Intensities of IR Bands as a Criterion for the Activation of Adsorbed Hydrocarbons

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Introduction

Classical IR Probe Molecule Spectroscopy

Probe molecules are chosen by a supposition of the nature of the active sites (e.g. NH_3 for acidic sites). Frequency shifts of vibrational bands of the probe itself and of surface functionalities upon formation of the surface-adsorbate complex are used as quantities to describe the site [1]. Frequency shifts may be small and do not always relate to catalyst performance, e.g. the extraordinary activity of sulfated zirconia in alkane isomerization could not be explained [2].

New Concept

(1) To characterize relevant sites, reactants of the catalytic process are used.
(2) IR spectral intensities are proportional to the change of the dipole moment during vibration and thus reflect charge dynamics. On surfaces, molecules may be polarized and band intensities should be indicators for activation of bonds. The intensity distribution of IR bands of hydrocarbons can change dramatically upon adsorption [3-5].

Experimental Strategy & Goals

Target reactions: Hydrocarbon (alkanes, alkenes) transformations
Catalysts: Zeolites with different cations, sulfated zirconia materials
(1) Find examples for variations in intensity patterns.
(2) Measure relative intensities and extinction coefficients.
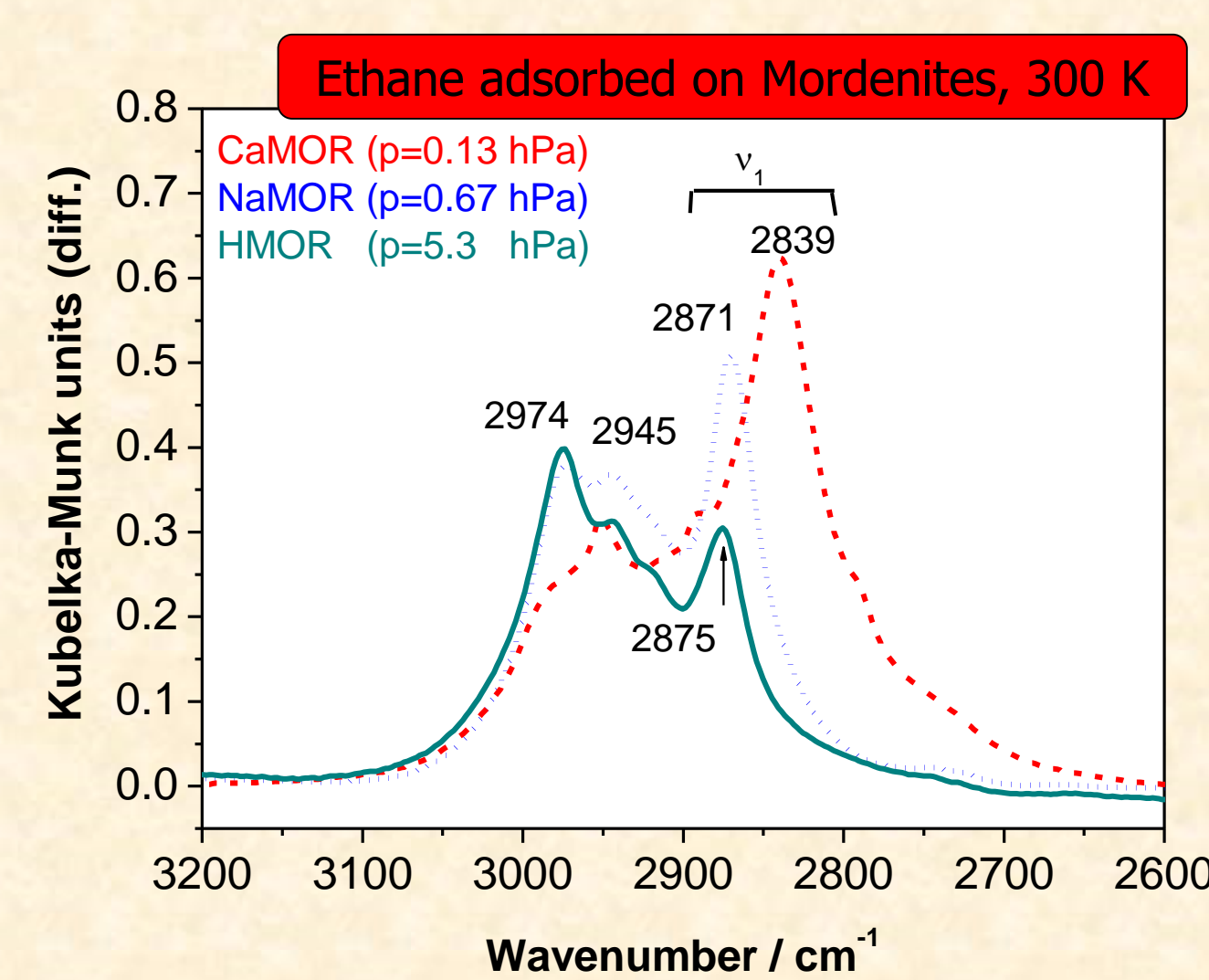(3) Correlate IR intensities and reactivity.

Intensity Patterns

Neopentane adsorption, 308 K
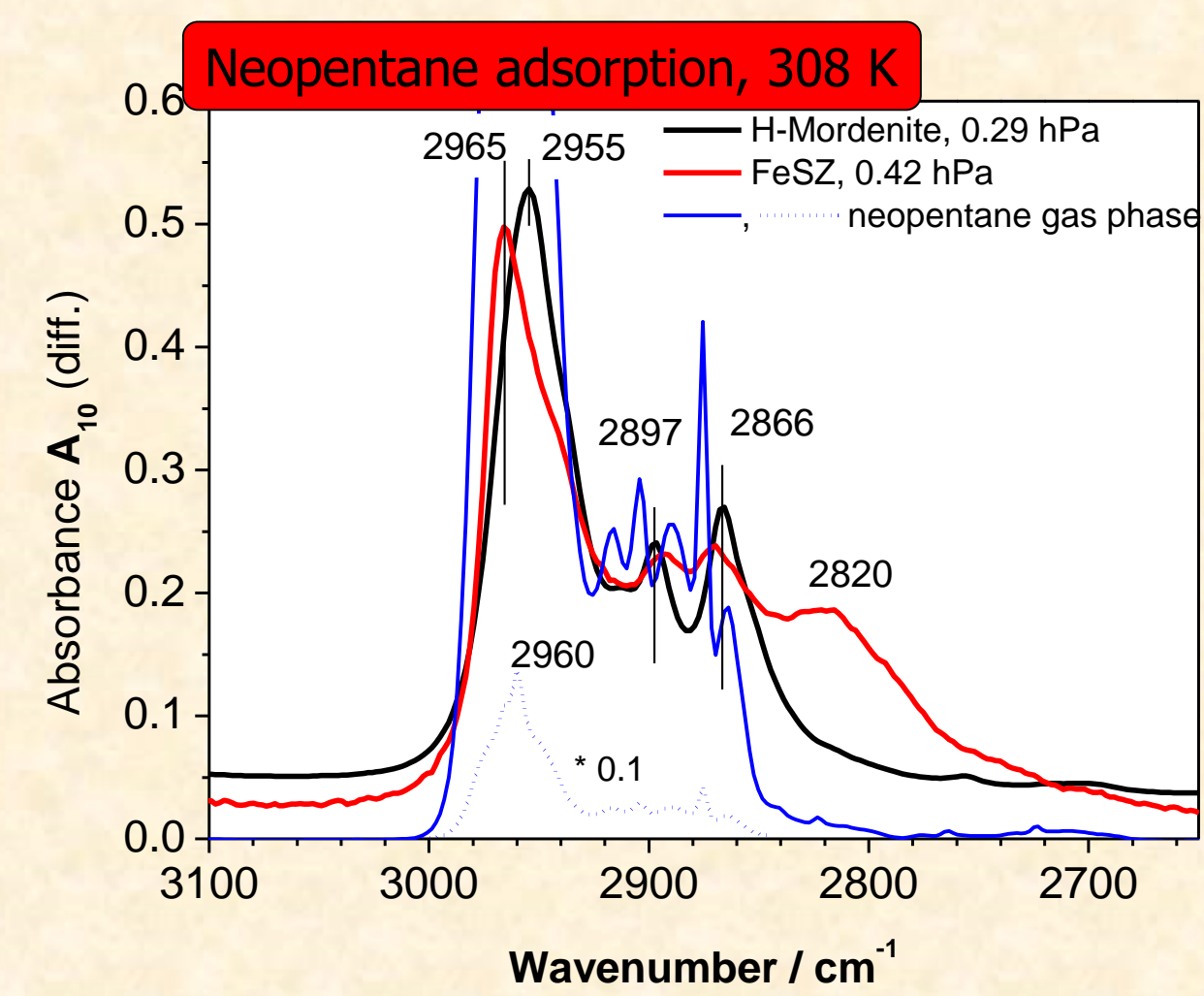
Transmission IR Spectroscopy

- most intense band, with a gas phase position of 2960 cm^{-1}, shifts upon adsorption, specifically 5 cm^{-1} to higher frequencies for SZ materials and 5 cm^{-1} to lower frequencies for H-Mordenite.

- other bands also shifted, but shifts are in general very small

- broad and intense band at 2820 cm^{-1} unique for FeSZ (and other SZ materials), not present in the spectrum for H-Mordenite.
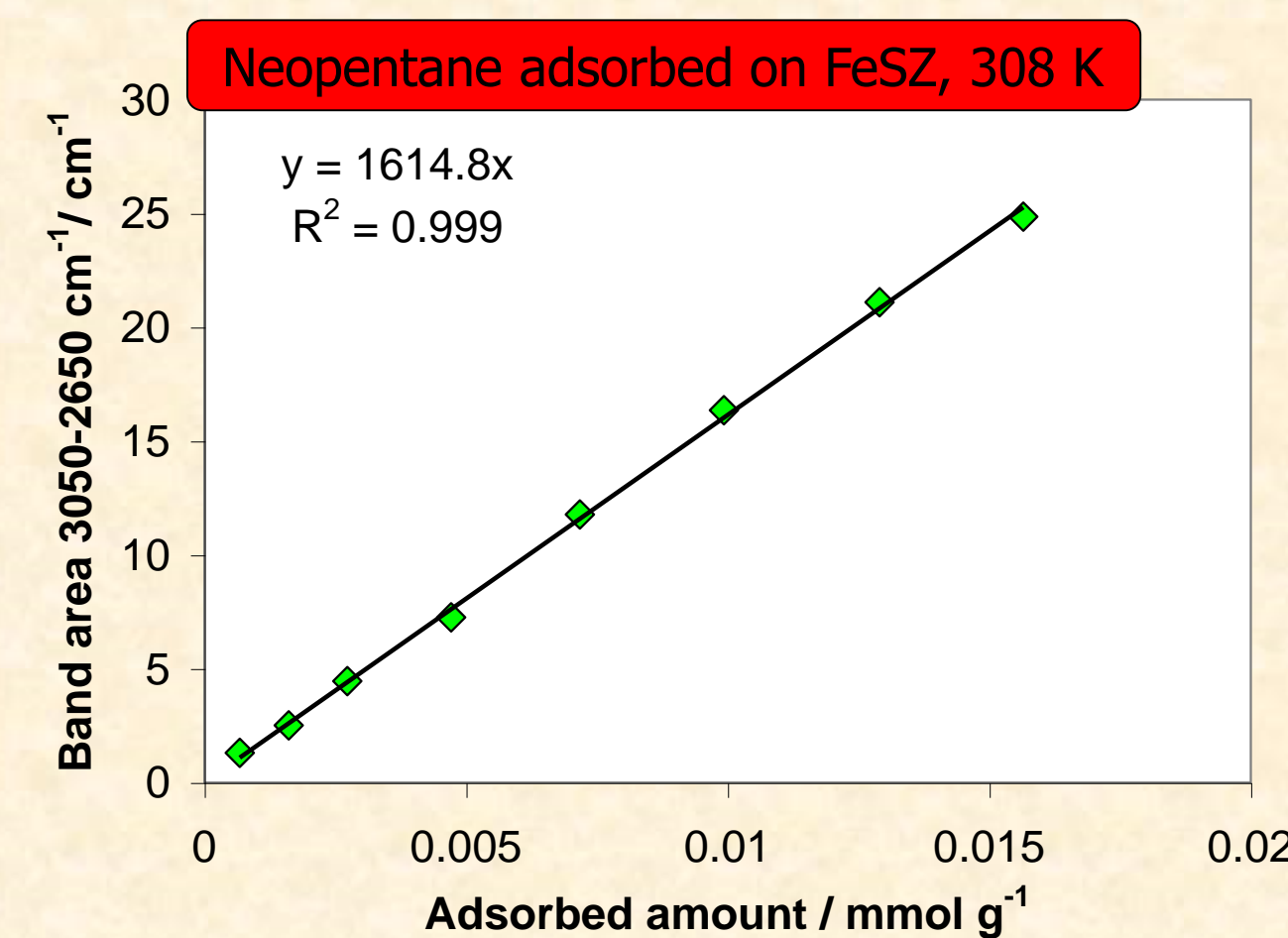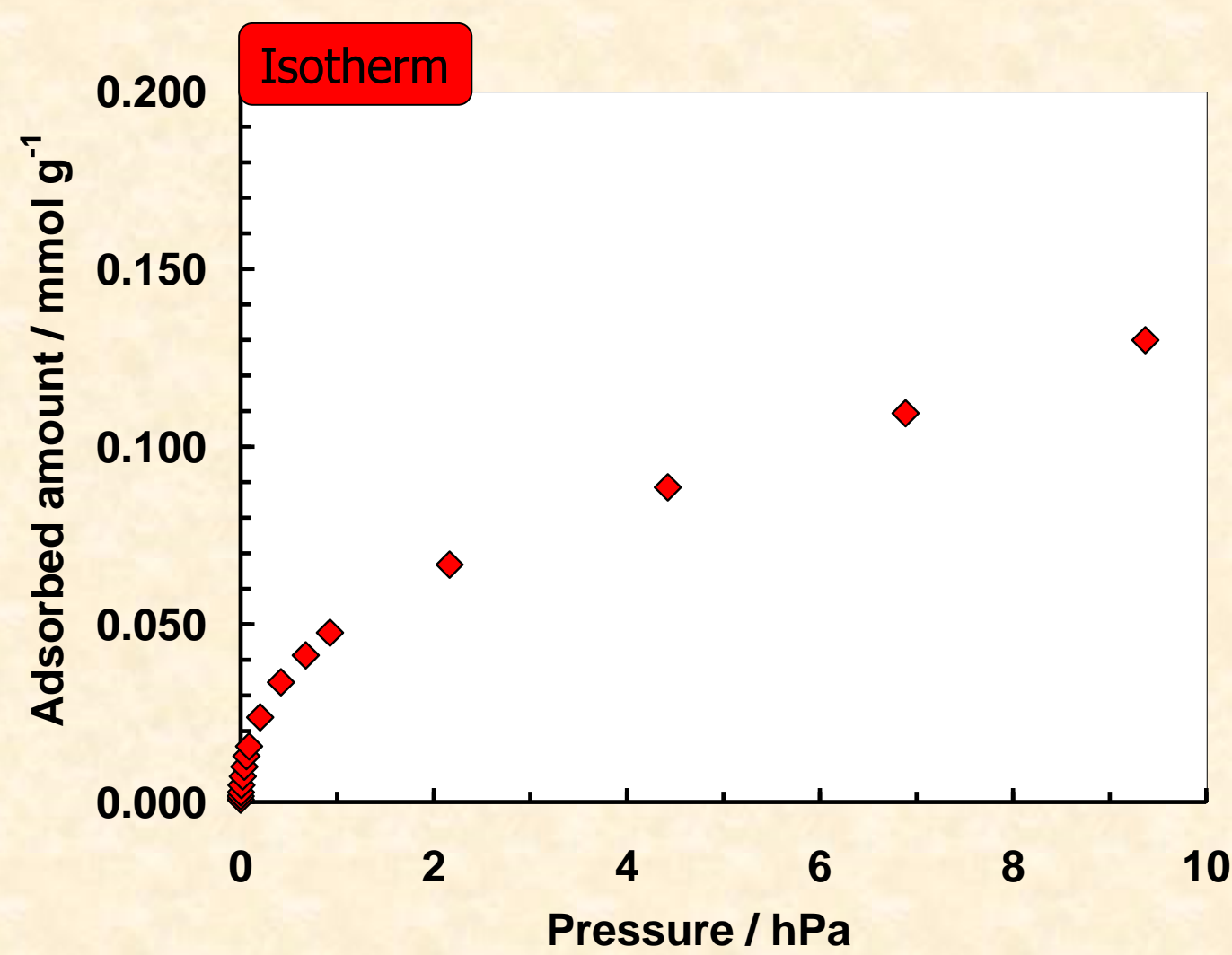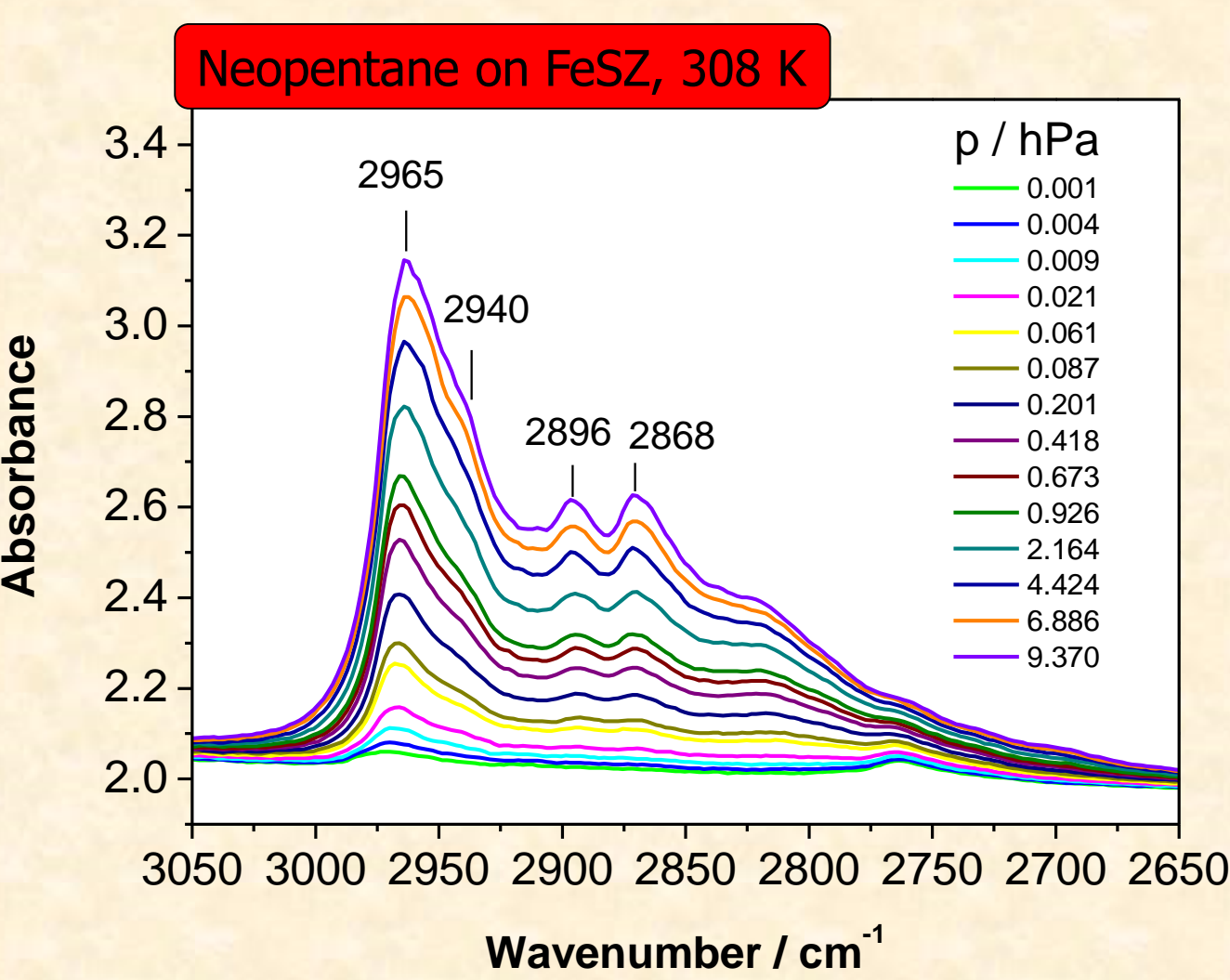
Diffuse Reflectance IR Spectroscopy

- low frequency band of υ_1 symmetric C-H stretching vibration more sensitive to nature of cations than asymmetric stretching bands

- high relative intensity of υ_1 band in comparison to other C-H bands indicates higher polarizability for corresponding vibrational mode

- relative intensity of symmetric stretching band decreases in the order: bivalent metal cation > monovalent metal cation > proton

Ethane adsorbed on Mordenites, 300 K

Proof of principle: extinction coefficient for a certain vibration of an adsorbed molecule is a quantity that is sensitive to the nature of the substrate
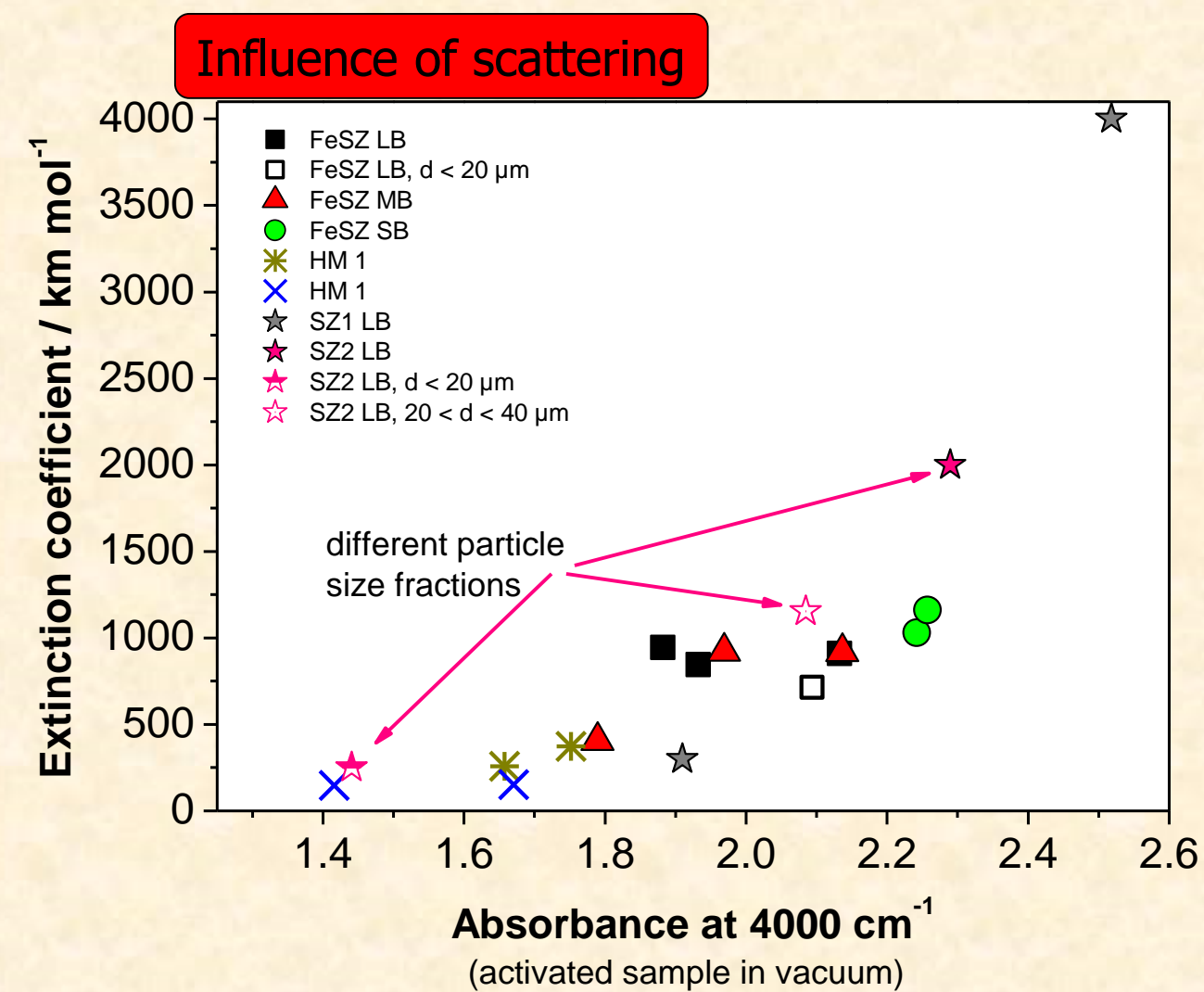
Extinction Coefficients

Neopentane on FeSZ, 308 K

Isotherm

Neopentane adsorbed on FeSZ, 308 K
y = 1614.8x
$R^2 = 0.999$

Influence of scattering

different particle size fractions

Neopentane gas phase CH stretching vibrations integral molar extinction coefficient: 165±2 km/mol

Lambert-Beer law: $A = \varepsilon\, c\, d$ $[c\, d] = \frac{mol}{cm^3} cm = \frac{mol}{cm^2}$

modified for wafers: $A = \varepsilon\, n_{ads}\, \rho_{2D}$ $[n_{ads}\, \rho_{2D}] = \frac{mol}{g} \frac{g}{cm^2} = \frac{mol}{cm^2}$

with A and ε: decadic absorbance and molar extinction coefficient, n_{ads} the adsorbed amount, and ρ_{2D} the wafer area weight
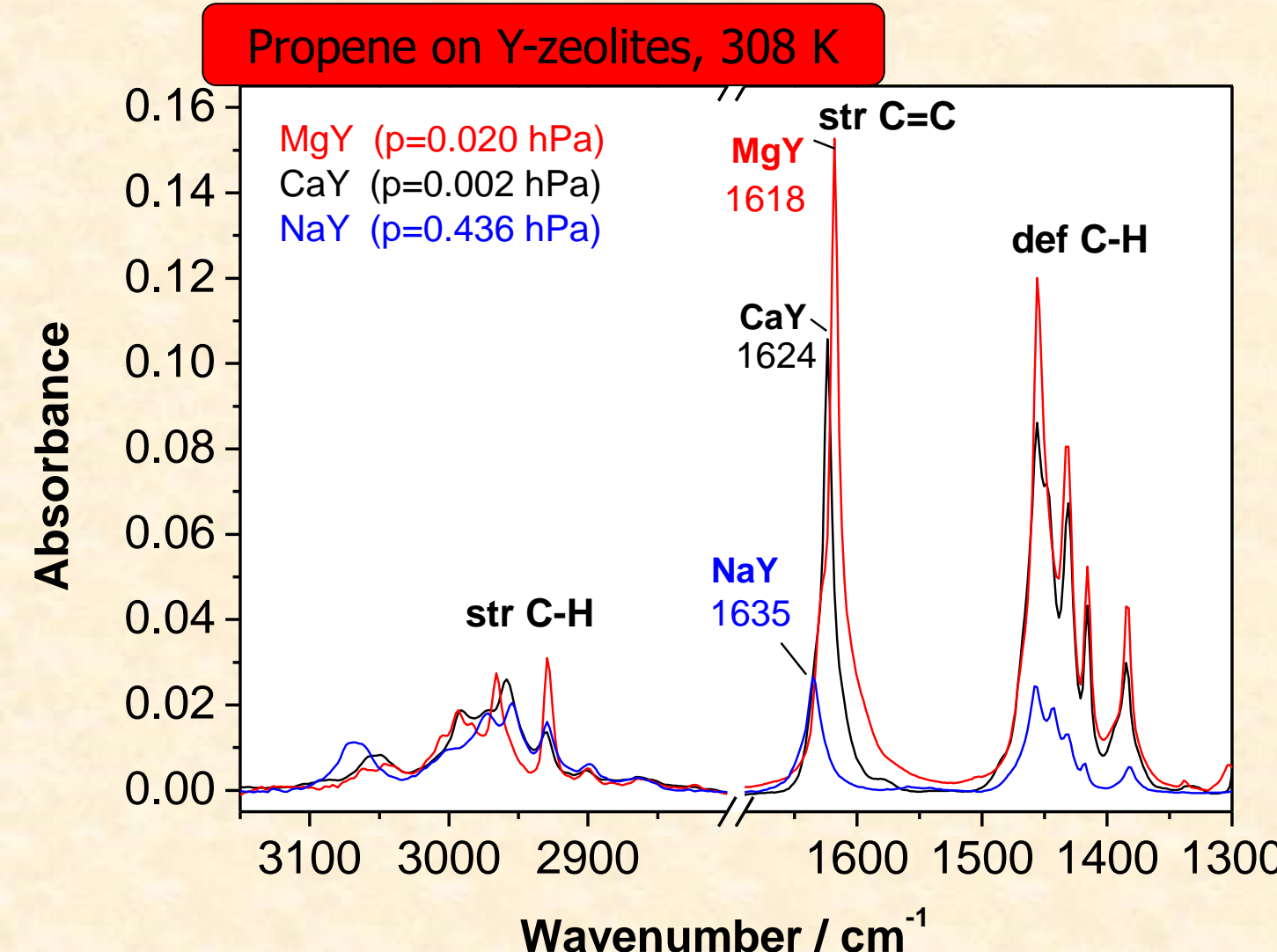
- previous transmission IR experiments on the adsorption of methanol on SiO_2 showed that the intensity of IR bands is not necessarily proportional to the adsorbed amount [6]; however, high pressures ($\geq$ 25 hPa) were considered

at low coverages (partial pressures) and with simultaneously measured isotherms, a **linear relationship** between integral IR intensity and adsorbed amount can be obtained

- it is assumed that the scattering of the sample is expressed by the absorbance in regions without discrete bands

- a general trend is found for different wafer preparations of one sample, namely the apparent extinction coefficient increases with the increasing absorbance (scattering)

- a method needs to be developed to eliminate the influence of scattering and to determine true extinction coefficients

- in regions with sufficient transmission (>10%), extinction coefficients can be determined

Intensities & Reactivity

Propene on Y-zeolites, 308 K

Propene on ZnY, 308 K

- CH deformation vibrations and the C=C stretching vibrations gain in relative intensity with increasing polarizing power of the cation (Na < Ca < Mg)
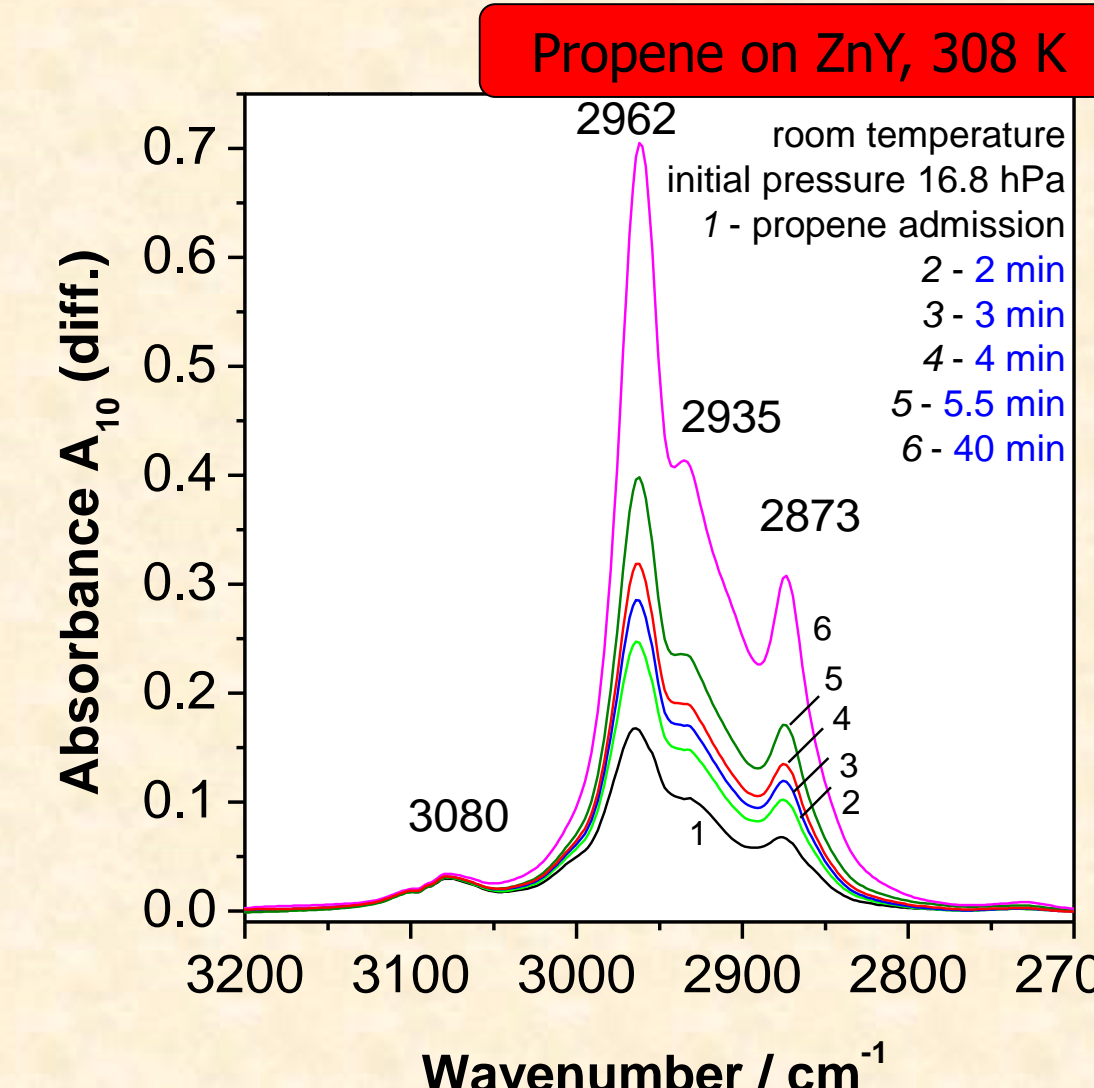
- Zn cations have sufficient polarizing power to initiate the polymerization of propene, C=C cannot be observed anymore and C-H stretching vibrations grow rapidly

Conclusions

1. CH bonds of alkanes experience a varying polarization upon adsorption, demonstrated for sulfated zirconia and zeolite samples with ethane and neopentane

2. Transmission IR and DRIFT spectroscopy are complementary and deliver high quality spectra in regions of low (transmission mode) or high scattering (reflection mode)

3. Measurement of extinction coefficients ε for vibrations of adsorbed species was attempted in transmission:
   - band areas are proportional to the adsorbed amount for low pressure (< 1 hPa)
   - absolute values of ε are obscured by scattering effects in self-supporting wafers Quantification in transmission is not generally easier than in diffuse reflectance; for catalyst powders, scattering in self-supporting wafers cannot be neglected

4. Reported extinction coefficients for probe molecules [7] may not be transferable:
   - for different polarization of the probe on a chemically different surface
   - for different scattering properties even for chemically identical surfaces

5. Intensities of IR bands of adsorbed propene (C=C stretching) reflect the trend in polarizing power of cations in zeolites

6. Correlation of reactivity to IR band intensity seems possible, prediction of selectivity will be evaluated in the future.

Experimental

Samples:
- different mordenites (Si/Al = 20) in H-form or exchanged with Na or Ca
- zeolite Y exchanged with Mg or Ca, or Zn (via evaporation onto HY)
- sulfated zirconia "SZ", prepared through calcination of $(NH_4)_2SO_4$ doped hydrous zirconia (MEL Cat. XZO 682/01) at 823 K for 3 h in a 20 g batch [8,9]
- 2 wt%Fe-promoted sulfated zirconia "FeSZ", prepared through impregnation of MEL Cat. XZO 682/01 with Fe(NO_3)$_3$ solution and subsequent calcination at 923 K for 3 h in differently sized batches [8,9]

Activation:
- vacuum treatments at 723–773 K

DRIFTS:
- Nicolet Impact 410 FTIR spectrometer in combination with self-made diffuse reflectance attachment (further developed version of the setup described in [10]); quartz cell with CaF_2 window

Transmission IR:
- Nicolet Protégé 466 FTIR spectrometer in combination with all-metal vacuum system with KBr windows; samples pressed (35 MPa, 3 s) into self-supporting wafers with area weights of 5 to 50 mg/cm^2
- simultaneously with the spectra, the amount adsorbed could be measured by recording the pressure drop upon adsorption in the system (total volume 375 ml).

Acknowledgements

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