

Degradation of Methyl Paraoxon in the Presence of Mg²⁺-Al³⁺ Mixed Oxides

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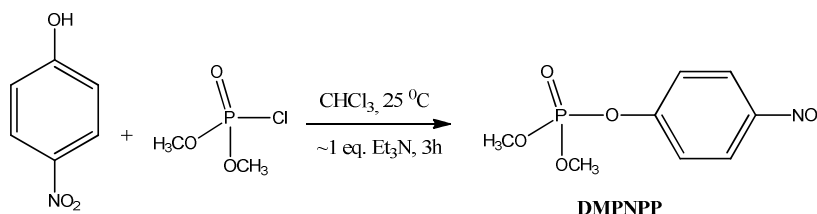
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1. Preparation, identification and purity of dimethyl 4-nitrophenyl phosphate

In the preparation of dimethyl 4-nitrophenyl phosphate CHCl_3 was used as solvent, and it was dried using molecular sieves 3 Å, and the reaction was carried out in anhydrous conditions under argon. Triethylamine (5.5 mmol) distilled on KOH was added to a solution of 4-nitrophenol (5 mmol.) (Fluka $\geq 99.5\%$ purity) in dry CHCl_3 (25 mL) under argon and with magnetic stirring. The system was kept on ice during 10 minutes, and a solution of $(\text{Me})_2\text{POCl}$ (5 mmol.) (Sigma Aldrich, 96%) was added dropwise (**Scheme 1**). Then the reaction was kept for 3 h at room temperature, washed with 25 mL of saturated NaHCO_3 twice and once with 25 mL of saturated NaCl . The organic layer was dried with MgSO_4 anhydrous (98% purity) and evaporated.



Scheme 1. Synthesis of **DMPNPP**.

Data acquisition parameters: GC-17A Ver.3. Column DB-5MS, length 30m, thickness 0.25 μm , diameter: 0.25 mm; Sampling time: 1 min; Injection Temp. 250 $^{\circ}\text{C}$; Interface Temp. 280 $^{\circ}\text{C}$; Control mode: Split; Column Flow: 1 mL min^{-1} ; Linear Velocity: 36.3 cm s^{-1} ; Split Ratio: 40; Total and Carrier Flow: 42.3 mL min^{-1} ; Oven Temp.: 50 $^{\circ}\text{C}$ – hold time: 5 min and follow the heating in a rate: 10 $^{\circ}\text{C min}^{-1}$ until 280 $^{\circ}\text{C}$ – hold time: 5 min. GC-MS QP5050A with DI; Acquisition Mode: Scan; Solvent cut time: 4 min; Start and End time: 4 and 32 min, respectively; Start and End m/z : 30 and 400 min, respectively; Scan Speed: 1000.

As shown in Figure S1, GC Chromatogram has only one peak, identified as the molecular ion of $m/z = 247$ by mass spectrometry (Figure S2), which agrees with the expected molecular mass. Table S1 shows proposed molecular ions detected by the fragmentation of $m/z = 247$. The ^{31}P NMR spectrum presents only one peak at -4.56 ppm (CDCl_3) relative to triester (Figure S3).

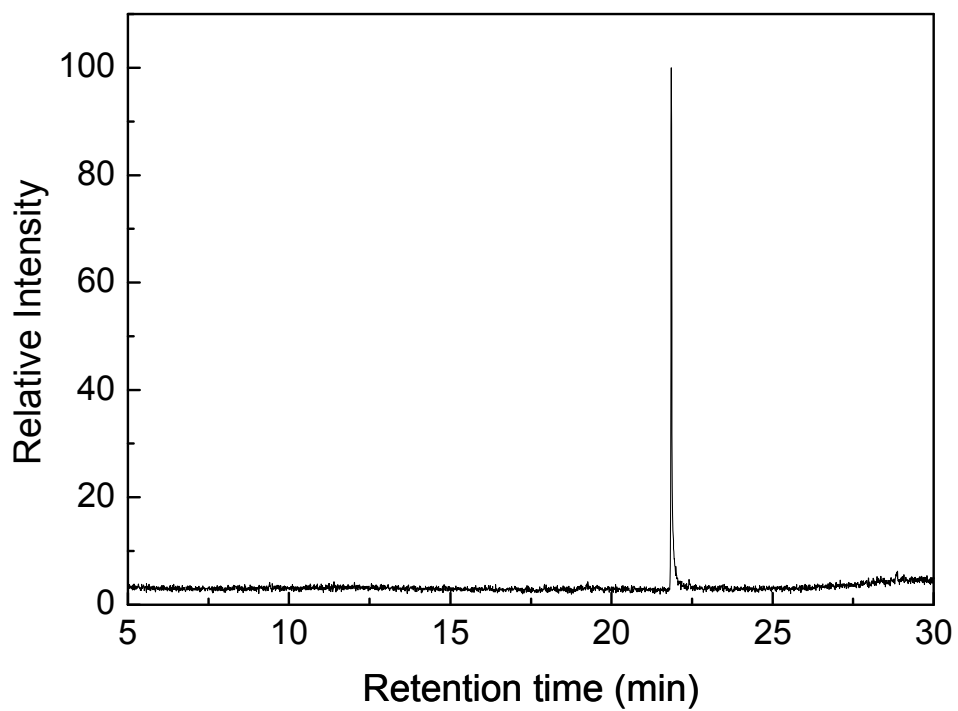


Figure S1. GC Chromatogram of compound DMPNPP.

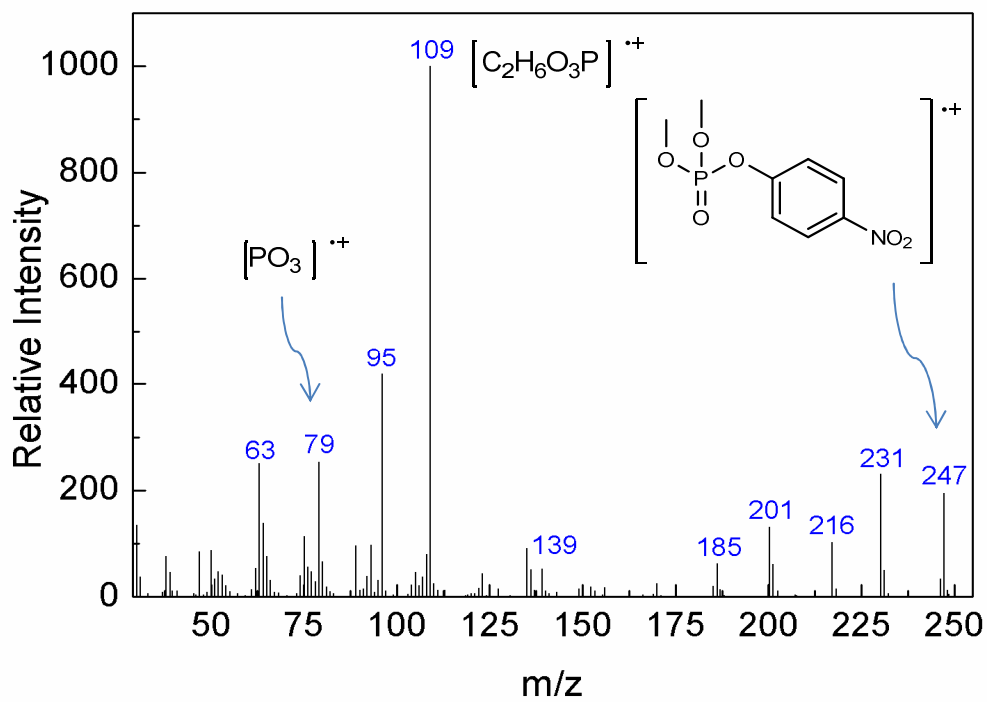


Figure S2. Fragmentation of molecular ion $m/z = 247$ at retention time 21.9 min.

Table S1. Proposed molecular ions detected by fragmentation of $m/z = 247$.

Molecular Formula	m/z	Molecular Formula	m/z
$[\text{C}_8\text{H}_{10}\text{NO}_6\text{P}]^+$	247	$[\text{C}_6\text{H}_6\text{NO}_3]^+$	139
$[\text{C}_8\text{H}_{10}\text{NO}_5\text{P}]^+$	231	$[\text{C}_2\text{H}_6\text{O}_3\text{P}]^+$	109
$[\text{C}_7\text{H}_7\text{NO}_5\text{P}]^+$	216	$[\text{PO}_4]^+$	95
$[\text{C}_6\text{H}_4\text{NO}_5\text{P}]^+$	201	$[\text{PO}_3]^+$	79
$[\text{C}_6\text{H}_4\text{NO}_4\text{P}]^+$	185	$[\text{PO}_2]^+$	63

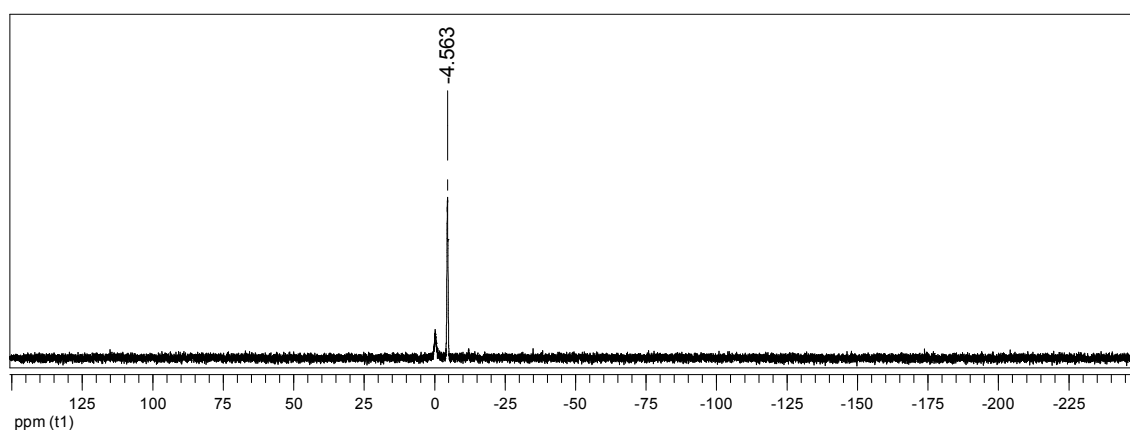


Figure S3. ^{31}P NMR spectrum (81 MHz) of the **DMPNPP** with external reference to 85% phosphoric acid at 0 ppm (200 MHz, CDCl_3).

2. Products identification

The chromatogram (Figure S4) is consistent with a reaction which proceeds largely via propanolysis when the catalyst is dried at 130 °C, and proceeds exclusively via propanolysis when the catalyst is dried at 450 °C.

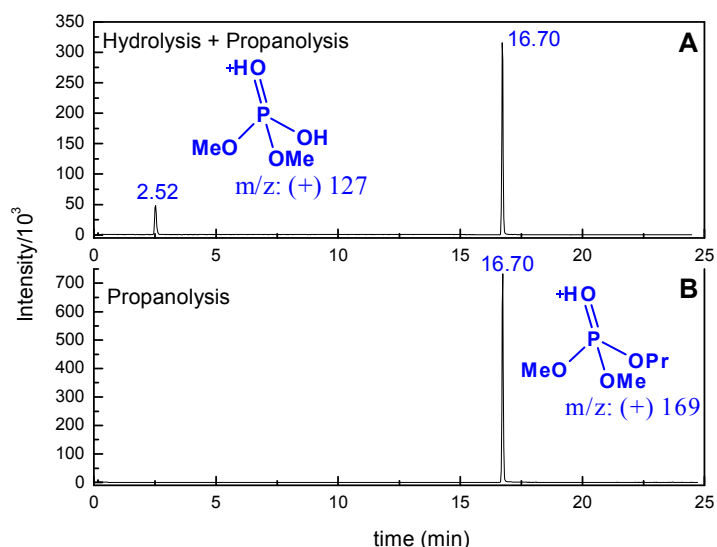


Figure S4. Chromatograms showing the products of hydrolysis and propanolysis, with a catalyst dried at 130 °C (A) and, exclusively a propanolysis product with the catalyst dried at 450°C (B), analyzed via LC-MS/MS ESI + MS/MS detection.

3. X-ray Diffraction (XRD)

The main characteristic peaks related to γ -Al₂O₃ and MgO samples were identified at the spectra shown in Figures S5 and S6, respectively. The identification was achieved by comparing the diffraction patterns with the standard peaks from CRYSMET Data.

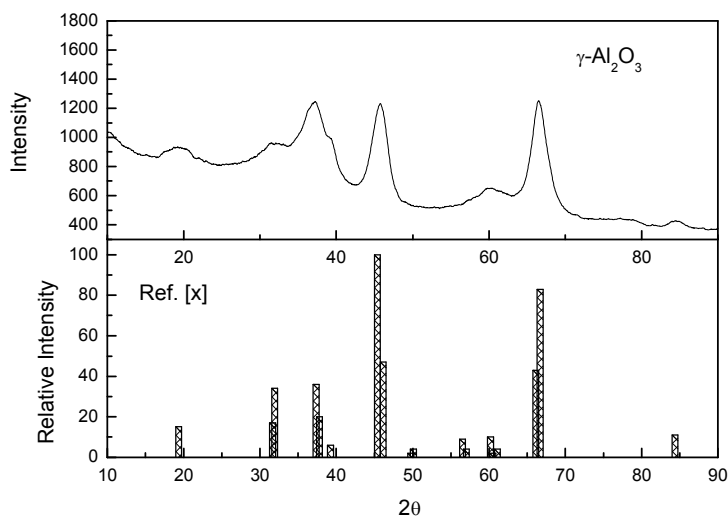


Figure S5. XRD for γ -Al₂O₃ and standard peaks from ID code 472864 CRYSTMET Data base.¹

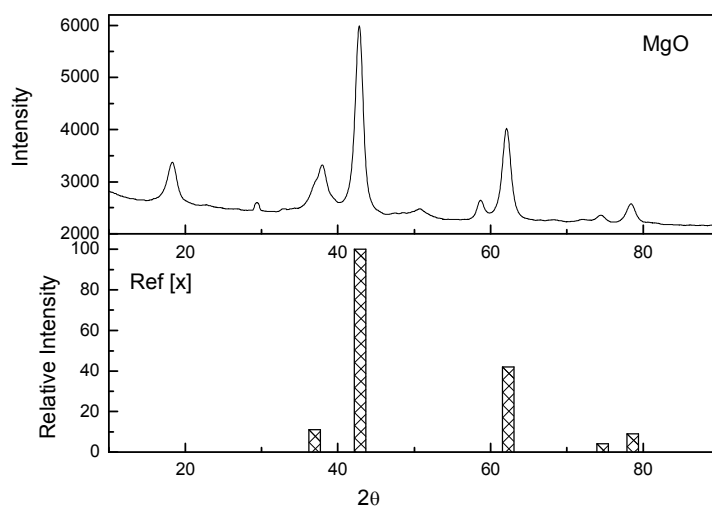


Figure S6. XRD for MgO and standard peaks from ID code 137946 CRYSMET Data base.²

4. Temperature Programmed Desorption of CO₂ (CO₂-TPD)

Figure S7 shows the deconvoluted desorption curves in three peaks for the catalyst 4. Deconvoluted curves and the red line were obtained by fitting data (blue line) with the QCfit application by ChemWin software.

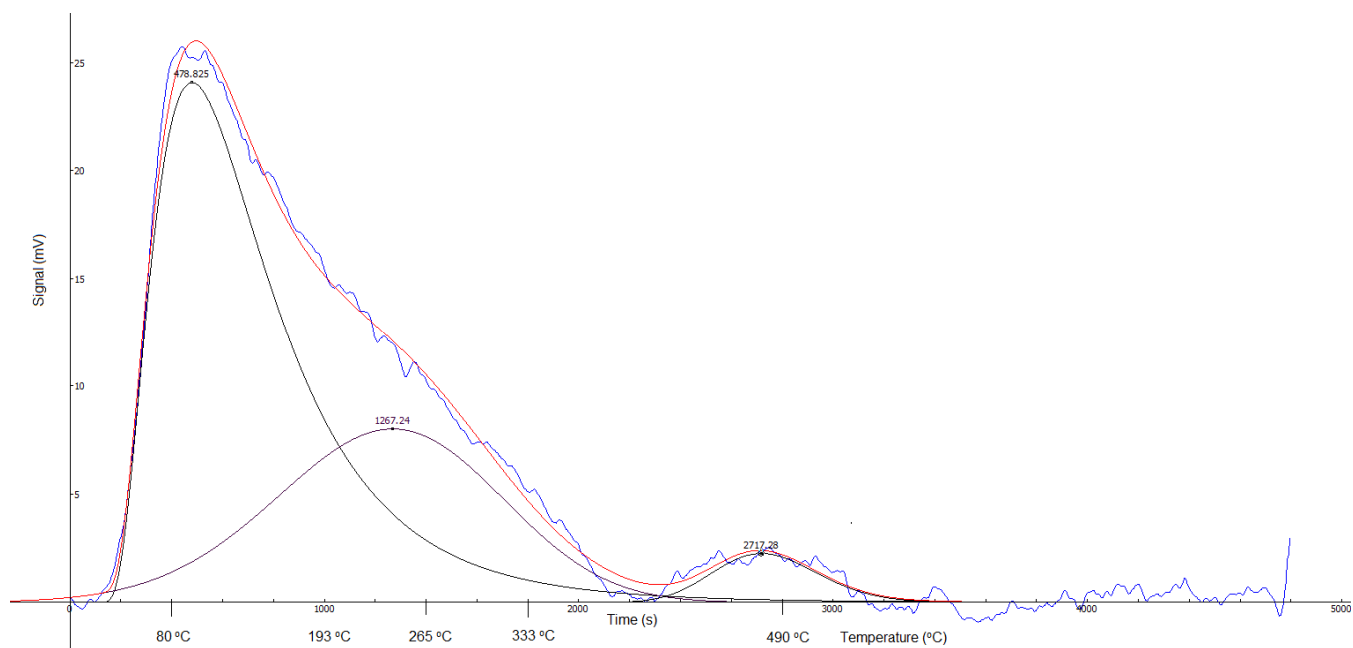


Figure S7. CO₂-TPD curves for catalyst 4.

5. Catalyst activity – kinetics measurements

The first order rate constants obtained by following the formation of the p-nitrophenolate anion at 405 nm, for all the different catalysts, are shown in Table S2.

Table S2. k_{obs} values for the reaction of $7.53 \times 10^{-5} \text{ mol L}^{-1}$ DMPNPP with different catalysts.

Catalyst	$k_{\text{obs}} (\text{s}^{-1})$	$t_{1/2} (\text{min})$	r^2
$\gamma\text{-Al}_2\text{O}_3$	$(5.50 \pm 0.28) \times 10^{-5}$	210	0.992
1	$(5.03 \pm 0.30) \times 10^{-5}$	230	0.995
2	$(3.25 \pm 0.25) \times 10^{-5}$	355	0.993
3	$(3.72 \pm 0.15) \times 10^{-5}$	311	0.996
4	$(3.80 \pm 0.11) \times 10^{-4}$	30	0.998
5	$(1.07 \pm 0.056) \times 10^{-4}$	108	0.995
MgO	$(1.52 \pm 0.04) \times 10^{-6}$	7130	0.963
$\text{H}_2\text{O} (k_0)^a$	2.92×10^{-9}	4.00×10^6	-
Propanol ^b	$< 1.50 \times 10^{-9}$	7.70×10^6	-

^aValue of k_0 taken from references 21 and 22.³⁻⁴ ^bValue of k_{obs} corresponds to experimental measurements in propanol.

The results for the effect of the calcination temperature (500 °C - 950 °C) for spinel are presented in Table S3.

Table S3. Texture parameters calculated from N₂ adsorption and desorption isotherms (drying temperature = 350 °C, 1.5 h) and k_{obs} values for the reaction of 7.53×10^{-5} mol L⁻¹ DMPNPP with different catalysts (drying temperature = 450 °C, 1.5 h).

Calcination Temperature (°C)	S _{BET} (m ² g ⁻¹) ^a	V _{BJH} (cm ³ g ⁻¹) ^b	RP (Å) ^c	k_{obs} (s ⁻¹)
500	147.2	0.55	74.46	$(1.00 \pm 0.04) \times 10^{-3}$
550	142.7	0.29	40.99	$(8.43 \pm 0.05) \times 10^{-4}$
650	103.0	0.26	50.49	$(8.97 \pm 0.06) \times 10^{-4}$
950	25.7	0.11	83.05	$(6.22 \pm 0.07) \times 10^{-5}$ ^d

^aS_{BET} = specific surface area. ^bV_{BJH} = pore volume. ^cRP = pores mean radius. ^dObtained by initial velocity method.

The results for the effect of the particle sizes for catalyst 4 are presented in Table S4.

Table S4. k_{obs} of the DMPNPP at 30 °C as a function of size distribution of the catalyst 4.

Particle size (μm)	k_{obs} (s ⁻¹)	r ²	S _{BET} (m ² g ⁻¹) ^a
≤ 20	$(4.65 \pm 0.34) \times 10^{-4}$	0.989	113.1
20 - 63	$(4.03 \pm 0.65) \times 10^{-4}$	0.990	127.4
≤ 63	$(3.80 \pm 0.41) \times 10^{-4}$	0.998	112.0

^aS_{BET} = specific surface area.

6. References

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