Catalytic upgrade of pyrolysis vapors: acetic acid chain-growth reactions on TiO_2

AUTHOR: ANDREA LOCATELLI

ADVISOR: ALESSANDRA BERETTA

CO-ADVISOR: VERONICA PIAZZA

ACADEMIC YEAR: 2021-2022

1 Introduction

The push for a transition towards a low carbon economy is asking for a lower dependence on fossil fuels. Different technologies have been developed during the years to achieve this goal, with a particular attention to the exploitation of renewable energy sources. Waste biomass valorization is among the proposed solutions, and it is widely used in the production of chemicals and biofuels.

Bio-oils, produced by pyrolysis of lignocellulosic biomass, are multicomponent mixtures characterized by a high content of water and C_2-C_4 oxygenated compounds, responsible for its well-known undesirable properties (high viscosity, high corrosivity, chemical instability and low heating value). A possible solution to improve bio-oil quality is the development of a catalytic upgrading stage of pyrolysis vapors aiming to convert these detrimental light oxygenates into useful products. A possible route involves C-C coupling processes, where C_2-C_4 oxygenates are converted to higher species via

chain-growth reactions, thus increasing the carbon-chain length while reducing the overall O/C ratio.

The objective of this thesis work is the experimental study of a model oxygenate and a model reacting system: acetic acid ketonization on TiO_2 catalyst. Carboxylic acids are in fact important light and undesired products of the pyrolysis of lignocellulosic biomass. Ketonization, then, is a reaction leading to the condensation of two molecules of acid with decarboxylation, than is loss of one C in the form of CO_2.

2 Materials and methods

2.1 Catalyst preparation

A commercial TiO_2 anatase in powder form (Tronox) was used for the catalyst preparation. A calcination in air was carried out to remove all volatiles and pre-treat the material to avoid morphological/chemical changes during the tests. Calcination procedure consisted in a controlled heating from T_{amb} to up to 400°C with a ramp rate of 1°C/min; after a hold of 3h at 400°C, the system

was cooled down to T_{amb} with a ramp rate of 2°C/min.

Ru/TiO$_2$ catalytic powder were prepared via incipient wetness impregnation technique, and two different precursors were used: RuCl$_3$ salt (39 wt. % Ru, Johnson Matthey) and Ru-Nitrosyl-Nitrate solution (1.4 wt. % Ru, Alfa Aesar).

2.2   Catalyst characterization

To better understand morphological and structural properties of the catalyst, BET measurements were carried out.

Temperature programmed reduction (TPR) was used to examine the surface chemistry of the catalyst. TPR tests were carried out with 20 NmL/min of 5% H$_2$ in Ar (T-ramp rate of 10°C/min up to 1000°C) in a TPDRO 1100 (Temperature Programmed Desorption Reduction Oxidation) by ThermoQuest© .TPR tests were repeated in a traditional fixed-bed configuration while analysing the composition of gas mixture in a online MS and IR analyzers: in this case, 100 Ncc/min of 4% H$_2$ in He was used, with a T-ramp of 10°C/min up to 800°C.

Temperature programmed desorption (TPD) with NH$_3$, CO$_2$ and Acetic acid as gas probes were performed; in particular NH$_3$ and CO$_2$ TPD tests were carried out to analyze acid and basic sites, respectively. Acetic acid TPD was instead carried out to comprehend how this molecule (reactant for ketonization tests) interacts with catalytic surface. TPD tests were performed sending 100 Nml/min of inert mixture (N$_2$/He or Ar/He) containing the probe gas (either 1% CO$_2$, 3% Acetic acid or 0,2% NH$_3$) in the adsorption phase. After a purge phase at 100Nml/min of inert mixture, a TPD T-ramp (10°C/min for CO$_2$ and NH$_3$, 5°C/min for Acetic acid) started, up to 600°C.

Temperature programmed oxidation (TPO) were performed to understand qualitatively and quantitatively the C-deposits formation on spent catalysts. TPO tests were performed with a controlled heating up to 600°C with a 2°C/min ramp, while subjected to an air flow of 25Nml/min.

2.3   Lab-scale apparatus for catalytic activity tests

Experiments were run in a lab-scale plant, using a traditional packed bed configuration where the catalyst was tested in powder form. Catalyst powders were sieved (mesh 140-200) and then loaded in a quartz reactor. The catalyst load

amounted to 150-300mg, corresponding to a bed height around 7-10 mm. A column of quartz grains (20-35 mesh) was loaded above the catalytic bed to obtain uniform flow distribution and pre-heating of the inlet stream. Before testing, H$_2$ pre-treatments with a GHSV of 6000 NL/h/kg$_{cat}$ up to 400°C with a ramp rate of 10°C/min (heating up/cooldown) were performed to reduce the catalyst surface.

Inlet composition to the reactor was provided by MFC controllers (model Brooks) for the gaseous species, while acetic acid was fed using a saturator, on which an He carrier flowed.

All composition analyses of reactants and products mixtures were carried out with an online GC-TCD (Gas Chromatography–Thermal Conductivity Detector) or an online a Micro-GC. Additionally, offline measurements were carried out in a GC-MS (Mass Spectrometer) to identify chemical structure of unknown species.

Standard ketonization tests were carried out with a GHSV of 20000 NL/h/kg$_{cat}$ of 3% Acetic acid, 20% H$_2$ (if co-fed), 10% N$_2$ in He.

Blank tests were carried out using Quartz instead of TiO$_2$ (same catalyst mesh of 140-200), with the same conditions of ketonization tests.
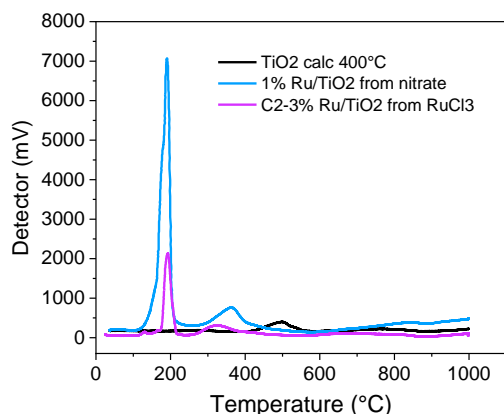
3   Results

3.1   Catalyst and surface characterization

3.1.1   Morphological analyses

BET measurements were performed on TiO$_2$ and TiO$_2$ spent after a ketonization test at 400°C for 4.5h. Results showed a decrease in surface area for the spent (from 80,3 to 64,9 m²/g$_{cat}$), with also a decrease for pore volume (From 0,38 to 0,32 cm³/g$_{cat}$). These results show a partial blockage of catalytic pores, likely due to the cumulation of carbonaceous deposits.

3.1.2   TPR

Figure 3.1 reports TPR results in terms of H$_2$ consumption (mV of detector) for TiO$_2$ and Ru/TiO$_2$ coming from two different precursors (RuCl$_3$ and Ru-Nitrosyl-Nitrate). In the Fig., a low-temperature H$_2$ consumption due to Ru cluster reduction[1] can be observed both for Cl (180-210°C) and Nitrate (150-220°C) precursors; a second peak is found between 250-400°C (Ru/TiO$_2$) and 400-600°C (TiO$_2$), attributed to oxygen vacancies formation due to partial surface reduction with H$_2$

Figure 3.1 - TPR results on TiO₂ and Ru/TiO₂
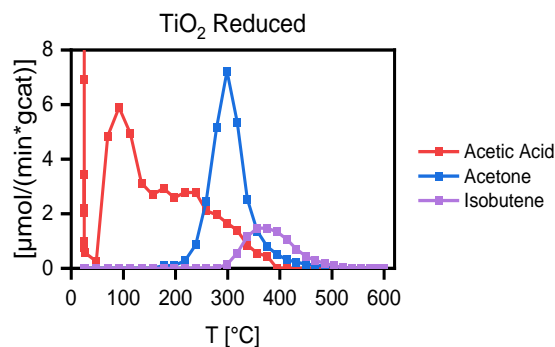

Figure 3.2 - Acetic Acid TPD on TiO₂

spillover[1]. Specific tests coupled with MS and IR showed that in this last temperature region also sulphates and other impurities are reduced. This observation confirms the importance and effectiveness of the H₂ pre-treatment process at 400°C.

3.1.3 TPD

NH₃ and CO₂ TPD tests were performed on three batches of TiO₂: TiO₂ fresh (no pre-treatments), a TiO₂ reduced with H₂ pre-treatment and TiO₂ spent (after ketonization up to 300°C) and then reduced. Results (Table 3.1) demonstrated that acid and basic sites are consistent with literature[2],[3], where TiO₂ demonstrates an acidic nature. However, it can be seen that the reduction pre-treatment allows to increase CO₂ adsorption; this suggest that favorable O-vacancies are formed on TiO₂. Instead, from the data collected during Acetic acid TPD on TiO₂ after a standard H₂ pre-treatment (Figure 3.2), it was discovered that acetic acid reacted as temperature increased, activating at least ketonization: when temperature conditions were enough, conversion from acetic acid into acetone started. Another major discovery is that isobutene is present because a cracking reaction took place. Faba et al.[4] reported that two acetone molecules combine into an intermediate C_6 that then cracks into an acetone

CO₂ and NH₃ integration results [mmol/g_cat]		
Catalyst type	CO₂	NH₃
TiO₂ fresh	0,021	0,244
TiO₂ reduced	0,034	0,168
Fresh TiO₂ spent then reduced	0,019	0,631

Table 3.1 - CO₂ and NH₃ integration results

molecule and isobutene.
Acetic acid TPD tests were also performed on Ru/TiO₂ catalysts, following the same procedure. The results (not reported here for the sake of brevity) showed similar trends, proving a major role of TiO₂ and a minor role of Ru for acetic acid surface reactions.
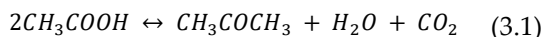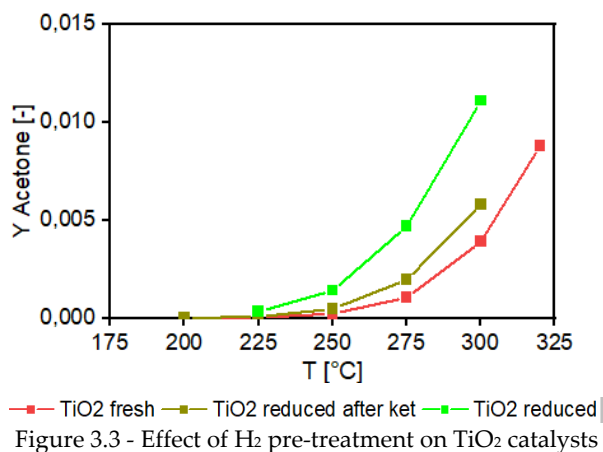
3.2 Ketonization tests

3.2.1 Blank tests

Blank tests of acetic acid ketonization were performed to evaluate the presence and effect of homogenous reactions. Results showed an impact of total inlet Flow rate and H₂ presence in the reacting mixture on homogeneous reactions onset. Operating conditions suitable for blocking homogeneous reactions and carrying out catalytic tests were identified. Moreover, in the past the quartz used to fill the quartz reactor (before the catalyst bed) was usually re-used for several reactor, after a thermal regeneration procedure. However, blank tests were carried out also on this regenerated quartz and showed an increased acetic acid conversion with respect to fresh quartz. For this reason, every reactor was prepared with a batch new quartz.

3.2.2 Ketonization on low temperature region

The first analyses involved an investigation of the low temperature range, up to 300°C for the ketonization reaction of acetic acid; as it was shown that in these conditions acetic acid ketonization reaction was the only active reaction pathway, with a reaction stoichiometry shown by Equation (3.1).

3

Figure 3.3 - Effect of H_2 pre-treatment on TiO_2 catalysts

$$2CH_3COOH \leftrightarrow CH_3COCH_3 + H_2O + CO_2 \quad (3.1)$$

Results of a standard acetic acid ketonization tests on TiO_2 is shown in Fig; being ketonization the only active reaction pathway, the only trend of acetone fully describes the catalyst performances. The effect of reduction pre-treatment was investigated, and results are shown in Figure 3.3, where "Fresh" refers to a non-pre-treated catalyst, while "reduced after ket" indicates a catalyst previously subjected to ketonization and then to a H_2 treatment.

It is observed that H_2 treatment has a positive effect on TiO_2 activity. However, if a reduction treatment performed after a ketonization test it is less effective; it is believed that C-species are formed on the surface and hinders the full development of reduction.

3.2.3 Ketonization on high temperature region

After the low temperature analyses, the catalytic system was tested in more severe conditions: in particular, temperature was increased from a range of 200-300°C to 300-400°C. In the previous thesis work[6], it was observed that carbon-balance to ketonization products (i.e. considering acetone and CO_2 only) declined above 275°C, indicating that ketonization alone could not explain high temperature conversion of acetic acid.

This observation suggested the onset of secondary reactions and the formation of secondary products. High temperature performances of TiO_2 were investigated by analyzing the catalyst activity at 400°C for 4.5 h while monitoring the evolution of product distribution. Effects of temperature (300-350-400°C), H_2 co-feed effect (0-20 %), and Ru addition were also explored.
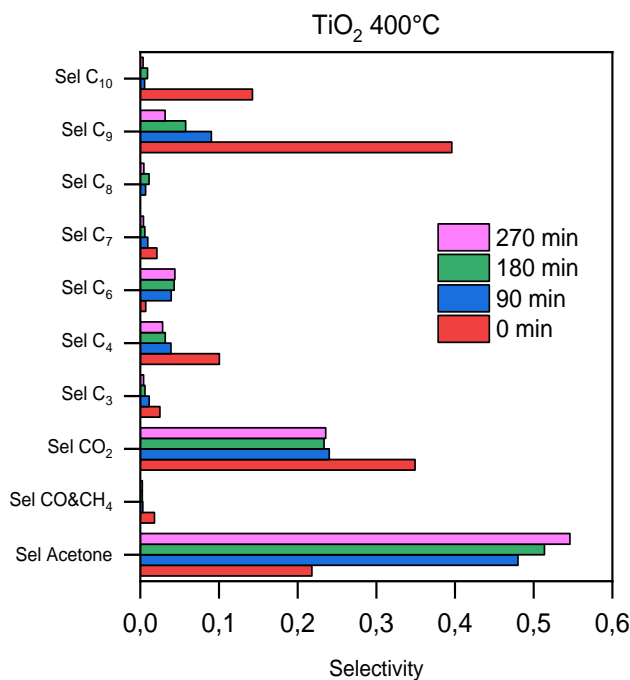

Figure 3.4 – C-selectivity of TiO_2

Analyzing the C-selectivity of products at 400°C, (Figure 3.4) at varying Time on Stream (ToS), it can be observed that C_4+ species justify a total selectivity of 66,3%, that is quite high, at the beginning of the test. However, at increasing ToS catalyst stability was not preserved: secondary-chain growth reactions were significantly hindered with time on stream, while acetone selectivity increased. Similar trends were obtained with Ru/TiO_2 as well as at lower operating temperature: surprisingly, also at 300°C heavy C_6+ species were seen among products at the beginning of the test. Considering the products, two secondary reactions can be found:

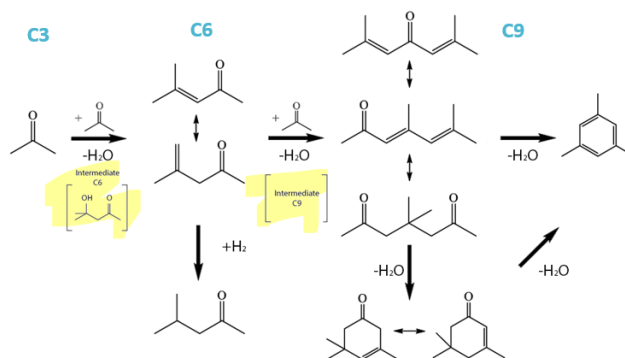**Consecutive self and cross condensation reactions of acetone**

Figure 3.4 – Condensation reactions overview

1. Self- and cross- aldol condensation reactions from acetone, to C_6, C_9 and C_{12} (reaction scheme presented in Figure 3.5)[4]
2. Cracking reactions, leading to the production of C_4, C_7, and C_{10} olefins with the elimination of a molecule of acetic acid(Figure 3.5)[4]

Among this wide products platform, mesitylene (the aromatic C_9H_{12} species) constitutes a good compound for blending in jet-fuels. Noticeably, it was proved that TiO_2 is able to produce it in significant amount (e.g. 40% selectivity reached in Figure 3.4), but only for a brief duration, because catalyst stability is not preserved.

3.2.4 TPO

Because phenomena of C-deposition were observed during ketonization, TPO tests were performed on spent catalyst. CO_2, H_2O and CH_4 amounts were monitored over the course of the experiment. Effect of temperature, H_2 co-feed and Ru addition were investigated.

Figure 3.6 reports the CO_2 trend seen in TPO on TiO_2 and Ru/TiO_2 after a ketonization test with or without H_2 at 400°C. It can be observed that Ru facilitates the combustion of the C-deposits near its vicinity, as a sharp CO_2 peak emerges at 220 °C. Moreover, an integration of the quantity of products over time also shows that the total amount of C-deposited on Ru/TiO_2 was lower by almost 25% (20 $mmol_C/g_{cat}$ on TiO_2, vs 15 $mmol_C/g_{cat}$ on Ru/TiO_2). An effect of H_2 co-feed in ketonization on C-deposits was also observed (Figure 3.7): indeed, carbon deposits on TiO_2 exposed to ketonization without H_2 co-feed were lower (15 $mmol_C/g_{cat}$).
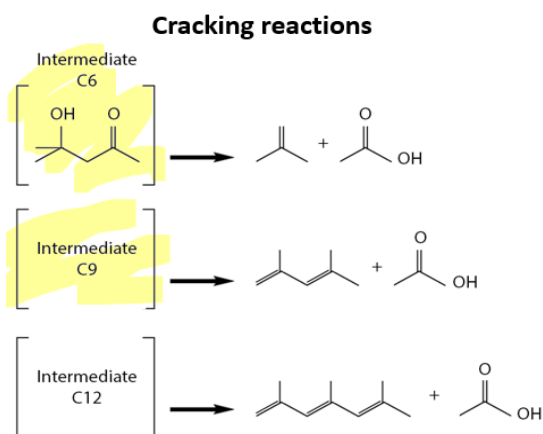

Cracking reactions

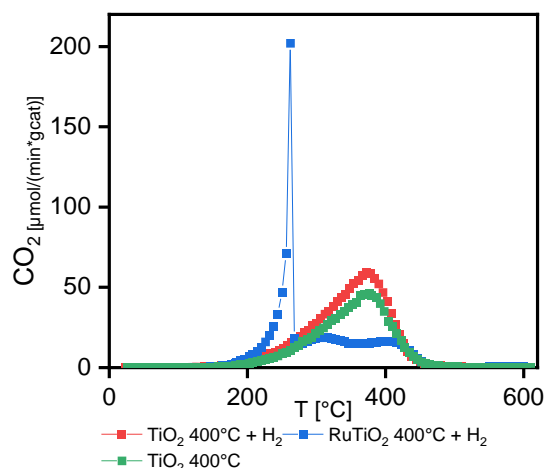Figure 3.5 – Cracking reaction pathways

Figure 3.6 – CO_2 amount over T during TPO of Ru/TiO_2 at 400°

4 Conclusions

The valorization of waste biomass is a resource for the current energy transition. However, the widespread use of bio-liquids is hampered by their negative features (e.g. low stability and heating value) caused by the presence of C_2-C_4 light oxygenates. In this context, the objective of this thesis is the study of light oxygenates catalytic C-C coupling reactions in order to increase C-chain length of bio-oil species while reducing the overall O/C ratio. On this purpose, a model oxygenate and a model reacting system were chosen: acetic acid ketonization on TiO_2 catalyst.

An in-depth catalyst characterization study was performed. CO_2 and NH_3 TPD tests proved the acidic nature of TiO_2 catalysts. However, results showed that H_2 pre-treatment contributed to the marginally increase of basic sites. Moreover, the CO_2 adsorption/desorption test seems to identify the H_2 pre-treated TiO_2 as the surface that is more prone to interact with an acidic and O-rich molecule as CO_2. Acetic acid Adsorption and TPD tests on TiO_2 and Ru/TiO_2 catalysts showed that acetic acid desorption was followed firstly by acetone formation, and then by isobutene formation, that is likely originated from the cracking of an intermediate C_6 component (from acetone condensation). In the presence of Ru, also CH_4 is observed desorbing at higher temperature, suggesting the onset of cracking reactions.

The effect of TiO_2 and Ru/TiO_2 pre-treatment in H_2 on low temperature (200-300°C) acetic acid ketonization were investigated. As a result, an appropriate protocol for catalyst pre-treatment

procedure was tuned, both for TiO$_2$ (6000 NL/h/kg$_{cat}$ of pure H$_2$, T-ramp of 10°C/min up to 400°C with 1h hold and subsequent cooldown at same rate) and for Ru/TiO$_2$ (the same reduction treatment performed on TiO$_2$ must be preceded by a ketonization test).

High temperature performances of TiO$_2$ were investigated by monitoring catalyst activity and product distribution at fixed temperature for 4.5 h. Effects of temperature (300-350-400°C), H$_2$ co-feed (0-20%) and Ru addition on the reaction were evaluated. Besides ketonization products, heavier species are detected among products due to the onset of secondary reactions at the beginning of the tests: self- and cross- aldol condensation reactions from acetone are activated, leading to the production of species with six C-atoms (Mesityl isobutyl ketone and Mesityl oxide) and 9 carbon atoms (Mesitylene). The presence of heavy olefins (C$_4$-C$_7$ and C$_{10}$) suggests instead the onset of cracking reactions (of the same surface intermediates produced in acetone condensation route). Among them, mesitylene and tetramethyl benzene, represent good products for jet-fuel blending. However, catalyst stability was not preserved at increasing ToS; moreover, neither the addition of Ru in catalyst recipe nor H$_2$ co-feed were successful in improving catalyst stability.

Challenges in terms of more detailed analyses in the higher temperature range are definitely a way forward, coupled with the possible improvement of TiO$_2$ properties, as they could lead to more selective reaction pathways for the intended goal pursued.

5   Bibliography

[1]   J. H. Shin, G. J. Kim, and S. C. Hong, "Reaction properties of ruthenium over Ru/TiO2 for selective catalytic oxidation of ammonia to nitrogen," *Appl. Surf. Sci.*, vol. 506, no. November 2019, p. 144906, 2020, doi: 10.1016/j.apsusc.2019.144906.

[2]   R. V. Mikhaylov, K. V. Nikitin, N. I. Glazkova, and V. N. Kuznetsov, "Temperature-programmed desorption of CO2, formed by CO photooxidation on TiO2 surface," *J. Photochem. Photobiol. A Chem.*, vol. 360, no. January, pp. 255–261, 2018, doi: 10.1016/j.jphotochem.2018.04.055.

[3]   S. Chai *et al.*, "Boosting CO2 methanation activity on Ru/TiO2 catalysts by exposing (001) facets of anatase TiO2," *J. CO2 Util.*, vol. 33, no. June, pp. 242–252, 2019, doi: 10.1016/j.jcou.2019.05.031.

[4]   L. Faba, J. Gancedo, J. Quesada, E. Diaz, and S. Ordóñez, "One-Pot Conversion of Acetone into Mesitylene over Combinations of Acid and Basic Catalysts," *ACS Catal.*, vol. 11, no. 18, pp. 11650–11662, 2021, doi: 10.1021/acscatal.1c03095.

[5]   S. Wang and E. Iglesia, "Experimental and theoretical assessment of the mechanism and site requirements for ketonization of carboxylic acids on oxides," *J. Catal.*, vol. 345, pp. 183–206, 2017, doi: 10.1016/j.jcat.2016.11.006.

[6]   P. Milano, "Catalytic upgrade of bio-vapours : Experimental analysis of acetic acid ketonization on TiO 2 catalyst," 2021.