Potassium Promoter for Palladium on Alumina Selective Hydrogenation Catalysts

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An enhancement in the rate and selectively to ethylene for the hydrogenation of traces of acetylene in ethylene may be obtained by the addition of potassium to Pd/Al_2O_3 catalysts.

The selective hydrogenation of traces of acetylene in raw streams is an important industrial process for the purification of ethylene streams.[1] Ethylene selectivity is a key objective in this process and, given the tremendous worldwide capacity for ethylene production, even a small increase in selectivity can represent a sizeable saving.

Potassium promoters are known to be effective for other catalytic processes including ammonia synthesis and CO hydrogenation.[2–4] However, we have been unable to find any reports in the open literature on the effect of potassium on Pd/Al_2O_3 for the selective hydrogenation of acetylene.

We have prepared two types of catalysts differing in the sequence of Pd and K addition. The first preparation method consists of adding K as aqueous K_2CO_3 to γ-Al_2O_3 by incipient wetness followed by calcination at 873 K. Pd as $Pd(NH_3)_4(NO_3)_2$ aqueous solution was then added to the K-containing Al_2O_3 by incipient wetness. In a second preparation, Pd [as $Pd(NH_3)_4NO_3$] was added to γ-Al_2O_3 followed by reduction at 773 K. K was post-impregnated on this material. Both types of material gave similar catalytic properties, indicating that the modification of the support is the important effect of K. We report here the properties of the materials where K has been added to the Pd/Al_2O_3 base material. The Pd loading in all cases was 1% (w/w) and 1% (w/w) K and 4% (w/w) K materials along with the base Pd/Al_2O_3 (0% K) are compared in this paper.

Catalytic reactions were performed on a batch recirculation reactor system constructed of Pyrex glass and having a total volume of about 700 cm^3. The catalyst charge was 100 mg in all cases and catalyst reduction was accomplished in 1 bar H_2 at 773 K for 1 h prior to the experiment. The catalyst was then flushed with He for 30 min. A mixture of H_2 and C_2H_2 (2 : 1 molar ratio) was first prepared, then the final reaction mixture consisting of 1% C_2H_2 in 99% C_2H_4 (w/w) (H_2 free basis) was

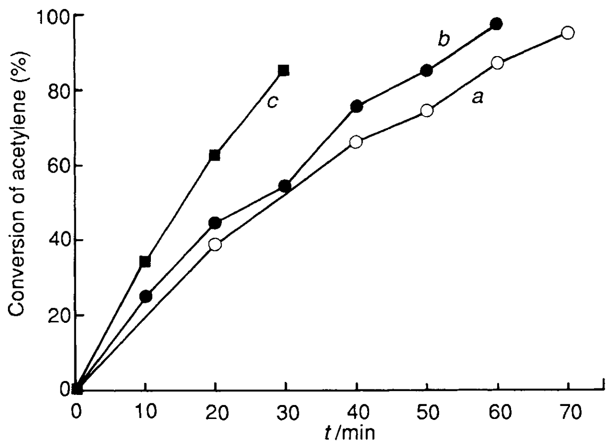

Fig. 1 Conversion of acetylene *vs.* time at 298 K, 100 mg of catalyst: *a*, 0% K; *b*, 1% K; *c*, 4% K

Table 1 Raw chromatographic results; wt% of hydrocarbon species

	0% K		1% K		4% K	
Reaction time/ min	Initial 0	Final 70	Initial 0	Final 60	Initial 0	Final 30
Methane	0.0014	0.0016	0	0	0	0.0014
Ethylene	98.93	99.44	98.99	99.67	98.94	99.60
Acetylene	1.0485	0.0556	0.9966	0.0299	1.0407	0.1509
Ethane	0	0.4008	0	0.2002	0	0.1580
Propylene	0.0109	0.0085	0.0095	0.0112	0.1175	0.0096
Propane	0.0112	0.0051	0.0048	0.0053	0.0053	0.0030
Bute-1-ne	0	0.0328	0	0.0307	0	0.0202
Butadiene	0	0.0298	0	0.0407	0	0.0398
trans-But-2-ene	0	0.0134	0	0.0122	0	0.0098
cis-But-2-ene	0	0.0076	0	0.0032	0	0.0059

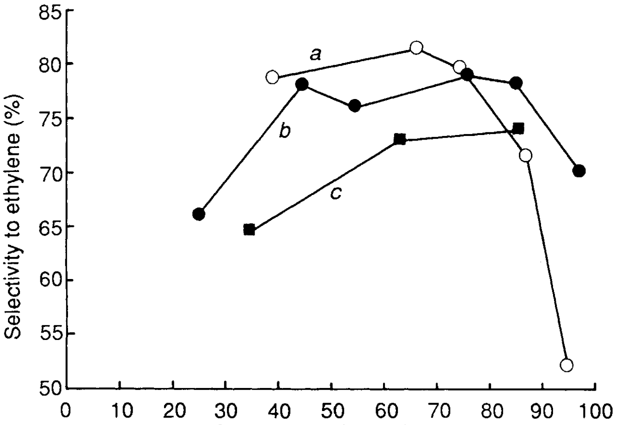

Fig. 2 Selectivity to ethylene at 298 K; *a*–*c* as in Fig. 1

prepared by successive dilution of the H_2–C_2H_2 mixture. Reactions were carried out at 298 K and 1.04 bar.

Products were analysed *via* capillary chromatography on a 60 m SE-30 column with a flame ionisation detector. Repeated analysis of the initial mixture showed a chromatographic reproducibility of about ±0.01 wt% C_2H_2 and a C_2H_2 dilution reproducibility of about ±0.03 wt% C_2H_2. The C_2H_2 and C_2H_6 detection limits were about 200 ppm while CH_4 and C_3 hydrocarbons (impurities in the feed reactants) and C_4 hydrocarbons (oligomerization products) could be detected to levels as low as about 25 ppm.

Table 1 gives a complete listing of initial mixtures and product analysis for >85% conversion for each of the three catalysts containing 0, 1 and 4% K. C_1 and C_3 reactant impurities are apparent but are quite insignificant. Acetylene conversion to ethylene, ethane and C_4 oligomerization products is evident. Fig. 1 shows conversion *vs.* time for each of the three catalysts and Fig. 2 shows ethylene selectivity, for all catalysts, as a function of conversion. Conversion and selectivity are defined by eqns. (1) and (2)

$$\%\mathrm{Conv.} = (W_{t,\mathrm{a}} - W_{0,\mathrm{a}})/W_{0,\mathrm{a}} \times 100 \qquad (1)$$

where: $W_{t,\mathrm{a}}$ is acetylene wt% at time t

$W_{0,\mathrm{a}}$ is the initial acetylene wt%

$$\%\mathrm{Selectivity} = (W_{t,i} - W_{0,i})/(W_{t,\mathrm{a}} - W_{0,\mathrm{a}}) \times 100 \qquad (2)$$

where: $W_{t,i}$ is the wt% of the ith component at time t

$W_{0,i}$ is the initial wt% of the ith component.

Several aspects of the effect of K may be noted from the Figures. First, the addition of K promotes the global reaction rate. The 1% K material also promotes higher ethylene selectivities at high conversions of acetylene which is particularly important since even higher conversions of acetylene are needed in industrial processes to reduce the acetylene content to less than 200 ppm. The ethylene selectivity over the 4% K material is generally less than that of the base material, and this effect may be related to its high activity. 4% K is probably beyond the optimal loading.

One of the surprising features of the K-promoted materials is the enhanced production of C_4 oligomers, particularly since Al_2O_3 acidity is thought to promote oligomerization[5,6] while K addition reduces the acidity of the support. NH_3 and acetylene temperature-programmed desorption experiments have confirmed the reduced acidity of these K-containing materials.

Further mechanistic work on acetylene and ethylene hydrogenation over K promoted Pd/Al_2O_3 will be reported elsewhere. Results of these studies which include temperature-programmed desorption of acetylene and NH_3, temperature-programmed reaction, and deuterium tracer techniques show that the effect of K is to shift the nature of the Al_2O_3 support from acidic to basic which causes a shift in electron density to Pd. This results in a weakened hydrocarbon strength of adsorption which favours ethylene desorption prior to hydrogenation to ethane and also favours the desorption of C_4 oligomerization products. This postulate is consistent with the data presented in this paper.

More investigations are necessary prior to aceptance of K promotion as a means to improve the process of removal of traces of acetylene from raw ethylene streams. Long-term catalyst stability studies are needed along with studies aimed at the effects of CO (which is already known to improve ethylene selectivity) on the K-promoted materials. Optimization of K loading also needs to be addressed.

We thank the Exxon Foundation for financial support of this project.

Received, 25th March 1991; Com. 1/01402A

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