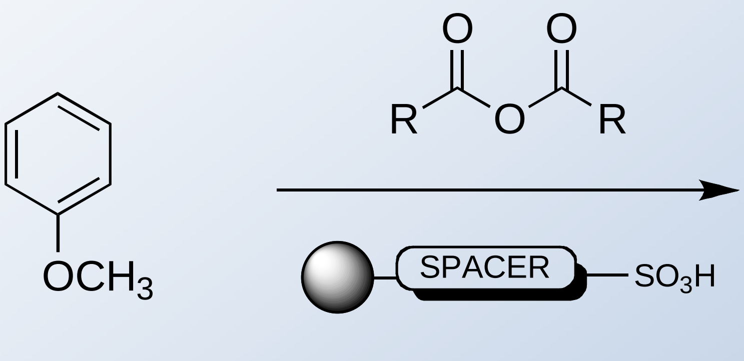
UNIVERSITÀ DEGLI STUDI DI PARMA

FRIEDEL-CRAFTS ACYLATION REACTION WITH ANHYDRIDES

SILICA SUPPORTED SULFONIC ACIDS AS GREEN AND EFFICIENT HETEROGENEOUS CATALYSTS



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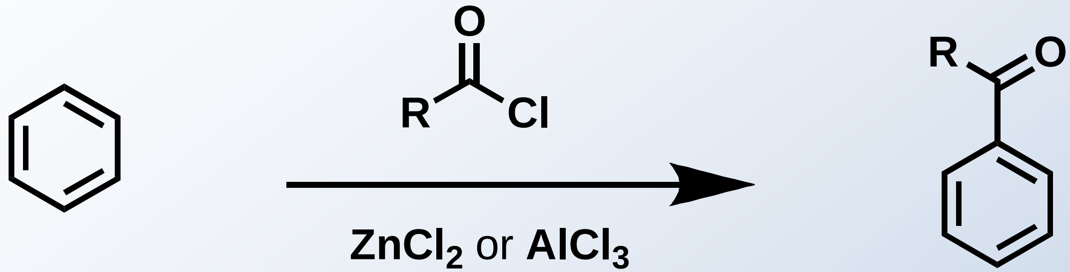
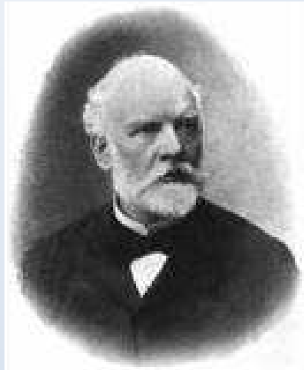
Calogero G. Piscopo*, Andrea Adorni, Raimondo Maggi, Giovanni Sartori

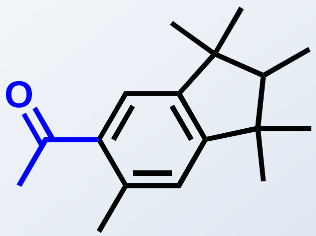
“Clean Synthetic Methodologies Group”
Dipartimento di Chimica Organica e Industriale
Università di Parma

Friedel-Crafts acylation reaction

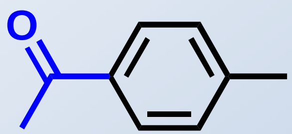
1877 : First paper reported by Friedel and Crafts



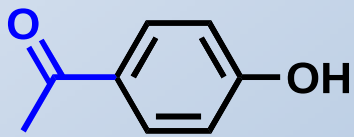




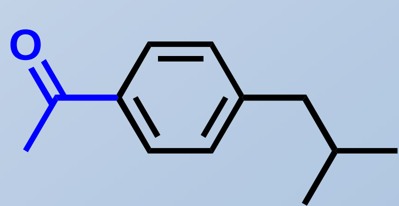
Musk fragrance



Mimosa fragrance



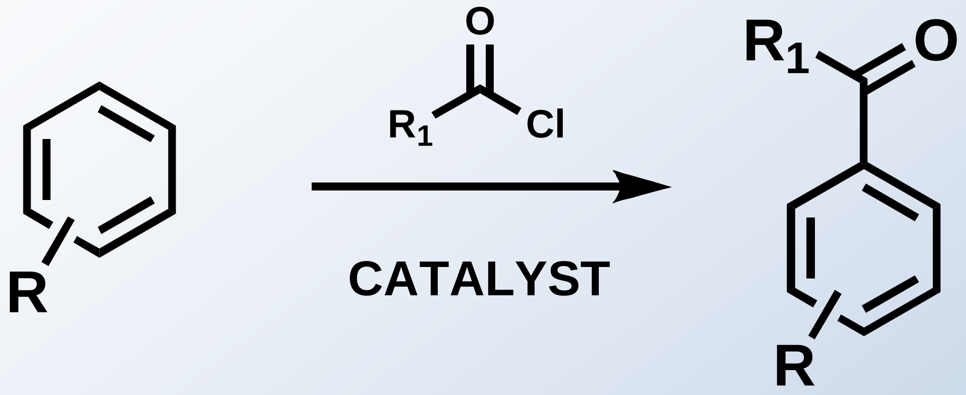
Paracetamol intermediate



Ibuprofene intermediate

G. Sartori, R. Maggi, “*Advances in Friedel-Crafts Acylation Reactions: Catalytic and Geen Processes*”, **2010**, CRC Press.

F.C. acylation reaction and environmental problems



CATALYST : Lewis or mineral acid

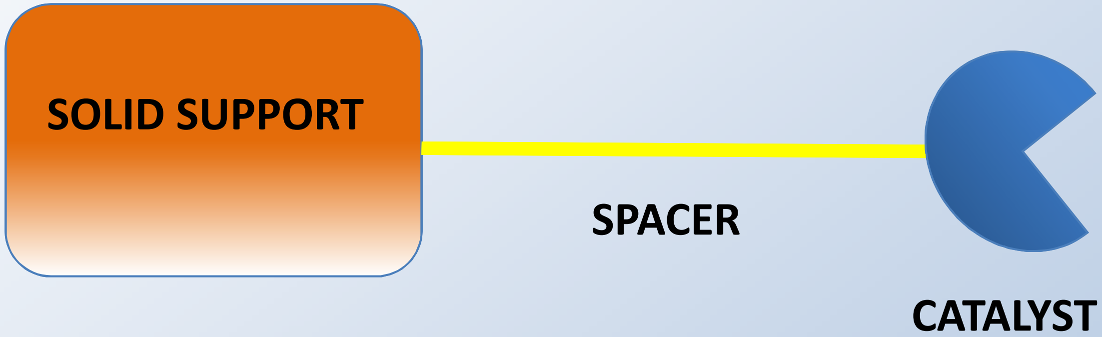
- **Stoichimoetric amount of catalyst**
- **Troublesome work-up steps**
- **Release of a great amount of anions in water (specially chloride)**

Friedel-Crafts acylation with heterogeneous catalysts

Solid acid catalysts:

Zeolites, clays, metal oxides, heteropoly acids.

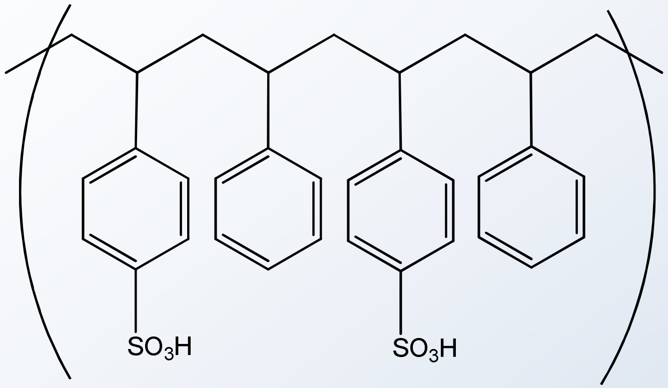
Supported catalysts:



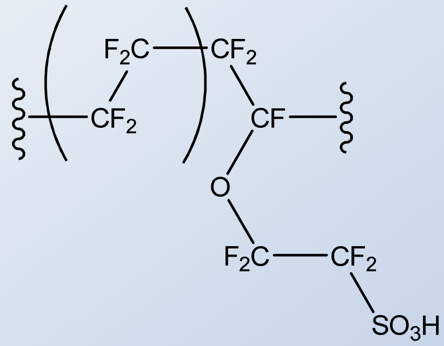
G. Sartori, R. Maggi *Chem. Rev.* **2006**, 106, 1077-1104.

Supported sulfonic acids

Resin supported sulfonic acids

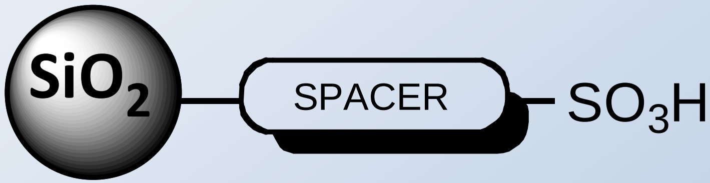


Amberlite or Amberlyst



Nafion-H

Silica supported sulfonic acids

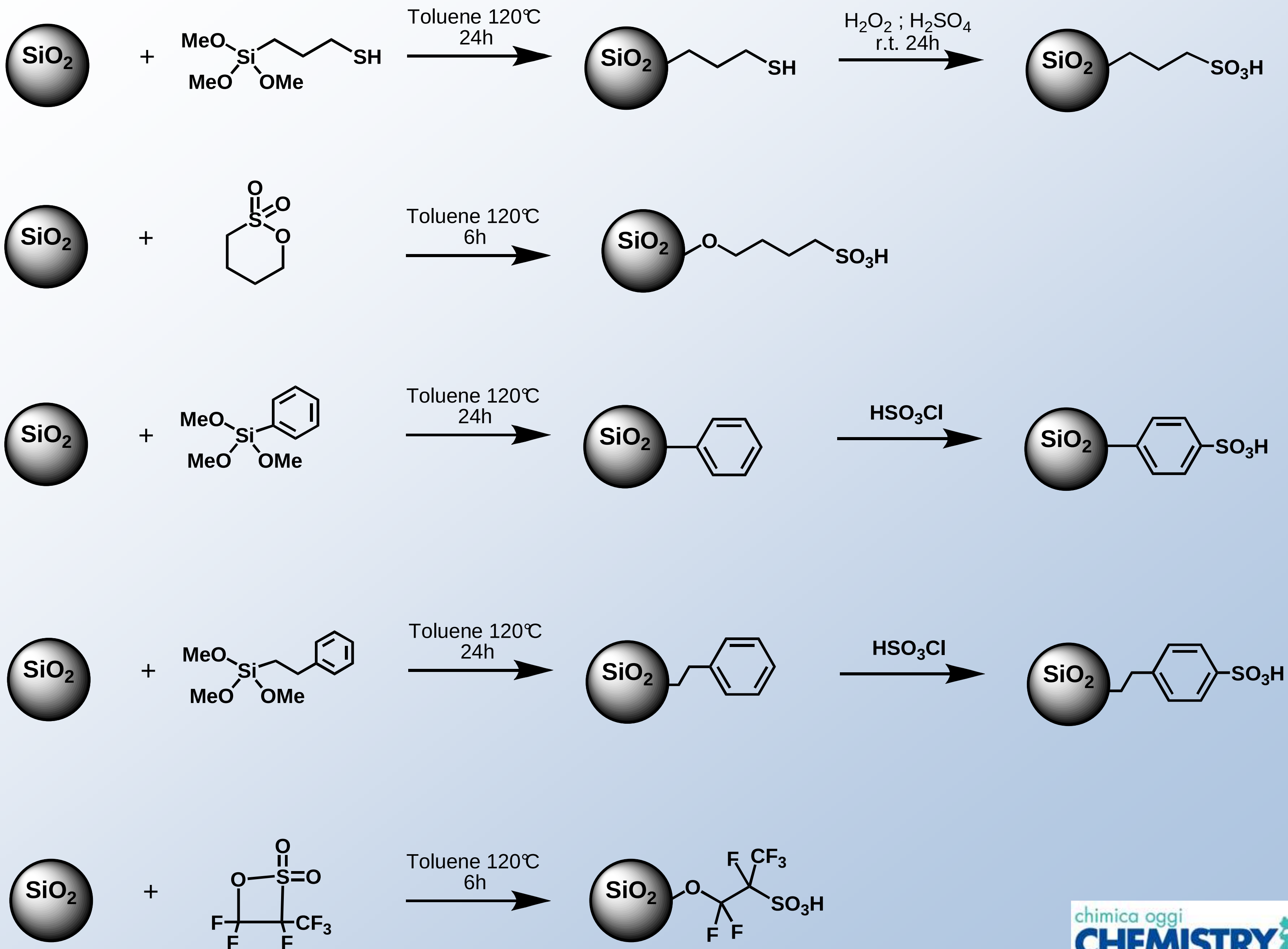


Surface Area:

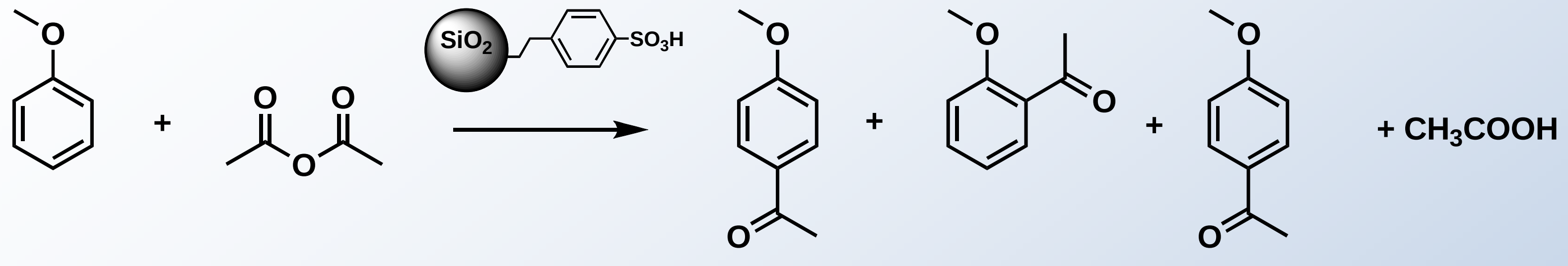
Polymer resin: <50 m^2/g

Amorphous silica: 400-600 m^2/g

Preparation of silica supported sulfonic acids



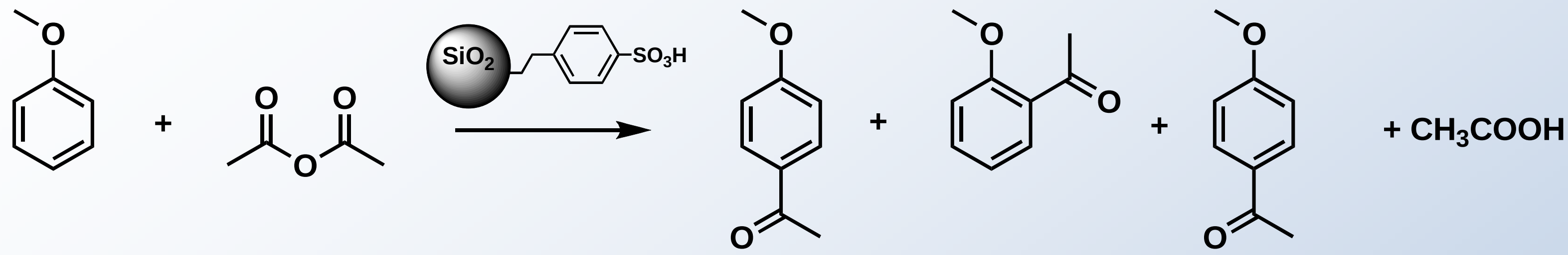
Acylation of anisole with acetic anhydride



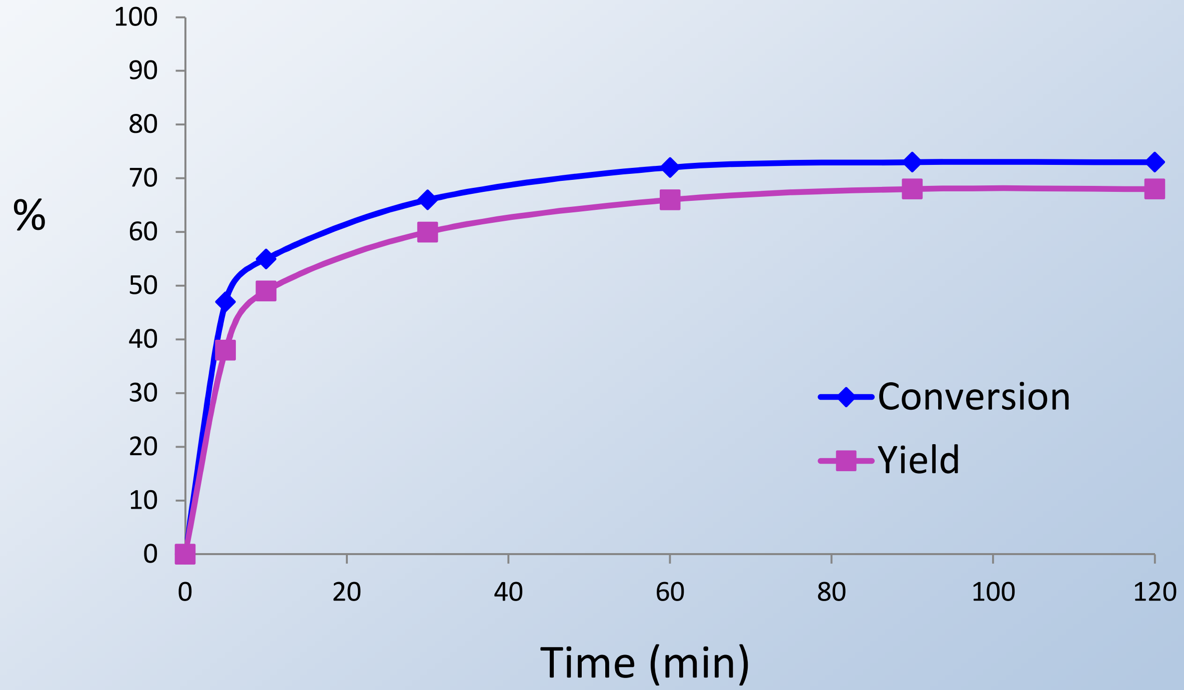
14 15 16 17 18 19

Entry	T (° C)	**14/15** molar ratio	Catalyst (%)	**14** Conversion (%)	**16** Selectivity (%)
1	60	1:1	5	31	87
2	80	1:1	5	35	89
3	120	1:1	5	48	83
4	120	1:3	2	49	88
5	120	1:3	5	60	92
6	120	1:3	10	73	93

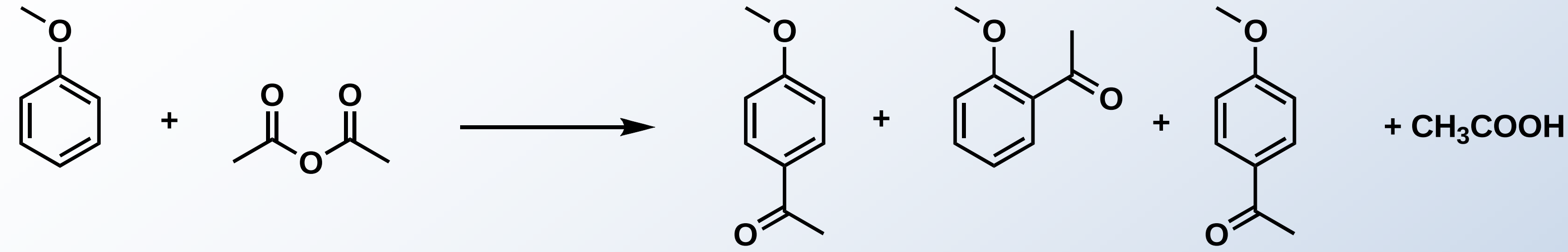
Reaction trend



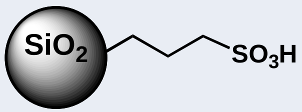
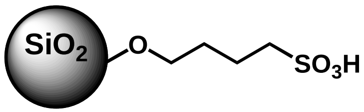
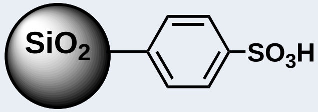
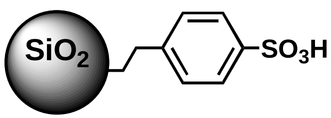
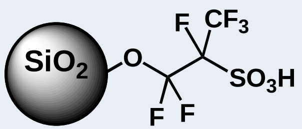
14 15 16 17 18 19



Catalyst's comparison



14 15 16 17 18 19

Catalyst	14 Conversion (%)	16 Selectivity (%)
3 	15	80
5 	20	80
8 	47	94
11 	73	93
13 	75	95

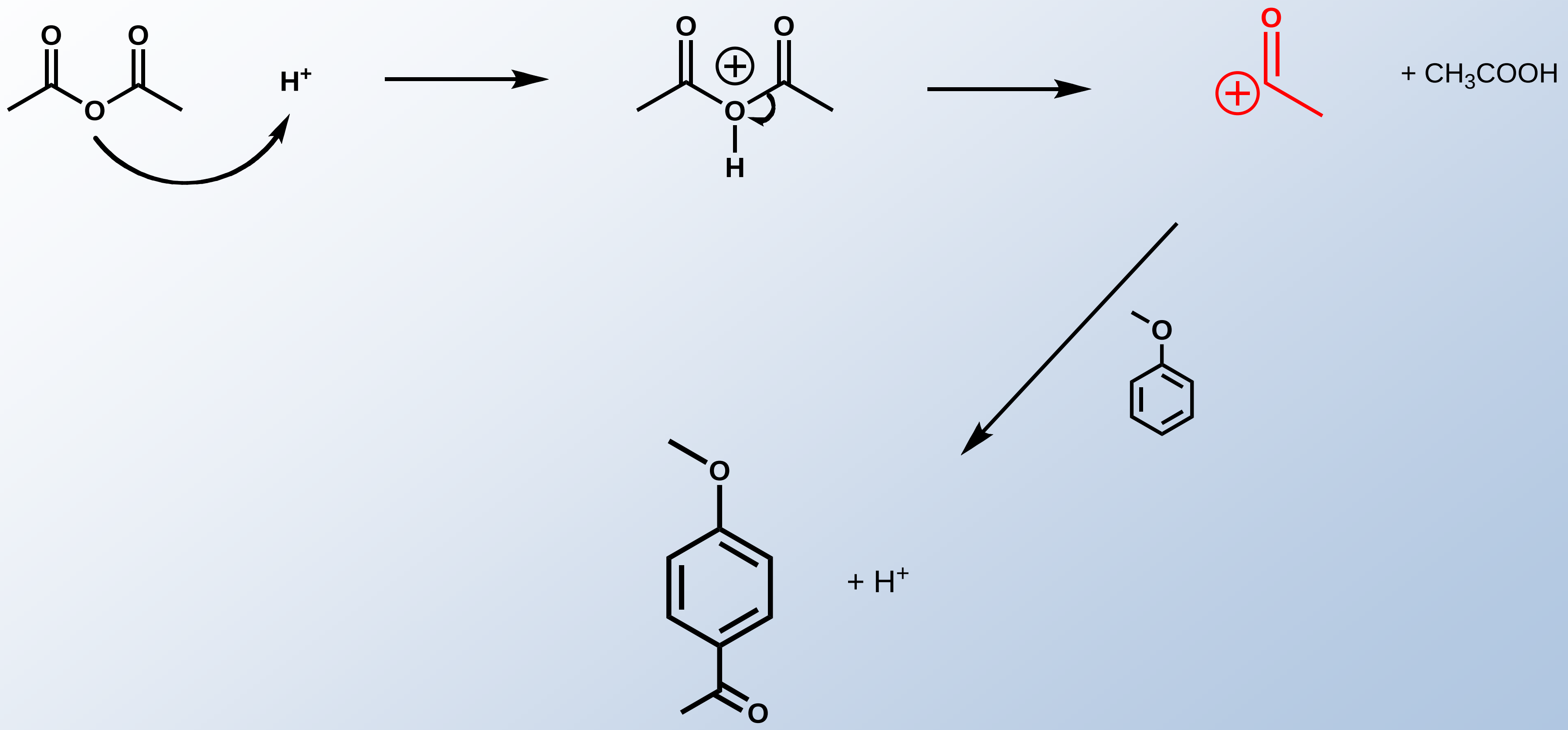
R-SO$_3$H pKa ≈ -2

Ar-SO$_3$H pKa ≈ -6,5

R$_F$-SO$_3$H pKa ≈ -13

ACIDITY

Reaction mechanism



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Conclusions and future developments

- These new materials could constitute a competitive alternative to traditional homogeneous systems conventionally used as catalysts in acylation processes.

- Such materials can represent interesting alternatives to commercially available sulfonated resins, which have low surface areas and poor thermal stabilities.

- Deactivation and regeneration of these catalysts as well as their catalytic behaviour with less activated aromatic compounds to settle its potential industrial applicability are currently under investigation.

Acknowledgements

“Clean Synthetic Metodologies Group”

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Prof. Raimondo Maggi
Andrea Adorni

Thank you for your kind attention!!!