

Electronic Supplementary Information

MOFs based on 1D structural sub-domains with Brønsted acid and redox active sites as effective bi-functional catalysts.

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Scheme S1. Synthesis procedures to obtain the metal-organic materials: (a) Al-ITQ-SH and Al-ITQ-SO₃H and (b) Al-ITQ-SH/Pd and Al-ITQ-SO₃H/Pd. Palladium nanoparticles were showed like dark circles.

Figure S1. TEM images: (a) and (b) Al-ITQ-SH and (c) and (d) Al-ITQ-SO₃H samples. Scale bars correspond to 100 nm for (a), (b) and (d) micrographs and 500 nm for (c) micrograph.

Figure S2. Al-ITQ-SO₃H/Pd sample: (a) and (b) TEM images, (c) and (d) HRTEM images and (e) photography of the obtained powder. Scale bars correspond to 100 nm for (a) micrograph, 20 nm for (b) and (c) micrographs and 10 nm for (d) micrograph.

Figure S3. TGA and DTA curves: (a) 3D standard MIL-53(Al), (b) Al-ITQ-SH, (c) Al-ITQ-SO₃H, (d) Al-ITQ-SH/Pd and (e) Al-ITQ-SO₃H/Pd.

Figure S4. ¹³C MAS NMR spectra: (a) Al-ITQ-SH, (b) Al-ITQ-SO₃H, (c) Al-ITQ-SH/Pd and (d) Al-ITQ-SO₃H/Pd.

Figure S5. ²⁷Al MAS NMR spectra: (a) Al-ITQ-SH, (b) Al-ITQ-SO₃H, (c) Al-ITQ-SH/Pd and (d) Al-ITQ-SO₃H/Pd.

Figure S6. IR spectra: (a) Al-ITQ-SH, (b) Al-ITQ-SO₃H, (c) Al-ITQ-SH/Pd and (d) Al-ITQ-SO₃H/Pd.

Figure S7. Argon isotherms and pore distribution for Al-ITQ-SH and Al-ITQ-SO₃H materials.

Figure S8. Argon isotherms and pore distribution for Al-ITQ-SH/Pd and Al-ITQ-SO₃H/Pd materials.

Figure S9. CO₂ isotherms: (●) Al-ITQ-SH, (■) Al-ITQ-SO₃H, (▲) Al-ITQ-SH/Pd and (×) Al-ITQ-SO₃H/Pd materials.

Figure S10. Yield of benzaldehyde dimethyl acetal was plotted versus time when the acetalization was carried out with different amount of acid sites ((▲) 5, (■) 7.5 and (●) 10 mol% SO₃H) using Al-ITQ-SO₃H as solid catalyst, methanol as solvent, at 30°C, under N₂ atmosphere.

Figure S11. (●) Yield of methyl hexanoate production was plotted versus time when the esterification was carried out in presence of Al-ITQ-SO₃H as catalyst, with 10 mol% SO₃H, methanol as solvent, at 60°C. (■) leaching test.

Figure S12. Yield of 2-methoxy-2-phenylethanol was plotted versus time when ring-opening reaction was carried out in the presence of Al-ITQ-SO₃H, with different amount of acid sites (▲) 5, (■) 7.5 and (●) 10 mol% SO₃H), in methanol, at 30°C.

Figure S13. Yield of benzaldehyde dimethyl acetal was plotted versus time when the acetalization was performed in the presence of (+) Al-ITQ-SH, (●) Al-ITQ-SO₃H, (▲) 4-mercaptobenzoic acid and (×) MIL-53(Al) (5 mol% SO₃H/Al), using methanol as solvent, at 30°C, under N₂ atmosphere. (■) Leaching test.

Figure S14. Yield of 2-methoxy-2-phenylethanol (●) was plotted versus time when ring-opening reaction was performed in presence of Al-ITQ-SO₃H catalyst, with 10 mol% SO₃H and using methanol as solvent, at 30°C. (■) leaching test.

Figure S15. XRD patterns of Al-ITQ-SO₃H catalyst used to produce benzaldehyde dimethyl acetal: (a) fresh, (b) first use, (c) second use, (d) third use and (e) fourth use.

Figure S16. XRD patterns of Al-ITQ-SO₃H catalyst used to produce methyl hexanoate: (a) fresh, (b) first use, (c) second use, (d) third use and (e) fourth use.

Figure S17. XRD patterns of Al-ITQ-SO₃H catalyst used to produce 2-methoxy-2-phenylethanol: (a) fresh, (b) first use, (c) second use, (d) third use, (e) fourth use and (f) fifth use.

Figure S18. Al-ITQ-SO₃H catalyst was used for four consecutive uses for benzaldehyde dimethyl acetal production. Reaction conditions: 5 mol% SO₃H as catalyst, in methanol as solvent, at 30°C, under N₂ atmosphere, being oxidized between each run, 7h of reaction time.

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Figure S20. Al-ITQ-SO₃H catalyst was used for four consecutive uses for methyl hexanoate production. Reaction conditions: 10 mol% SO₃H, methanol as solvent, at 60°C, being oxidized between each catalytic cycle, 20h of reaction time.

Figure S21. XRD patterns of Al-ITQ-SO₃H catalyst used to produce methyl hexanoate: (a) fresh and (b) fourth use being oxidized after each run.

Figure S22. (●) Kinetics of oxidation reaction (step I) in presence of Al-ITQ-SO₃H/Pd catalyst with 3 mol% Pd and (■) leaching test. Reaction conditions: benzonitrile as solvent at 100°C under O₂ atmosphere.

Figure S23. XRD patterns of Al-ITQ-SO₃H/Pd catalyst used in the oxidation-acetalization reaction: (a) fresh, (b) first use, (c) second use, (d) third use and (e) fourth use.

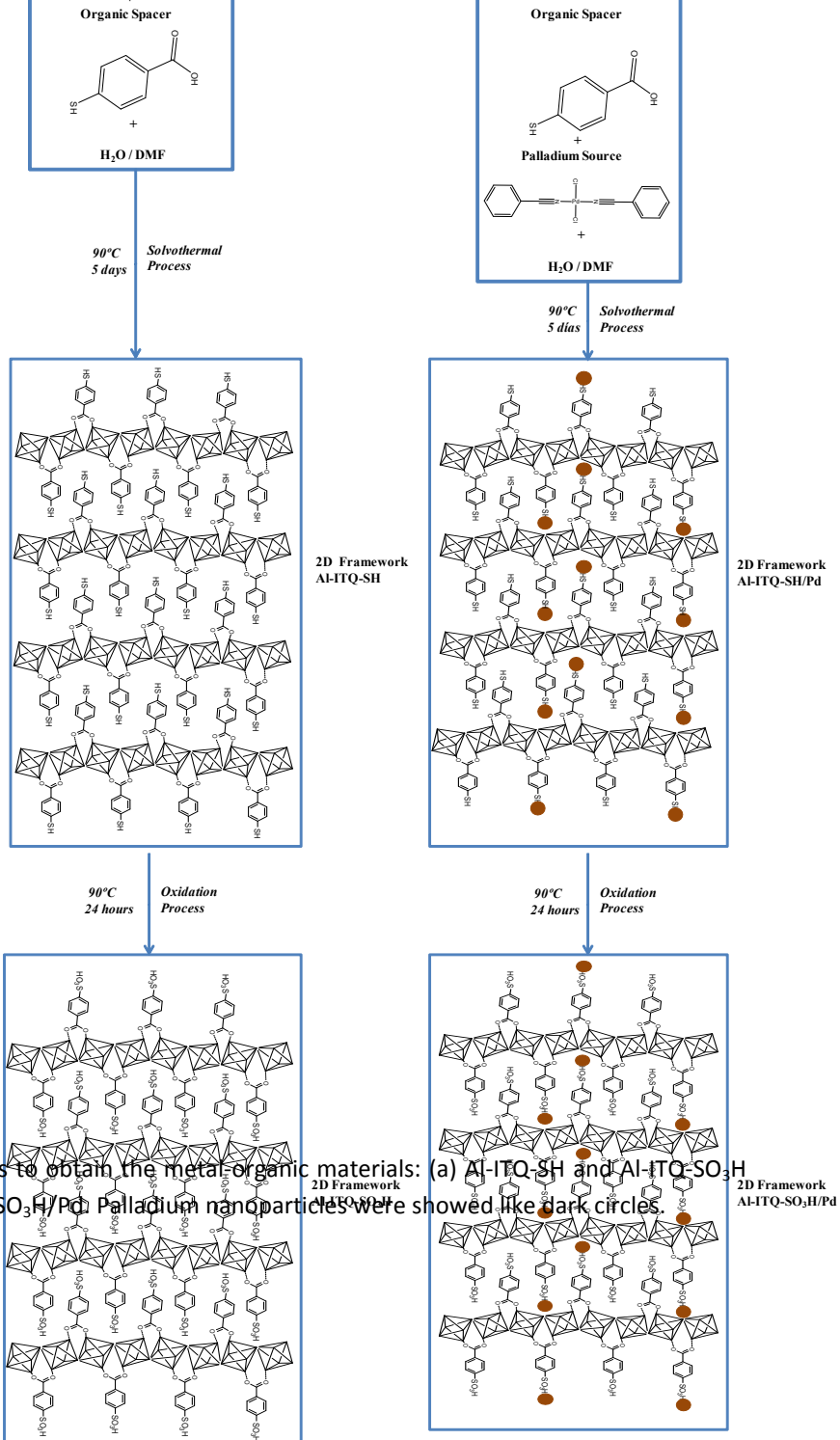
Table S1. CO₂ adsorbed for the lamellar and standard hybrid materials.

Table S2. Yields of methyl hexanoate production in presence of Al-ITQ-SO₃H, using methanol as solvent.

Table S3. Yields of 2-methoxy-2-phenylethanol production in presence of Al-ITQ-SO₃H and conventional MOFs as catalyst, using methanol as solvent.

Table S4. Yields of oxidation reaction in presence of Al-ITQ-SO₃H/Pd.

Schemes



Figures

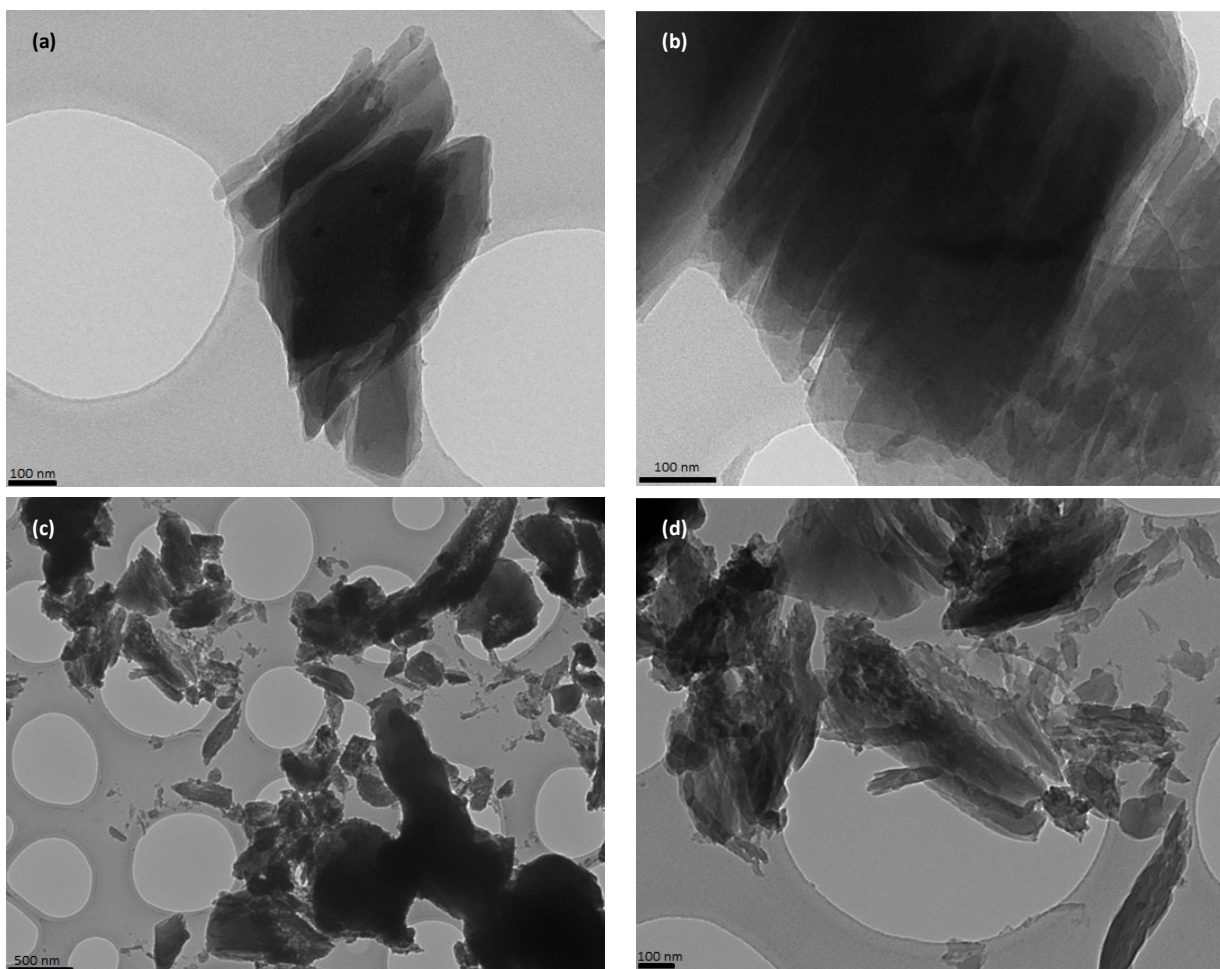


Figure S1. TEM images: (a) and (b) Al-ITQ-SH and (c) and (d) Al-ITQ-SO₃H samples. Scale bars correspond to 100 nm for (a), (b) and (d) micrographs and 500 nm for (c) micrograph.

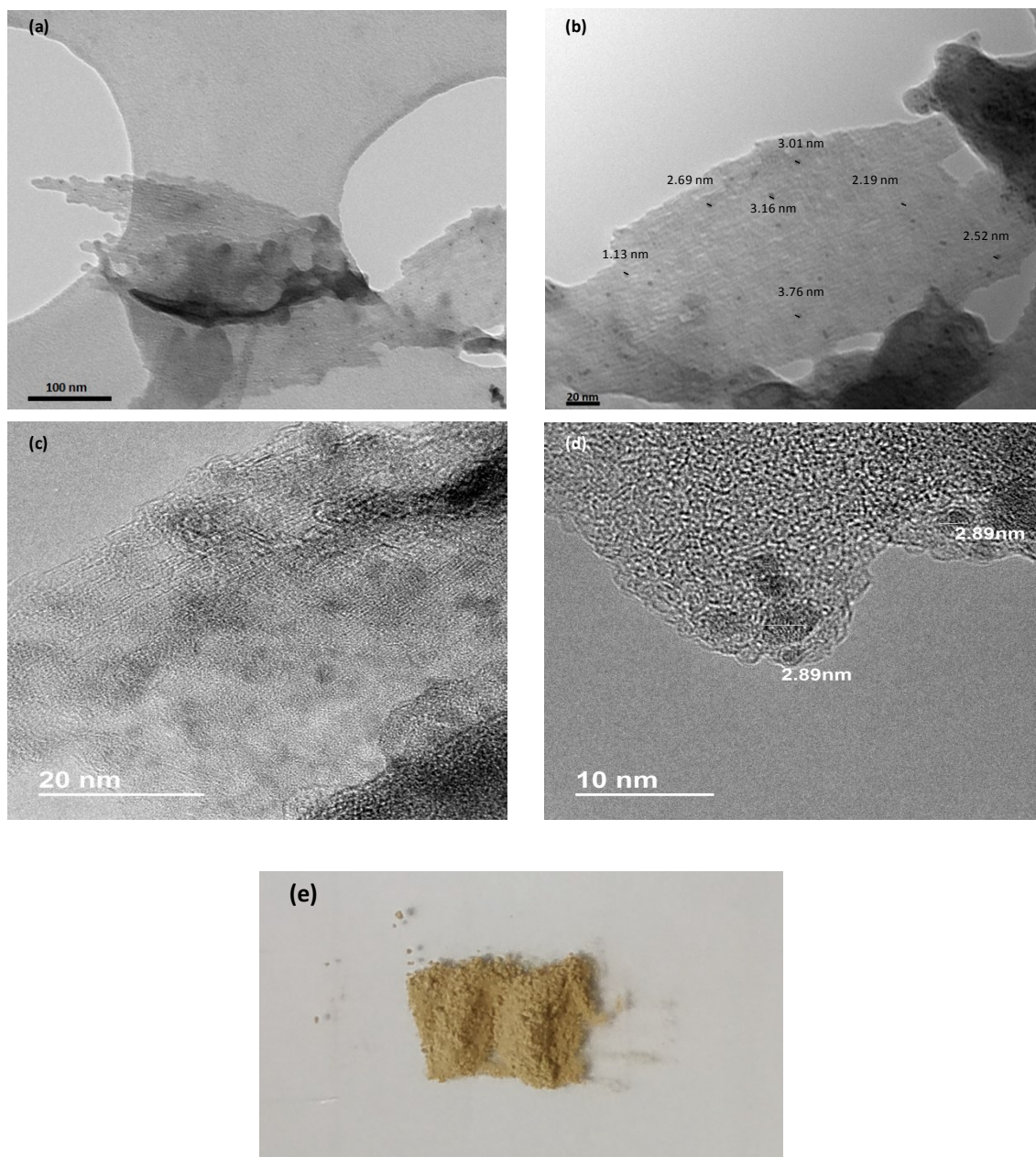


Figure S2. Al-ITQ-SO₃H/Pd sample: (a) and (b) TEM images, (c) and (d) HRTEM images and (e) photography of the obtained powder. Scale bars correspond to 100 nm for (a) micrograph, 20 nm for (b) and (c) micrographs and 10 nm for (d) micrograph.

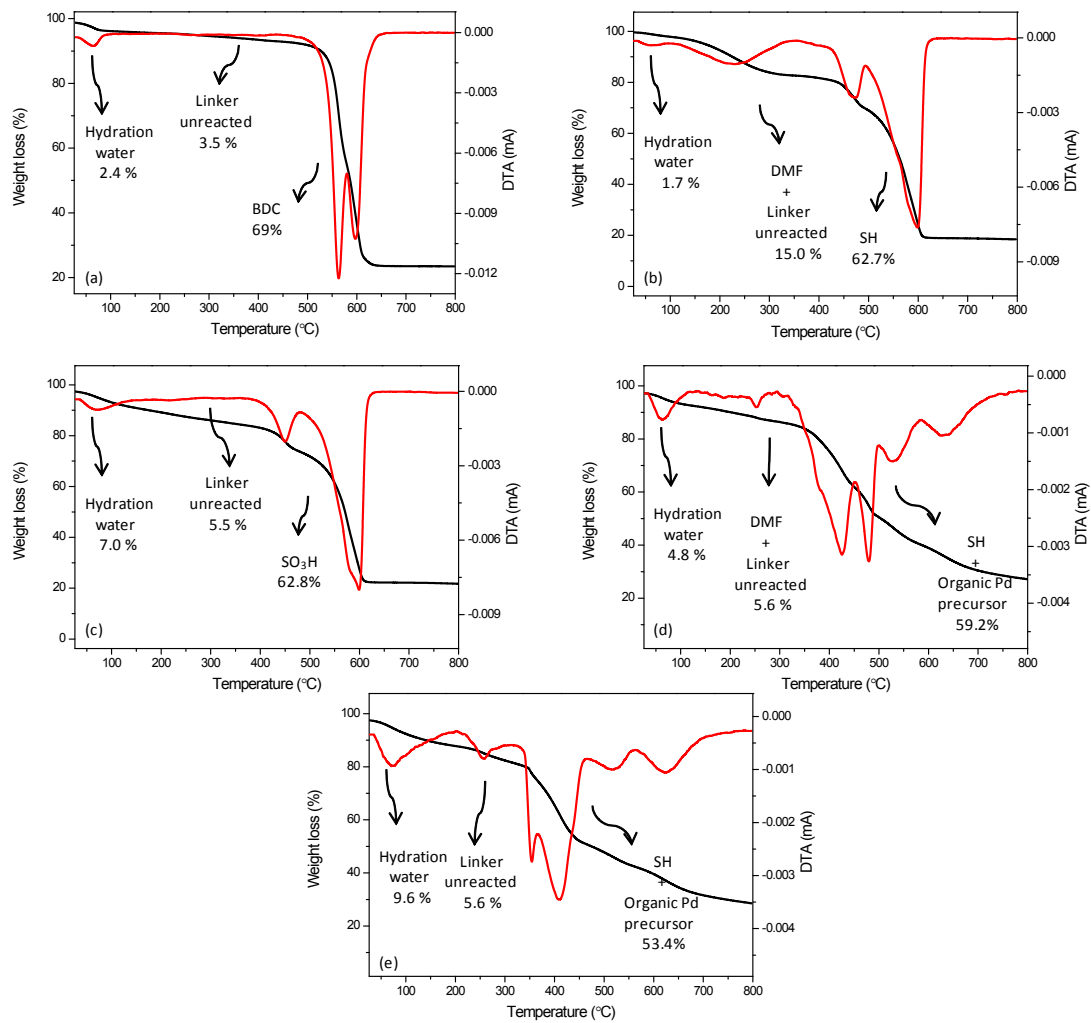


Figure S3. TGA and DTA curves: (a) 3D standard MIL-53(Al), (b) Al-ITQ-SH, (c) Al-ITQ-SO₃H, (d) Al-ITQ-SH/Pd and (e) Al-ITQ-SO₃H/Pd.

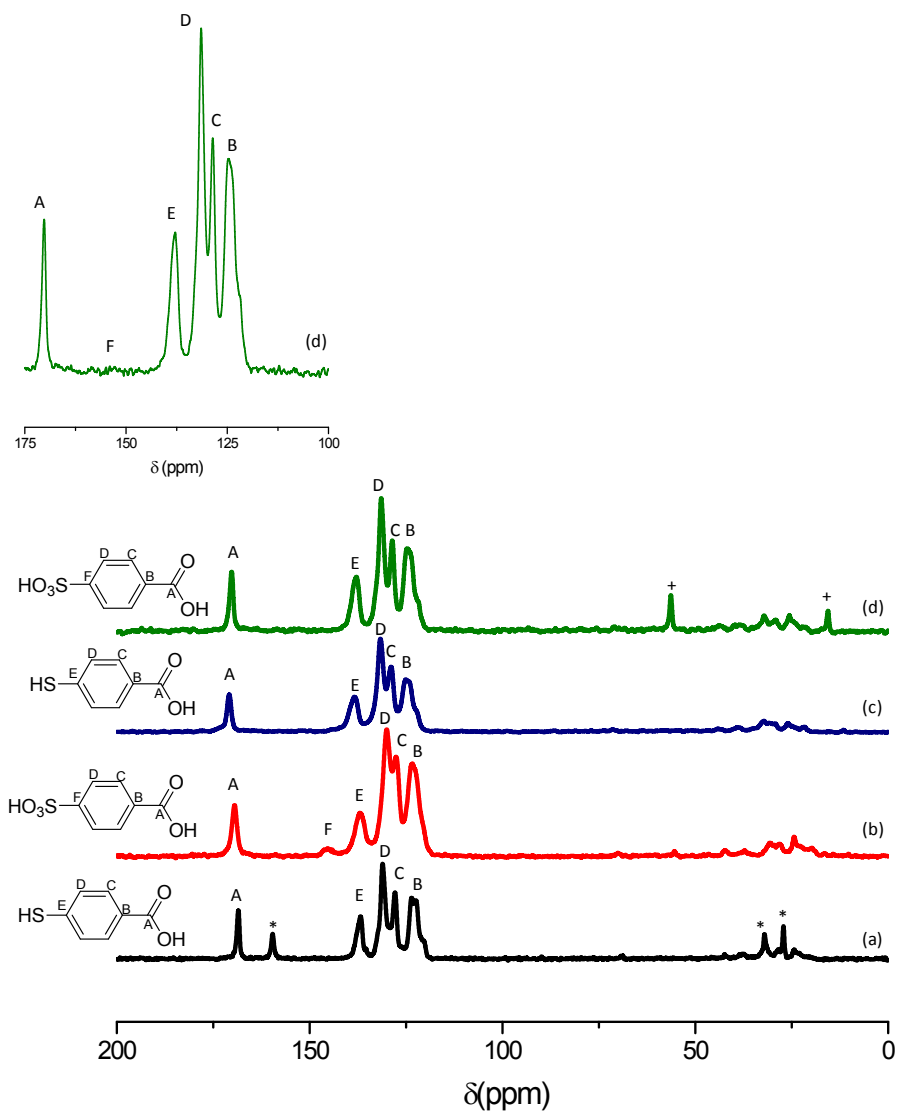


Figure S4. ^{13}C MAS NMR spectra: (a) Al-ITQ-SH, (b) Al-ITQ-SO₃H, (c) Al-ITQ-SH/Pd and (d) Al-ITQ-SO₃H/Pd. (*) DMF. (+) Ethanol.

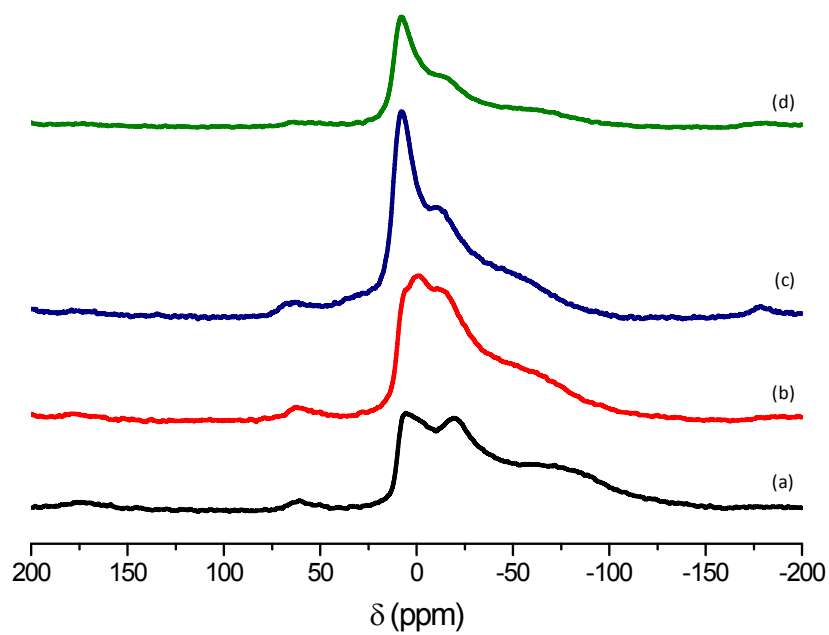


Figure S5. ^{27}Al MAS NMR spectra: (a) Al-ITQ-SH, (b) Al-ITQ-SO₃H, (c) Al-ITQ-SH/Pd and (d) Al-ITQ-SO₃H/Pd.

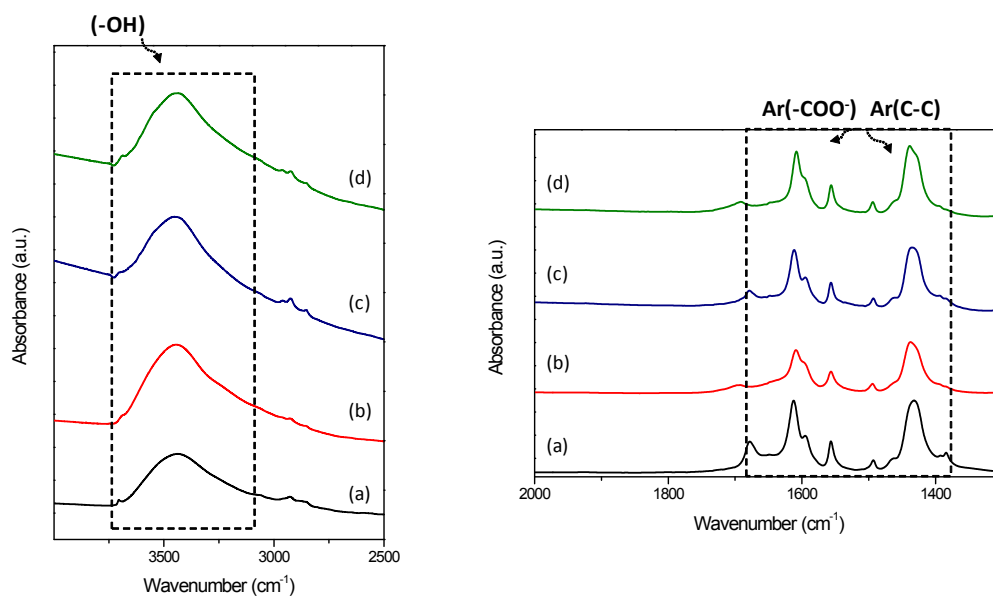


Figure S6. IR spectra: (a) Al-ITQ-SH, (b) Al-ITQ-SO₃H, (c) Al-ITQ-SH/Pd and (d) Al-ITQ-SO₃H/Pd.

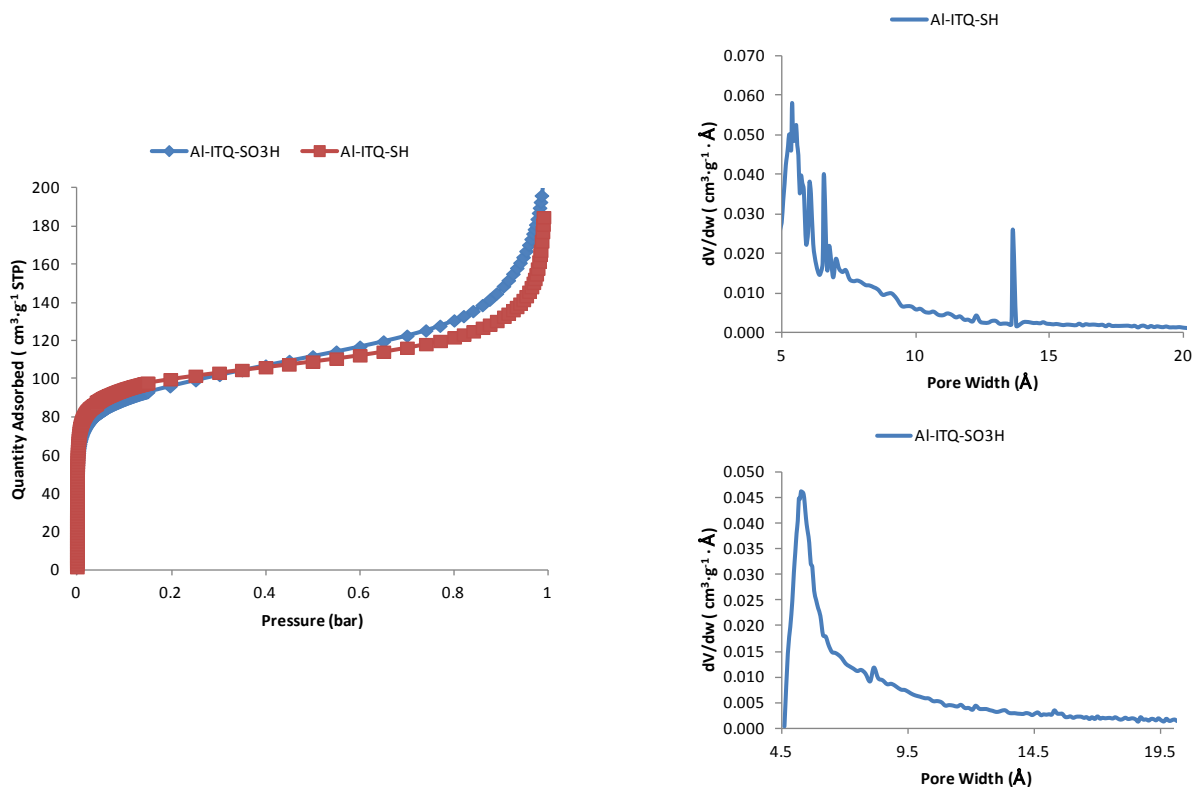


Figure S7. Argon isotherms and pore distribution for Al-ITQ-SH and Al-ITQ-SO₃H materials.

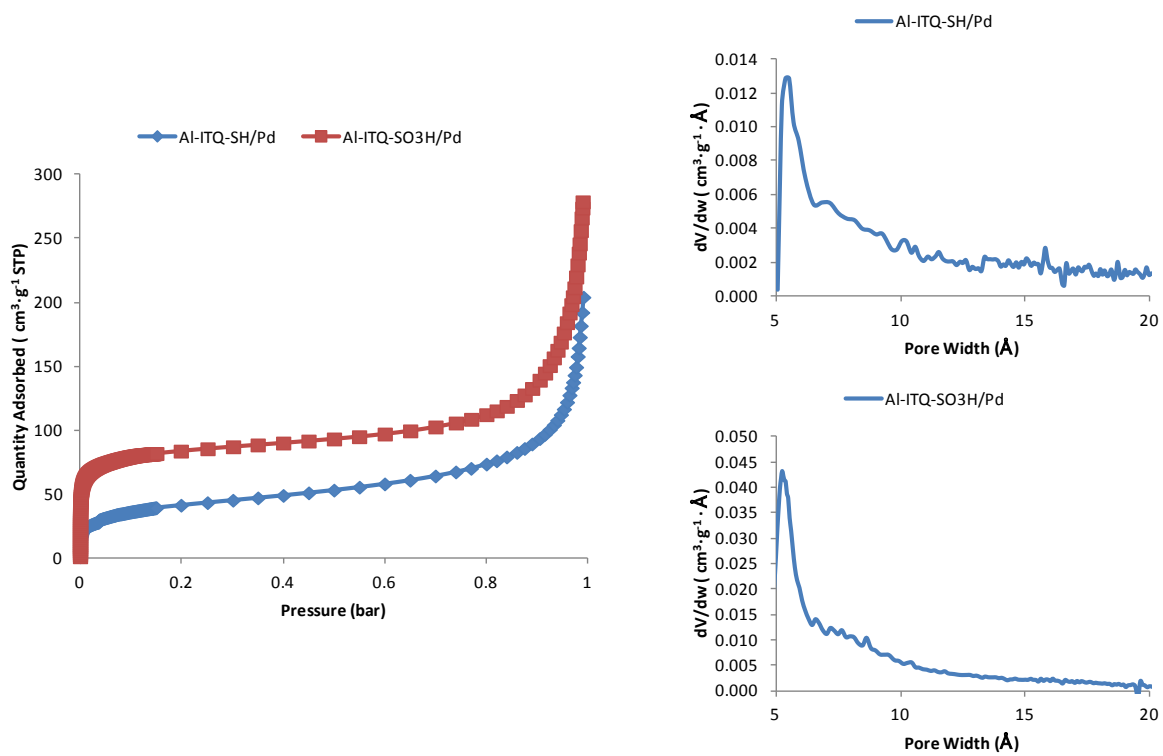


Figure S8. Argon isotherms and pore distribution for Al-ITQ-SH/Pd and Al-ITQ-SO₃H/Pd materials.

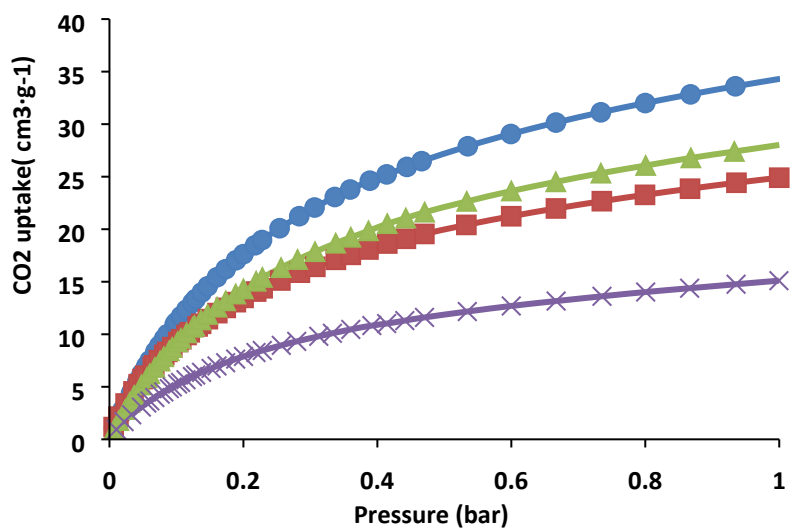


Figure S9. CO₂ isotherms: (●) Al-ITQ-SH, (■) Al-ITQ-SO₃H, (▲) Al-ITQ-SH/Pd and (×) Al-ITQ-SO₃H/Pd materials.

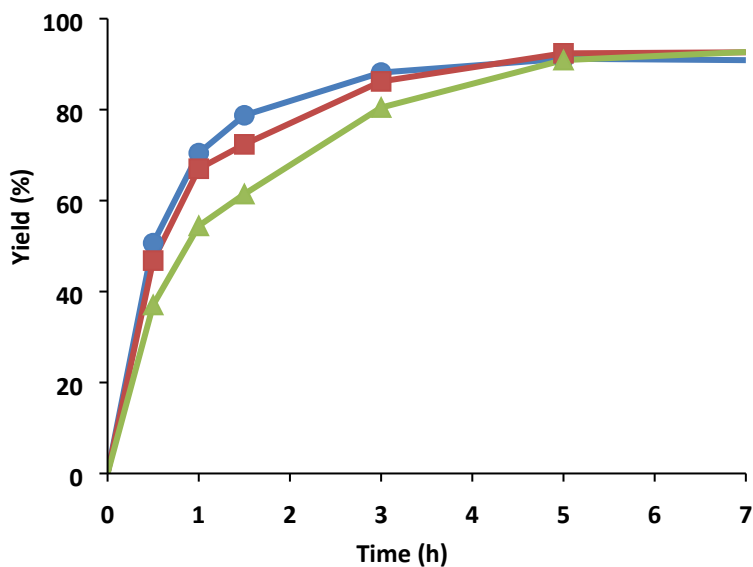


Figure S10. Yield of benzaldehyde dimethyl acetal was plotted versus time when the acetalization was carried out with different amount of acid sites ((▲) 5, (■) 7.5 and (●) 10 mol% SO₃H) using Al-ITQ-SO₃H as solid catalyst, methanol as solvent, at 30°C, under N₂ atmosphere.

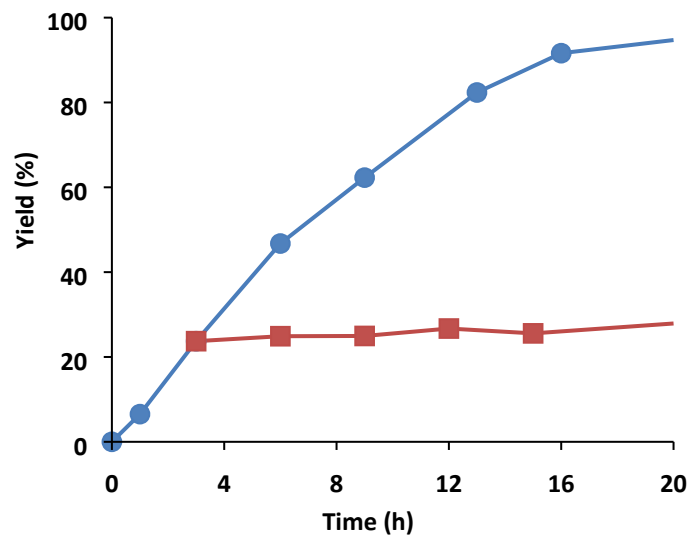


Figure S11. (●) Yield of methyl hexanoate production was plotted versus time when the esterification was carried out in presence of Al-ITQ-SO₃H as catalyst, with 10 mol% SO₃H, methanol as solvent, at 60°C. (■) leaching test.

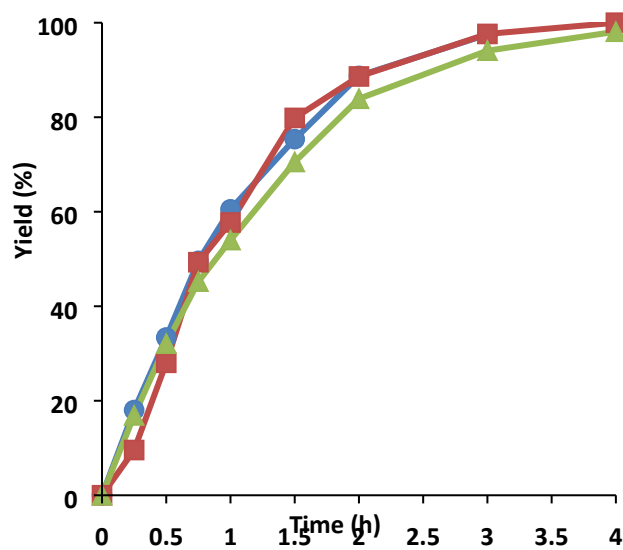


Figure S12. Yield of 2-methoxy-2-phenylethanol was plotted versus time when ring-opening reaction was carried out in the presence of Al-ITQ-SO₃H, with different amount of acid sites (▲) 5, (■) 7.5 and (●) 10 mol% SO₃H, in methanol, at 30°C.

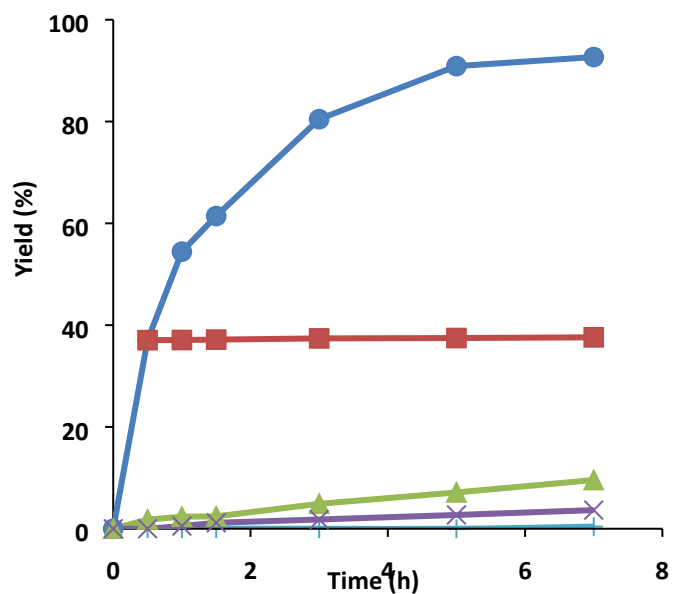


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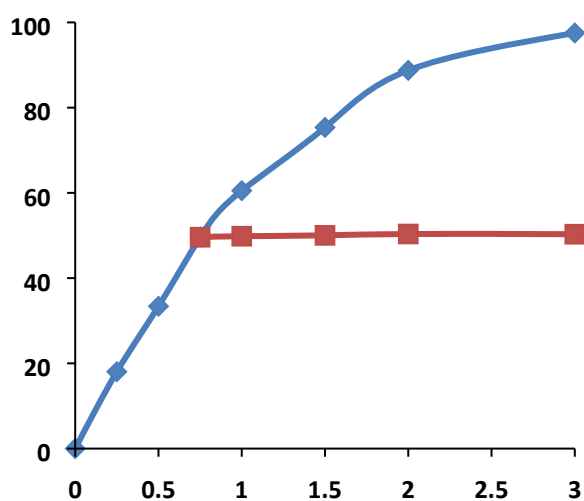


Figure S14. Yield of 2-methoxy-2-phenylethanol (◆) was plotted versus time when ring-opening reaction was performed in presence of Al-ITQ-SO₃H catalyst, with 10 mol% SO₃H and using methanol as solvent, at 30°C. (■) leaching test.

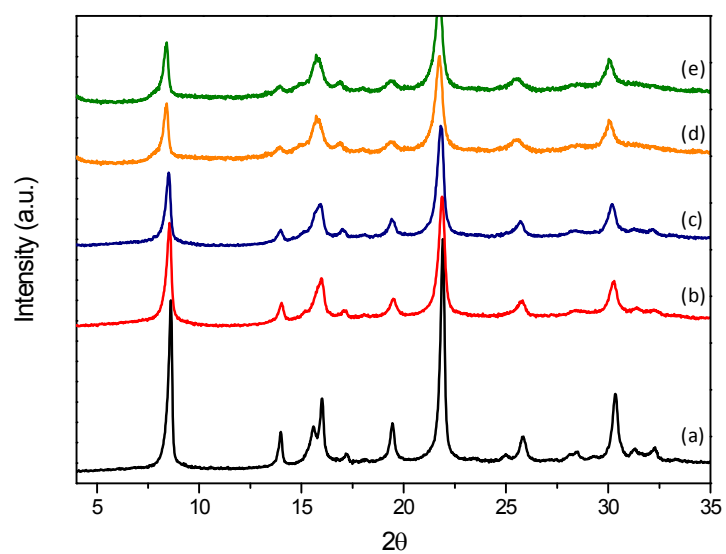


Figure S15. XRD patterns of Al-ITQ-SO₃H catalyst used to produce benzaldehyde dimethyl acetal: (a) fresh, (b) first use, (c) second use, (d) third use and (e) fourth use.

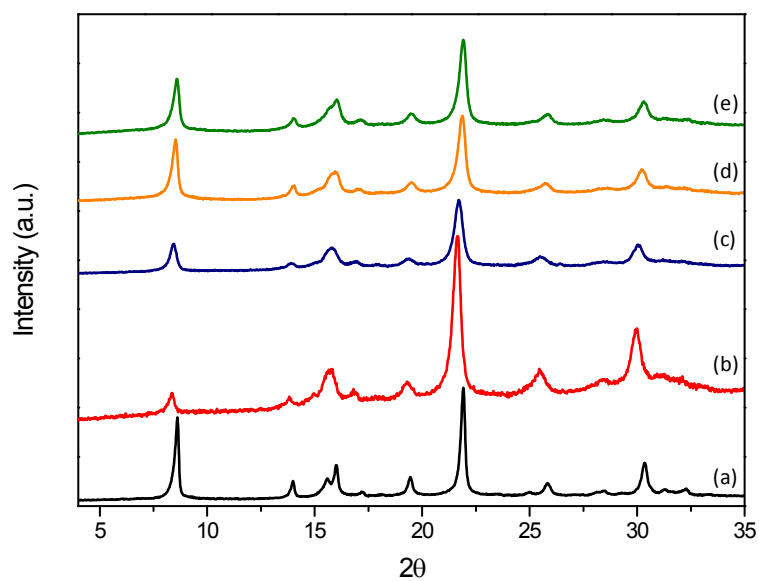


Figure S16. XRD patterns of Al-ITQ-SO₃H catalyst used to produce methyl hexanoate: (a) fresh, (b) first use, (c) second use, (d) third use and (e) fourth use.

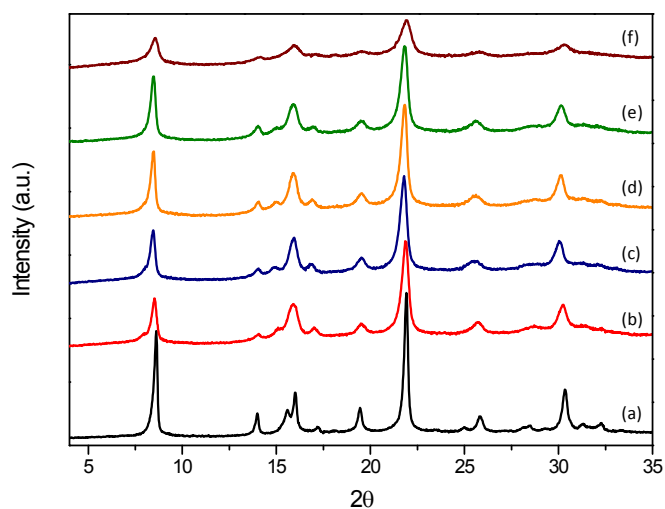


Figure S17. XRD patterns of Al-ITQ-SO₃H catalyst used to produce 2-methoxy-2-phenylethanol: (a) fresh, (b) first use, (c) second use, (d) third use, (e) fourth use and (f) fifth use.

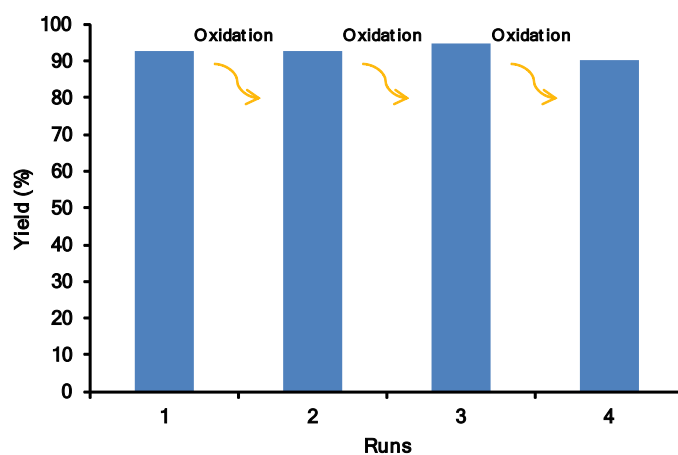


Figure S18. Al-ITQ-SO₃H catalyst was used for four consecutive uses for benzaldehyde dimethyl acetal production. Reaction conditions: 5 mol% SO₃H as catalyst, in methanol as solvent, at 30°C, under N₂ atmosphere, being oxidized between each run, 7h of reaction time.

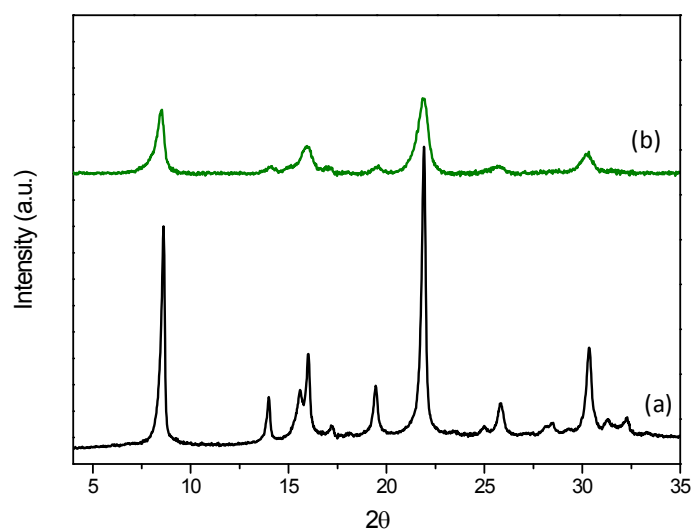


Figure S19. XRD patterns of Al-ITQ-SO₃H catalyst used to produce benzaldehyde dimethyl acetal: (a) fresh and (b) fourth use, being oxidized after each run.

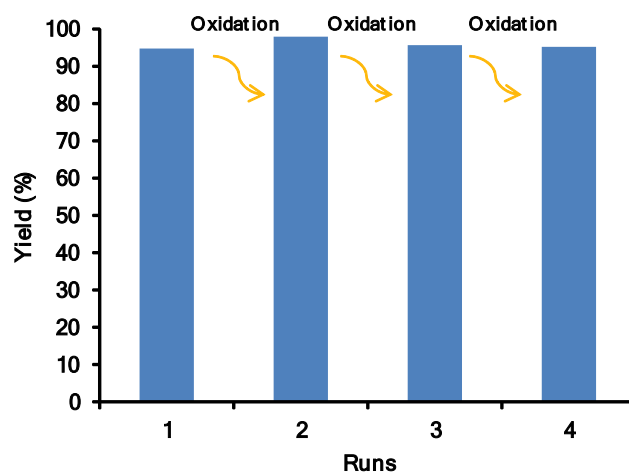


Figure S20. Al-ITQ-SO₃H catalyst was used for four consecutive uses for methyl hexanoate production. Reaction conditions: 10 mol% SO₃H, methanol as solvent, at 60°C, being oxidized between each catalytic cycle, 20h of reaction time.

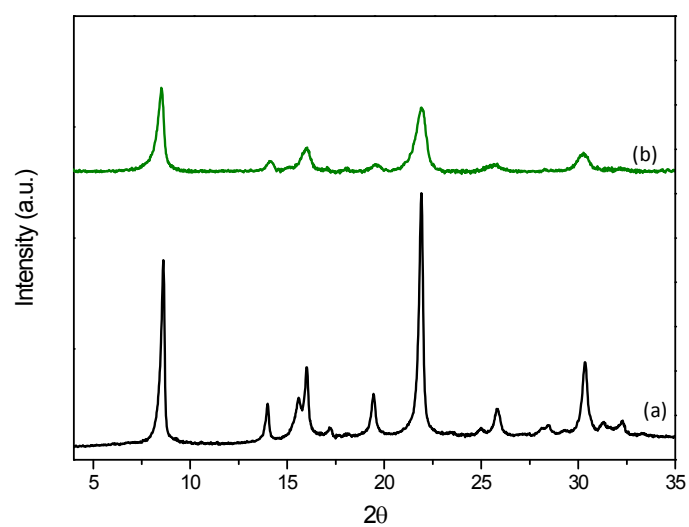


Figure S21. XRD patterns of Al-ITQ-SO₃H catalyst used to produce methyl hexanoate: (a) fresh and (b) fourth use being oxidized after each run.

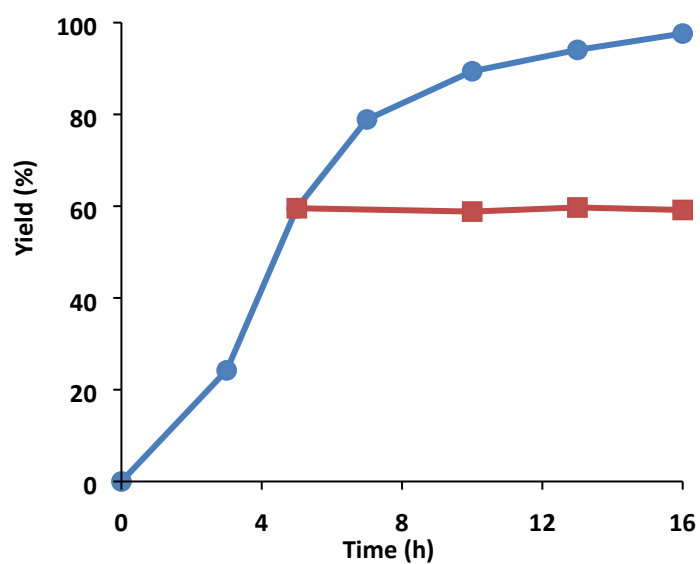


Figure S22. (●) Kinetics of oxidation reaction (step I) in presence of Al-ITQ-SO₃H/Pd catalyst with 3 mol% Pd and (■) leaching test. Reaction conditions: benzonitrile as solvent at 100°C under O₂ atmosphere.

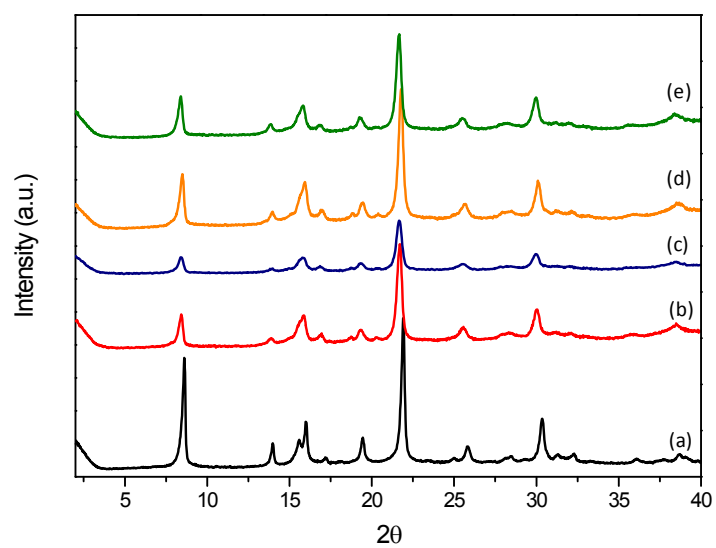


Figure S23. XRD patterns of Al-ITQ-SO₃H/Pd catalyst used in the oxidation-acetalization reaction: (a) fresh, (b) first use, (c) second use, (d) third use and (e) fourth use.

Tables

Table S1. CO₂ adsorbed for the lamellar and standard hybrid materials.

Samples	Volume CO ₂ (cm ³ ·g ⁻¹)
Al-ITQ-SH	34.3
Al-ITQ-SO ₃ H	24.9
Al-ITQ-SH/Pd	28.0
Al-ITQ-SO ₃ H/Pd	15.1
UiO66(Zr)-(SH) ₂ ¹	35.0
UiO66(Zr)-(SO ₃ H) ₂ ¹	15.0
DUT-4(SO ₃ H) ₅₀ ²	33.5

Table S2. Yields of methyl hexanoate production in presence of Al-ITQ-SO₃H, using methanol as solvent^a.

Catalysts	Load catalyst (mol%SO ₃ H)	Temperature (°C)	Yield (%)
Al-ITQ-SH	10	60	2
MIL-53(Al)	10	60	3
4-Mercaptobenzoic acid	10	60	5
4-Mercaptobenzoic acid	5	60	4
4-Mercaptobenzoic acid	3	60	4
Blank	---	60	3

^aReaction conditions: hexanoic acid (0.4 mmol), methanol (1 mL), 10 mol% SO₃H, 60°C at 20 h.

Table S3. Yields of 2-methoxy-2-phenylethanol production in presence of Al-ITQ-SO₃H and conventional MOFs as catalyst, using methanol as solvent^a.

Catalysts	Load catalyst (mol%)	Yield (%)	TON	TOF (h ⁻¹) ^b
Al-ITQ-SO ₃ H	10	98	10	8
Al-ITQ-SH	10	---	---	---
MIL-53(Al)	10	---	---	---
Ácido 4-mercaptobenzoico	10	37	---	---
Ácido 4-mercaptobenzoico	5	25	---	---
Ácido 4-mercaptobenzoico	1	5	---	---
Blanco	---	---	---	---
HKUST-1 ^{c3}	10	44	4	0.65
HKUST-1 ^{c3}	12.5	89	7	3.5
Basolite F300 ^{c3}	10	99	10	5.6
UiO66 ^{c3}	10	26	3	3.1

^aReaction conditions: styrene oxide (0.25 mmol), methanol (1 mL), 30°C, 3 h. ^bCalculated at initial reaction rate.

^cReactions conditions: styrene oxide (2.0 mmol), methanol (5 mL), 40°C at 24 h.

Table S4. Yields of oxidation reaction in presence of Al-ITQ-SO₃H/Pd^a.

Catalysts	Load catalyst (mol%)	Yield (%)	TON
Al-ITQ-SO ₃ H/Pd	5	98	20
Al-ITQ-SO ₃ H/Pd	3	98	33
Al-ITQ-SO ₃ H/Pd	1	88	88
Al-ITQ-SH	3	2	0.7
Al-ITQ-SO ₃ H	3	2	0.7
MIL-53(Al)	3	---	---
Ácido 4-mercaptobenzoico	10	2	---
Cloruro de bis(benzonitrilo)paladio (II)	3	12	---
Blank	---	4	---
Pd@UiO67 ^{b 4}	1	99	99
Pd@MIL-101 ^{c 5}	1	99	99
Pd@Cu-MOF ^{d 6}	5	95	19

^aReaction conditions: benzyl alcohol (0.20 mmol), benzonitrile (1 mL), 16 h, 100°C, O₂. ^bReaction conditions: benzyl alcohol (1.0 mmol), toluene (10 mL), 20 h, 100°C. ^cReaction conditions: benzyl alcohol (1.0 mmol), toluene (10 mL), 1.5 h, 80°C, O₂. ^dReaction conditions: benzyl alcohol (0.21 mmol), xylene (3 mL), 25 h, 130°C.

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