

ADVANCES IN OLEFIN PURIFICATION VIA CATALYSIS AND SORBENT MATERIALS

A technical investigation
commissioned by the members of the
Catalytic Advances Program (CAP)

Client Private
October 2014





The Catalytic Advances Program (CAP)

The Catalytic Advances Program (CAP) is an information resource for research and development organizations in the petroleum, chemical, and polymer industries. By the direction of the member companies (through balloting and other interactive means), the program delivers a range of timely and insightful information and analyses which are accessible exclusively to members and protected by confidentiality agreements. The objective is to provide a technical update on commercially viable advances in catalysis as well as benchmark commercial advances in catalysis and process technology.

Members receive three in-depth **CAP Technical Reports** which are written and peer reviewed by leading scientists and experienced industry professionals in areas selected by the membership (via ballot); weekly *CAP Communications* (delivered via e-mail) which provide the latest updates on technical breakthroughs, commercial events and exclusive development opportunities; and attendance at the **CAP Annual Meeting**.

The **Catalytic Advances Program (CAP)** is available on a membership basis from The Catalyst Group Resources (TCGR). For further details, please contact Matthew A. Colquitt at Matthew.A.Colquitt@catalystgrp.com or +1.215.628.4447 (x1130).



P.O. Box 680
Spring House, PA 19477 U.S.A.
ph: +1.215.628.4447
fax: +1.215.628.2267
website: www.catalystgrp.com

CONTENTS

EXECUTIVE SUMMARY	xxi
1. INTRODUCTION.....	1
2. OLEFIN PURIFICATION VIA CATALYSIS.....	5
2.1 INTRODUCTION.....	5
2.2 LOWER OLEFINS	9
2.2.1 Selective hydrogenation of acetylene in ethylene production.....	15
2.2.1.1 Evolution of catalysts	18
2.2.1.2 Catalyst deactivation	22
2.2.1.3 Relative adsorption.....	23
2.2.1.4 Oligomers (green oil) formation.....	23
2.2.1.5 Catalyst poisons and inhibitors of Pd catalysts	26
2.2.1.6 Recent advances in catalysts and reaction mechanism	28
2.2.2 Selective hydrogenation of MAPD in propylene production.....	44
2.2.2.1 Catalyst development	48
2.2.2.2 Reaction mechanism.....	49
2.2.3 Selective hydrogenation of byproducts in C ₄ and C ₅ cut production	51
2.2.4. Selective catalytic removal of other contaminants.....	53
2.2.5 Current R&D and future developments.....	54
2.3 ALPHA OLEFINS	55
2.3.1 Introduction	55
2.3.1.3 Industrial production of alpha-olefins	55
2.3.1.2 Applications.....	59
2.3.1.3 By-products	60
2.3.2 Advances	61
2.3.2.1 Removal internal olefins	62
2.3.2.2 Vinylidene removal	63
2.3.2.3 1-Hexene purification.....	63
2.3.3 Current R&D and future developments.....	64

2.4 REFERENCES	66
3. OLEFIN PURIFICATION VIA SORBENT MATERIALS	79
3.1 INTRODUCTION	79
3.2. TRADITIONAL POROUS MATERIALS AS ADSORBENTS	81
3.2.1 Activated Carbon	81
3.2.2 Alumina	82
3.2.3 Mesoporous Silica	82
3.2.4 Zeolites	83
3.2.4.1 Olefin/paraffin separation.....	83
3.2.4.2 Removal of polar impurities	85
3.3 NOVEL ADSORBENTS.....	86
3.3.1 Carbon nanotubes	86
3.3.2 Ionic liquids	86
3.3.3 Ionic crystals.....	87
3.3.4 Covalent organic frameworks.....	87
3.3.5 Metal–organic frameworks.....	89
3.3.5.1 Olefin/Paraffin separation.....	89
3.3.6 Organic polymers.....	95
3.4 MEMBRANES	96
3.4.1 Purely organic-based polymer membranes.....	96
3.4.2 Metal ion-incorporated polymer membranes.....	97
3.4.3 Supported ionic liquid membranes	98
3.4.4 Membranes-based on carbon molecular sieves	100
3.4.5 Membranes-based on metal–organic frameworks (MOFs)	101
3.4.6 Membrane–distillation hybrids	102
3.5 CONCLUSIONS AND FUTURE DIRECTIONS	102
3.6 REFERENCES	103
4. INDEX	109

FIGURES

Figure 2.1	Typical FCCU product recovery scheme showing some of the off gas.....	6
Figure 2.2	Process flowsheet showing enhanced recovery of olefins and hydrogen.	6
Figure 2.3	Typical processing schemes for refinery off gas.....	7
Figure 2.4	Simplified reaction network in the steam cracking to produce lower olefins. The formation of acetylenic compounds is highlighted.....	10
Figure 2.5	Basic flow sheet of steam cracking process to produce ethylene. The main purification steps are shown as well as the catalytic hydrogenation steps to remove acetylene and MAPD.....	11
Figure 2.6	Basic flowsheet of two front-end systems for acetylene removal by selective hydrogenation: front-end de-ethaniser (a) and front-end depropaniser (b).	12
Figure 2.7	Typical reactor configurations for front- and tail-end processes.	18
Figure 2.8	Progresses in catalyst performances from 2 nd to 3 rd generation (stabilized) catalysts for acetylene selective hydrogenation.	19
Figure 2.9	Operating windows of second- and third-generation catalysts at 500 ppm and 100 ppm CO levels.	21
Figure 2.10	Green oil and polymer formation in standard and promoted (by Ag) Süd-Chemie acetylene selective hydrogenation catalyst. Test conditions: 1% C ₂ H ₂ , 1.5% H ₂ , SV = 5000 h ⁻¹ , T = 500°C.	25
Figure 2.11	Typical reactor configuration for in-situ regeneration (tail-end configuration) during acetylene selective hydrogenation.	27
Figure 2.12	Typical temperature programmed profile under different atmospheres for tail-end acetylene selective hydrogenation catalyst regeneration.....	28
Figure 2.13	Selectivity (left) and conversion (right) of PdGa (40 mg), Pd ₃ Ga ₇ (100 mg), Pd/Al ₂ O ₃ (0.15 mg), and Pd ₂₀ Ag ₈₀ (200 mg) in acetylene hydrogenation in a mixture of 0.5 % C ₂ H ₂ + 5 % H ₂ + 50 % C ₂ H ₂ in helium at 473 K.	29
Figure 2.14	Selectivity and specific activity (per mol Pd) in acetylene selective hydrogenation of Pd-based catalysts (in red intermetallic Pd-Ga supported catalysts).	30
Figure 2.15	(a) Ethylene selectivity versus conversion in acetylene hydrogenation (H ₂ /acetylene = 2, T = 60°C): Pd/SiO ₂ ; and Pd–Si/SiO ₂ (Si/Pd = 0.095). (b) Deactivation of catalyst, before and after regeneration, with accumulated amounts of converted acetylene (regeneration condition: O ₂ = 20 ml/min, temperature = 600°C for 2 h): Pd/SiO ₂ ; (b) Pd–Si/SiO ₂ , fresh and after regeneration.....	31
Figure 2.16	IR spectra of CO adsorbed on various catalysts: Pd/SiO ₂ ; Pd–0.095Si/SiO ₂ ; Pd– 0.19Si/SiO ₂	32
Figure 2.17	Changes in the ethylene selectivity with conversion in acetylene hydrogenation for different sample catalysts (H ₂ /acetylene = 2, reduction temperature = 300°C	

or 500°C, reaction temperature = 60°C): (a) Pd/300; (b) Pd/500; (c) Pd–Ti/300; (d) Pd–Ti/500; (e) Pd–La/300; (f) Pd–La/500; (g) Pd–Nb/300; (h) Pd–Nb/500..	33
Figure 2.18 (A) results of acetylene hydrogenation obtained using Pd/Al ₂ O ₃ containing either Ag or Cu: (a) Pd; (b) Pd–0.08Cu (SR); (c) Pd–0.41Cu (SR); (d) Pd–0.79Cu (SR); (e) Pd–0.08Ag (SR); (f) Pd–0.38Ag (SR); (g) Pd–0.58Ag (SR). (B) Dependence of acetylene conversion on the amount of either Ag or Cu, which was added by the surface redox (SR) method: (a) Pd–xCu (SR); (b) Pd–xAg (SR).....	33
Figure 2.19 Reaction results obtained using (a) 1 wt.% Pd/Al ₂ O ₃ , (b) 3 wt.% Pd/Al ₂ O ₃ prepared using conventional impregnation (I), and (c) 3 wt.% cubic Pd/Al ₂ O ₃ (Catalyst I), (d) 3 wt.% spherical Pd/Al ₂ O ₃ (Catalyst II).	34
Figure 2.20 Reaction steps involved in acetylene hydrogenation process.....	35
Figure 2.21 The amounts of green oil deposited on Pd/SiO ₂ (■) and Pd–0.5Ag/SiO ₂ (●), analyzed by TGA (—) and EA (—).	36
Figure 2.22 (a) Acetylene hydrogenation performance of CeO ₂ : selectivity to ethylene and oligomers as a function of the acetylene conversion (at T = 523 K, H ₂ /C ₃ H ₄ = 30, τ = 0.12 ⁻¹ s). The experiments were conducted at 1 bar. (b) Reaction energy profile for acetylene hydrogenation on CeO ₂ (111). All energies are referenced to the total energy of H ₂ (g), C ₂ H ₂ (g), and the clean CeO ₂ (111) surface (state A). States A–L stand for minima and their structures are schematically shown in the insets, whereas transition structures are indicated by R2–R17. Colors indicate different pathways: partial hydrogenation of acetylene to ethylene via R5 (black line) or via dissociative acetylene adsorption (light brown), and total hydrogenation to C ₂ H ₆ (red line).	38
Figure 2.23 (a) Transition-state structures of C ₂ H ₂ , C ₂ H ₃ , and C ₂ H ₄ hydrogenation on Pd(111), Pd(100), Pd(211), and Pd(211)-defect surfaces. Those low-coordinated Pd atoms of Pd(211) and Pd(211)-defect surfaces are shown in red. (b) Energy profiles of C ₂ H ₂ hydrogenation on Pd(111), Pd(100), Pd(211), and Pd(211)-defect surfaces under the standard pressure; the entropy effect is considered for the adsorption and desorption processes here. G* _{ad} is the transition-state energy of the adsorption of C ₂ H ₂ on all the surfaces.....	40
Figure 2.24 Tail-End Acetylene Hydrogenation Unit.....	46
Figure 2.25 Hydrorefining of the propylene rich cut in liquid phase. IFP technology employing chamber-type reactors.....	47
Figure 2.26 Engelhard (now BASF) upflow reactor system.....	53
Figure 2.27 Block diagram of the Linear-1 process.....	57
Figure 2.28 α-SABLIN® overall process.	58
Figure 2.29 LAOs are used as co-monomer for polymers, as synthetic lubricants, as additives to detergents and for paper treating chemicals.	59

Figure 2.30	Catalytic distillation processes: (a) Conventional process; (b) Novel process; (c) Propylene catalytic distillation unit; (d) Comparison between new and conventional processes.....	66
Figure 3.1	Adsorption isotherms of ethane (\blacktriangle) and ethylene (\bullet) on 36 wt% CuCl/NaX and the ideal selectivity (\blacklozenge) for ethylene over ethane at 373 K.....	84
Figure 3.2	Structures of MCOF-1, diamondyne, and PAF-302.....	88
Figure 3.3	Crystallographic structure of common MOFs studied for olefin purification.....	89

TABLES

Table 2.1	Typical impurities in refinery off gas and their effect (Hawkins, 2014).....	7
Table 2.2	Typical impurities in refinery off gas and their removal (Hawkins, 2014).....	8
Table 2.3	Ethylene product specification for export to polymer plants (Rahimpour et al., 2012).....	8
Table 2.4	Typical compositions of the outlet stream from different process configurations for the acetylene removal unit and relative operative conditions for the hydrogenation reactor. (Hawkins, 2014).....	13
Table 2.5	Comparison of tail- and front-end configurations for acetylene hydrogenation (Adapted from Spaether, 2013)	14
Table 2.6	Distribution of technologies for acetylene removal (Rahimpour et al., 2013)....	15
Table 2.7	Main requirements for selective hydrogenation catalysts depending on process configuration, and some examples of commercial catalysts for the tail- and front-end configurations (Spaether, 2013)	17
Table 2.8	Evolution of catalyst generations for tail-end and front-end configurations in acetylene selective hydrogenation (Spaether, 2013)	18
Table 2.9	CO swing tests for second- and third-generation selective acetylene hydrogenation catalysts (Xu et al., 2013).....	21
Table 2.10	Composition of propylene cuts and commercial propylenes (Wang, 2007).....	44
Table 2.11	Composition of propylene cut for different steam cracking feeds (Wang, 2007).....	45
Table 2.12	Industrial statistical ethylene oligomerization processes (Belov and Matkovsky, 2010).....	56
Table 3.1	Typical composition of cracked gas stream	80
Table 3.2	Relevant physical properties of ethane (C_2H_6), ethylene (C_2H_4), propane (C_3H_8), and propylene (C_3H_6) (Geier et al., 2013)	80
Table 3.3	Column efficiency data of modified and bare alumina columns.....	82

Table 3.4	The solubility of C ₃ H ₆ and C ₃ H ₈ in IL or IL/salt at 298K.....	87
Table 3.5	Isosteric Heats of Adsorption of Propane and Propylene at Zero Coverage for various adsorbents (Bao et al., 2011).....	91

SCHEMES

Scheme 3.1	Suggested flow scheme for the separation of the C ₅ -cut from a steam cracker	94
Scheme 3.2	Synthesis and metallation of A ₂ B ₁ and A ₁₀ B ₁ to generate CuA ₂ B ₁ and CuA ₁₀ B ₁	95
Scheme 3.3	Synthesis of phenanthroline-based polymer 3 and its metallated analogue 4: (a) Pd(PPh ₃) ₂ Cl ₂ , CuI, triethylamine, THF, 70 °C, 77%; (b) AgOTf, acetone, CH ₂ Cl ₂ , 95%.....	96