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Operando FT-IR Studies of heterogeneous catalytic reactions:

1. Pitfalls
2. Benefits.

Pitfalls:
- Temperature control
- Flow control

in IR reaction cells
Catalytic reactor and spectroscopic IR cells

U-shaped quartz reactor in a tubular furnace

Transmission IR cell (ca. 20 mg wafer)

Heat loss through IR windows

Diffuse reflectance IR cells

Harrick (powder, up to 80 mg)

Modified Spectra-Tech (powder, up to 60 mg)
Measure-thermocouple positioning

Figure 1. Schematic representation of the various sample beds used in this study: (A) in the U-shaped quartz reactor, (B) in the “Sandwich” transmission cell, (C) in the Harrick DRIFTS cell and (D) in the Spectra-Tech DRIFTS cell.
CO methanation as a “bulk temperature probe”

Figure 3. (A) Arrhenius-type plots relating the natural logarithm of the reaction rate of CO methanation to the reciprocal temperature. (B) Same plots as (A), except that the reaction temperature of the IR cells was corrected by the value given in the legend. Feed 10% CO + 35% H₂ in Ar.
DRIFTS: bed surface (top) temperature

Typical analysis depth: < few 100 μm

Bed depth: 2-5 mm
Figure 6. Comparison of the temperature read using the optical pyrometer on the various IR cells and the corresponding sample bed temperature. The sample bed temperature was measured with a thermocouple located in the cell as described in Table 1 and Fig. 1. The optical pyrometer was held at about 20 cm from the sample bed filled with the powdered form (for the Spectra-Tech and Harrick DRIFTS cells) and a self-supported wafer (in the case of the Sandwich transmission cell) of the Ni/alumina
Supported CoOx for CO hydrogenation in custom-made DRIFTS cell: reduction at 450°C?
Spectra-tech DRIFTS cell hydrodynamics: “ill-defined” reactor

Fig. 4. Kr mass spectrometer signal during a switch from 2% Kr/Ar to pure Ar and the corresponding normalized residence time distribution (RTD). The total flowrate was always 100 ml min\(^{-1}\).

Artistic impression of a post-experiment wafer (NOx storage-Reduction)

Aabspec

Inlet  

Carbonaceous deposits?  

Outlet  

16 mm
Alcohol condensation at 300 °C using the same catalyst

Temperature (mis)control and bad hydrodynamics?
Modified DRIFTS cell from Spectra-Tech.

**CO + O₂ over 2% Pt/CeO₂.**

Validation of modified DRIFTS cell

Au-Ce-La-O catalyst
Water-gas shift: 2 % CO + 7 % H₂O

Ensure kinetic relevance of the IR cell-based data

Validation of modified DRIFTS cell

CO hydrogenation (30% CO + 60 % H\textsubscript{2} at 1 bar) on 14 wt.% Co (8 nm) /Al\textsubscript{2}O\textsubscript{3}: TOF = 14 \times 10^{-3} \text{ s}^{-1}

DeJong et al., J. AM. CHEM. SOC. 2006, 128, 3956

Figure 8. The influence of cobalt particle size on the TOF (220 °C, H\textsubscript{2}/CO = 2, 1 bar).
Operando FT-IR Studies of heterogeneous catalytic reactions: pitfalls and benefits.

Benefits:
- transport in zeolites
- CO heat of adsorption
- catalyst surface poisoning
- adsorbate reactivity
Isooctane transport in large and small H-ZSM-5

1 mg powder is enough!

H-ZSM-5: pore diameter ca. 0.55 nm

kinetic diameter = 0.62 nm
Isooctane in H-ZSM-5: effect of mesoporosity

ca. 4-fold reduction in the characteristic diffusion path length

CO adsorption on Pt-Sn/Al₂O₃ pre-reduced at 400°C

- Feed: 2%CO/H₂
- T decreased from 325-50°C

IR determines the nature and coverage of sites

325°C: CO coverage = ~0
1. CO bonding much weaker on Pt-Sn / Pt

2. Effect of surface coverage on ΔH not significant for Pt-Sn

Introduction of O$_2$ at 225°C (Red spectrum is under CO/H$_2$/Ar only)


$\text{H}_2 \leftrightarrow \text{Atmosphere} \rightarrow \text{CO:O}_2$

G.A. Somorjai et al., *J. Catalysis*, 2014, 312, 17-25
Impact of the Reconstruction of Gold Particles on the Heats of Adsorption of Linear CO Species Adsorbed on the Au Sites of a 1% Au/Al₂O₃ Catalyst

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IR is site and coordination-specific!
Toluene hydrogenation: Effect of CO₂

0.17 % toluene + 17 % H₂ + 1.7 % CO₂

75°C

In presence of CO₂:
Pt: fast and total deactivation
Rh: slow and limited deactivation: why?

Various Rh-CO are formed, but no CO(g)
Correlation between toluene conversion and Pt-CO

Conversion correlates Pt-CO signal whatever [CO₂]
**Rh/Al₂O₃ (D= 55%): linear carbonyls assignment**

High-wavenumber carbonyls, on dense plans, displaced by toluene.

Low-wavenumber carbonyls, on low coordination sites, more stable.

→ Low dispersion samples should be more resistant to deactivation.


*Ferri et al., PCCP, 2002, 4, 2667.*
Rh/Al₂O₃ (D=55 %) vs Rh/SiO₂ (D=19 %)

Feed: 0.8 % toluene + 57 % H₂

No carbonyl nor carbonate formation on Rh/SiO₂ when CO₂ is added.

Scalbert et al., J. Catal 318 (2014) 61
DRIFTS + MS + SSITKA
(SSITKA: Steady-State Isotopic Transient Kinetic Analysis)


**DRIFTS: Formate exchange over Pt-CeO$_2$**

$2\% \text{^{12}CO} + 7\% \text{H}_2\text{O} \rightarrow 2\% \text{^{13}CO} + 7\% \text{H}_2\text{O}$

**Slope = k**
Formate DRIFT signal calibration

Na-formate deposition (by IWI) over the CeO$_2$ support
Spectra recorded at 100°C under Ar

Wavenumber /cm$^{-1}$

Calibration standards

Abs

WGS at 220°C

0.66 wt.%

0.33 wt.%

Wavenumber /cm$^{-1}$

Formate DRIFT signal /a.u.

wt.% formate

[formates] can be determined accurately
Pt/CeO$_2$: rate of CO$_2$ formation vs. rate of formate decomposition

\[ \text{Formate decomposition rate to CO}_2 = k \ [\text{formate}] \times 100\% \]

Formate decomposition during CO hydrogenation on 14% Co/Al₂O₃

30% CO + 60% H₂ at 1 bar, 220°C


Two-type of formates: fast and slow
Conclusions

Operando FT-IR Studies of heterogeneous catalytic reactions: pitfalls and benefits.

- Necessity to compare activity in IR cell and standard reactor
- Understand the origin of the differences, if any. (impurities, bed by-pass, temperature gradients)
- Improve cell design.

- Many relevant information for kinetic modelling can be obtained (using differential conditions): transport, nature(s) and coverage of sites, heat and mode of adsorption, poisoning, adsorbate reactivity….