ended up in that product. For products resulted from the coupling between propane and nitrobenzene, their yields were analyzed by dividing the molecules into the aromatic portion and the side chain(s) attached. The mass of the aromatic portion of these products was counted towards nitrobenzene conversion, and the carbon atoms on the side chain(s) attached were counted towards propane conversion. Finally, selectivity towards a product is defined as its yield divided by the total yield of the propane-derived products or nitrobenzene-derived products.

3. Results and discussion

SEM images of fresh (i.e., untreated and unreacted) Pt/Al_2O_3 powders exhibited a wide range of particle size (Fig. 1a), from sub-micron to more than 25 μm. The shape of the catalyst particles appeared to be irregular. SEM images under a higher magnification suggest the alumina support in layered structures (Fig. 1a-c). Using the backscattered mode, the bright spots on the SEM images were identified as Pt based on its higher atomic weight compared to Al and O, with particle size less than 15 nm (Fig. 1d). The EDS analysis (Fig. 1e) confirmed that the Pt loading was approximately 6 wt% (0.7 at%) in the catalyst, which was close to the 5 wt% value reported by the vendor. The O to Al atomic ratio was measured to be 1.2, slightly lower than the theoretical ratio of 1.5. Since EDS analysis for low-Z atoms like C, N, and O were less reliable due to X-ray adsorption in a thick sample, this O to Al was still within a reasonable range of error.

The XRD spectrum of the catalyst showed characteristic peaks for Pt and γ-alumina and the patten was identified via the American Mineralogist Crystal Structure Database. The peaks at 32°, 37°, 45°, and 67° were associated with γ-alumina. The peaks at 40°, 46°, 67°, and 81° were associated with Pt. The peaks at 46° and 67° showed overlap between Pt and γ-alumina. The noise level was relatively high, likely due to the low crystallinity of the sample.



Element	wt%	At%
O	38.6	53.8
Al	55.1	45.5
Pt	6.3	0.7

Fig. 1. (a)-(d) SEM images of the Pt/Al_2O_3 catalyst used in this study. (a)-(c) A wide range of particle size in between sub-micron to more than 25 μm observed; (d) the backscattered mode image from a small area of (c) at high magnification, where the bright spots were identified as the dispersed Pt based on the larger atomic number of Pt compared to Al and O; (e) the EDS spectrum with weight and atomic ratios of Oxygen (O), Aluminum (Al), and platinum (Pt) tabulated; (f) the XRD pattern for the Pt/Al_2O_3 catalyst used in this study.

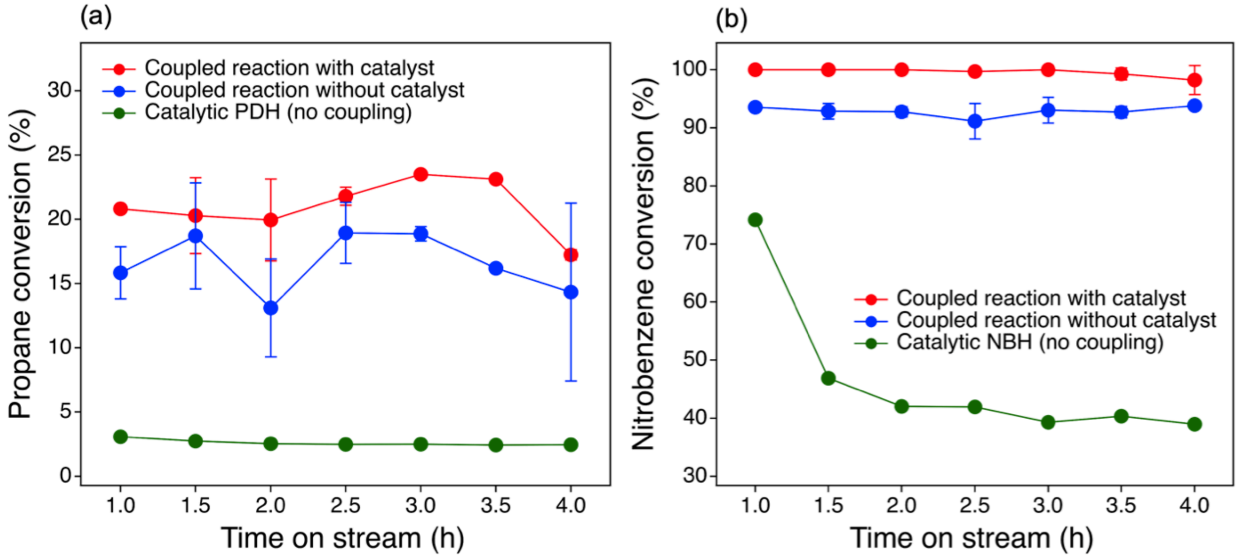


Fig. 2. Effect of reaction coupling and the use of catalysts on (a) PDH conversion and (b) NBH conversion. Reaction temperature: 550 °C.

Fig. 2a illustrates propane conversion when PDH was coupled with NBH over the Pt/Al_2O_3 catalyst. As a comparison, propane conversion was lower than 5% without reaction coupling. This value was smaller than the typical literature values [35], indicating that the Pt/Al_2O_3 catalyst used in our experiments was not at optimal activity, likely due to the absence of a promoter, such as Sn. Nevertheless, when PDH was coupled with NBH, propane conversion increased to approximately 15% even without the use of the catalysts. This marked increase in propane conversion due to reaction coupling was evident. Catalyst seemed to further improve propane conversion, although the effect appeared to be small (< 5%). Reaction coupling also significantly accelerated NBH, revealed by the increased conversion of nitrobenzene (Fig. 2b). Particularly, the presence of propane provided a rich source of hydrogen to continually convert NB at approximately 92% even without the use of catalysts. The addition of catalysts further increased NB conversion to almost

100% (Fig. 2b).

Note that our product analysis did not consider coke formation due to three reasons. First, we observed that the amount of carbon atoms existing the reactor exceed those entering the reactor by approximately 20% (Fig. S1), with an error bar of 20%. This suggests that not many propane-derived carbon atoms were available for coke formation. Second, very small amount (< 0.5 wt%) of polyaromatic hydrocarbons (such as naphthalene), known coke precursors, were observed in the product stream. Third, there was almost negligible weight increase in the spent catalysts after 4 hours of time-on-stream reactions. These observations suggest that the formation of coke might be minimal in our reaction system. It is known that for Pt-based catalysts under propane dehydrogenation conditions, the presence of steam (i.e., water vapor) reduces coke formation [35]. It is possible that steam produced from reaction coupling reduced coke formation from PDH. However, extended use of catalysts in the presence of steam may also result in sintering of the catalyst [35], particularly for the alumina support, which could reduce catalyst activity. Although we did not observe reduced propane and nitrobenzene conversions after 4 hours of usage in our experiments, the change in catalyst structure due to steam formation or the deposition of coke on catalyst surfaces cannot be totally ruled out. Consequently, the validity and mechanism by which reduced coke formation in our experiments, as well as the role of steam in the reaction coupling scheme, need to be further researched and clarified in future experiments.

Different product distributions were observed due to the use of the catalyst during reaction coupling of PDH with NBH. As depicted in Fig. 3, when the catalyst was not used, approximately the same amount of propylene, ethylene, and methane were produced. Adding Pt/Al_2O_3 shifted product distribution towards propylene, the target product. This suggests that there is a new surface reaction route on Pt/Al_2O_3 that allows hydrogen abstraction from the center propane carbon atom, leading to the formation of a *i*-C_3H_7 complex [35] which serves as a propylene precursor. The yields of coupling products were at approximately 3% regardless the use of the catalyst.

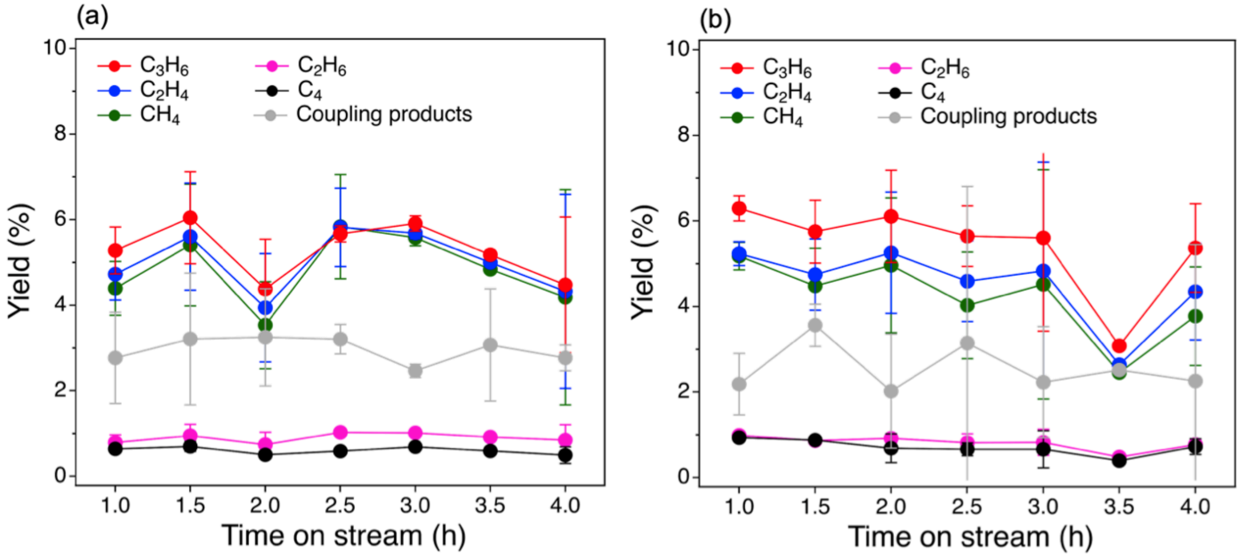


Fig. 3. The yields of propane-derived products during reaction coupling of PDH with NBH: (a) without Pt/Al_2O_3, and (b) with Pt/Al_2O_3. Reaction temperature: 550 °C.

Fig. 4 shows the yields of nitrobenzene-derived products during reaction coupling of PDH with NBH at 550 °C with or without the addition of Pt/Al_2O_3. When the catalyst was not used, products derived from nitrobenzene pyrolysis, primarily benzene, phenol, benzonitrile, and biphenyl [31], were dominant with combined yields of approximately 50–60% (Fig. 4a). Products resulted from the coupling between PDH and NBH (i.e., toluene, ethylbenzene, styrene, propyl benzene, and *n*-methylaniline) and nitrobenzene hydrogenation (i.e., aniline and azobenzene) had similar yields of approximately 15–20% (Fig. 4a). In the presence of Pt/Al_2O_3, yields PDH/NBH coupling products remained similar. However, yields of the nitrobenzene hydrogenation products increased to approximately 30%, while yields of the pyrolysis products slightly decreased to approximately 50% (Fig. 4b). The increased yields of the hydrogenation products in the presence of the catalyst suggests higher coverage of propane-derived complexes on the Pt/Al_2O_3 surfaces and increased catalytic hydrogen abstraction from propane, accelerating nitrobenzene hydrogenation.

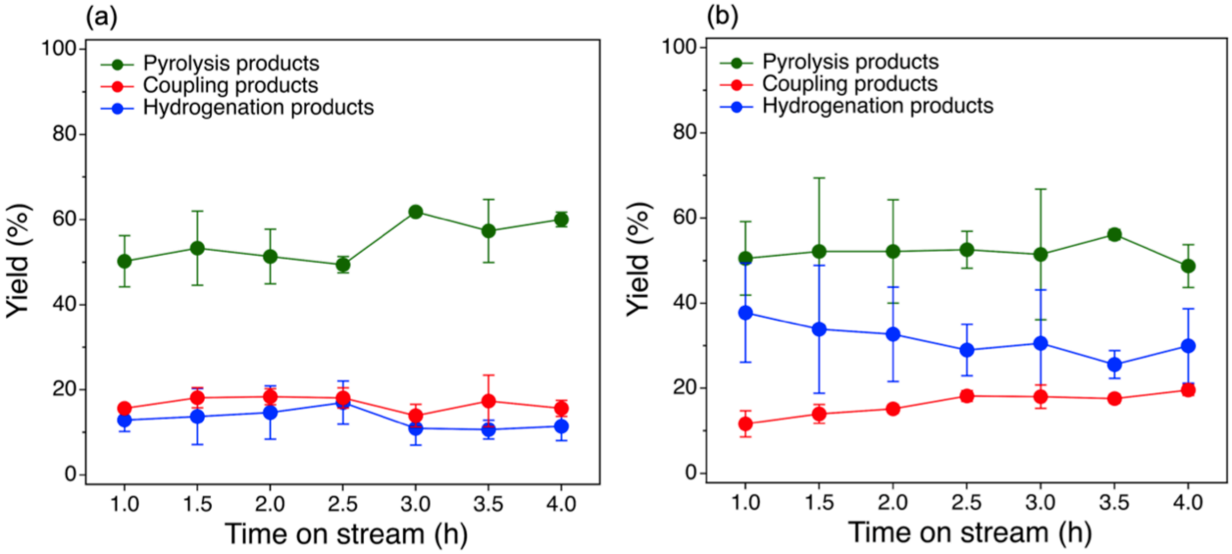


Fig. 4. The yields of nitrobenzene-derived products during reaction coupling of PDH and NBH: (a) without Pt/Al_2O_3, and (b) with Pt/Al_2O_3. Reaction temperature: 550 °C.

The effect of reaction temperature on the catalytic reaction coupling of PDH with NBH is shown in Fig. 5. It was observed that propane conversion increased from approximately 5% at 450 °C to approximately 10% at 500 °C and 20% at 550 °C (Fig. 5a). Nitrobenzene conversion also increased drastically from approximately 40 % at 450 °C to over 80% at 500 ºC and close to 100% at 550 ºC (Fig. 5b). Product selectivity was also found to be affected by the reaction temperature. Particularly, propylene selectivity (Fig. 6a) in propane-derived products slightly decreased at higher temperatures due to more dominant pyrolysis reactions. Higher reaction temperatures also favored nitrobenzene pyrolysis products (Fig. 6b), whereas selectivity towards products from nitrobenzene hydrogenation (Fig. 6c) decreased at higher temperatures. This is consistent with conventional understanding that pyrolysis reactions are more endothermic and have higher activation energies than nitrobenzene hydrogenation. Selectivity towards products

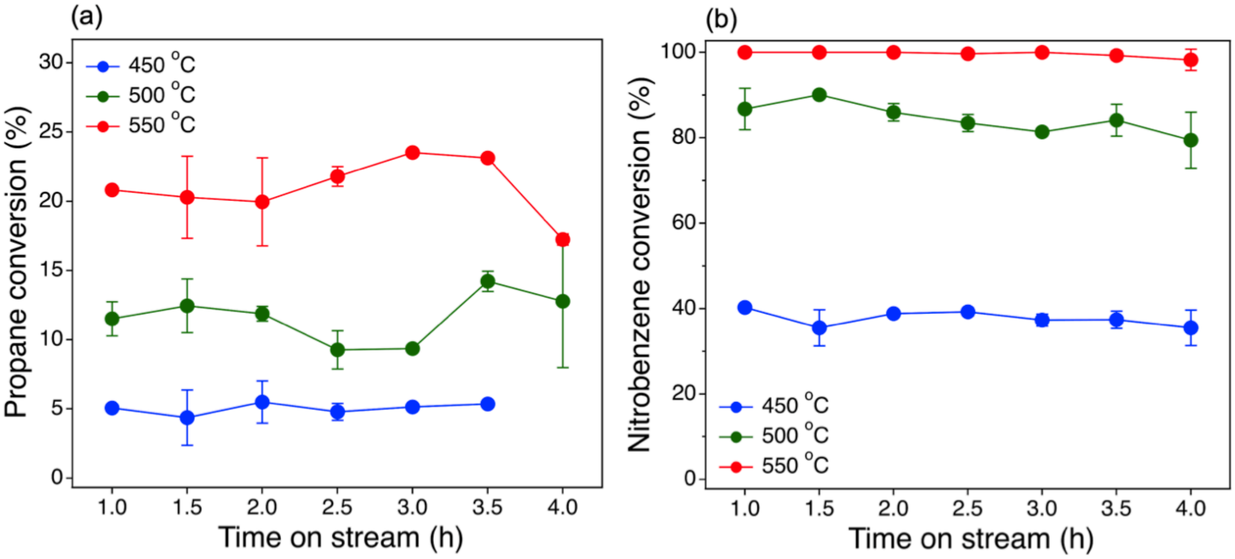


Fig. 5. The effect of reaction temperature on the conversion of: (a) PDH and (b) NBH in the presence of the Pt/Al_2O_3 catalyst during the catalytic reaction coupling of PDH with NBH.

from PDH/NBH reaction coupling remained similar regardless reaction temperature tested.

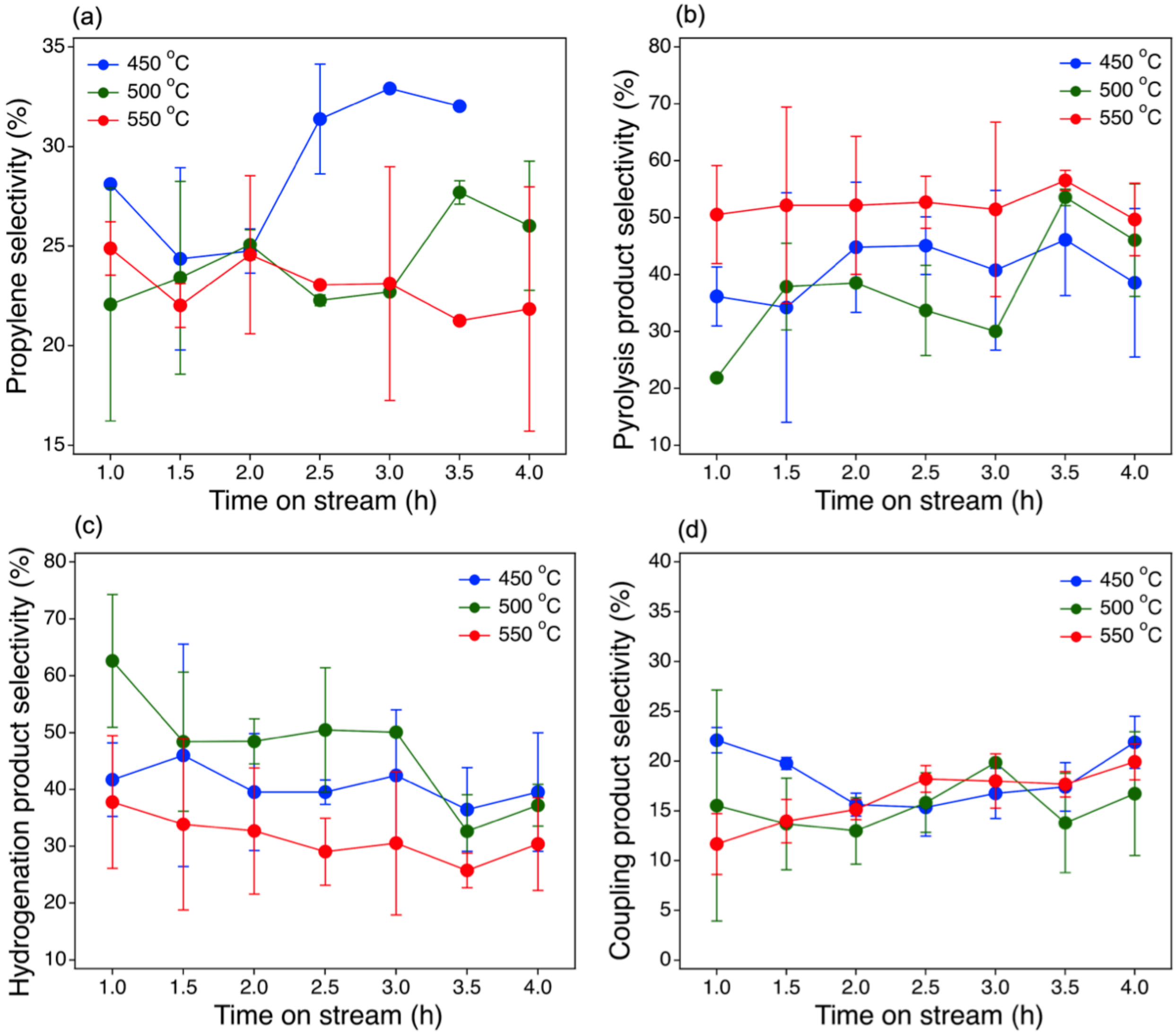


Fig. 6. The effect of reaction temperature on the selectivity towards: (a) propylene produced from PDH, (b) products from nitrobenzene pyrolysis, (c) products of nitrobenzene hydrogenation, and (d) products resulted from the coupling of PDH with NBH, in the presence of the Pt/Al_2O_3 catalyst during the catalytic reaction coupling of PDH with NBH.

Based on our experimental findings, reaction pathways of catalytic reaction coupling between PDH and NBH are hypothesized and depicted in Fig. 7. Regardless the presence of the catalyst, both propane and nitrobenzene undergo pyrolysis through free radical pathways, leading to the formation of propyl and phenyl radicals, respectively. Our previous work [31] has shown that during co-pyrolysis of propane and nitrobenzene, nitrobenzene-derived phenyl radicals accelerate propane pyrolysis, leading to increased propylene yields at the expense of decreased selectivity. Simultaneously, propane-derived hydrogen radicals facilitate nitrobenzene hydrogenation, enabling the formation of aniline and azobenzene. Coupling products such as ethylbenzene, styrene, and propyl benzene are also produced in the gas phase due to radical–radical recombination. In the presence of the Pt/Al_2O_3 catalyst, new pathways of propane adsorption followed by hydrogen abstraction occur on the surfaces, promoting the formation of propylene. This explains why increased propylene selectivity was observed in our experiments (Fig. 3). In addition, surface adsorbed hydrogen atoms enable a new route for nitrobenzene hydrogenation, which explains the increased selectivity towards hydrogenation products observed (Fig. 4). The hypothesized mechanism qualitatively explains some of the important observations in our experiments. To obtain quantitative kinetic parameters and detailed pathways of the reaction system, however, future in-depth studies employing differential reactors are needed. These future studies can also help determine the formation rates of important products under different conditions (e.g., various feed ratios and system pressures), limiting scenarios, and roles of critical species such as steam, hydrogen atoms from different sources, and coke.

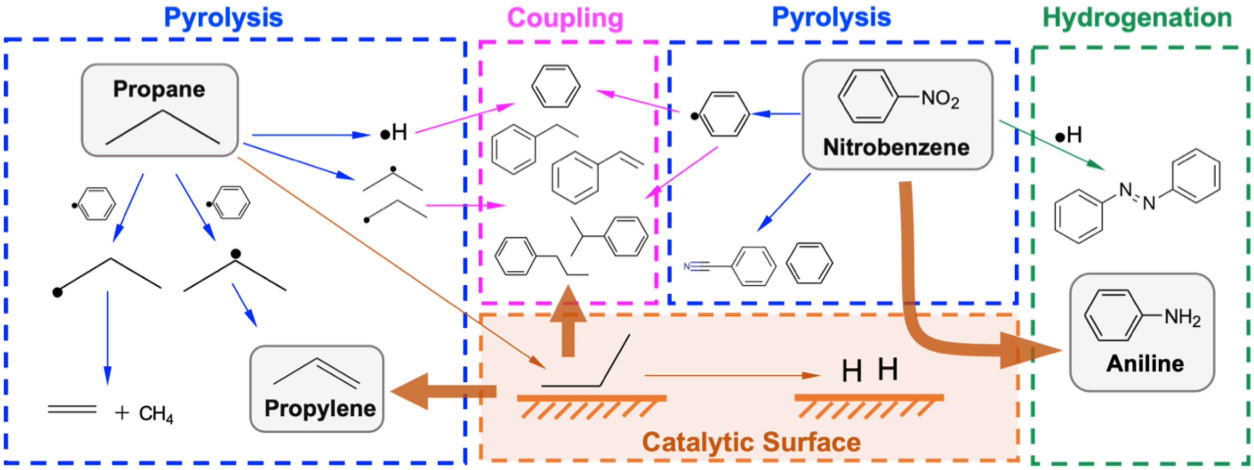


Fig. 7. Hypothesized reaction pathways of catalytic reaction coupling of PDH with NBH over Pt/Al_2O_3 surfaces.

4. Conclusion

Catalytic reaction coupling of propane dehydrogenation (PDH) with nitrobenzene hydrogenation (NBH) over Pt/Al_2O_3 was studied with a laboratory-scale fixed bed reactor between 450 and 550 °C. It was found that the coupling of the two reaction systems drastically increased the conversions of propane and nitrobenzene regardless the presence of the catalyst. The use of Pt/Al_2O_3 further increased both conversions. The catalyst also increased the selectivity towards propylene and nitrobenzene hydrogenation products, whereas the selectivity towards nitrobenzene pyrolysis products decreased, both of which desired outcomes. Higher reaction temperatures were found to favor the selectivity towards propane and nitrobenzene pyrolysis products. Reaction pathways of this catalytic reaction coupling system are hypothesized to explain our experimental findings. Our work suggests that catalytic design to maximize propylene adsorption and hydrogen abstraction and minimize C–C bond cleavage on the catalyst surfaces should be explored to enable optimal concurrent production of propylene and aniline from this reaction coupling concept.

Acknowledgements

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