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CONTENTS / СОДЕРЖАНИЕ

**Dmitry V. Kazachkin, David R. Luebke,
 Vladimir I. Kovalchuk, and Julie L. d'Itri**
 Hydrogen-Assisted 1,2-Dichloroethane Dechlorination Catalyzed
 by Pt-Cu/SiO₂: Insights into the Nature of Ethylene-Selective
 Active Sites

— 303 —

**Alexey N. Lukianov, Olga N. Kononova
 and Sergey V. Kachin**
 Calculation of Protolytic Equilibria Parameters on a Surface of
 Some Carbon Adsorbents According to Potentiometric Titration
 Data

— 326 —

**Tatiana G. Shendrik, Valentina V. Siminova,
 Nikolai V. Chesnokov and Boris N. Kuznetsov**
 Properties of Active Carbons Produced by Thermochemical
 Transformation of Lignin, Brown Coal and Oil Slime Mixtures

— 336 —

Anatoly I. Rubailo and Andrey V. Oberenko
 Polycyclic Aromatic Hydrocarbons as Priority Pollutants

— 344 —

**Irina G. Sudakova, Boris N. Kuznetsov,
 Natalia V. Garyntseva, Nina I. Pavlenko
 and Natalia M. Ivanchenko**
 Functional and Thermal Analysis of Suberin Isolated from Birch
 Bark

— 355 —

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**Valeri E. Tarabanko, Olga A. Ulyanova,
 Galina S. Kalachova, Valentina V. Chuprova
 and Nikolai V. Tarabanko**

Study of Plant Growth Promoting Activity and Chemical Composition of Pine Bark after Various Storage Periods

— 363 —

**Владимир А. Левданский, Александр В. Левданский,
 Борис Н. Кузнецов**

Влияние ортофосфорной кислоты на химические превращения бетулинова в бутаноле, изобутаноле и уксусной кислоте

— 369 —

**Светлана А. Козлова, Владимир А. Парфенов,
 Людмила С. Тарасова, Сергей Д. Кирик**

Состояние сilanольного покрытия мезоструктурированного силикатного материала MCM-41 в результате постсинтетической активации

— 376 —

**Светлана И. Цыганова, Александр Н. Швецов,
 Ирина В. Королькова, Николай В. Чесноков,
 Борис Н. Кузнецов**

Влияние модифицирующих добавок на карбонизацию смесей березовых опилок с каменноугольным пеком

— 389 —

Светлана А. Быстрякова, Людмила П. Рубчевская

Состав фосфолипидов хвои сосны сибирской

— 399 —

Правила представления статей для публикации

— 405 —

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Hydrogen-Assisted 1,2-Dichloroethane Dechlorination Catalyzed by Pt-Cu/SiO₂: Insights into the Nature of Ethylene-Selective Active Sites

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Differently pretreated silica-supported Pt, Cu, and Pt-Cu catalysts with Cu to Pt atomic ratio of 1 to 6 have been investigated by a combination of reaction kinetics and FTIR spectroscopic studies in order to understand the factors that control the selectivity toward ethylene and ethane in the CH₂ClCH₂Cl+H₂ reaction. Carbon monoxide adsorption was used to probe the electronic modification of Pt and Cu as well as the nature of ethylene-selective active sites. It was shown that there is a very limited, if any, electronic interaction between Pt and Cu in the bimetallic catalysts reduced at 493 K. However, the Pt-Cu catalysts, for which no dipole-dipole coupling shift was observed in the IR spectra of adsorbed CO suggesting extremely small Pt ensembles on the catalyst surface, demonstrated high ethylene selectivity in the 1,2-dichloroethane dechlorination. Electronic interactions between Pt and Cu have been discovered for the Pt-Cu/SiO₂ catalysts reduced at 773 K. The interactions manifested themselves by a higher stability of Cu⁰-CO adsorption complexes in vacuum and by an increase in intensity of the Pt-CO band in the FTIR spectra upon evacuation of CO from the gas phase suggesting the formation of Pt-Cu solid solutions. The higher temperature reduction resulted in the dipole-dipole coupling shift of 6 to 19 cm⁻¹ in the FTIR spectra of adsorbed CO. The initial ethylene selectivity of the catalysts was inversely proportional to the dipole-dipole coupling shift. The observations are consistent with the idea that the nature of the Pt-Cu species, viz., alloy particles as opposed to Cu/Pt overlayers, does not control the reaction selectivity, which is a function of the Pt ensemble size on the surface of Pt-Cu moieties.

Keywords: hydrogen-assisted dechlorination, 1,2-dichloroethane, ethylene, Pt-Cu catalysts, infrared spectroscopy, singleton frequency, dipole-dipole coupling.

Introduction

It has been discovered a decade ago that a combination of Pt or Pd with another metal deposited on a solid support catalyzes hydrodechlorination of vicinal dichloroalkanes such as 1,2-dichloroethane and 1,2-

dichloropropane toward the formation of the corresponding alkene, viz., ethylene or propylene [1-3]. Such a chemistry looks surprising because any catalyst that activates H₂ should also hydrogenate the product olefin. As chloroalkanes are common environmental pollutants and alkenes

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