

Electronic Supplementary Information (ESI)

Selective C–O bond cleavage in diphenyl ether via catalytic transfer hydrogenolysis over Ru-decorated nanocrystalline H-ZSM-5

Atul Kumar^a, and Rajendra Srivastava^{a*}

^aCatalysis Research Laboratory, Department of Chemistry, Indian Institute of Technology
Ropar, Rupnagar-140001, India

*Email: rajendra@iitrpr.ac.in

*Phone: +91-1881-232064

1. Materials

All the chemicals and materials were of AR grade, and used without further purification. The [Poly(ethylene glycol)]-block-[poly(propylene glycol)]-block-[poly(ethylene glycol)] (Pluronic®P123, $M_n = 5800$), tetraethylorthosilicate (TEOS, 98%), propyltriethoxy silane (PrTES, 97%) tetrapropylammonium hydroxide (TPAOH), sodium aluminate and ruthenium (III) chloride hydrate, and 2-propanol (IPA) were purchased from Sigma Aldrich. Sodium borohydride (98%) was purchased from Loba Chemie Pvt. Ltd. Diphenyl ether (99.89%) and other substrates were purchased from BLD pharmatech (India) Pvt. Ltd, India. The other solvents (>99%) used in this work were obtained from Merck Lifescience Private Limited, India.

2. Characterization

The powder X-ray diffraction pattern of the prepared materials was recorded on a Rigaku Miniflex III diffractometer. The diffraction intensities were measured in the 2θ range of $5-80^\circ$ with a Cu $K\alpha$ ($\lambda = 0.15406$ nm) radiation (40 kV, 15 mA) at a scanning speed of $10^\circ/\text{min}$. The Si/Al ratio and Ru metal loading in the prepared zeolite materials were analyzed by microwave plasma atomic emission spectroscopy (MP-AES). The analysis was carried out in a single spray chamber by injecting the samples into a stream of nitrogen plasma. The textural properties of the prepared samples were analyzed by N_2 -adsorption isotherms using Quantachrome autosorb-iQ₂-TPX surface area instrument. All the samples were preheated up to 300°C for 3 h under vacuum. The specific surface area and the pore diameter estimation in the prepared catalyst were calculated using Brunauer Emmett-Teller (BET) equation in the relative pressure range of 0.05-0.3 and Barrett-Joyner-Halenda (BJH) equation, respectively. The morphological investigation of the prepared materials was recorded in scanning electron microscopy (JEOL JSM-6610LV) instrument. The transmission electron microscopy obtained the in-depth investigation of the morphology in the prepared material (FEI Tecnai G2, F30) operated at an accelerating potential of 200 kV. The elemental analysis and oxidation states of the elements present in the catalysts were examined by X-ray photoelectron spectroscopy (XPS) on PHI 5000 VersaProbeII (ULVAC- PHI, INC, Japan) operating with a microfocus ($100\ \mu\text{m}$, 25 W, 15 kV) monochromatic Al- $K\alpha$ source ($h\nu = 1486.6$ eV) equipped with a hemispherical analyzer and a multichannel detector. The Bruker Tensor-II F-27 Fourier transform Infra-Red (FT-IR) instrument was used, and pyridine used as a probe molecule for Py FT-IR study. The total acidity (NH_3 -TPD) and reducibility (H_2 -TPR) of the prepared materials were examined through Temperature Programmed Desorption/Reduction experiments on a Quantachrome Autosorb-iQ₂-TPX, CHEMBET™ TPR/TPD instrument. For the NH_3 -TPD analysis, the prepared

samples were pre-treated to 300 °C at the ramp rate of 10 °C/min under He flows for 30 min. After the pre-treatment, the sample cell was cooled to 50 °C, and the NH₃ (10% in He) was adsorbed by flowing the gas for 1 h in the sample cell with a flowing rate of 10 mL/min. After adsorption, the excess or physically adsorbed NH₃-gas was removed by passing the He gas at 50 mL/min for 30 min. The amount of desorbed gas was analyzed on a thermal conductivity detector (TCD) against temperature with a heating rate of 10 °C/min in the temperature range from 50-800 °C. For the H₂-TPD analysis, H₂ gas (10% H₂ in Ar) was taken instead of NH₃ gas. The temperature-programmed reduction was performed on Quantachrome Autosorb-iQ2-TPX, CHEMBET™ TPR/TPD instrument. During the analysis, the temperature was increased from room temperature to 800 °C with a heating rate of 5 °C/min in 10% H₂/Ar flow (30 mL/min).

3. Catalyst preparation

3.1 Synthesis of N-HZSM-5

Nanocrystalline zeolite (N-HZSM-5) was prepared via a reported procedure with some modification.^{S1} In a typical synthesis process, 6.355 g of TPAOH and 0.241 g of sodium aluminate (53 wt% Al₂O₃, 43 wt% Na₂O) were dissolved in 18.686 g of deionized water (DI water), and the solution was stirred for 30 min at room temperature (25 ± 2 °C) until the solution becomes clear. To this solution, 1.031 g of PrTES was added and stirred for another 5 min; after that, 9.36 g of TEOS was added. The mixed solution was stirred for another 6 h at room temperature (25 ± 2 °C). The obtained gel mixture has a molar composition of 90TEOS/10PrTES/2.5Al₂O₃/3.3Na₂O/25TPAOH/2500H₂O. This mixed solution was transferred into a 100 mL Teflon-lined autoclave and then hydrothermally treated at 170 °C for 72 h under static conditions. The obtained white-colored material was filtered in a vacuum filtration assembly, washed with 500 mL DI water, and dried at 80 °C for 12 h. The dried material was calcined at 550 °C for 5 h at a heating rate of 2 °C/min in a muffle furnace. The ion-exchange process produced the acidic form of the material designated as N-HZSM-5 prepared by stirring with 1 M aqueous NH₄Cl solution at 80 °C for 5 h. This ion-exchange step was repeated thrice, followed by calcination at 550 °C for 5 h at a heating rate of 2 °C/min. For the comparison, conventional HZSM-5 material was synthesized using the same procedure mentioned above for the N-HZSM-5, but without adding PrTES additive.

3.2 Synthesis of Ru(x%)/N-HZSM-5

The impregnation method was used to prepare the metal NPs based catalytic materials. In a typical process, 500 mg of N-HZSM-5 was dispersed in the 50 mL of ethanol: water (2:1) system and then sonicated for 20 min. In a separate beaker, the necessary quantity of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (at $x = 1, 2, 3,$ and 5 wt.% or 10.22, 20.45, 30.67, and 51.10 mg respectively w.r.t support) was dissolved in 10 mL of water. The aqueous metal salt solution was added dropwise to the dispersed N-HZSM-5 solution under stirring and stirred for 24 h at room temperature. After the impregnation, the water evaporated at $50\text{ }^\circ\text{C}$ (total evaporation time ~ 9 h). The metal salt-impregnated precursor was dried and grounded by mortar & pestle. The metal salt-impregnated precursor was reduced by the chemical reduction process. The metal salt-impregnated precursor was subjected to a chemical reduction process. In this procedure, a limited volume of NaBH_4 (30 mL) was used, with a NaBH_4 to Ru weight ratio of 15. Depending on the Ru loading (1, 2, 3, or 5 wt.%), 75, 150, 225, or 375 mg of NaBH_4 were taken. To this NaBH_4 solution, the metal salt-impregnated precursor was slowly added. Then this mixed solution was stirred for 1 h in an ice bath ($4 \pm 2\text{ }^\circ\text{C}$) and another 24 h at room temperature ($25 \pm 2\text{ }^\circ\text{C}$). Then, reduced catalysts were washed with excess DI water and dried at $50\text{ }^\circ\text{C}$ under a vacuum oven (~ 0.09 MPa) for 12 h. The reduced material is termed Ru(x%)/N-HZSM-5, where $x = 1, 2, 3,$ and 5 . The corresponding loading of the Ru NPs was further confirmed by the MP-AES analysis (Table-1). The surface area of H-ZSM-5 was $304\text{ m}^2/\text{g}$. The Ru content was determined to be 2.88 wt% in Ru(3%)/H-ZSM-5.

3.3 Synthesis of Ru(3%)/SBA-15

SBA-15 material was synthesized via a reported method.^{S2} In a typical process, 2g of P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) were dissolved in the 45 mL of HCl solution (1.6 mol/L), and then the mixture was stirred in a $40\text{ }^\circ\text{C}$ water bath for 3 h. To this mixture, 4.25 g of TEOS was added and stirred for another 24 h, at $40\text{ }^\circ\text{C}$. After stirring, the mixed solution was aged for another 24 h at $100\text{ }^\circ\text{C}$. The precipitate was washed enough with water and ethanol, dried in an oven, and then calcined at $550\text{ }^\circ\text{C}$ for 6 h at a $2\text{ }^\circ\text{C}/\text{min}$ heating rate. The Ru(3%)/SBA-15 material was synthesized using the same method as Ru(x%)/N-HZSM-5. The surface area of SBA-15 was $698\text{ m}^2/\text{g}$. The Ru content was determined to be 2.89 wt% in Ru(3%)/SBA-15.

Calculation regarding the formation of acetone during CTH of DPE (GC-FID data):

From the Fig. S20 a and b,

The percentage of acetone formed during the 3 h of CTH of DPE = 10.078 %

The amount of IPA taken in reaction mixture = 10 mL

The amount of acetone formed after CTH of DPE = $10 \times \frac{10.078}{100} = 1.0078 \text{ mL}$

$$\text{Density of acetone (d)} = 0.784 \text{ g mL}^{-1} = \frac{\text{Mass (m)}}{\text{Volume (V)}}$$

Mass of acetone (m) = $d \times V = 0.784 \text{ g mL}^{-1} \times 1.0078 \text{ mL} = 0.79011 \text{ g}$

Moles of acetone formed during CTH of DPE = Mass of acetone $\times \frac{1 \text{ mole}}{58.08 \text{ g}}$

Moles of acetone formed during CTH of DPE = $0.79011 \text{ g} \times \frac{1 \text{ mole}}{58.08 \text{ g}} = 0.01360 \text{ M}$
= 13.60 mmol .

Calculation for the formation of acetone during CTH process (¹H-NMR data):

From Fig. S21,

Acetone yield (%)

= $\frac{[(\text{Acetone (product) i. e. area under the peaks correspond to acetone } (-\text{CH}_3)\text{protons})]}{[(\text{area under the peaks correspond to IPA } (-\text{CH}_3)\text{protons}) + (\text{Acetone (product) i. e. area under the peaks correspond to acetone } (-\text{CH}_3)\text{protons})]} \times 100$

$$\text{Acetone yield (\%)} = \frac{0.68}{6 + 0.68} \times 100 = 10.17 \%$$

The amount of IPA taken in reaction mixture = 10 mL

The amount of acetone formed after CTH of DPE = $10 \times \frac{10.17}{100} = 1.017 \text{ mL}$

$$\text{Density of acetone (d)} = 0.784 \text{ g mL}^{-1} = \frac{\text{Mass (m)}}{\text{Volume (V)}}$$

Mass of acetone (m) = $d \times V = 0.784 \text{ g mL}^{-1} \times 1.017 \text{ mL} = 0.7973 \text{ g}$

$$\text{Moles of acetone formed during CTH of DPE} = \text{Mass of acetone} \times \frac{1 \text{ mole}}{58.08 \text{ g}}$$

$$\begin{aligned} \text{Moles of acetone formed during CTH of DPE} &= 0.7973 \text{ g} \times \frac{1 \text{ mole}}{58.08 \text{ g}} = 0.01372 \text{ M} \\ &= \mathbf{13.72 \text{ mmol}} . \end{aligned}$$

Table S1 Assessing catalytic efficiency in the conversion of DPE using Ru/Zeolite-based catalysts in CTH.

S. No.	Catalyst	Reaction condition	Selectivity of HYD product (%)	Limitations	Reference
1	Ru/HZSM-5-OM	150 °C, 4 h, 4.0 MPa of H ₂ , 50 mg of catalyst, 1 mmol of substrate, 8 mL of water	100	Use of high pressure H ₂ gas (4.0 MPa)	S3
2	Ru/ZSM-5	reaction temperature (200 °C), WHSV (0.0867 min ⁻¹), 0.3 g catalyst, P _{H₂} (4.0 MPa), H ₂ flow rate (120 mL/min), guaiacol flow rate (0.026 g/min)	100	Use of high pressure H ₂ gas (4.0 MPa)	S4
3	Microporous Beta, Y, and ZSM-5 zeolites	1.0 g lignin, 0.5 g catalyst, and 100 mL ethanol, 280 °C, 6 h	-	High reaction temperature (280 °C) Lignin ethanolysis to produce the aromatic monomers not fuel range chemicals.	S5
4	Ru/H-Beta	1 mmol substrate, 0.1 g catalyst, 4 mL H ₂ O, 4.0 MPa H ₂ , temperature 140 °C	100	Use of high pressure H ₂ gas (4.0 MPa)	S6
5	Ru/HZSM-5	100 mg of DPE, 20 mL of n-hexane, 30 mg of 5% Ru/HZSM-5 catalyst, 1 MPa H ₂ , 2 h, 210 °C	100	Reaction temperature 210 °C, Use of 1 MPa H ₂ pressure, high Ru- metal loading (5 wt.%)	S7
6	Ru@H-ZSM-5	150 °C, 5.0 MPa H ₂ , phenol (2.13 mmol), catalyst (200 mg), and water (10 mL)	100	Use of high pressure H ₂ gas (4.0 MPa)	S8
7	Ru(3%)/N-HZSM-5	DPE (1 mmol), IPA (10 mL), catalyst (100 mg), temperature (170 °C), time (3 h), and N ₂ (1 MPa)	100	Sustainable CTH process (Lower reaction temperature < 180 °C) (Alcohol as H-donor)	Present work

Table S2

Ratio of Ru⁰/RuO_x calculated using a high-resolution Ru 3p XPS spectrum of Ru(3%)/N-HZSM-5.

Peaks	Binding energy	Area
Ru ⁰ 3p _{3/2}	462.18 eV	11905
Ru ⁰ 3p _{1/2}	484.16 eV	4901
RuO _x 3p _{3/2}	466.48 eV	4256
RuO _x 3p _{1/2}	486.78 eV	2519
Ru ⁰ 3p _{3/2} + Ru ⁰ 3p _{1/2}	Ru ⁰	16806
RuO _x 3p _{3/2} + RuO _x 3p _{1/2}	RuO _x	6775
	Ru ⁰ / RuO _x	2.48
	{Ru ⁰ / (Ru ⁰ + RuO _x)} ×100	71.26%

Table S3

Ratio of Ru⁰/RuO_x calculated using high-resolution Ru 3p XPS spectrum of Ru(3%)/N-HZSM-5- spent.

Peaks	Binding energy	Area
Ru ⁰ 3p _{3/2}	462.18 eV	10788
Ru ⁰ 3p _{1/2}	484.16 eV	3969
RuO _x 3p _{3/2}	466.48 eV	3978
RuO _x 3p _{1/2}	486.78 eV	1558
Ru ⁰ 3p _{3/2} + Ru ⁰ 3p _{1/2}	Ru ⁰	14766
RuO _x 3p _{3/2} + RuO _x 3p _{1/2}	RuO _x	5536
	Ru ⁰ / RuO _x	2.66
	{Ru ⁰ / (Ru ⁰ + RuO _x)} ×100	72.73%

Table S4

The acidity measurements determined from NH₃-TPD.

S. N.	Catalyst	Acidity ($\mu\text{mol g}^{-1}$) ^a			
		Weak	Medium	Strong	Total
1	HZSM-5	40.2	9.0	-	49.2
2	Ru(3%)/HZSM-5	40.5	14.6	-	55.1
3	SBA-15	-	-	-	-
4	Ru(3%)/SBA-15	6.6	26.9	-	33.5

^aCalculated by the NH₃-TPD analysis.

Table S5

Catalytic reaction data for the control reactions and analysis of the products yield.

S. N.	Catalyst	Con. (%)	Product Yield (%)						HYD yield (%)	Aromatic yield (%)
			BEZ	CHE	PHE	CHO	CHL	CPE		
1	Ru(3%)/N-HZSM-5	50.9 ^a	6.2	14.7	8.7	4.3	16.7	0.3	36.0	14.9
2	Ru(3%)/N-HZSM-5	41.5 ^b	2.3	14.9	2.6	4.2	17.6	0.2	36.9	4.9
3	Ru(3%)/N-HZSM-5	56 ^c	7.9	18.1	9.0	1.5	19.3	0.1	39.0	16.9
4	Ru(3%)/N-HZSM-5	100 ^d	-	49.9	-	-	49.8	0.3	100	-
5	Ru(3%)/HZSM-5	80 ^d	9.1	26.5	11.3	4.6	28.2	0.3	59.6	20.4

^aReaction conditions: DPE (1 mmol), IPA (10 mL), catalyst (100 mg), temperature (150 °C), time (3 h), and N₂ (1 MPa).

^bReaction conditions: DPE (1 mmol), IPA (10 mL), catalyst (100 mg), temperature (170 °C), time (1 h), and N₂ (1 MPa).

^cReaction conditions: DPE (1 mmol), dodecane (10 mL), catalyst (100 mg), temperature (170 °C), time (3 h), and H₂ (1 MPa).

^dReaction conditions: DPE (1 mmol), IPA (10 mL), catalyst (100 mg), temperature (170 °C), time (3 h), and N₂ (1 MPa).

Table S6 Controlled CTH reactions with different substrates.

S. N.	Substrate	Conversion (%) ^a	Product (yield (%))
1	Benzene ^b	100	Cyclohexane (100)
2	Phenol ^b	100	Cyclohexane (2.8), Cyclohexanol (97.2)
3	Toluene ^c	<2	Methylcyclohexane (100)
4	Ethylbenzene ^c	22.3	Ethylcyclohexane (100)

^aReaction conditions: Substrate (1 mmol), IPA (10 mL), catalyst (100 mg), temperature (170 °C), and N₂ (1 MPa).

^bTime 2 h.

^cTime 3 h.

Table S7 Comparative catalytic activity for the CTH of DPE with the reported catalysts.

Entry	Catalyst	H-Donor	Reaction conditions (Temperature/Time/Pressure)	DPE Conv. (%)	Product Sele. (%)		Yield (%)		Ref.
					HYD Sele.	Aromatic Sele.	HYD Yield	Aromatic Yield	
1	RANEY Ni	2-propanol	80 °C/12 h/-	100	52	48	-	-	S9
2	Ni/Al ₂ O ₃ -650 °C	2-propanol	150 °C/5 h/1 MPa(N ₂)	100	-	-	100	100	S10
3	20% Ni/CNT	2-propanol	240 °C/2/-	100	-	-	CHE (88) CHL (82)	-	S11
4	Pt/C	ethanol-water-mixture	300 °C/12h/0.1 MPa (N ₂)	100	-	100	-	-	S12
5	Ru/hydroxyapatite	2-propanol	150 °C/10 h/-	100	-	-	73.7	26.3	S13
6	Au ₁ Pd ₁ /CeO ₂	HCOOH	180 °C/ 24 h/-	100	-	100	-	-	S14
7	Ru(3%)/N-HZSM-5	2-propanol	170 °C/ 3h/1 MPa (N ₂)	100	100	-	100	-	This work

Table S8

Ru contents in Ru(3%)/N-HZSM-5 catalyst.

Catalyst	Ru metal loading weight (%)
Ru(3%)/N-HZSM-5	2.94
Ru(3%)/N-HZSM-5-spent ^a	2.92

^aRu content after five recycling experiment.

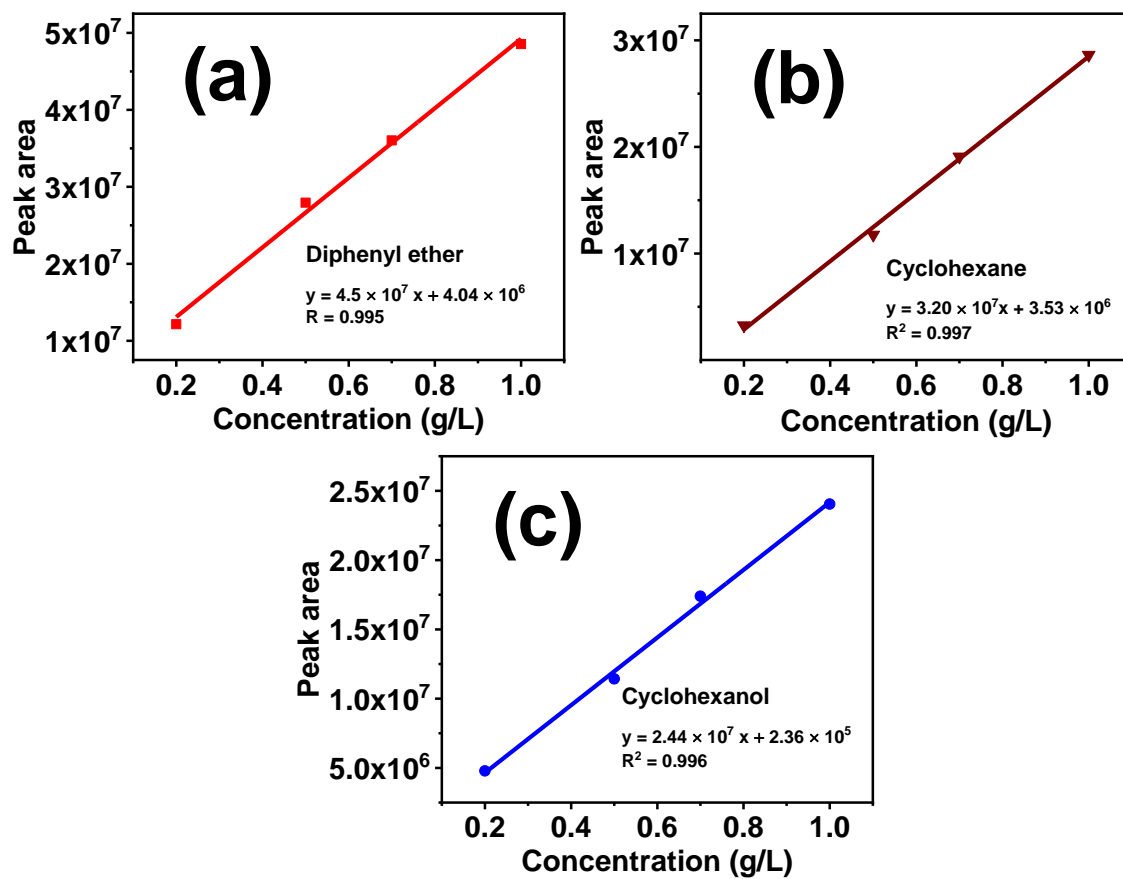


Fig. S1 Calibration plots of (a) diphenyl ether, (b) cyclohexane, and (c) cyclohexanol.

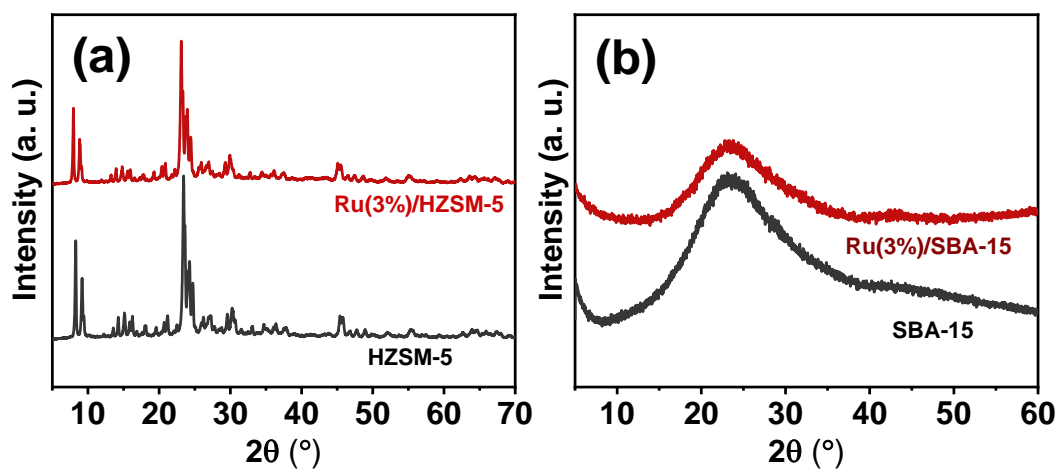


Fig. S2 PXRD patterns of the (a) HZSM-5 and Ru(3%)/HZSM-5, (b) SBA-15 and Ru(3%)/SBA-15.

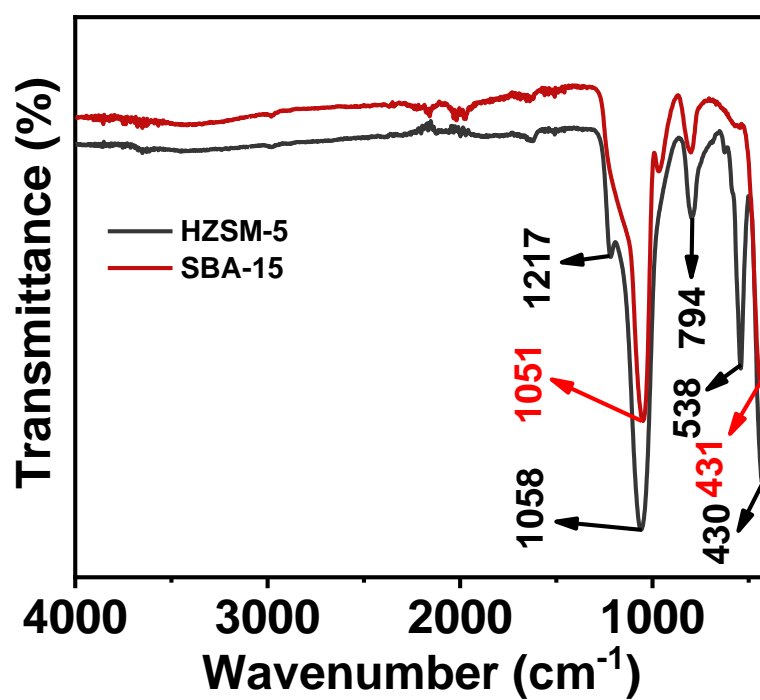


Fig. S3 FT-IR spectra of the HZSM-5 and SBA-15.

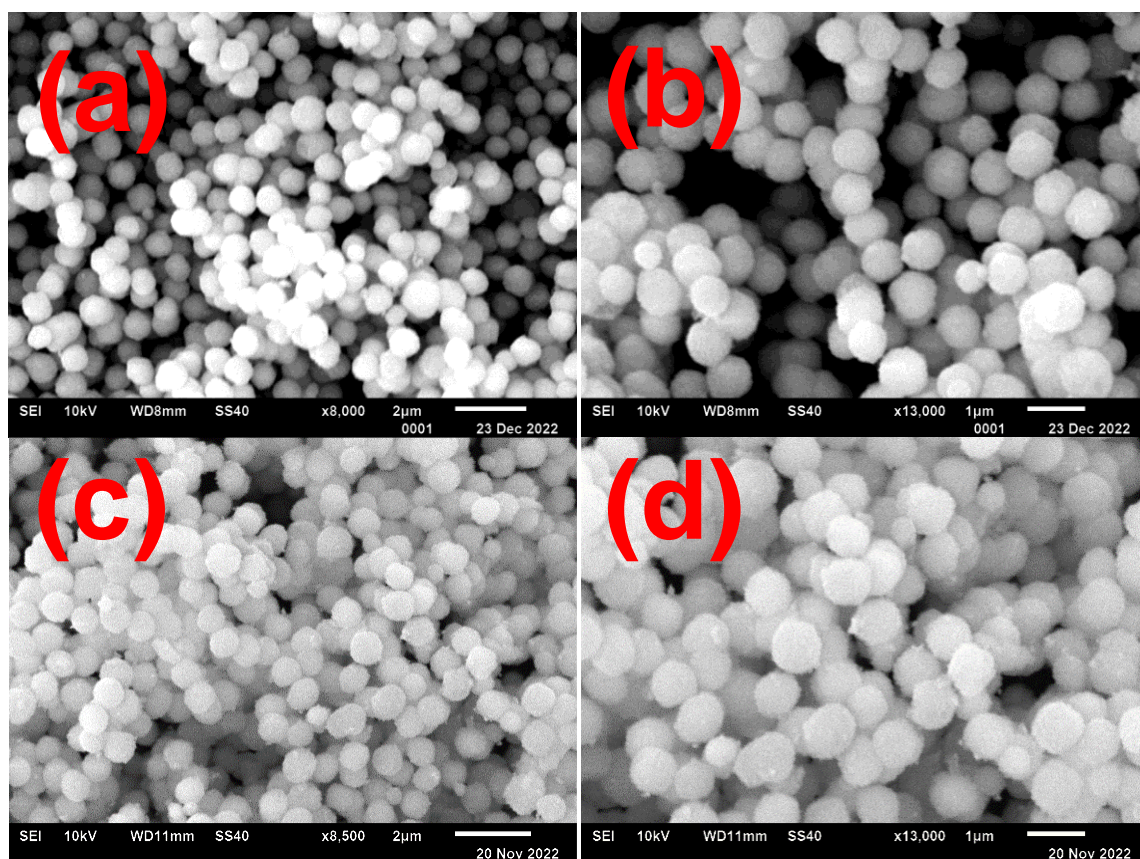


Fig. S4 SEM images of the (a, b) N-HZSM-5, and (c, d) Ru(3%)/N-HZSM-5.

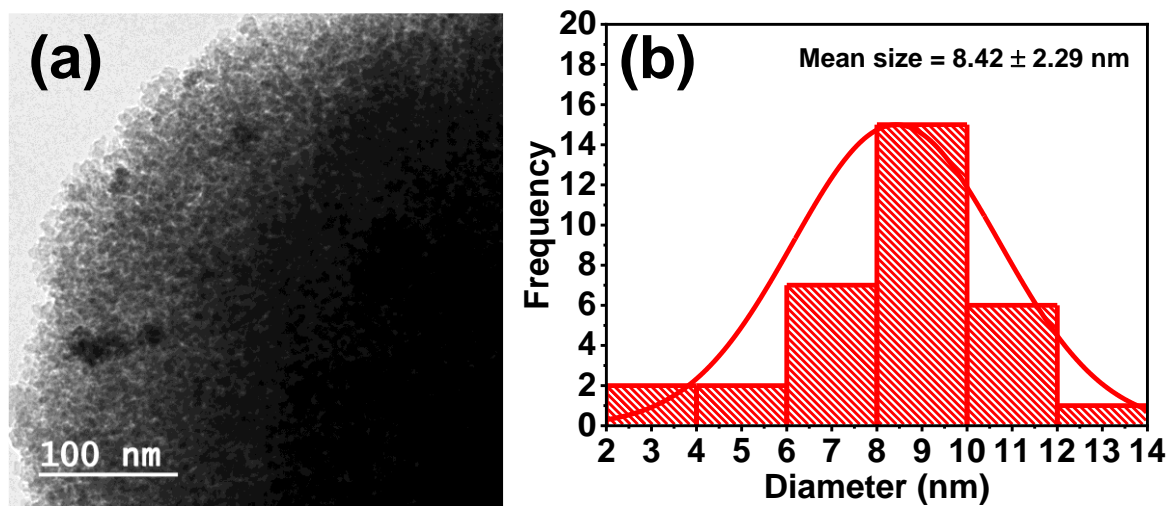


Fig. S5 (a) TEM image and (b) size distribution of Ru NPs in Ru(3%)/N-HZSM-5.

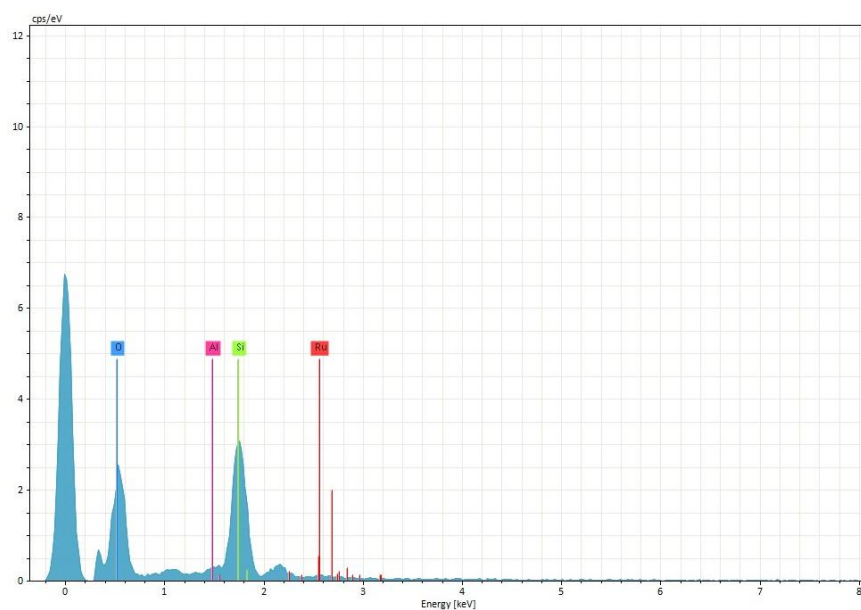


Fig. S6 EDAX spectrum of Ru(3%)/N-HZSM-5 catalyst.

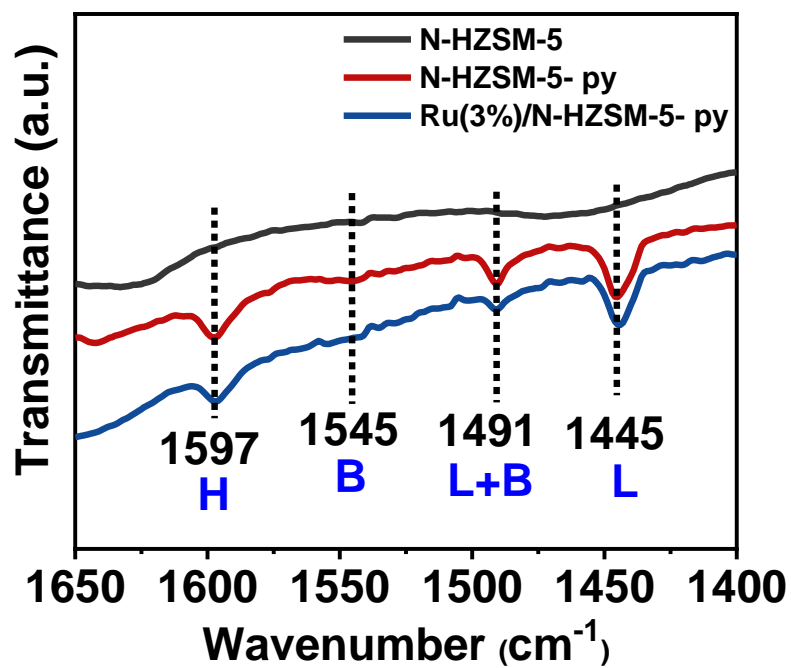


Fig. S7 FT-IR spectra of N-HZSM-5 support, Py-IR spectra of N-HZSM-5 and Ru(3%)/N-HZSM-5 catalyst.

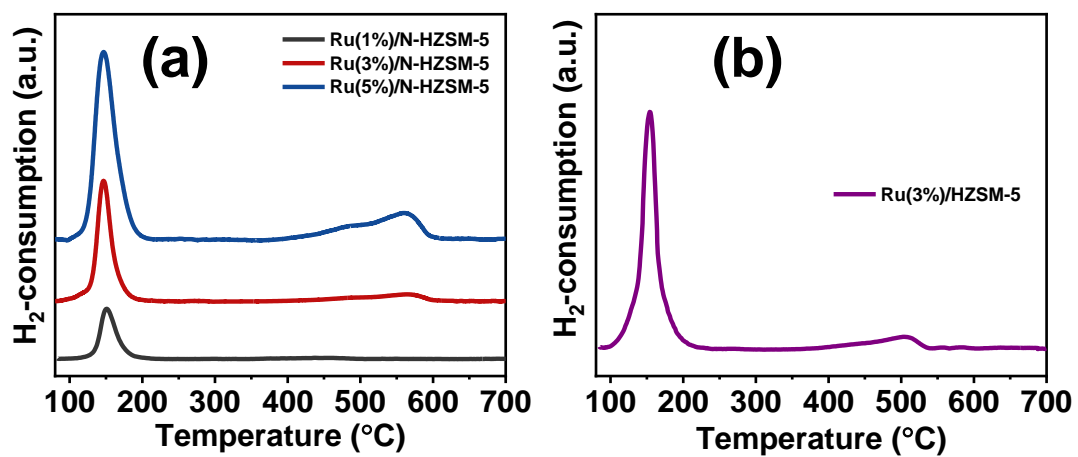
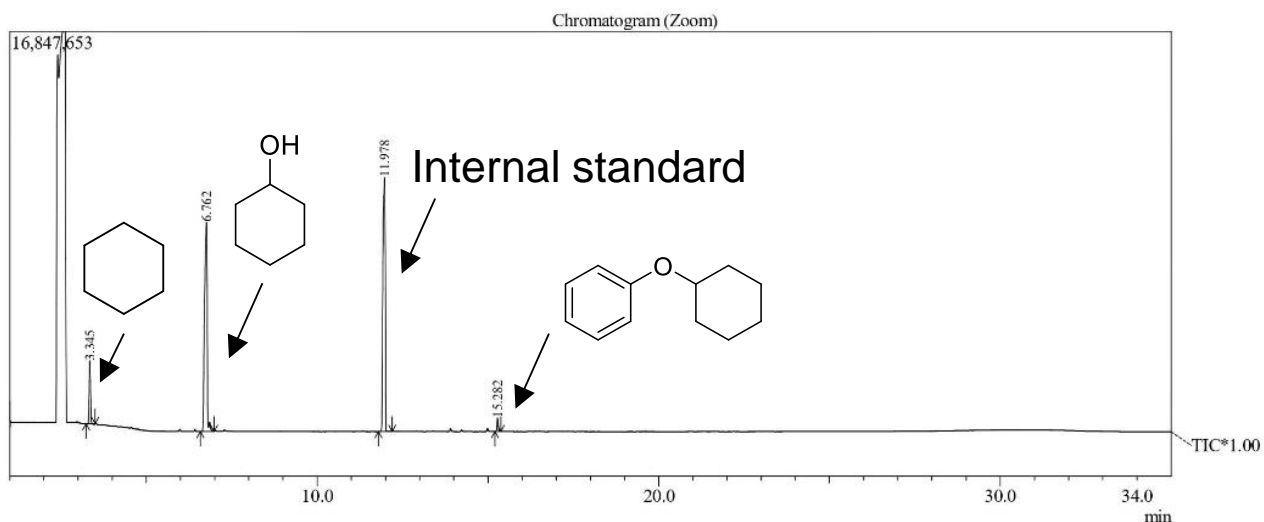
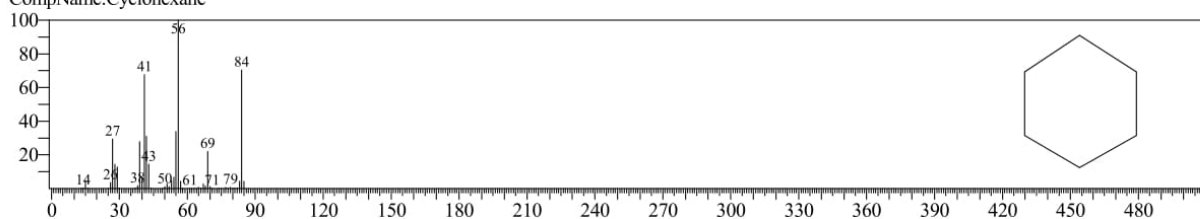


Fig. S8 H₂-TPR profiles of (a) Ru(x%)/N-HZSM-5 (where x = 1, 3, 5) and (b) Ru(3%)/HZSM-5 catalyst.

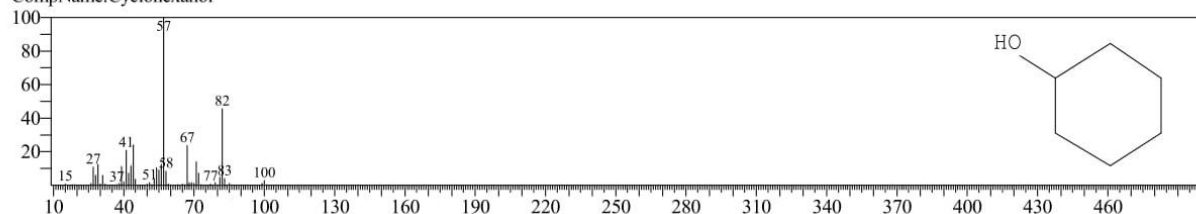


Spectrum

Hit#:2 Entry:1693 Library:NIST17.lib
 SI:90 Formula:C₆H₁₂ CAS:110-82-7 MolWeight:84 RetIndex:719
 CompName:Cyclohexane



Hit#:1 Entry:4372 Library:NIST17.lib
 SI:97 Formula:C₆H₁₂O CAS:108-93-0 MolWeight:100 RetIndex:908
 CompName:Cyclohexanol



Hit#:1 Entry:48825 Library:NIST17.lib
 SI:94 Formula:C₁₂H₁₆O CAS:2206-38-4 MolWeight:176 RetIndex:1430
 CompName:Benzene, (cyclohexyloxy)-

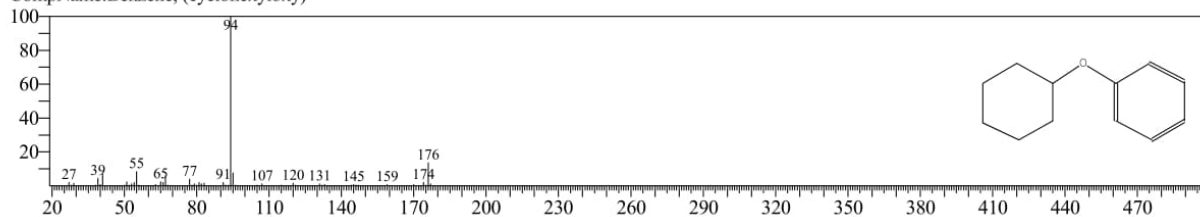


Fig. S9 GC-MS chromatogram of CTH of DPE after 3 h (at 100% conversion) (Reaction conditions: DPE (1 mmol), Ru(3%)/N-HZSM-5 (100 mg), IPA (10 mL), N₂ (10 bar), Temperature (170 °C), Time (3 h) internal standard (n-dodecane).

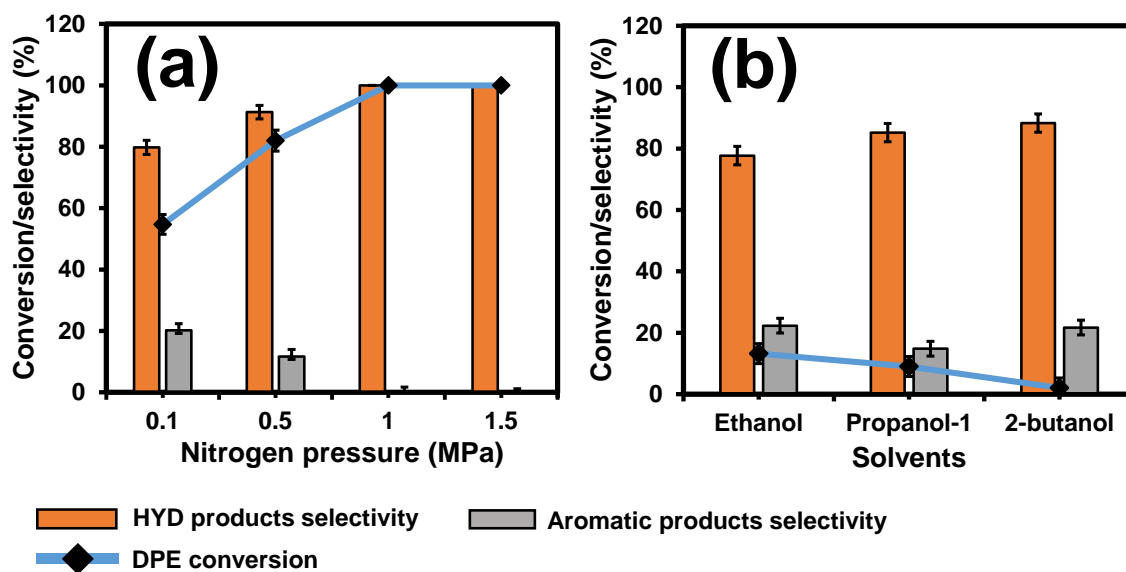


Fig. S10 (a) Influence of N₂-pressure [Reaction conditions: DPE (1 mmol), IPA (10 mL), catalyst (100 mg), temperature (170 °C), and time (3 h)] and (b) solvent [Reaction conditions: DPE (1 mmol), solvent (10 mL), catalyst (100 mg), temperature (170 °C), time (3 h), and N₂ (1 MPa)] in the CTH of DPE over Ru(3%)/N-HZSM-5.

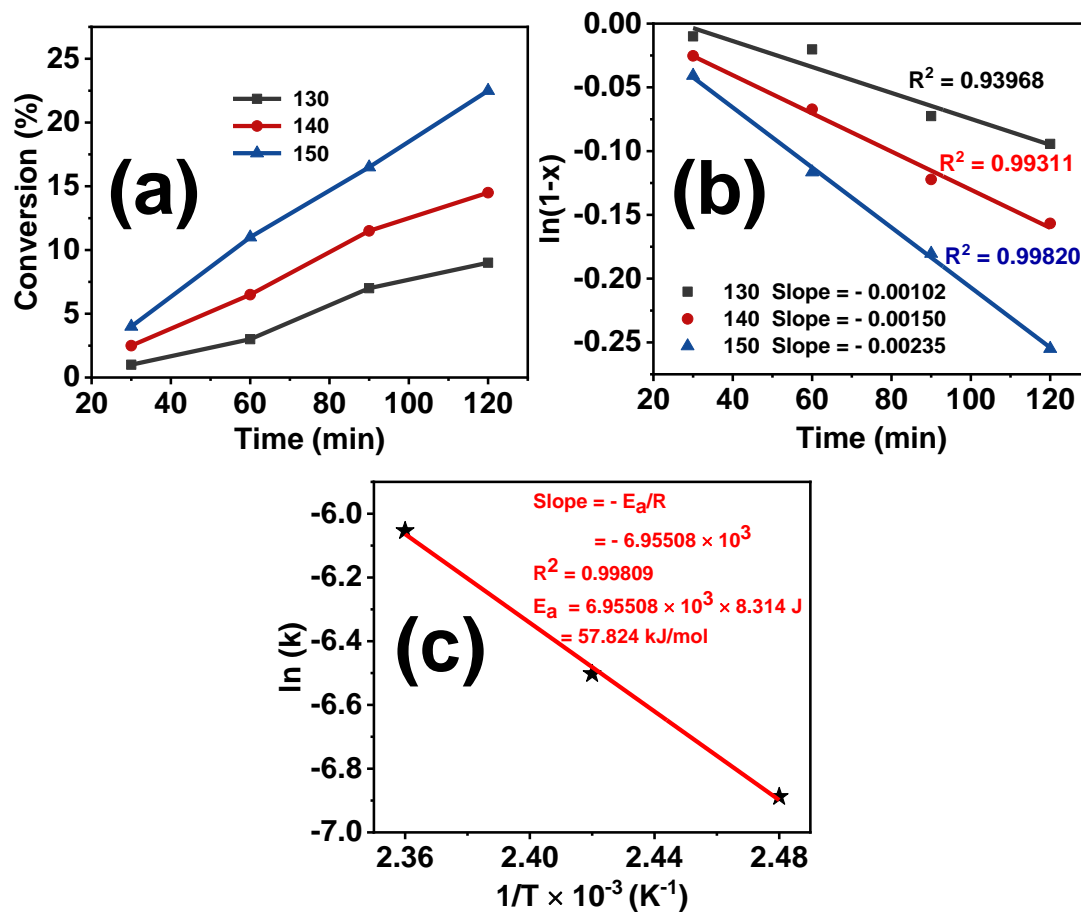


Fig. S11 Kinetic plots for the CTH of DPE (a) relationship between DPE conversion and reaction time, (b) relationship between $-\ln(1-x)$ and reaction time, and (c) relationship between $\ln k$ and $1/\text{Temperature}$ ($1/T$). [Reaction condition: DPE (1 mmol), Ru(3%)/N-HZSM-5 (100 mg), IPA (10 mL), N_2 (10 bar)]

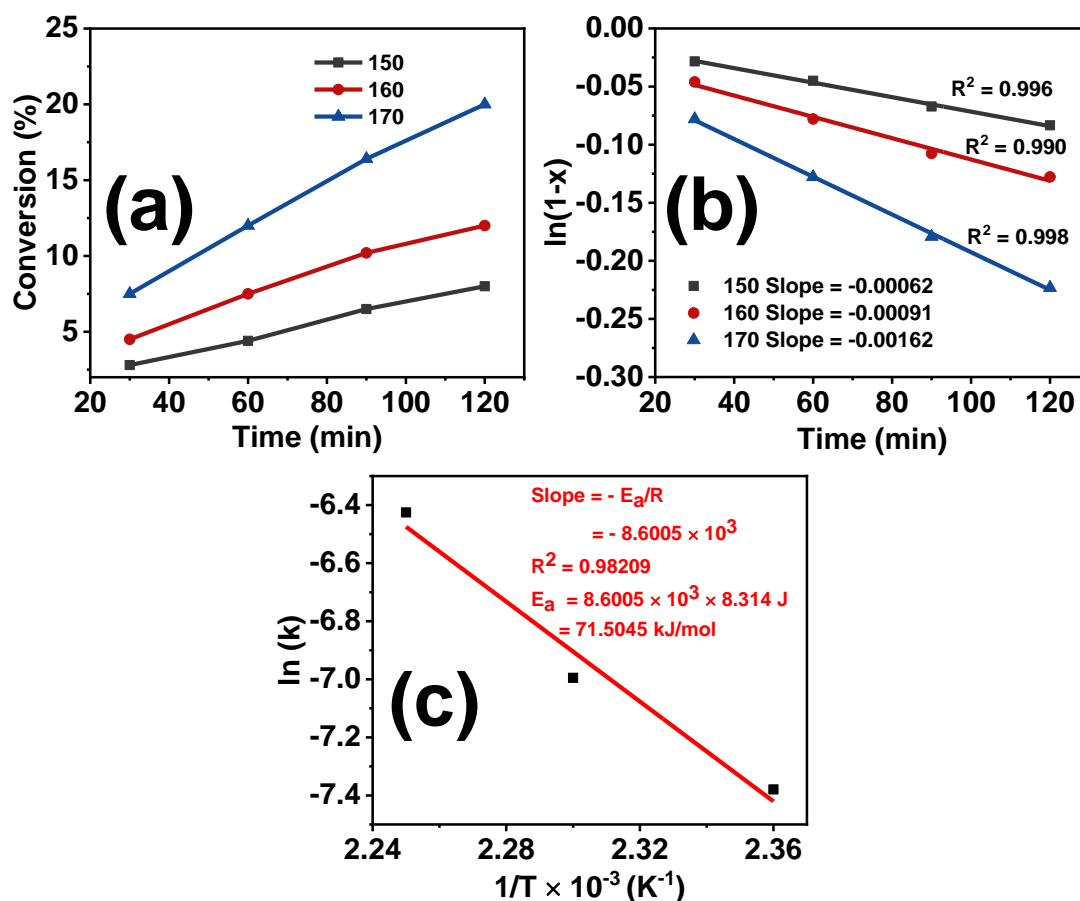


Fig. S12 Kinetic plots for the CTH of DPE (a) relationship between DPE conversion and reaction time, (b) relationship between $-\ln(1-x)$ and reaction time, and (c) relationship between $\ln k$ and $1/\text{Temperature}$ ($1/T$). [Reaction condition: DPE (1 mmol), Ru(1%)/N-HZSM-5 (100 mg), IPA (10 mL), N_2 (10 bar)]

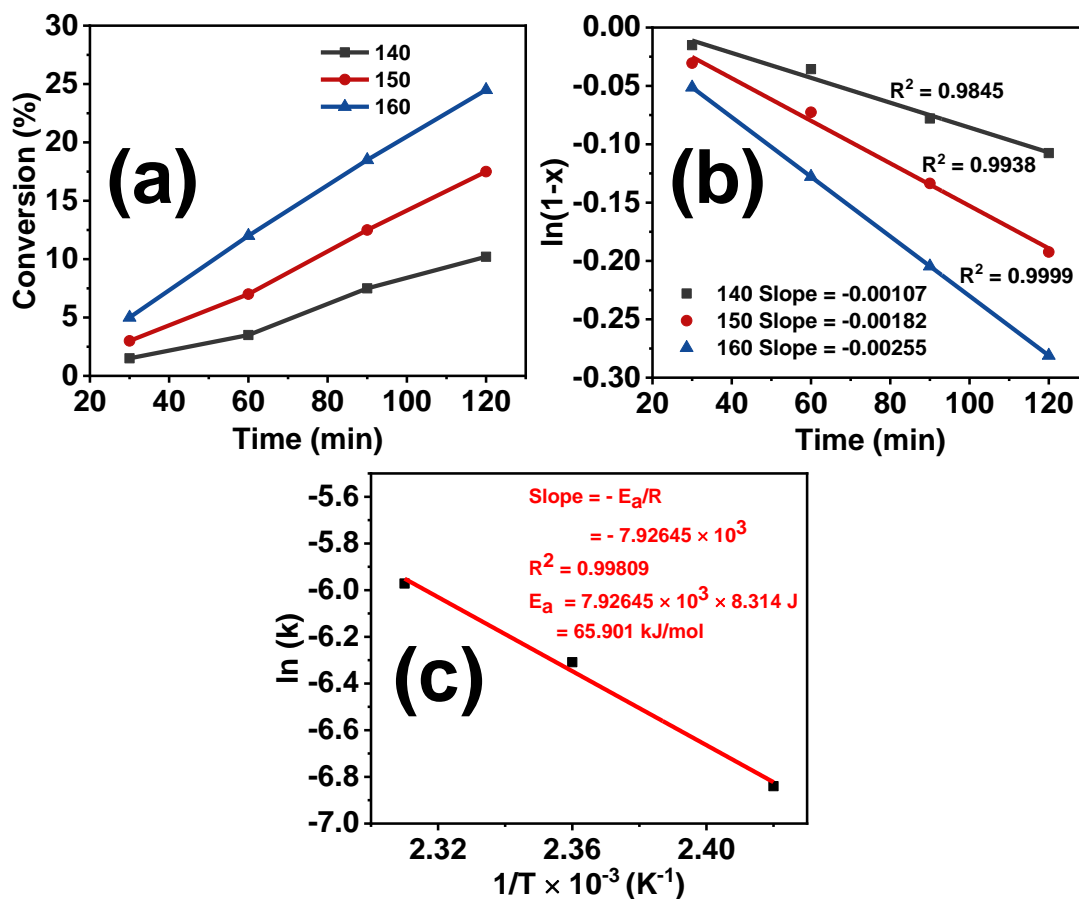


Fig. S13 Kinetic plots for the CTH of DPE (a) relationship between DPE conversion and reaction time, (b) relationship between $-\ln(1-x)$ and reaction time, and (c) relationship between $\ln k$ and $1/\text{Temperature}$ ($1/T$). [Reaction condition: DPE (1 mmol), Ru(3%)/HZSM-5 (100 mg), IPA (10 mL), N_2 (10 bar)]

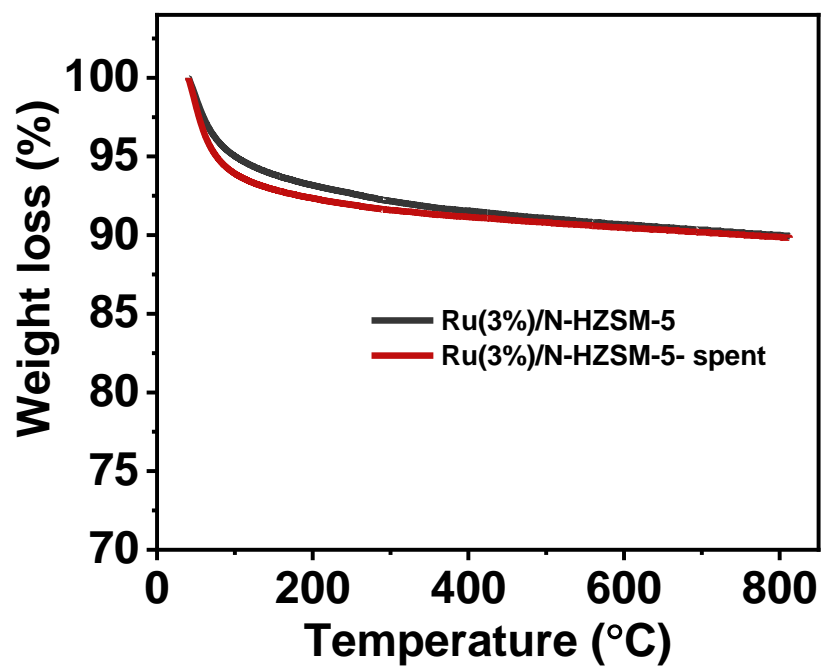


Fig. 14 Thermograms of the fresh and spent Ru(3%)/N-HZSM-5 catalyst.

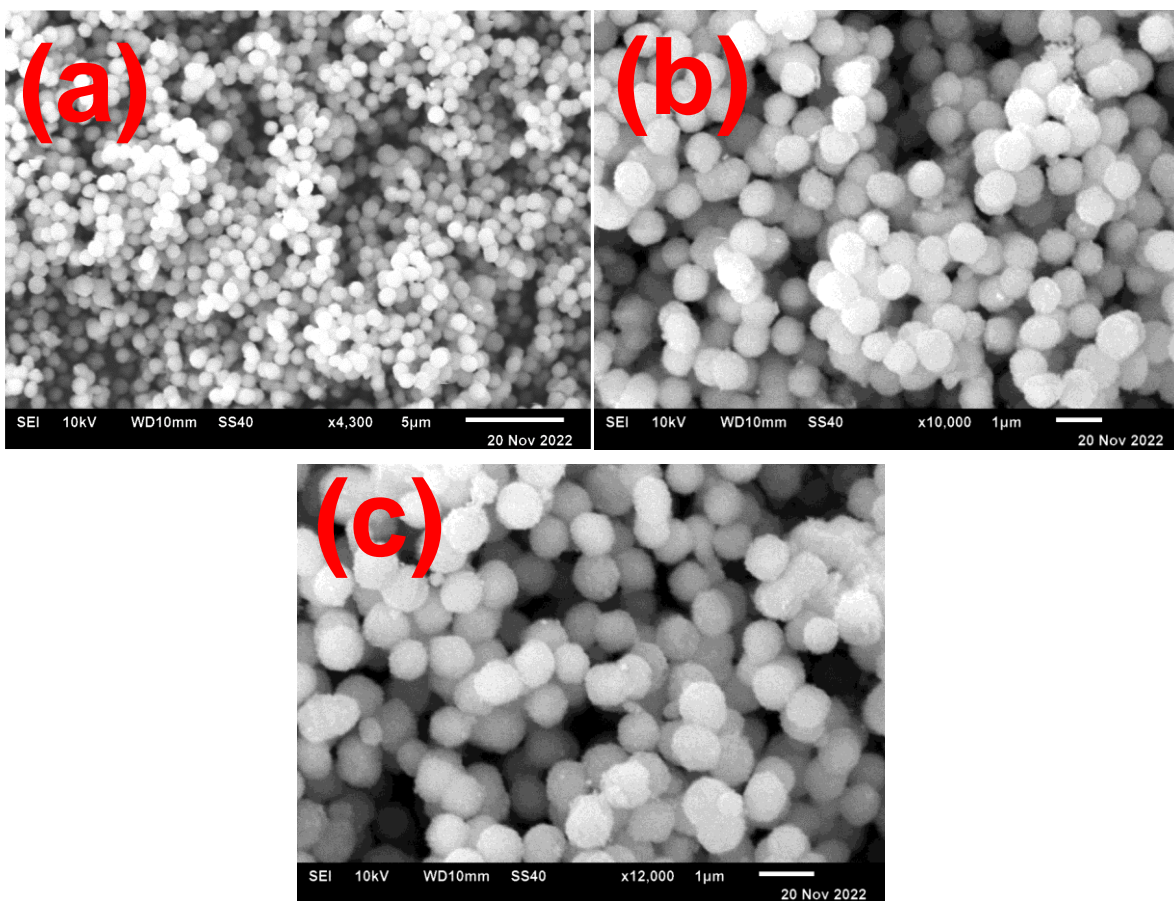


Fig. S15 SEM images (a, b, and c) of the Ru(3%)/N-HZSM-5-spent.

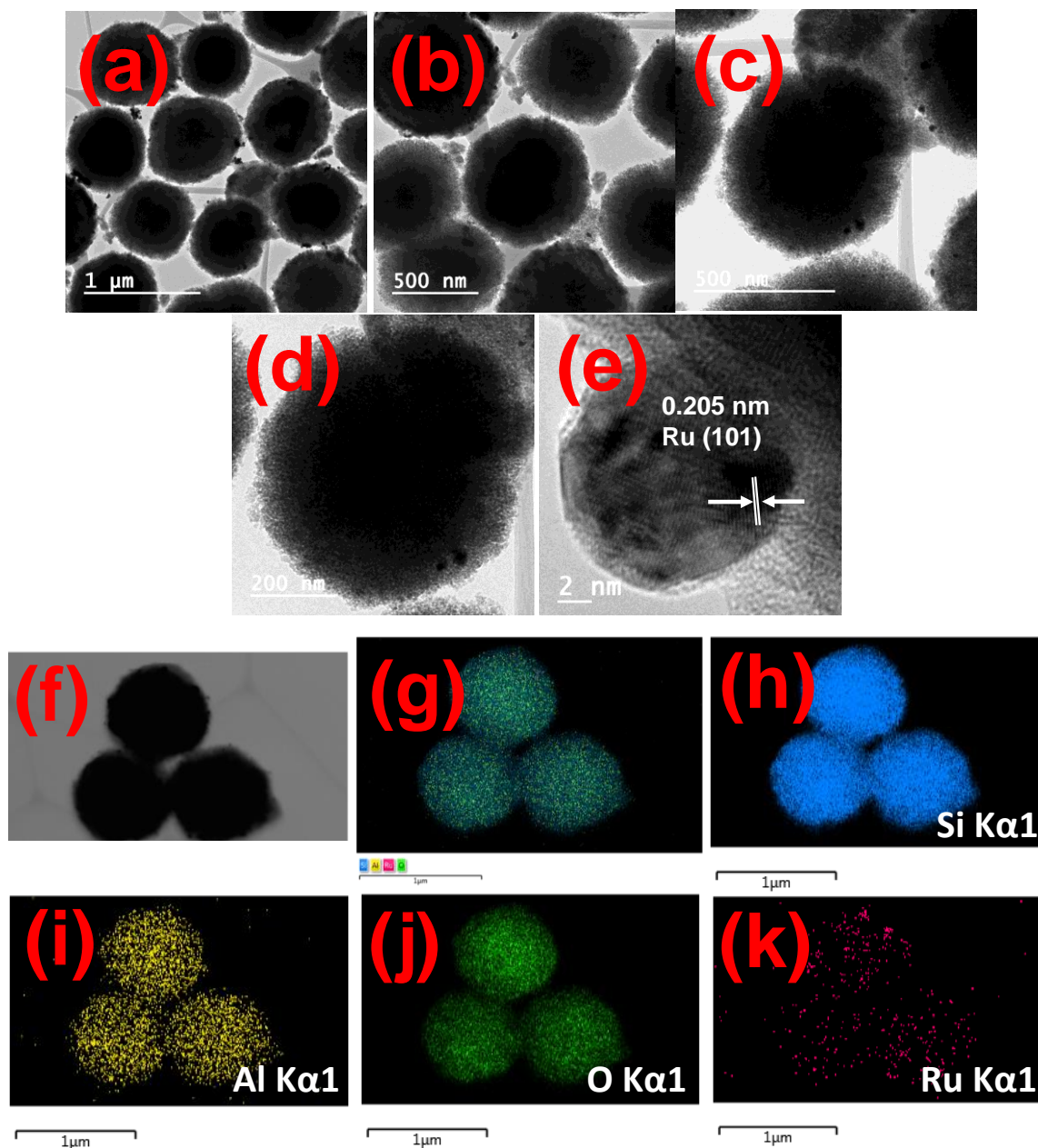


Fig. S16 (a) TEM images, (b, c, d and e) HR-TEM images at different magnifications (illustrating the Ru (101) lattice fringes), (f) the region selected for elemental mapping, and elemental mapping for (g) combined Ru, Al, Si, O, (h) Si, (i) Al, (j) O (k) Ru elements in the Ru(3%)/N-HZSM-5-spent.

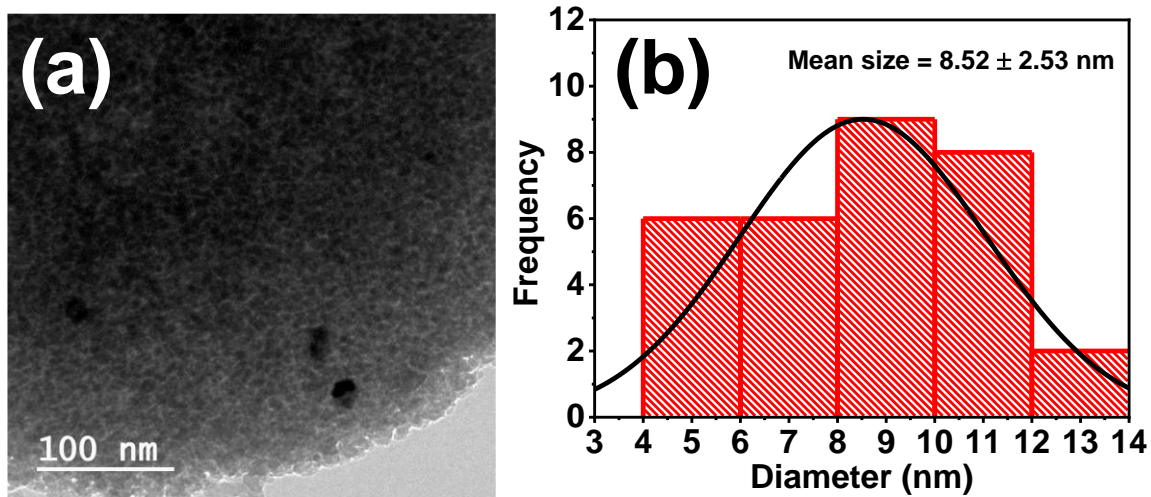


Fig. S17 (a) TEM image and (b) Ru NPs size distribution of the Ru(3%)/N-HZSM-5-spent catalyst.

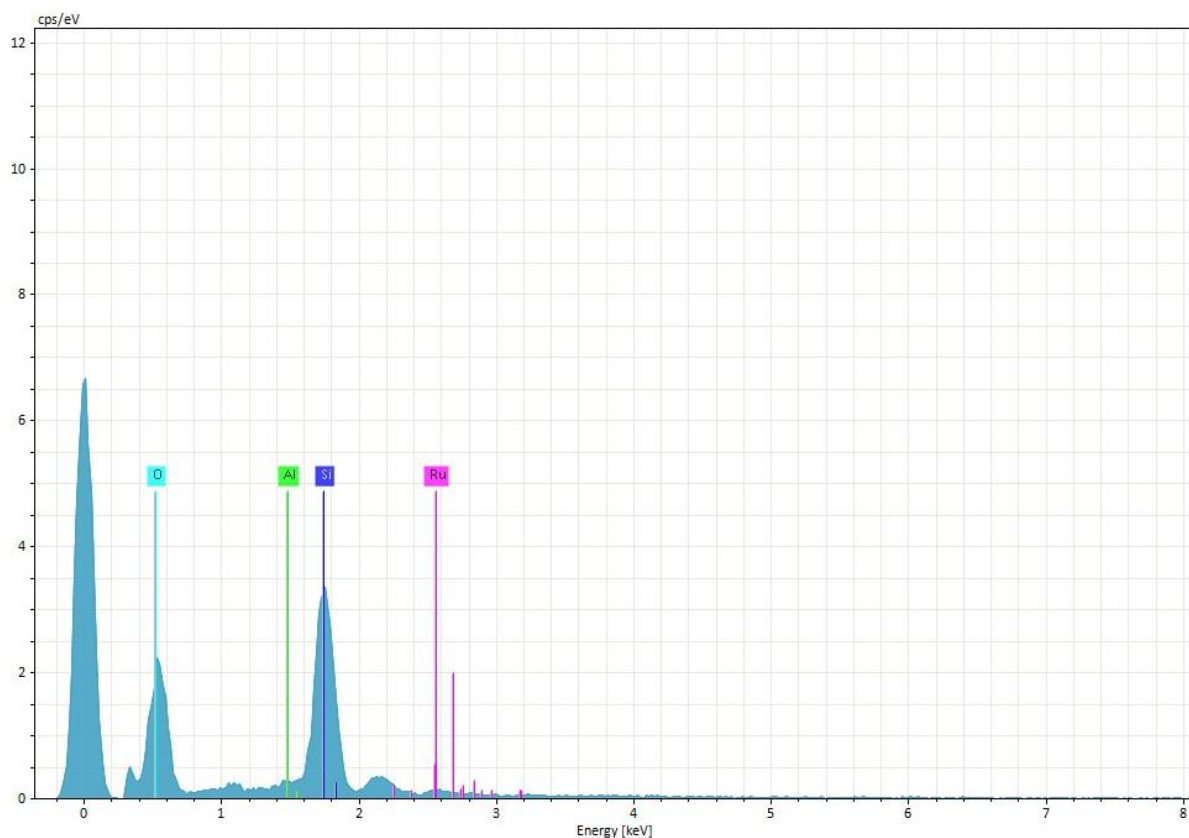
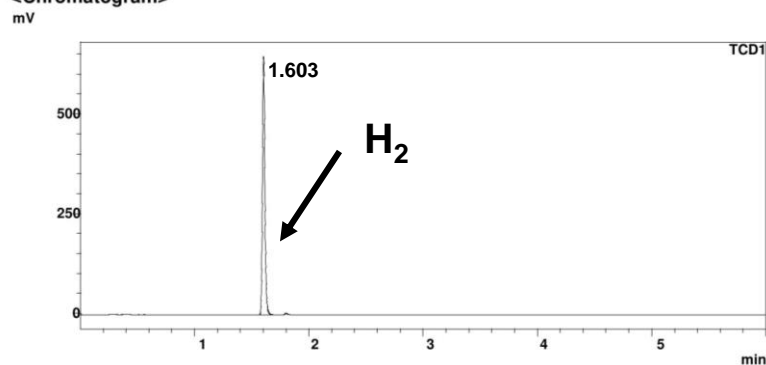


Fig. S18 EDAX spectrum of the Ru(3%)/N-HZSM-5-spent catalyst.

<Sample Information>

Sample Name : AT-1
 Sample ID : AT-1
 Data Filename : AT-1.gcd
 Method Filename : GAS ANALYSIS.gcm
 Batch Filename :
 Vial # : 1
 Injection Volume : 1 uL
 Date Acquired : 22-09-2023 15:24:32
 Date Processed : 22-09-2023 16:56:29
 Sample Type : Gas
 Acquired by : IIT ROPAR
 Processed by : IIT ROPAR

<Chromatogram>



<Peak Table>

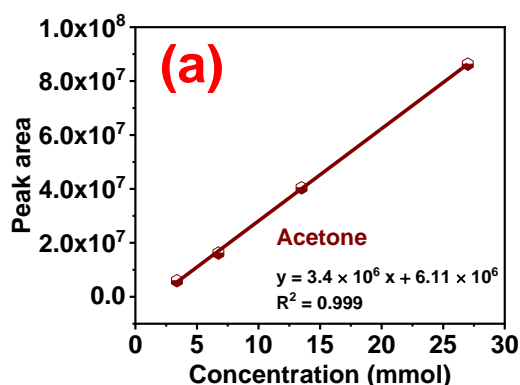
Peak#	Ret. Time	Area	Height	Area (%)	Unit	Mark	Name
1	1.603	937859	630991	100.000		M	H ₂
Total		937859	630991				

Fig. S19 GC-TCD chromatogram showing the gas phase GC chromatogram from the IPA mediated CTH of DPE. Reaction conditions: DPE (1 mmol), IPA (10 mL), catalyst (100 mg), temperature (170 °C), time (3 h) and N₂ (1 MPa). GC instrument information: The reaction mixture was analyzed by gas chromatography (GC) (Shimadzu 2010 Plus; SH-Rt®-Q-BOND; capillary column: SH; 30m × 0.32mm ID × 10µm df) equipped with thermal conductivity detector (TCD) detector. Oven Temperature: 36 °C (hold 6 min), Nitrogen, Constant Flow @ 1.20 mL/min.

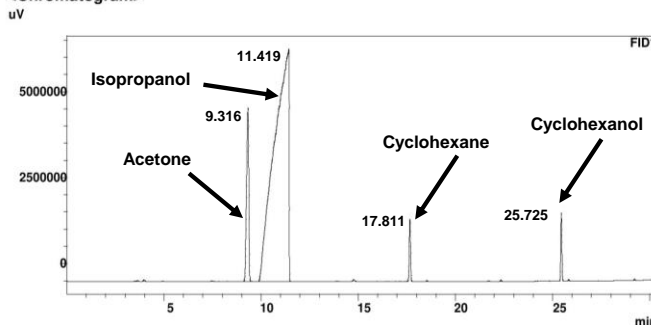
<Sample Information>

Sample Name : AT-1
 Sample ID : AT-1
 Data Filename : AT-1.gcd
 Method Filename : FID-BHASKAR_35C_ISO_ACETONE-IPA.gcm
 Batch Filename :
 Vial # : 2
 Injection Volume : 1 uL
 Date Acquired : 29-09-2023 10:17:01
 Date Processed : 29-09-2023 22:43:45
 Sample Type : Liquid
 Acquired by : IIT ROPAR
 Processed by : IIT ROPAR

(b)



<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%	Mark	Name
1	9.316	39087132	5044791	10.078	M	Acetone
2	11.419	348761533	6757871	89.922	M	Isopropanol
Total		387848665	11802663	100.000		

Fig. S20 (a) Calibration data for the assessment of the acetone formation during the catalytic process, (b) GC-FID chromatogram showing the liquid phase from the IPA mediated CTH of DPE. Reaction conditions: DPE (1 mmol), IPA (10 mL), catalyst (100 mg), temperature (170 °C), time (3 h) and N₂ (1 MPa). GC instrument information: The reaction mixture was analyzed by gas chromatography (GC) (Shimadzu 2010 Plus; Rxi-624 Sil MS; capillary column: Restek; 30m × 0.32mm ID × 1.8µm df) equipped with flame ionization (FID) detector. Oven Temperature: 35 °C (hold 13 min) to 225 °C @ 30 °C/min (hold 7 min), Nitrogen, Constant Flow @ 0.80 mL/min.

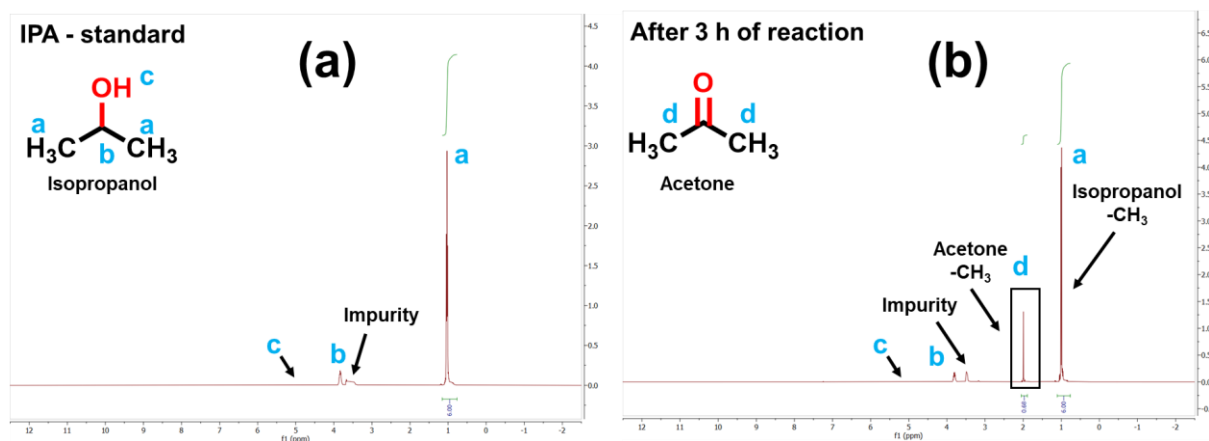


Fig. S21 (a) ¹H NMR spectra recorded before reaction, (b) ¹H NMR spectra recorded after reaction demonstrating the acetone formation.

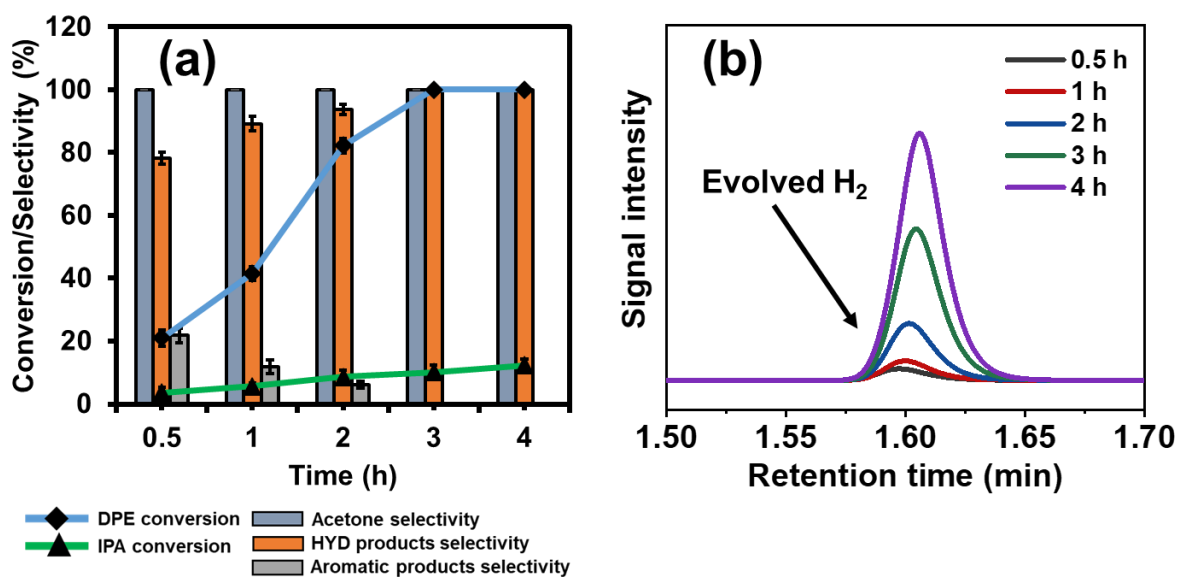


Fig. S22. (a) the IPA and DPE conversion and products selectivity during the course of the reaction. (b) Gas chromatogram (TCD) of gaseous phase in the CTH of DPE during the course of reaction (Shimadzu 2010 Plus; SH-Rt®-Q-BOND; capillary column: SH; 30m × 0.32mm ID × 10µm df).

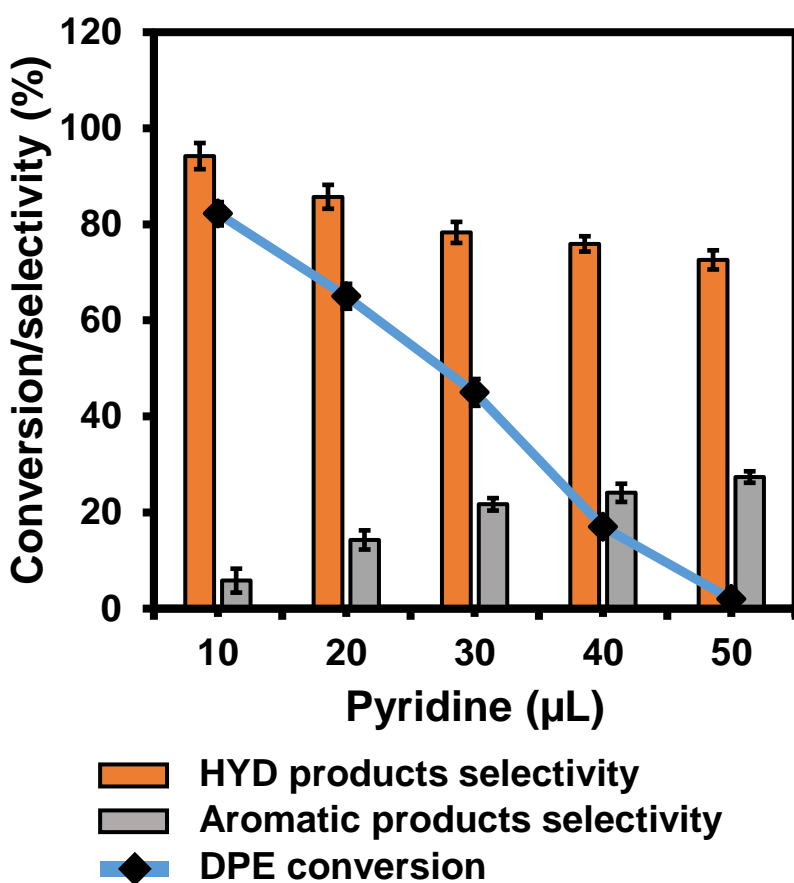
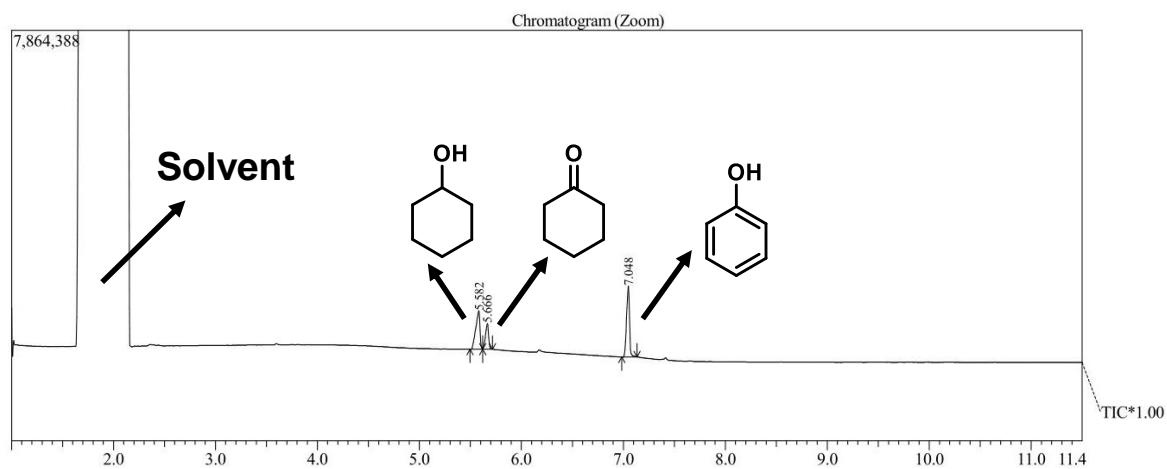
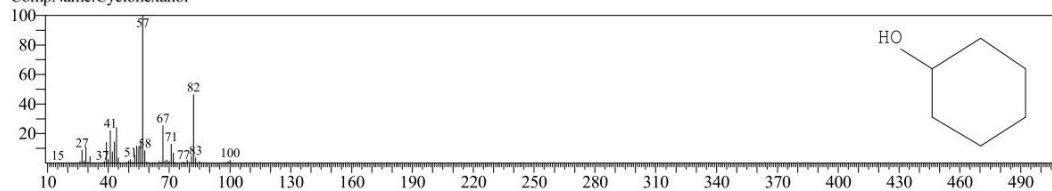


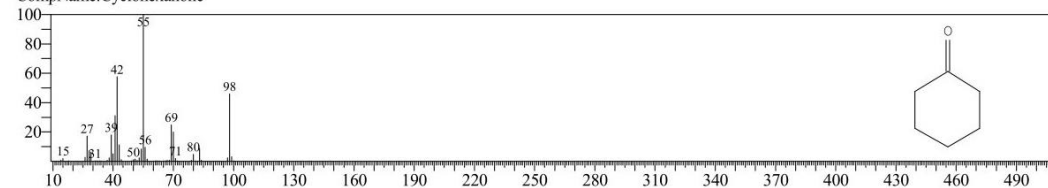
Fig. S23 Poisoning test with pyridine in the CTH of DPE over Ru(3%)/N-HZSM-5.



Hit#:1 Entry:4257 Library:NIST17.lib
 SI:90 Formula:C6H12O CAS:108-93-0 MolWeight:100 RetIndex:908
 CompName:Cyclohexanol



Hit#:1 Entry:3618 Library:NIST17.lib
 SI:83 Formula:C6H10O CAS:108-94-1 MolWeight:98 RetIndex:891
 CompName:Cyclohexanone



Hit#:1 Entry:2878 Library:NIST17.lib
 SI:96 Formula:C6H6O CAS:108-95-2 MolWeight:94 RetIndex:901
 CompName:Phenol

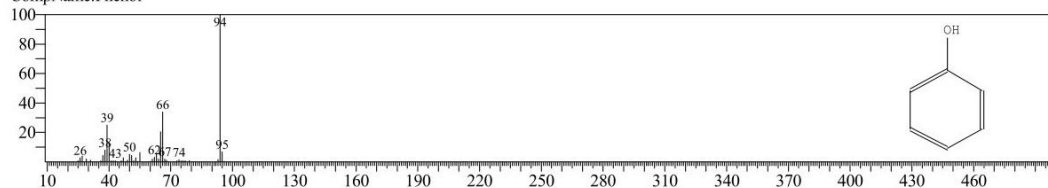
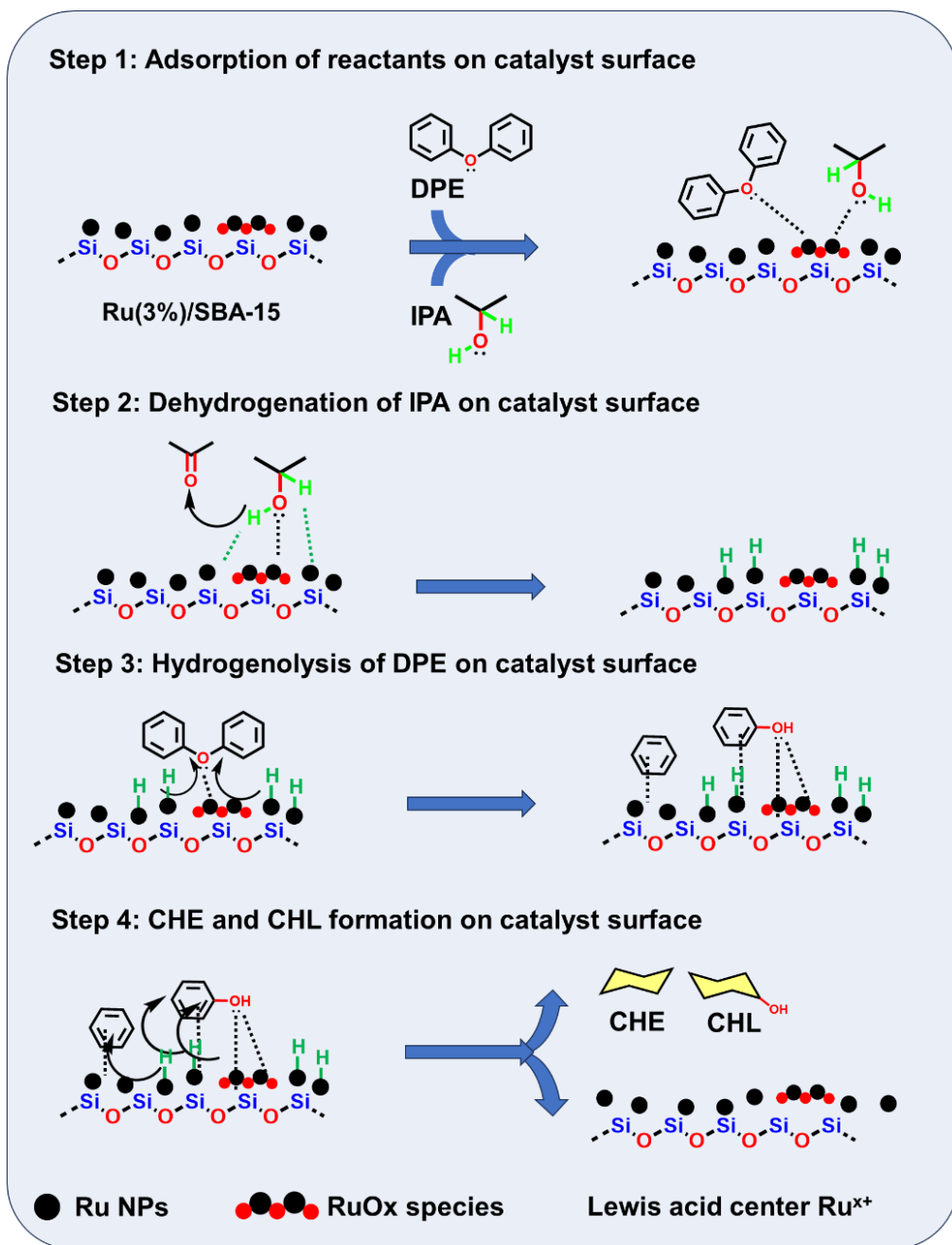


Fig. S24 GC-MS chromatogram of CTH of phenol after 1 h (at 60% conversion) [Reaction conditions: phenol (1 mmol), Ru(3%)/N-HZSM-5 (100 mg), IPA (10 mL), N₂ (10 bar), Temperature (170 °C), Time (1 h)].



Scheme S1 Proposed mechanism for the CTH of DPE over Ru(3%)/SBA-15.

Reference

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