Relationships between the Hydrogenation and Dehydrogenation Properties of Rh-, Ir-, Pd-, and Pt-Containing Zeolites Y

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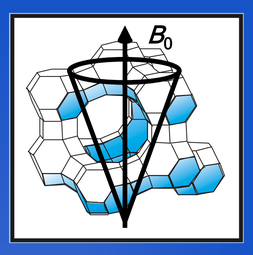


INTRODUCTION

Despite the high importance of transition and noble metals for heterogeneous catalysis, only few systematic studies exist, which compare the hydrogenation and dehydrogenation activities of homologous series of solid catalysts containing different metal types. Based on the results of complementary spectroscopic and analytical methods, the effect of the H_2/metal interaction on the hydrogenation and dehydrogenation activities of homologous series of Rh-, Ir-, Pd-, and Pt-containing zeolites Y was investigated.

Therefore, the intrinsic hydrogenation activities of noble metal-containing zeolites Y, i.e. of the hydrogenation of acrylonitrile, were studied by in situ solid-state NMR spectroscopy under semi-batch conditions and compared with the turn-over-frequencies of the dehydrogenation of propane under continuous flow-conditions in a conventional fixed-bed reactor. To discuss the influence of the H_2/metal interaction on the hydrogenation and dehydrogenation reactions, temperature-programmed desorption of hydrogen (H_2-TPD) was performed.

EXPERIMENTAL SECTION

Commercial zeolite Na-Y (Degussa AG, Germany) was exchanged with different amounts of $RhCl_3 \cdot xH_2O$, $[Ir(NH_3)_5Cl]Cl_2$, $[Pd(NH_3)_4]Cl_2$ or $[Pt(NH_3)_4]Cl_2$ via ion exchange in aqueous suspension. The noble metal-containing catalyst powders were calcined in synthetic air for 3 h (1.0 bar, 300 °C) and subsequently reduced in H_2 for 2 h (1.0 bar, 350 °C).[1]

For the hydrogenation of acrylonitrile, the reduced catalysts were loaded with acrylonitrile via distillation. The hydrogenation was determined at T = 298 K under semi-batch conditions using a Bruker 4 mm MAS NMR probe, modified for continuously flowing hydrogen (300 mL/min).[2]

The dehydrogenation of propane was studied under continuous-flow conditions in a fixed-bed reactor (ca. 200 mg of catalyst) with a *WHSV* = 3 h^{-1} at T = 828 K. The hydrocarbons in the product flow were determined by on-line gas chromatography.[2]

Table 1 Sample designations, ratios of noble metal (NM) atoms per unit cell (u.c.), and noble metal dispersions ,*D*.

Catalyst	NM/u.c.	Dispersion *D* / %
0.4Rh/H,Na-Y	0.4±0.04	54±2.7
2.3Rh/H,Na-Y	2.9±0.29	80±4.0
0.8Ir/H,Na-Y	0.6±0.06	121±6.1
4.7Ir/H,Na-Y	3.3±0.33	130±6.5
0.4Pd/H,Na-Y	0.5±0.05	19±1.0
2.8Pd/H,Na-Y	3.4±0.34	43±2.2
0.8Pt/H,Na-Y	0.5±0.05	73±3.7
4.5Pt/H,Na-Y	3.1±0.31	92±4.6

HYDROGENATION OF ACRYLONITRILE

The intrinsic hydrogenation activities of the noble metal-containing zeolites Y were studied by in situ solid-state NMR spectroscopy under semi-batch conditions. For these experiments, a Bruker 4 mm MAS NMR probe, modified as shown in Figure 2, was used.

Results and discussion:

- All catalysts were loaded with a similar density of acrylonitrile per supercage (0.6-0.9 ACN/s.c.), except catalyst 0.8Ir/H,Na-Y (0.5 ACN/s.c.) due to the very long reaction time (see Table 2, column 2)
- Reaction rates were determined by the quantitative evaluation of the intensities of the peaks at 5.8 ppm and 6.3 ppm (see Scheme 1 for closer explanation and Figure 1 for generic ^{1}H MAS NMR spectra)
- For both series of catalysts, with low or high noble metal content, the sequences of the reaction rates, *r*, are the same (see also Table 2, column 4):

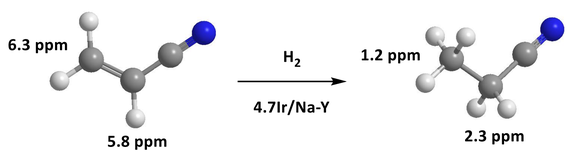
Pd/H,Na-Y > Rh/H,Na-Y > Pt/H,Na-Y > Ir/H,Na-Y

Conclusions:

- High-temperature (HT) peaks for the catalysts 2.8Pd/H,Na-Y, 2.3Rh/H,Na-Y, and 4.7Ir/H,Na-Y show the same sequence as the reaction rates, *r*, for these catalysts (see also Table 3, column 2):

2.8Pd/H,Na-Y (723 K) > 2.3Rh/H,Na-Y (713 K) > 4.7Ir/H,Na-Y (663 K)

- High-temperature peaks for the catalyst 4.5Pt/H,Na-Y (848 K and 738 K) don‘t fit to the sequence of the reaction rates, *r*



Scheme 1 Reaction scheme of the in situ ^{1}H MAS NMR hydrogenation of acrylonitrile on zeolite 4.7Ir/H,Na-Y with the chemical shift values (δ_{1H}) for the reactants.

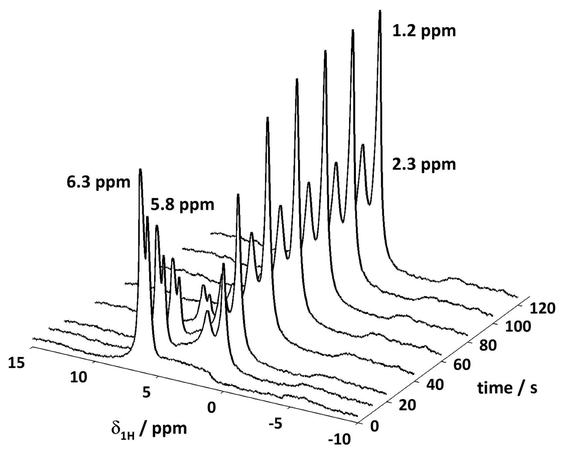


Figure 1 Stack plot of the in situ ^{1}H MAS NMR spectra recorded during the hydrogenation of acrylonitrile on zeolite 4.7Ir/H,Na-Y under semi-batch conditions at 298 K.

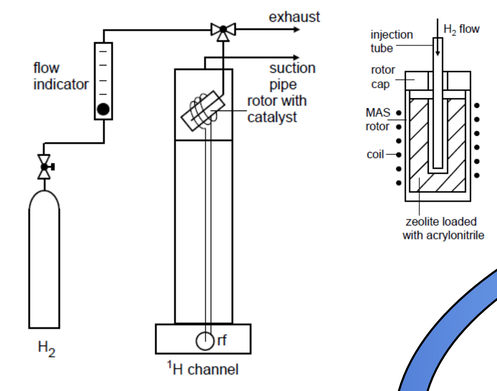


Figure 2 Scheme of the modified MAS NMR probe for in situ use (left) and schematic view on the semi-batch reactor (Bruker 4 mm rotor, right).[3]

Table 2 Loadings of acrylonitrile (ACN) per supercage (s.c.), velocity rate constants, *k*, and reaction rates, *r*, for the hydrogenation of acrylonitrile.

Catalyst	ACN/s.c.	*k* / s^{-1}	*r* / mmol s^{-1}
0.4Pd/H,Na-Y	0.81±0.04	1.1±0.3	$(2.7\pm1.0)\cdot10^{-2}$
0.4Rh/H,Na-Y	0.68±0.03	$(3.4\pm0.3)\cdot10^{-2}$	$(6.8\pm1.0)\cdot10^{-4}$
0.8Pt/H,Na-Y	0.65±0.03	$(1.1\pm0.1)\cdot10^{-2}$	$(2.3\pm0.4)\cdot10^{-4}$
0.8Ir/H,Na-Y	0.52±0.03	$(6.7\pm0.7)\cdot10^{-4}$	$(1.1\pm0.2)\cdot10^{-5}$
2.8Pd/H,Na-Y	0.86±0.04	$(7.6\pm2.5)\cdot10^{-1}$	$(2.0\pm1.0)\cdot10^{-2}$
2.3Rh/H,Na-Y	0.71±0.04	$(7.0\pm2.4)\cdot10^{-1}$	$(1.6\pm1.0)\cdot10^{-2}$
4.5Pt/H,Na-Y	0.82±0.04	$(5.1\pm0.5)\cdot10^{-2}$	$(1.4\pm0.2)\cdot10^{-3}$
4.7Ir/H,Na-Y	0.81±0.04	$(7.6\pm0.8)\cdot10^{-3}$	$(2.3\pm0.3)\cdot10^{-4}$

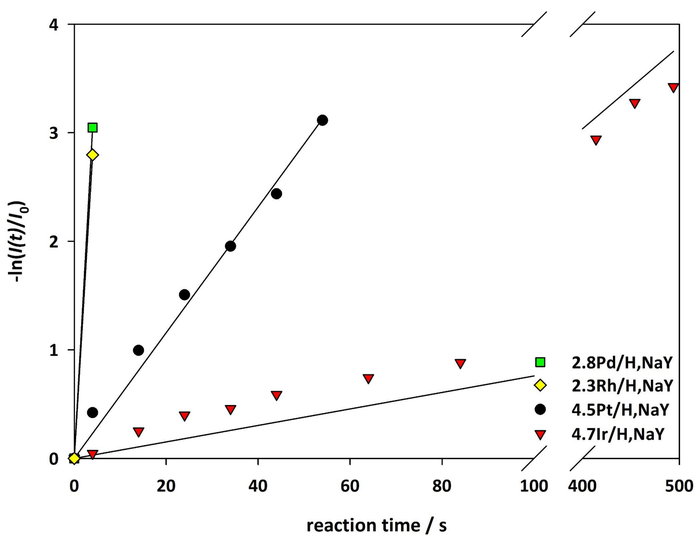
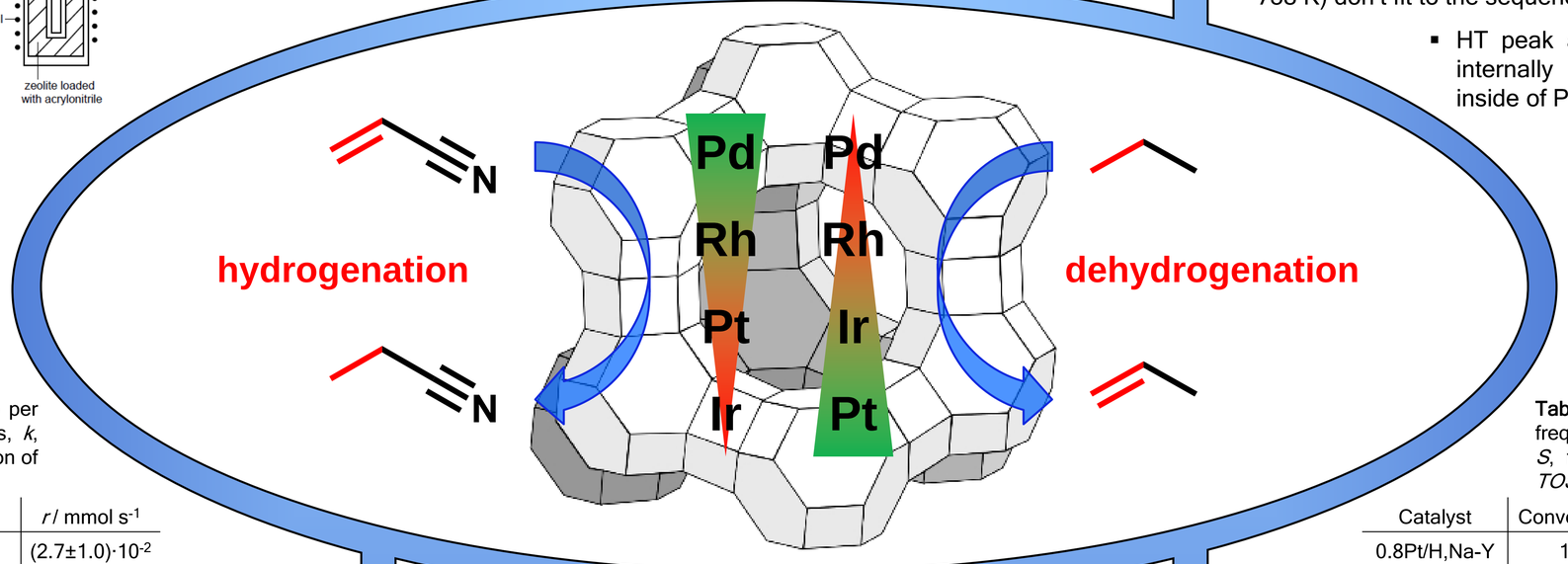


Figure 3 Negative logarithms of the intensity ratios *I*(t)/I_0 of the ^{1}H MAS NMR signals of acrylonitrile plotted as a function of the reaction time, *t*, for the hydrogenation of acrylonitrile.



H_2-TPD

Temperature-programmed desorption of hydrogen was utilized to gain an insight into the strength of the hydrogen adsorption on the metal species in the zeolite catalysts under study.

The high-temperature (HT) peaks of the H_2-TPD for the Rh-, Ir-, and Pd-containing catalysts are related to the reaction rates, *r*, for the hydrogenation and to the *TOF* values of the dehydrogenation in a systematic manner:

r: Pd/H,Na-Y > Rh/H,Na-Y > Ir/H,Na-Y

HT: 723 K > 713 K > 663 K

TOF: Pd/H,Na-Y < Rh/H,Na-Y < Ir/H,Na-Y

The HT peaks (738 K and 848 K) for the Pt-containing catalyst don‘t fit in this sequence. This could be due to the presence of internally chemisorbed hydrogen species inside of Pt clusters, as described in [4].

Table 3 High-temperature (HT) peaks of the H_2-TPD of the catalysts with a high noble metal content.

Catalyst	HT-peak / K
4.5Pt/H,Na-Y	738 & 848
2.8Pd/H,Na-Y	723
2.3Rh/H,Na-Y	713
4.7Ir/H,Na-Y	663

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[1] U. Obenaus, M. Dyballa, S. Lang, M. Scheibe, M. Hunger *Journal of Physical Chemistry C* **119** (2015) 15254-15262.

[2] U. Obenaus, F. Neher, M. Scheibe, M. Dyballa, S. Lang, M. Hunger *Journal of Physical Chemistry C* **120** (2016) 2284-2291.

[3] H.Henning, M. Dyballa, M. Scheibe, E. Klemm, M. Hunger *Chemical Physics Letters* **555** (2013) 258-262.

[4] C.Jensen, D.Buck, H.Dilger, M.Bauer, F.Phillipp, E. Roduner *Chemical Communications* **49** (2013) 588-590.

DEHYDROGENATION OF PROPANE

The dehydrogenation of propane was investigated under conventional continuous-flow conditions in a fixed-bed reactor with a *WHSV* = 3 h^{-1} at T = 828 K.

Results and Discussion:

- For both series of catalysts, with low or high noble metal contents, the sequences of propane conversion are the same (see also Table 4, column 2):

Pt/H,Na-Y > Ir/H,Na-Y > Rh/H,Na-Y ≈ Pd/H,Na-Y

- For both series of catalysts, with low or high noble metal contents, the sequences of the turn-over-frequencies are the same (see also Table 4, column 3):

Pt/H,Na-Y > Ir/H,Na-Y > Rh/H,Na-Y > Pd/H,Na-Y

- Pt-containing catalysts show roughly one order of magnitude higher *TOF* values than the other catalysts under study (see Table 4, column 3)

Conclusions:

- Sequence of the high-temperature (HT) peaks for the catalysts 2.8Pd/H,Na-Y (723 K) > 2.3Rh/H,Na-Y (713 K) > 4.7Ir/H,Na-Y (663 K) is reversed to the sequence of the *TOF* values for these catalysts
- Preferred adsorption of H_2 on the metal surface of Pd- compared with Rh- or Ir-containing catalysts
  - → Hindered product desorption and lower *TOF* values
- High-temperature peaks for the catalyst 4.5Pt/H,Na-Y (848 K and 738 K) don‘t fit to the sequence of the *TOF* values
  - HT peak at 848 K hints at the presence of internally chemisorbed hydrogen species inside of Pt clusters[4]
    - This may lead to a faster desorption of the surface hydrogen and, therefore, to a higher *TOF* value

Table 4 Conversion of propane, *X*, turn-over-frequencies, *TOF*, and selectivity to propene, *S*, for the dehydrogenation of propane at *TOS* = 35 min.

Catalyst	Conversion *X* / %	*TOF* / s^{-1}	Selectivity *S* / %
0.8Pt/H,Na-Y	18±0.36	8.4±0.4	69±1.4
0.8Ir/H,Na-Y	6±0.12	2.7±0.1	63±1.3
0.4Rh/H,Na-Y	2±0.04	1.1±0.05	74±1.5
0.4Pd/H,Na-Y	2±0.04	1.0±0.05	49±1.0
4.5Pt/H,Na-Y	33±0.66	2.7±0.1	51±1.2
4.7Ir/H,Na-Y	8±0.16	0.7±0.05	57±1.1
2.3Rh/H,Na-Y	3±0.06	0.2±0.01	80±1.6
2.8Pd/H,Na-Y	3±0.06	0.2±0.01	62±1.2

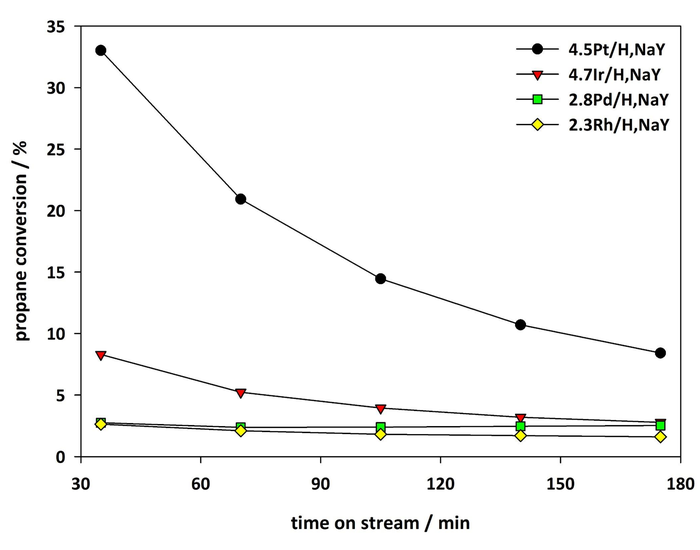

Figure 4 Conversion of propane during the dehydrogenation on Pt-, Ir-, Pd-, and Rh-containing zeolites Y under continuous-flow conditions plotted as a function of the time on stream, *TOS*.