Selective Hydrogenation of Acetylene in the Presence of Ethylene Using Zeolite-Supported Bimetallic Catalysts

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Introduction

Novel catalysts have been synthesized and evaluated by supporting Pd-based bimetallic nanocatalysts on zeolites to achieve higher selectivity for the selective hydrogenation of acetylene in a stream containing excess ethylene at relatively low temperatures (300-339K). Low-temperature hydrogenation offers the opportunity of using competitive adsorption to achieve preferential hydrogenation of acetylene. Previous work from our group has found that bimetallic catalysts favor low temperature hydrogenation.[1-3] Results from many other groups have also shown that Pd is a good catalyst for the selective hydrogenation of alkynes in excess ethylene. Therefore the strategy of the present work was to modify Pd catalysts and to embed bimetallic nanoparticles in an environment that is highly selective for acetylene hydrogenation [4].

Cation-π interaction offers the potential for selective adsorption of acetylene on the zeolite supports. In the current work we used the ion-exchanged β-type zeolite [5,6] as the support of the bimetallic catalysts. The zeolite structure should have multiple dimensions and contain large pores, in order to house the bimetallic nanoparticles inside the pores.

Materials and Methods

Supported catalysts were prepared by the incipient impregnation method. Flow reactor studies using GC, batch reactor studies using FTIR, EXAFS and CO-Chemisorption evaluations have been performed.

Results and Discussion

Our results indicate that the Pd-Ag bimetallic catalyst has a much higher selectivity for acetylene hydrogenation in excess ethylene than either Pd or Ag. Kinetic modeling of reactions results from FTIR shows significant differences in the hydrogenation rate constant, adsorption equilibrium constant, as well as the selectivity of the γ-Al_2O_3 supported catalysts and β-zeolites supported catalysts. As summarized in Table 1, β-zeolite supported catalysts show much higher selectivity than the γ-Al_2O_3 supported catalysts. [4]

Table 1. Reaction rate constants and adsorption equilibrium constants fitted from experimental data

Catalysts	k_1 (min^{-1})	k_2 (min^{-1})	K_1 (cm^3/mol)	K_2 (cm^3/mol)	S=(k_1/ k_2)* (K_1/ K_2)
Pd/γ-Al_2O_3	43.4±1.1	17.3±1.8	1.9±0.5	3.3±0.3	1.4
PdNi/γ-Al_2O_3	33±0.5	6.8±0.1	0.6±0.2	2.2±0.5	1.3
PdAg/γ-Al_2O_3	35.2±1.0	16.4±2.0	0.8±0.2	0.8±0.1	2.1
Pd/Na-β-zeolite	21.4±7.1	36.5±0.9	2.7±0.2	0.6±0.3	2.6
PdNi/Na-β-zeolite	20.5±5.5	28.6±1.3	3.3±0.3	0.6±0.2	3.9
PdAg/Na-β-zeolite	5.1±0.6	26.5±5.9	5.2±0.3	0.15±0.05	6.8
Ag/γ-Al_2O_3[3]	5.5	0.8	0.4	6.1	-
Ni/Na-β-zeolite	4.8	2.0	3.1	1.8	-
Ag/Na-β-zeolite[3]	1.7	0.9	5.9	3.3	-

[1] is for acetylene, [2] is for ethylene, [3] is calculated per gram of catalysts

$$r_{C_2H_2} = -\frac{k_1 K_1 \sqrt{K_{H_2}}\, P_{C_2H_2} \sqrt{P_{H_2}}}{(1 + K_1 P_{C_2H_2} + K_2 P_{C_2H_4} + \sqrt{K_{H_2} P_{H_2}})^2}$$

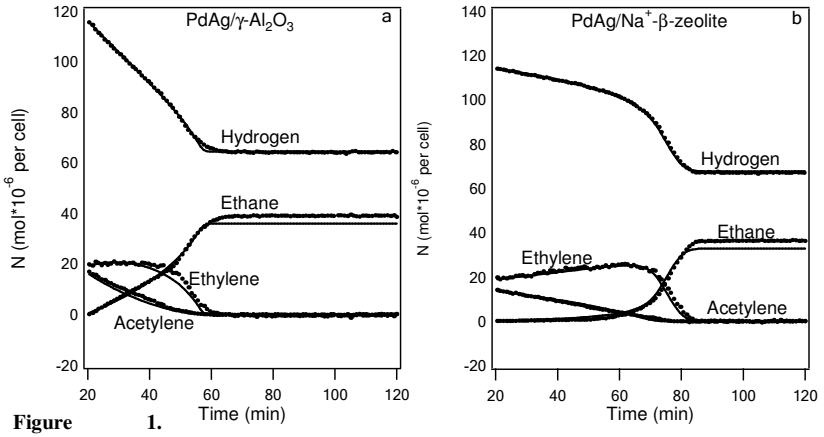

Figure 1. Comparison of FTIR measurements (dots) and fitted concentrations (solid lines) of gas-phase C_2H_2, C_2H_4 and C_2H_6 on a) PdAg/γ-Al_2O_3 and b) PdAg/Na^+-β-zeolite

Significance

It is critical to reduce acetylene concentration in alkenes to prevent the polymerization catalyst poisoning. In particular, industrial feedstocks for the production of ethylene polymers must contain no more than 5 ppm of acetylene. Therefore selective hydrogenation of small amounts of alkynes in the presence of large amounts of ethylene is an important target of the polymer industry.

References

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