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Comparative texture study of dried and reduced Ni/silica gel catalyst precursors for vegetable oil hydrogenation

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The catalytic partial hydrogenation of vegetable oils:

$$C_{18}H_{30}O_2 + H_2 \rightarrow C_{18}H_{32}O_2 + H_2 \rightarrow C_{18}H_{34}O_2 + H_2 \rightarrow C_{18}H_{36}O_2$$

is widely used in the manufacture of margarines, cooking, frying and salad oils, chocolates, ice-creams, shortenings and bakery products.





Most commonly used catalyst for vegetable oil hydrogenation is metallic nickel (22–25 wt.%) supported on different natural sources of SiO_2 as diatomite, bentonite, clay minerals as well as different types of zeolites

Disadvantages of the natural SiO_2 sources

- variation of composition from batch to batch
- remarkable content of different metals as aluminum, iron and heavy metals

Silica gels as synthetic catalyst supports are an alternative to the natural silica sources because of their

- purity
- controlled pore system
- surface properties

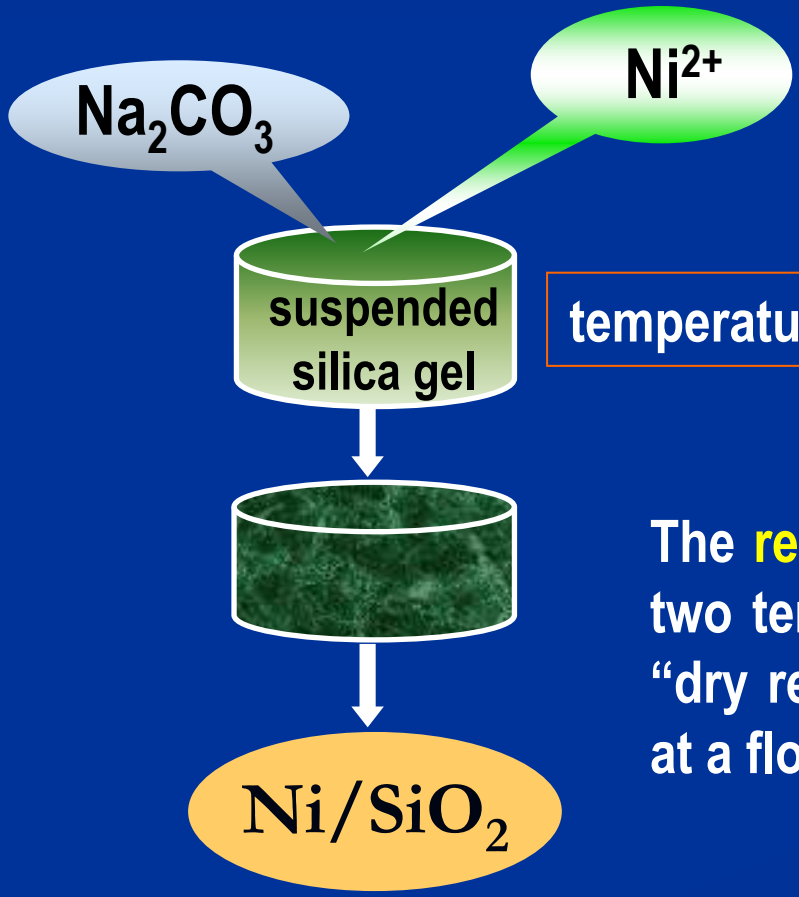
The aim of this work is to study the texture properties after drying and after reduction- activation of Ni/silica gel catalyst precursors at two different temperatures (430 and 530°C).

These properties are important for the sorption and transport of the large triglyceride molecules.

Synthesis of precursors

Three types of silica gel (SIG) with different pore structures:

- ⇨ SIG-A (prepared at acidic pH)
- ⇨ SIG-B (prepared at neutral pH)
- ⇨ SIG-C (prepared at alkaline pH)

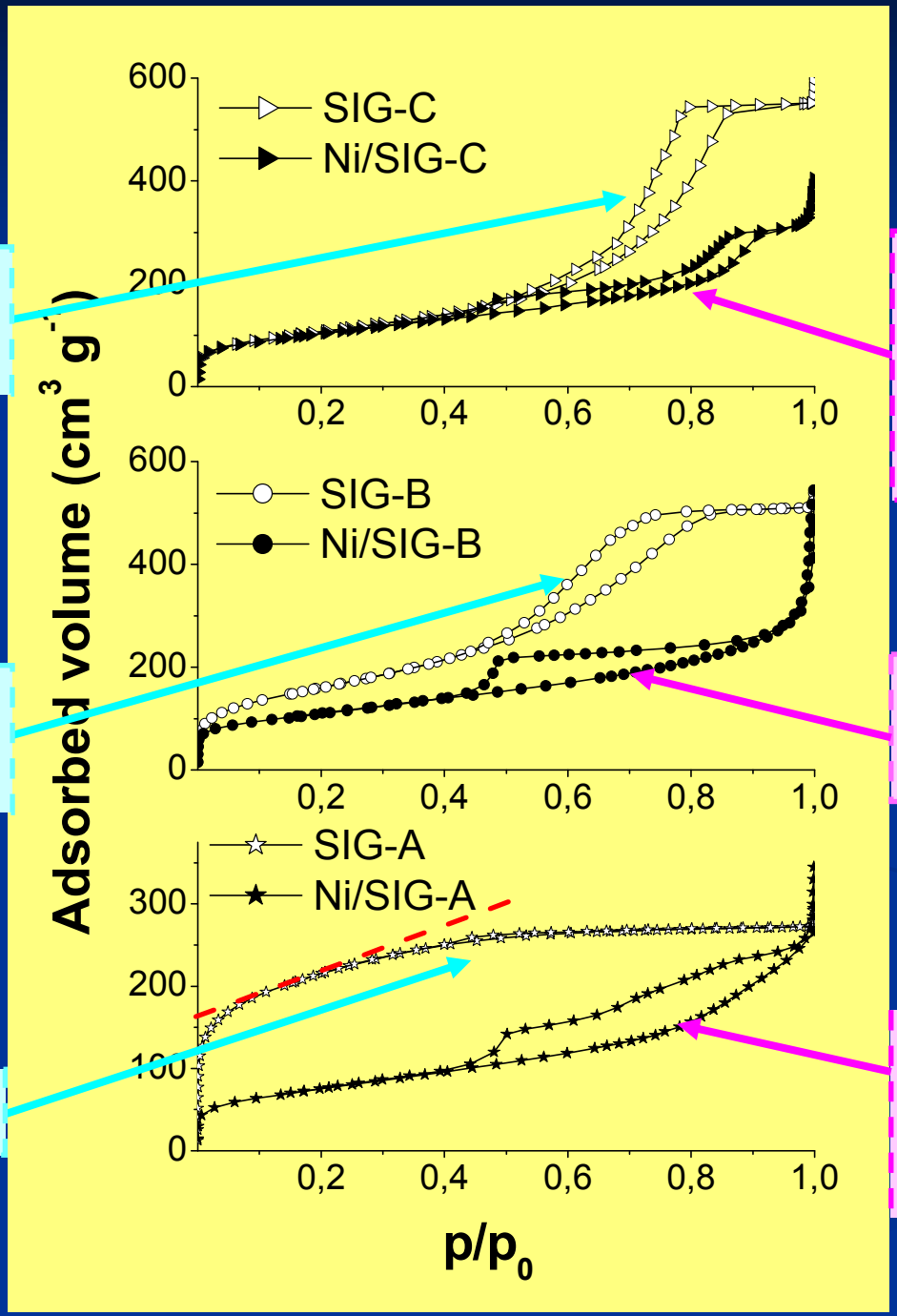


The precursors were synthesized with identical composition (SiO_2/Ni=1.0 corresponding to NiO content of 55.4 mass.%)

temperature = 90°C; pH = 9

The reduction-activation of the precursors was performed at two temperatures 430 and 530°C in a laboratory set-up by a "dry reduction" method with a gas mixture of H_2/N_2 (1/1 v/v) at a flow rate of 10 dm^3h^{-1}.

Nitrogen adsorption-desorption isotherms of the SIG supports and dried Ni/SIG precursors



isotherm: type IV
hysteresis loop: H2 type

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hysteresis loop: H2 type

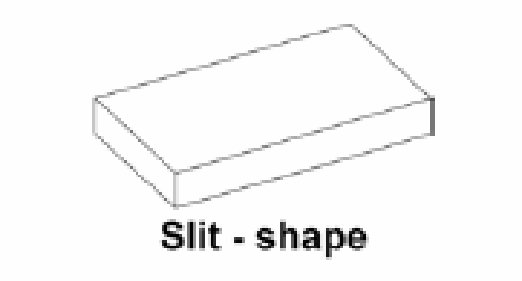
isotherm: type Ib

isotherm: type IV
hysteresis loop:
a combination between
H2 and H3 types

isotherm: type IIb
hysteresis loop: H3 type

isotherm: type IIb (pseudo-type II)
hysteresis loop: H3 type

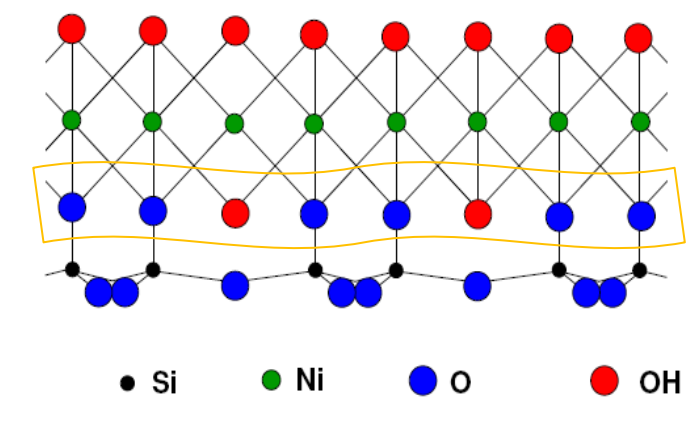
Obviously, the texture of all dried precursors is characterized by the presence of aggregates of plate-like particles having non-rigid slit-shaped mesopores as a common feature of the Ni-containing phase formed on SIG supports.



(Kaneko classification)

This aggregates may consist of $Ni(OH)_x(CO_3)_y$ and/or Ni^{2+}-O(OH)-Si entities.

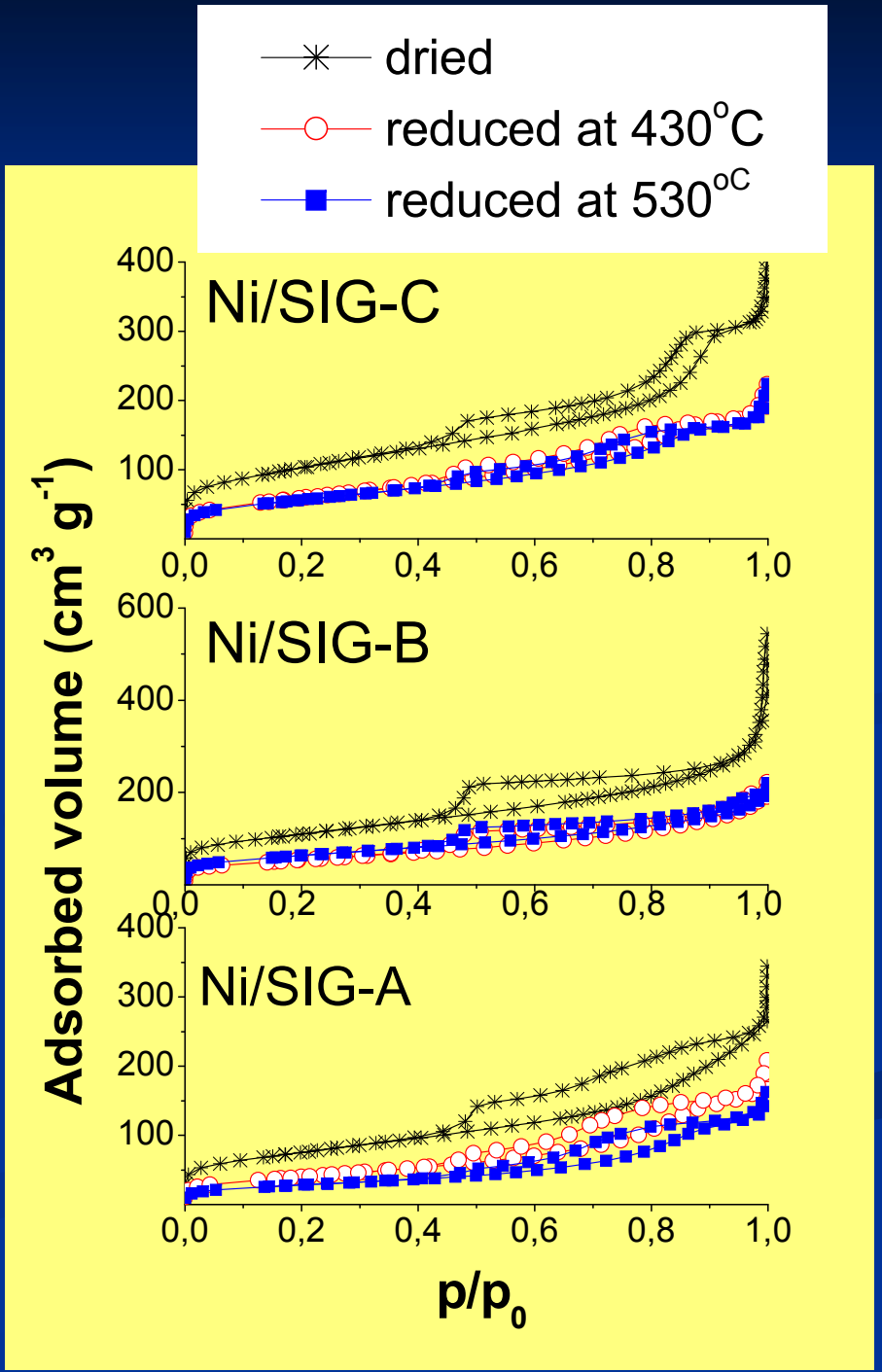
Ni-phyllosilicate layers →



Nitrogen adsorption-desorption isotherms of the reduced Ni/SIG precursors at 430 and 530°C

After the reduction-activation procedure, the isotherm shape and the type of hysteresis loop are preserved at both temperatures.

Only filling of the pores has occurred.



Ttexture parameters

Sample	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	$d_{average}$ (nm)	C
SIG-A	777	0.44	0.28	0.17	2.7	179
SIG-B	581	0.83	0.21	0.83	4.9	92
SIG-C	387	0.96	0.14	0.92	7.3	110
Dried precursors						
Ni/SIG-A	269	0.53	0.10	0.32	8.8	135
Ni/SIG-B	392	0.84	0.15	0.39	6.7	182
Ni/SIG-C	367	0.63	0.13	0.46	10.2	139
Reduced at 430°C						
Ni/SIG-A	146	0.31	0.05	0.22	8.9	84
Ni/SIG-B	193	0.32	0.07	0.19	7.0	123
Ni/SIG-C	216	0.34	0.07	0.22	7.0	76
Reduced at 530°C						
Ni/SIG-A	101	0.24	0.04	0.19	9.5	105
Ni/SIG-B	227	0.33	0.08	0.18	6.7	116
Ni/SIG-C	206	0.34	0.07	0.21	7.5	87

- **C constant** is proportional to the heat of adsorption and is associated with the force of interaction between adsorbent and adsorbate

$$C \sim e^{H_1 - H_L / RT}$$

H_1 - the heat of adsorption of the first adsorbate layer

H_L - the heats of adsorption of the second and the next layers

- values of C<20 show a lack of monolayer formation;
- values of C>100 show a strong interaction between adsorbent and adsorbate as well as presence of micropores.

CONCLUSIONS

- The texture of all dried precursors was characterized by the presence of aggregates of plate-like particles containing non-rigid slit-shaped mesopores as a common feature of the Ni-containing phase formed on SIG supports.

- The formation of the mesoporous Ni-containing phase changes the polarity of the surface in different way because of its different extent of presence and location. This phase may consists of $Ni(OH)_x(CO_3)_y$ and/or Ni^{2+}-O(OH)-Si entities.

- The specific location of the Ni-containing entities in the dried nickel-silica gel catalyst precursors is preserved after the reduction-activation procedure at 430°C as well as at 530°C.

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Thanks for your attention!