SUPPLEMENTARY INFORMATION

# "Enhancing Butadiene Yield and Catalyst Stability via Aqueous Feed Dilution in 1,3-Butanediol Dehydration"

Andrea C. Rodriguez, María E. Sad, Cristina L. Padró

*Catalysis Science and Engineering Research Group (GICIC), Instituto de Investigaciones en Catálisis y Petroquímica – INCAPE - (UNL-CONICET), CCT Santa Fe, Colectora RN 168 km 0, Paraje El Pozo, (3000), Santa Fe, Argentina.*

## S1. Identification and quantification of products

The products generated during the reaction were injected into a mass spectrometer (GC-MS) using a Thermo Scientific ISQ QD single quadropole mass spectrometer (TR-5MS) column (30 m x 0.25 mm x 0.25 μm). Product assignment was performed by comparing each signal with the corresponding spectra in the NIST database. Since the chromatograph and GC-MS columns were of the same type, the peak order was identical. A typical chromatogram of the reaction obtained by GC-MS is shown in Figure S1. The signals observed at the bottom of Figure S1 correspond to the fractionation standard for the compound with a retention time of 8.29 minutes, which is identified in the database as 1,3-butanediol.

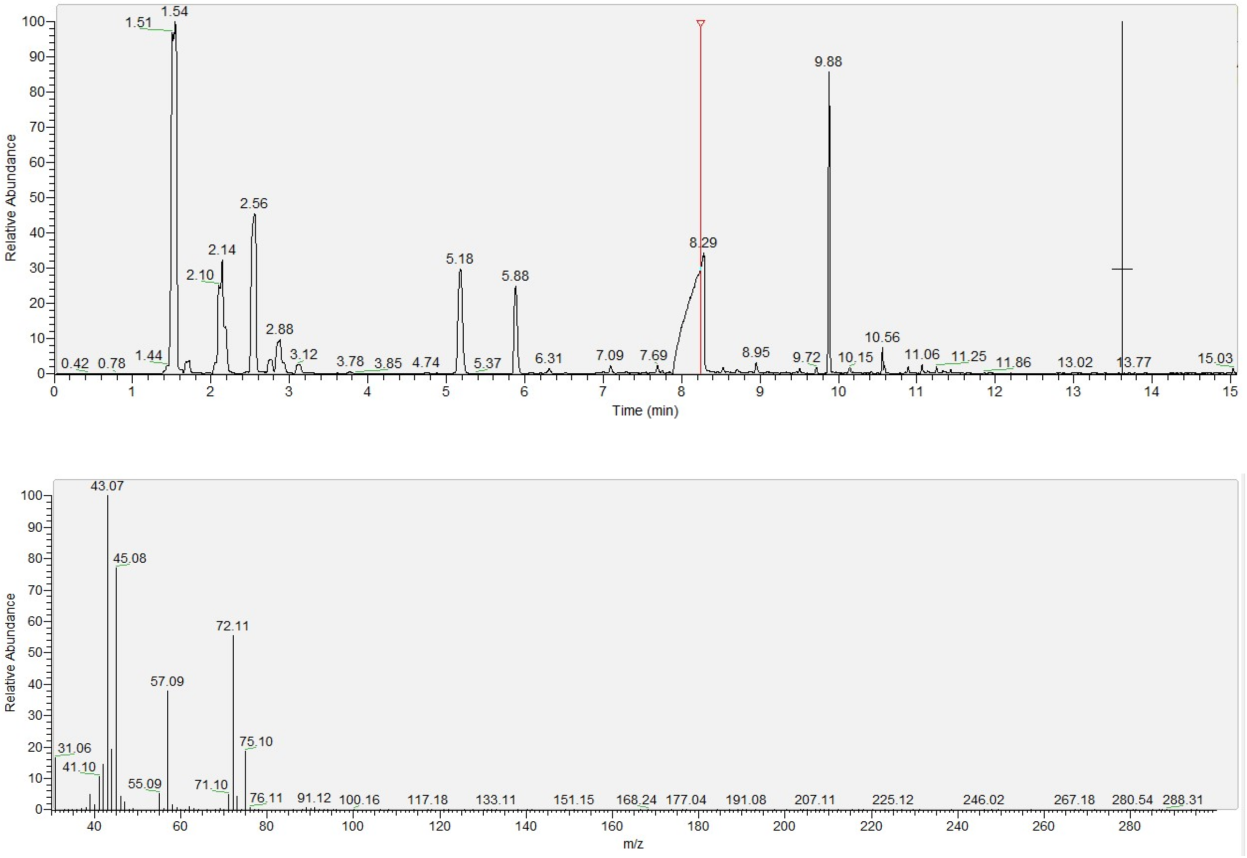

**Figure S1.** Typical chromatogram obtained by GC-MS spectrometry. [$SiO_2/Al_2O_3$, $W/F^{0}_{1,3BDOL}$ = 29.9 g h/mol, T=250 °C, $P_T$=1 atm, $P_{1,3BDOL}$=0.0182 atm, balance $N_2$].

Based on the results obtained by mass spectrometry, the products generated in the reaction were identified (Figure S2).

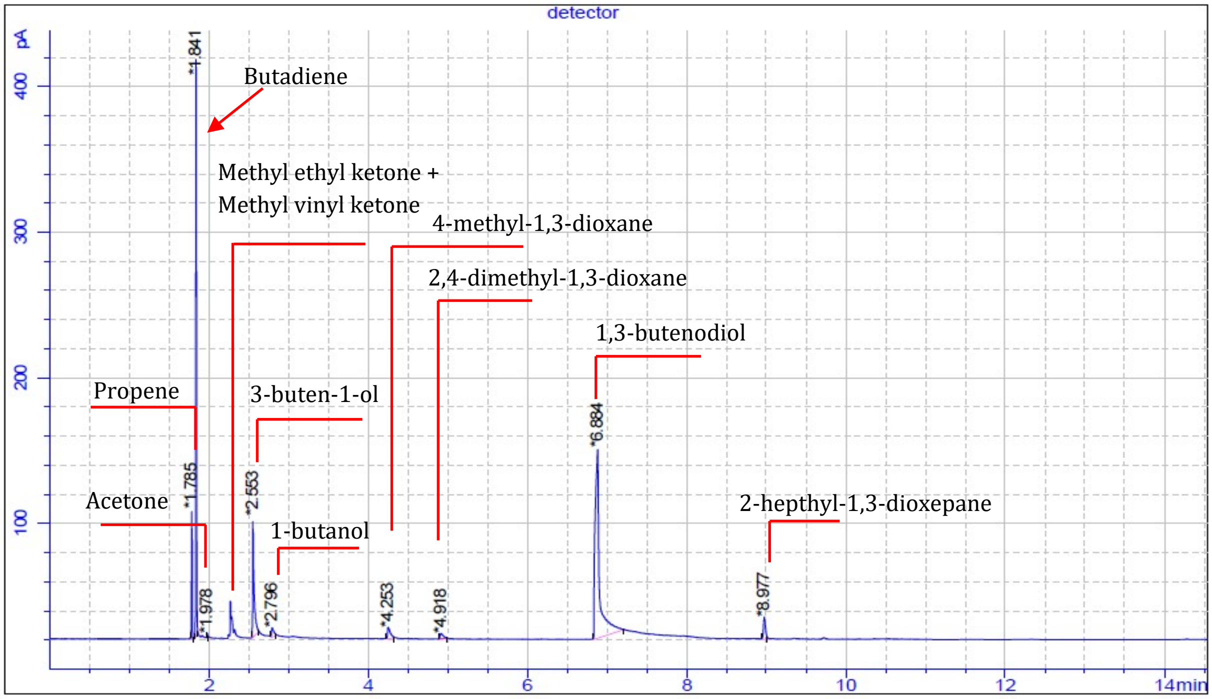

**Figure S2.** Typical chromatogram for the 1,3BDOL reaction obtained by gas chromatography. [$SiO_2/Al_2O_3$, $W/F^0_{1,3BDOL}$ = 29.9 g h/mol, T=250 °C, $P_T$=1 atm, $P_{1,3BDOL}$=0.0182 atm, balance $N_2$].

The relative response factors calculated for the different compounds are shown in Table S1. The standards used were Ethanol (Sigma-Aldrich, ACS reagent), acetone (Baker, >99.9%), 3-buten-2-ol (Sigma-Aldrich, >96.5%), methyl vinyl ketone (Sigma-Aldrich, >93.5%), methyl ethyl ketone (Sigma-Aldrich, 99.9%), butanal (Sigma-Aldrich, >99.5%), 3-buten-1-ol (Merck, 96%), 1-butanol (Sigma-Aldrich, ACS reagent), 4-methyl-1,3-dioxane (Thermo Scientific, >99%), 2,4-dimethyl-1,3-dioxane (MCE, >98%) and 1,3-butanediol (Sigma-Aldrich, >99%).

**Table S1.** Relative response factors of the different compounds.

| Compound | Relative response factor ($F_{Ri}$) |
|---|---|
| Propene | 0.98 |
| 1,3-Butadiene | 1 |
| Ethanol | 0.46 |

| | |
|---|---|
| Acetone | 0.49 |
| 3-Buten-2-ol | 0.62 |
| Methyl vinyl ketone | 0.60 |
| Metyl ethyl ketone | 0.59 |
| Butanal | 0.59 |
| 3-Buten-1-ol | 0.67 |
| 1-Butanol | 0.65 |
| 4-Methyl-1,3-dioxane | 0.42 |
| 2,4-Dimethyl-1,3-dioxane | 0.49 |
| 1,3-Butanediol | 0.42 |
| 2-Heptyl-1,3-dioxepane | 0.71 |

## S2. Acid sites characterization by FTIR of pyridine

The acidity of the catalysts was analyzed by FTIR using pyridine as a probe molecule, which helps identify the density, type, and strength of acid sites. Pyridine adsorbed on Lewis acid sites shows IR bands at 1440–1465 cm$^{-1}$, 1480–1500 cm$^{-1}$, and around 1600 cm$^{-1}$. Brønsted acid sites, in contrast, lead to pyridinium ion bands at 1540 cm$^{-1}$, 1480–1500 cm$^{-1}$, 1610 cm$^{-1}$, and 1630–1640 cm$^{-1}$ (1).

Figure S3 shows the FTIR spectra after pyridine adsorption and desorption at 423 K. TPA/$SiO_2$ displayed mainly Brønsted acidity (bands at 1540, 1610, and 1636 cm$^{-1}$), with a minor Lewis acid band at 1450 cm$^{-1}$. HZSM5 showed overlapping Lewis acid bands at ~1445–1455 cm$^{-1}$ (Na and Al sites) and bands at 1600 and 1620 cm$^{-1}$; the 1540 cm$^{-1}$ band confirmed Brønsted acidity. $SiO_2/Al_2O_3$ exhibited mainly Lewis acidity (1455 and 1620 cm$^{-1}$) with some Brønsted contribution (1540 and 1637 cm$^{-1}$). $Al_2O_3$ showed only Lewis acidity (bands at 1450 and 1620 cm$^{-1}$), linked to low-coordination $Al^{3+}$ sites. The absence of 1540 and 1635 cm$^{-1}$ bands indicated no Brønsted acidity.

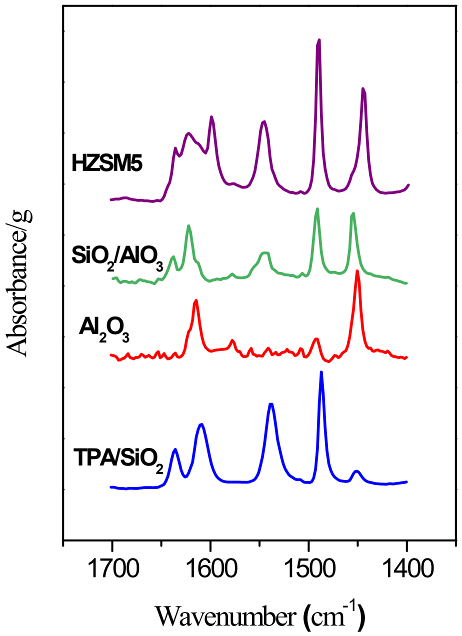

**Figure S3.** FTIR spectra of pyridine adsorbed at 298 K on TPA/SiO$_2$, Al$_2$O$_3$, SiO$_2$/Al$_2$O$_3$ and HZSM5 and evacuated at 423 K for 30 min

## S3. Catalytic results

Minor product selectivity corresponding to Figure 2 as a function of the reaction time using pure 1,3BDOL ($P_{1,3BDOL}$= 1.84 kPa) and 10 wt% aqueous solution of 1,3BDOL ($P_{1,3BDOL}$=0.36 kPa) as reagent at the same contact time ($W/F^{0}_{1,3BDOL}$= 29.9 g h/mol) are displayed in Tables S2 – S5.

**Table S2.** Temporal evolution of minor product selectivities on HZSM5.

***Pure 1,3BDOL***

| t (min) | $S_{P+F}$ | $S_{MVK+MEK}$ | $S_{C4AL+C4OL}$ | $S_{Others}$ |
|---|---|---|---|---|
| 9.51 | 9.51 | 7.63 | 5.90 | 1.19 |
| 7.77 | 7.77 | 7.52 | 5.03 | 1.00 |
| 8.50 | 8.50 | 6.90 | 3.83 | 1.17 |
| 9.02 | 9.02 | 7.28 | 4,64 | 0.87 |
| 8.91 | 8.91 | 6.36 | 3,41 | 0.74 |
| 8.38 | 8.38 | 5.86 | 3.30 | 1.19 |
| 9.32 | 9.32 | 4.83 | 1.88 | 0.95 |

***1,3BDOL 10 wt% aqueous solution***

| $S_{P+F}$ | $S_{MVK+MEK}$ | $S_{C4AL+C4OL}$ | $S_{Others}$ |
|---|---|---|---|
| 17.05 | 11.96 | 2.28 | 0.80 |
| 13.25 | 13.41 | 1.47 | 1.37 |
| 12.80 | 14.27 | 1.51 | 1.52 |
| 10.46 | 12.14 | 2.35 | 1.00 |
| 11.34 | 12.53 | 1.76 | 1.34 |
| 11.01 | 12.82 | 1.35 | 2.17 |
| 12.38 | 13.57 | 1.40 | 1.80 |

| | | | | |
|---|---|---|---|---|
| 8.20 | 8.20 | 5.07 | 2.35 | 1.49 |

| | | | |
|---|---|---|---|
| 12.54 | 13.78 | 1.53 | 1.08 |

**Table S3.** Temporal evolution of minor product selectivities on $SiO_2/Al_2O_3$

***Pure 1,3BDOL***

| t (min) | $S_{P+F}$ | $S_{MVK+MEK}$ | $S_{C4AL+C4OL}$ | $S_{Others}$ |
|---|---|---|---|---|
| 20 | 18.53 | 9.55 | 4.64 | 1.15 |
| 44 | 15.30 | 9.57 | 4.14 | 0.91 |
| 68 | 12.39 | 8.11 | 3.20 | 1.07 |
| 93 | 13.32 | 9.56 | 3.25 | 1.07 |
| 116 | 12.43 | 9.06 | 3.37 | 1.05 |
| 141 | 11.97 | 8.18 | 3.14 | 1.29 |
| 163 | 14.67 | 10.08 | 3.57 | 1.26 |
| 192 | 12.42 | 8.89 | 3.36 | 1.44 |

***1,3BDOL 10 wt% aqueous solution***

| $S_{P+F}$ | $S_{MVK+MEK}$ | $S_{C4AL+C4OL}$ | $S_{Others}$ |
|---|---|---|---|
| 26.98 | 11.70 | 3.45 | 5.16 |
| 21.02 | 11.78 | 3.78 | 2.00 |
| 14.76 | 12.22 | 0.66 | 0.45 |
| 15.33 | 13.31 | 1.04 | 1.94 |
| 19.80 | 12.16 | 3.10 | 1.42 |
| 17.83 | 11.83 | 2.61 | 1.28 |
| 16.78 | 11.10 | 3.60 | 1.33 |
| 17.36 | 12.79 | 0.83 | 1.00 |

**Table S4.** Temporal evolution of minor product selectivities on $Al_2O_3$.

***Pure 1,3BDOL***

| t (min) | $S_{P+F}$ | $S_{MVK+MEK}$ | $S_{C4AL+C4OL}$ | $S_{Others}$ |
|---|---|---|---|---|
| 21 | 43.89 | 13.23 | 4.83 | 2.54 |
| 46 | 46.42 | 11.49 | 4.59 | 1.92 |
| 63 | 53.11 | 11.75 | 7.69 | 2.27 |
| 87 | 47.11 | 10.14 | 4.66 | 1.76 |
| 116 | 45.81 | 10.41 | 3.05 | 1.35 |
| 141 | 55.12 | 10.69 | 6.71 | 2.48 |
| 166 | 53.06 | 10.22 | 6.59 | 2.18 |
| 188 | 48.08 | 9.36 | 2.41 | 1.35 |

***1,3BDOL 10 wt% aqueous solution***

| $S_{P+F}$ | $S_{MVK+MEK}$ | $S_{C4AL+C4OL}$ | $S_{Others}$ |
|---|---|---|---|
| 65.03 | 8.40 | 6.98 | 3.27 |
| 63.25 | 9.46 | 5.41 | 3.52 |
| 59.73 | 10.13 | 5.36 | 3.68 |
| 61.61 | 9.56 | 6.98 | 4.19 |
| 63.90 | 9.12 | 4.16 | 2.42 |
| 67.44 | 9.24 | 4.76 | 2.63 |
| 68.64 | 8.23 | 3.62 | 3.38 |
| 63.66 | 10.20 | 2.12 | 1.62 |

**Table S5.** Temporal evolution of minor product selectivities on $TPA/SiO_2$

***Pure 1,3BDOL***

| t (min) | $S_{P+F}$ | $S_{MVK+MEK}$ | $S_{C4AL+C4OL}$ | $S_{Others}$ |
|---|---|---|---|---|
| 20 | 8.55 | 9.20 | 0.47 | 0.49 |
| 45 | 9.30 | 8.39 | 0.38 | 0.39 |
| 73 | 8.87 | 7.08 | 0.12 | 0.71 |
| 93 | 8.77 | 6.76 | 0.15 | 0.81 |
| 115 | 9.00 | 6.57 | 0.21 | 0.87 |
| 137 | 9.17 | 5.96 | 0.19 | 0.71 |
| 158 | 8.55 | 5.81 | 0.15 | 1.14 |
| 181 | 8.58 | 5.64 | 0.16 | 1.01 |

***1,3BDOL 10 wt% aqueous solution***

| $S_{P+F}$ | $S_{MVK+MEK}$ | $S_{C4AL+C4OL}$ | $S_{Others}$ |
|---|---|---|---|
| 7.85 | 15.12 | 0.00 | 0.33 |
| 6.85 | 13.81 | 0.00 | 0.00 |
| 6.92 | 12.36 | 0.00 | 0.14 |
| 6.57 | 12.19 | 0.00 | 0.22 |
| 6.70 | 11.81 | 0.00 | 0.30 |
| 7.05 | 12.48 | 0.00 | 0.08 |
| 7.40 | 12.01 | 0.00 | 0.09 |
| 7.60 | 11.38 | 0.00 | 0.10 |

## S4. Catalysts deactivation

Figure S4 shows the variation of the activity ($a_{1,3\mathrm{BDOL}}$) as a function of the reaction time using pure 1,3BDOL and 1,3BDOL 10 wt% aqueous solution as reagent, respectively, for HZSM5, $SiO_2/Al_2O_3$, $Al_2O_3$, and $TPA/SiO_2$ at similar initial conversions.

The activity was determined as $a_{1,3BDOL} = r_{(t)}/r^{0}_{(t=0)}$ where $r_{(t)}$ and $r^{0}_{(t=0)}$ are the 1,3BDOL conversion rates at t=t and t=0, respectively.

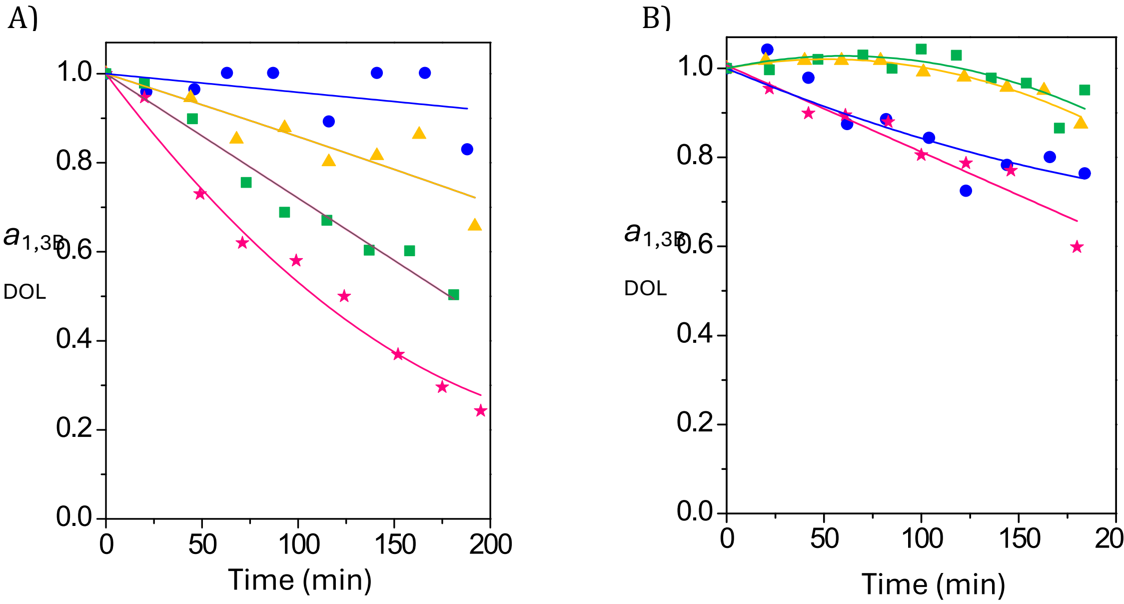

**Figure S4.** Activity decay at 523 K and isoconversion (95-98 %). A) 1,3BDOL, B) 1,3BDOL 10 wt % aqueous solution. □ $SiO_2/Al_2O_3$, ● $Al_2O_3$, ★ HZSM5□ and ○ $TPA/SiO_2$.

$Al_2O_3$ exhibited slight deactivation on stream while $SiO_2/Al_2O_3$, $TPA/SiO_2$ and HZSM5 showed a progressive decline in activity over time, with the zeolite experiencing the greatest deactivation after 3 h of reaction, as shown in Figure SI.2A. During the first two hours of reaction co-feeding water, no loss of activity was observed on $SiO_2/Al_2O_3$ and $TPA/SiO_2$; after two hours a slow deactivation was observed in Figure SI.2B. As mentioned above, $Al_2O_3$ suffered a more pronounced loss of activity during the reaction using reagent with water. Although HZSM5 showed a drop in activity when using a 10 wt% aqueous solution of 1,3BDOL as reagent, this was less pronounced than when using pure 1,3BDOL and differences in both curves can be noted.

## S5. Characterization of spent catalysts

XRD analysis on fresh HZSM5 and TPA/$SiO_2$ samples, as well as after being used in the reaction with a feed of 1,3BDOL diluted in water, were conducted. TPA is highly dispersed on $SiO_2$, therefore the signals in DRX are very weak both before and after reaction. No significant changes in the corresponding diffraction signals water were observed after the reaction with1,3BDOL diluted in as shown in Figure S5.

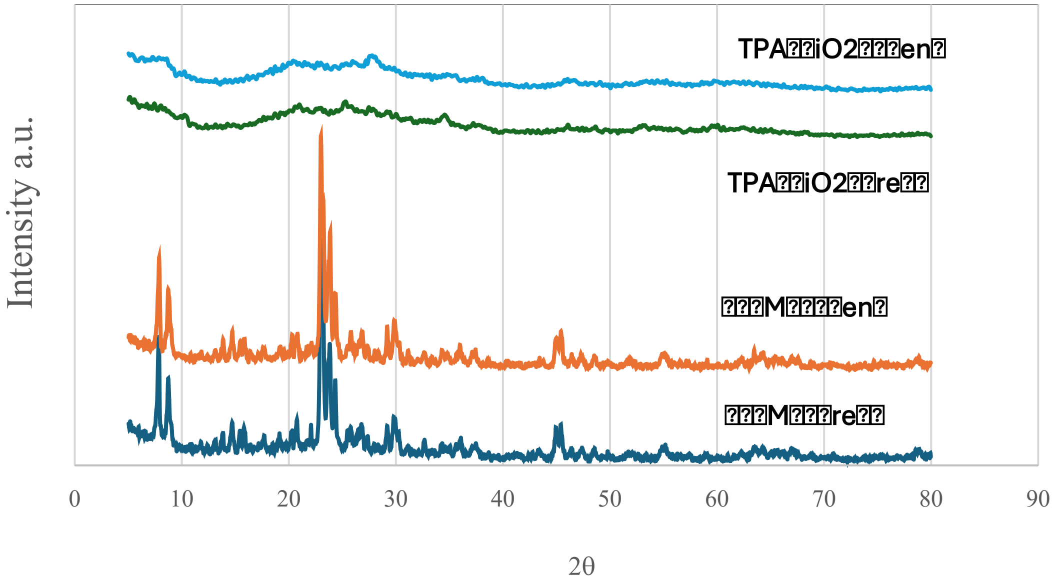

**Figure S5.** XRD diffractograms for fresh HZSM5 and TPA/$SiO_2$ samples and after being used in the reaction with a feed of 1,3BDOL diluted in water (spent).