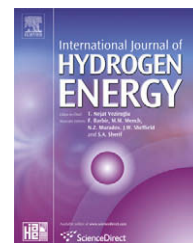


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Hydrogen from oxygenated solvents by steam reforming on Ni/Al₂O₃ catalyst

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ABSTRACT

Industrial wastes from the semiconductor industry comprise solvent mixtures of organic oxygenated compounds. Steam reforming of three alcohols and three oxygenated molecules (aldehydes and ketones), normally used in the electronics industry, was carried out at 1073 K by using a Ni/Al₂O₃ catalyst. Hydroxyl and carbonyl groups show highly different reactivities and coke formation from molecules containing a hydroxyl group is higher than for those with a carbonyl group. Thermodynamic considerations on the basis of the outlet compositions have allowed calculation of the mass action ratio (MAR) for the main equilibria involved: (i) methane steam reforming (MSR); (ii) water–gas shift reaction (WGSR); (iii) methane pyrolysis (PYR); and (iv) Boudouard reaction (BOUD). We suggest that MAR_{MSR} is lower than equilibrium value and excess of methane is always present in the reaction atmosphere.

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1. Introduction

Today hydrogen production is studied intensively, because the demand for hydrogen is expected to increase considerably in the coming years both in existing industries and in new technologies like fuel cells (DMFC, PEM and SOFC) [1–3]. In particular, numerous studies have focused on the synthesis of H₂ from oxygenated hydrocarbons for fuel cell applications [4–16] or from waste materials obtained from fermentation and decomposition of vegetable biomass [17–19]. Recently, researchers have investigated the possibility of using catalytic steam reforming (SR) to convert hazardous industrial wastes such as alcohols and chlorinated and non-chlorinated organics [20–22].

The economically highly important electronics industry is facing exhaustion of scarce resources, treatment of industrial wastes, and recycling [23]. Semiconductor processes generate

industrial basic wastes, which are frequently composed of solvent mixtures containing ethanol, isopropanol, acetone, 1-methoxy-2-propanol and 2-butanone [20,24–26]. Some of these solvents, which cannot be recovered economically from the effluents of the semiconductor industry, are supplied to special waste treatment plants, thus increasing the cost to industry. The components of these solvent mixtures are difficult to separate, and therefore they are burnt in boilers and their chemical energy is partly recovered as thermal energy.

Isopropanol is widely employed in manufacturing semiconductor wafers for removal of water from the wafer surface after cleaning operations [25]. Mizuno et al. [20,24] have recently studied steam reforming of isopropanol (IPA) on supported Rh catalysts.

This work aims at investigating the possibility of obtaining H₂ from mixtures of oxygenated solvents starting from the

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behaviour of the pure components. In order to increase the applicability of the laboratory tests, steam reforming was carried out using a commercial Ni/Al₂O₃ catalyst on six probe molecules that are often used as solvents in the semiconductor industry. In particular, three alcohols and three oxygenated products (aldehydes and ketones) were selected, namely different C₂ to C₄ isomers, in order to evaluate the influence of the functional group (–OH or C=O).

2. Experimental

2.1. Catalytic tests

A commercial Ni/Al₂O₃ steam reforming catalyst (Girdler catalyst G-56A, SÜD-CHEMIE AG, München) has been used throughout. The G-56 composition is typical of an MSR catalyst, nominally made by 15 wt% of Ni supported on α -Al₂O₃ (73 wt%) and CaO (8 wt%) mixture. Carbon content is less than 2 wt%, while traces of other constituents (i.e., SiO₂, Na, S) can hardly be detected (<0.1 wt%). BET surface area of the catalyst was 43.7 m² g⁻¹. All reagents (aldehydes and ketones, cf. Table 1) were supplied by Sigma–Aldrich.

Catalytic experiments were performed at atmospheric pressure in a fixed-bed linear quartz microreactor ($\phi_{\text{int}} = 4$ mm; $h_{\text{bed}} = 1.0$ – 2.0 cm) charged with 0.01–0.06 g of catalyst (40–70 mesh) and diluted with 200 mg of similar sized inert material (i.e., SiC). Before each test run, catalysts were reduced “in situ” at $T = 1073$ K for 1 h. Water/hydrocarbon mixtures were fed by an isocratic HP 1100 pump and vaporized at $T = 400$ K in a N₂ stream. Experiments were performed at $T = 1073$ K with a hydrocarbon gas hourly space velocity (GHSV_{HC}) of 40,000 h⁻¹ and steam-to-carbon molar ratio S/C of 4.0 mol/mol. The reaction stream was analyzed “on line” by a Hewlett Packard GC-TCD/FID model 6890 Plus, equipped with a three-columns (Molecular Sieve 5 Å, Porapak Q and Hysep) system. Nitrogen (10 vol%) was used as an internal standard to evaluate the carbon balance. GC data were acquired and elaborated by the Hewlett–Packard Interface Bus system (HP Chemstation).

2.2. Characterisation of used catalyst

TEM observations were made by using a Philips CM12 instrument equipped with a high resolution camera that allows acquisition and evaluation (i.e., of the particle size distribution) of TEM images. Specimens were prepared by ultrasonic

dispersion of catalyst samples in isopropyl alcohol depositing a drop of suspension on a Formvar carbon grid Cu 400. The overall amount of coke deposited on the catalytic surface after each test run has been determined by CHNS elemental analysis of the discharged sample performed by a Carlo Erba Elemental Analyzer.

3. Results

The initial catalytic activity determined from the outlet composition after 0.5 h is shown in Fig. 1. The C₂–C₄ alcohol conversion is independent of the number of carbon atoms of the reagent, whereas the conversion of molecules containing carbonylic oxygen (aldehydes or ketones) decreases with carbon atom number. Figs. 2 and 3 show the initial hydrogen and methane selectivity, respectively, expressed as mole of H₂ and CH₄ produced per mole of reagent converted (molar ratio). Hydrogen selectivity decreases with the carbon atom number from 46.8% using ethanol to 29.0% using 2-butanol, and from 52.7% using acetaldehyde to 31.7% using 2-butanone. Methane selectivity increases with carbon atom number from 0.3% using ethanol to 1.3% using 2-butanol and from 0.05% using acetaldehyde to 1.1% using 2-butanone. The overall catalytic selectivity is described more appropriately by considering the mass action ratio (MAR) determined from the H₂, CO₂, CO and CH₄ concentrations in the outlet gas. Fig. 4 reports the initial MAR for the reactions involving C₁ compounds. We notice that the water–gas shift (Eq. (1)) and methane pyrolysis (Eq. (2)) reactions are approaching equilibrium, while the methane steam reforming (Eq. (3)) and Boudouard (Eq. (4)) reactions are shifted to the left and right sides of the reaction equation, respectively, because the CO concentration in the outlet is very low and far from equilibrium.



Obviously, considerations based on a specific coking reaction (i.e., PYR and BOUD) do not take into account the overall

Table 1 – Coke formation evaluated by CHNS analysis on used catalysts

Catalyst sample #	Oxygenated compound	Abbreviation ^a	C atom number	Coke (wt%)	Time on stream (h)	wt%/h
CS1	Ethanol	EtOH	2	7.97	19	0.4
CS2	Acetaldehyde	AcHO	2	4.36	13	0.3
CS3	Isopropanol	iso-PrOH	3	6.65	6	1.1
CS4	Acetone	–	3	6.56	27	0.2
CS5	1-Methoxy-2-propanol	MePrOH	4	16.32	20	0.8
CS6	2-Butanol	2ButOH	4	21.55	3.5	6.2
CS7	2-Butanone	2ButONE	4	6.52	20	0.3

a cf. Figs. 5 and 7.

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