TiO$_2$ nanoparticles for CO$_2$ photoreduction: a combined experimental and periodic DFT study of the active sites

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Background of the study and investigation techniques

Study of the TiO$_2$ exposed surface sites by CO adsorption

CO$_2$ interaction with dehydroxylated and hydrated TiO$_2$ anatase surfaces

Conclusions and perspectives
Background of the study and investigation techniques

- Study of the TiO$_2$ exposed surface sites by CO adsorption
- CO$_2$ interaction with dehydroxylated and hydrated TiO$_2$ anatase surfaces
- Conclusions and perspectives
Already in 1979 Honda and coworkers reported the photoreduction of CO$_2$ to form formic acid, formaldehyde, methyl alcohol and methane in aqueous suspension of TiO$_2$.

Despite a considerable amount of subsequent studies, the conversion efficiency of CO$_2$ into useful hydrocarbons is still too low for large-scale technological applications.

**surface study at an atomic/molecular level**
The key role of surface sites
Shape dependent properties

M.V. Dozzi et al., Catalysts 2013, 3, 455

Background of the study and investigation techniques
Background of the study and investigation techniques

Nanoparticle morphology
Electron microscopy

- TiO$_2$ HT
- TiO$_2$ P25 (Evonik)
- TiO$_2$ T-SP (Solaronix)


study at an atomic level

Information on exposed surfaces

more complex morphology: how can we study the surface?
Nanoparticle morphology and surface properties
FTIR spectroscopy of adsorbed probe molecules

TiO₂ surface
Nanoparticle morphology and surface properties
FTIR spectroscopy of adsorbed probe molecules

Effect of the interaction with surface sites on the ν of the internal mode
FTIR spectroscopy of adsorbed probe molecules
Carbon monoxide

The higher is the blue-shift, the greater is the Lewis acidity of the metal cation

Information on surface properties and morphology

Stretching frequency of adsorbed CO is also influenced by the lateral interactions occurring in the adlayers

2143 CO gas

v increases

\[ \tilde{v} \ (\text{cm}^{-1}) \]

\( \sigma \)-donation
(TMI: e.g. Ti\(^{4+}\))

\( \pi \)-backdonation

\( v \) decreases
The use of a cryostat allowed us go below the liquid nitrogen temperature obtaining spectra of considerably improved quality.

Study of the TiO$_2$ exposed surface sites by CO adsorption

- Background of the study and investigation techniques
- Study of the TiO$_2$ exposed surface sites by CO adsorption
- CO$_2$ interaction with dehydroxylated and hydrated TiO$_2$ anatase surfaces
- Conclusions and perspectives
Anatase TiO$_2$ nanocrystals

HRTEM and FTIR of CO adsorbed at 60 K


Study of the TiO$_2$ exposed surface sites by CO adsorption
Anatase surfaces modeled with bidimensional slabs characterized by two infinite dimensions \((x, y)\) and a finite thickness exploiting the CRYSTAL09 code and the PBE0 functional.


Study of the TiO\(_2\) exposed surface sites by CO adsorption
Periodic DFT calculations
CO adsorption on the main anatase surfaces

Study of the TiO$_2$ exposed surface sites by CO adsorption
Periodic DFT calculations
Main computed parameters

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<tr>
<th>Surface</th>
<th>θ</th>
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CO adsorbed at 60 K on nanoanatase
Complete spectral assignment

Rutile TiO$_2$
Modeling of CO adsorption

L. Mino et al., J. Phys. Chem. C 2013, 117, 11186

<table>
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<th>surface</th>
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Rutile TiO$_2$ model system
FESEM and FTIR of CO adsorbed at 60 K

BET surface area: 2 m$^2$/g

Reconstructed (110)

0.3 a.u.

(110)

OH $\cdots$ CO

L. Mino et al., J. Phys. Chem. C 2013, 117, 11186

Oxide surface properties and particle morphology
Mixture of different polymorphs
Evonik (Degussa) TiO₂ P25

Mixture of about 85% anatase and 15% rutile with a surface area of 60 m²/g prepared by flame hydrolysis of TiCl₄.
Its outstanding photocatalytic activity makes it a benchmark for testing new synthesized materials.

HRTEM particles in 10-50 nm range
XRD anatase 26 nm – rutile 42 nm
Oxide surface properties and particle morphology

TiO$_2$ P25
Ingredients for complete spectral assignment

Anatase

CO adsorption at 60 K

HRTEM

P25

Periodic DFT calculations (PBE0 functional)

Oxide surface properties and particle morphology
TiO$_2$ P25
Complete spectral assignment


Information on face distribution, surface regularity and crystallinity
Anatase TiO$_2$ model system

FTIR of CO adsorbed at 100 K

CO$_2$ interaction with dehydroxylated and hydrated TiO$_2$ anatase surfaces

Section

- Background of the study and investigation techniques
- Study of the TiO$_2$ exposed surface sites by CO adsorption
- CO$_2$ interaction with dehydroxylated and hydrated TiO$_2$ anatase surfaces
- Conclusions and perspectives
Dehydroxylated TiO$_2$ anatase surfaces

The CO surface picture

Nanoanatase outgassed for 2h at 823 K

CO$_2$ interaction with dehydroxylated and hydrated TiO$_2$ anatase surfaces
Dehydroxylated TiO$_2$ anatase surfaces

FTIR of adsorbed CO$_2$ (pressure up to 10 mbar)

Nanoanatase outgassed for 2h at 823 K

Dehydroxylated TiO$_2$ anatase surfaces
Possible adsorption geometries on the (101) surface

$\Delta E_{\text{form}} = -9.5$ Kcal/mol

$\Delta E_{\text{form}} = -7.8$ Kcal/mol

$\Delta E_{\text{form}} = -8.5$ Kcal/mol

$\Delta E_{\text{form}} = 2.7$ Kcal/mol
Dehydroxylated TiO$_2$ anatase surfaces
Possible adsorption geometries on the (001) surface

$\Delta E_{\text{form}} = -5.3$ Kcal/mol

CO$_2$ interaction with dehydroxylated and hydrated TiO$_2$ anatase surfaces

$\Delta E_{\text{form}} = -30.1$ Kcal/mol

$\Delta E_{\text{form}} = -3.4$ Kcal/mol

$\Delta E_{\text{form}} = -20.9$ Kcal/mol
# Dehydroxylated TiO$_2$ anatase surfaces

## Computed vibrational frequencies

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<td>1335 (0)</td>
<td>1340 (14)</td>
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<tr>
<td>$\nu_{\text{B(OCO)}}$</td>
<td>652 (694)</td>
<td>642 (108)</td>
<td>652 (98)</td>
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<table>
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<td>663 (23)</td>
<td>610 (6)</td>
<td>648 (98)</td>
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Dehydroxylated TiO$_2$ anatase surfaces
Experimental vs simulated FTIR spectra

CO$_2$ interaction with dehydroxylated and hydrated TiO$_2$ anatase surfaces
Hydrated TiO$_2$ anatase surfaces
The CO surface picture

Nanoanatase outgassed for 2h at 823 K and then partially rehydrated

- (101) halved intensity
- (001) missing
- Low coordinated Ti sites missing
- OH ··· CO more intense
- Physisorbed CO

CO$_2$ interaction with dehydroxylated and hydrated TiO$_2$ anatase surfaces
Hydrated TiO$_2$ anatase surfaces

FTIR of adsorbed CO$_2$ (pressure up to 10 mbar)


Nanoanatase outgassed for 2h at 823 K and then partially rehydrated
Hydrated TiO$_2$ anatase surfaces
Possible bicarbonates on the (001) surface

$\Delta E_{\text{form}} = -10.3$ Kcal/mol

$-14.6$ Kcal/mol
$-4.3$ Kcal/mol
$-1.5$ Kcal/mol
$0.1$ Kcal/mol
$3.5$ Kcal/mol
$8.6$ Kcal/mol

CO$_2$ interaction with dehydroxylated and hydrated TiO$_2$ anatase surfaces
Hydrated TiO$_2$ anatase surfaces
Bicarbonate computed vibrational frequencies

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<td>664 (13)</td>
<td>670 (18)</td>
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Hydrated TiO$_2$ anatase surfaces
Experimental vs simulated FTIR spectra

CO$_2$ interaction with dehydroxylated and hydrated TiO$_2$ anatase surfaces
Conclusions and perspectives

- The use of adsorbed CO as probe molecule allowed us to highlight the exposed surface sites and to determine the average nanoparticle morphology.

- Study of mixtures of different polymorphs or mixtures of different oxides.

- On the most stable anatase (101) surface CO$_2$ is weakly adsorbed and retains its molecular properties.

- On the dehydroxylated anatase (001) surface the formation of monodentate carbonates occurs.

- On the partially hydrated (001) surface the formation of bidentate bicarbonates is favored.

- Basis for future *in situ* study under UV irradiation.
Acknowledgments

A. Zecchina  
S. Bordiga  
C. Negri

Thank you for the kind attention