

Zirconia: Selective oxidation catalyst for removal of tar and ammonia from biomass gasification gas

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Abstract

Catalysts containing zirconia and alumina were tested for their activity in the selective oxidation of tar and ammonia in biomass gasification gas. Their performance was compared with that of nickel and dolomite catalysts. Synthetic gasification gas with toluene as tar model compound was used as feed. In the presence of oxygen, zirconia and alumina-doped zirconia gave high toluene and ammonia conversions even below 600 °C. They were the most active catalysts for toluene oxidation below 700 °C and for ammonia oxidation below 650 °C. At higher temperatures than these, the impregnated ZrO₂/Al₂O₃ catalysts performed better: oxidation selectivity was improved and toluene and ammonia conversions were higher. The presence of both zirconia and alumina in the catalyst promoted toluene and ammonia conversions at low temperatures: zirconia enhanced the oxidation activity, while alumina improved the oxidation selectivity. The presence of H₂S had little effect on the activity of alumina-doped zirconia.

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1. Introduction

Growing energy demand and the environmental burden of fossil fuels have created wide interest in renewable energy sources. Biomass is an abundant renewable energy source, and its gasification is an environmentally attractive method of energy production. A variety of biomasses—wood residues, straw, peat and waste materials—are suitable as gasifier feedstock. The main components of gasification gas are CO, H₂, CO₂, CH₄ and H₂O, plus N₂ in the case of air gasification. Biomass-derived gasification gas also contains harmful components, such as tar (polyaromatic hydrocarbons) and nitrogen and sulphur compounds [1]. Tar is likely to cause operational problems in downstream processing, for example, by blocking gas coolers, filter elements and engine suction channels. Gasification gas needs to be cleaned, therefore, before it is cooled down for filtration or

combusted in gas engines or turbines. Nitrogen compounds, particularly NH₃, are potential sources of NO_x emissions during gas combustion and may cause corrosion in the process equipment. Catalytic gas cleaning units that decompose tar and NH₃ to gaseous components are being widely studied as an approach to solve these problems.

A recent review by Sutton et al. [2] summarises the current status of catalysts in gasification gas cleaning. Until now, the research in this field has mainly focused on nickel-based steam-reforming catalysts and dolomites. Nickel catalysts are active in decomposition of both tar and ammonia and have been studied by many research groups [3–14]. Almost complete tar and high ammonia conversions can be achieved with nickel catalysts. Unfortunately, nickel catalysts are easily poisoned by H₂S, and deactivation due to coke deposits has been reported [5–7,9,13,14]. Operating temperatures of 800–900 °C are required to circumvent these drawbacks. Nickel catalysts also decompose light hydrocarbons, which with their high heating value are useful components in many combustion applications. Unless

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synthesis gas is the desired product, these light hydrocarbons should be retained in the gas.

Carbonate rocks, mainly dolomites, are effective in tar decomposition [14–19]. Since carbonate rocks are active only in calcined state, they too require operating temperatures above 800 °C under gasification conditions and are not suitable for pressurised applications. Carbonate rocks are low-cost materials, but they are not active in ammonia decomposition. They are also sensitive to attrition, which, in practice, means there is a considerable need for make-up catalyst.

As reviewed by Yamaguchi [20], zirconia is a suitable catalyst, promoter or support for a variety of applications. Zirconia possesses an unusual set of acidic, basic, oxidising and reducing surface properties [21]. One relevant example of the oxidising character of zirconia is the partial oxidation of methane on yttria-stabilised zirconia yielding CO, CO₂, H₂O and H₂ [22]. Moreover, zirconium oxide gives high conversion of peat pyrolysis products with high hydrogen to carbon monoxide ratio in the product gas [23].

We tested a new and promising catalytic material, zirconia, for removal of tar and ammonia from biomass gasification gas. Bulk zirconia and alumina-supported zirconia catalysts are compared with nickel and dolomite catalysts.

2. Experimental

2.1. Catalyst preparation

The bulk zirconia materials, undoped MEZR 0404 T1/8 pellets and alumina-doped MEZR 0500 E1/8 extrudates, were from MEL Chemicals. They were calcined at 800 °C for 1 h and cooled in a desiccator. The MEZR 0500 catalyst was crushed and sieved to particle size 2–3.15 mm after calcination. Kalkkimaä dolomite was from the Kalkkimaä quarry in Northern Finland. It was crushed and sieved to particle size 2–3.15 mm and calcined in situ in nitrogen stream for 1 h at 900 °C. The 3 mm alumina pellets used as bulk alumina catalyst and as support for the impregnated zirconia and nickel catalysts were from Engelhard. The pellets used as bulk alumina catalyst were calcined in a similar manner to the bulk zirconia materials, and those used

as support for the impregnated catalysts were pretreated at 500 °C overnight and cooled in a desiccator. Impregnation of alumina was by incipient wetness method. Zirconium nitrate solution from MEL Chemicals (20 wt.% ZrO₂ content) was used as zirconium oxide precursor. Ni(NO₃)₃·6H₂O (p.a. purity) from Merck was selected as nickel precursor. The 5 wt.% ZrO₂/Al₂O₃ and NiO/Al₂O₃ catalysts were prepared in a single impregnation step, while the 10 and 20 wt.% ZrO₂/Al₂O₃ catalysts required two and four impregnations, respectively. After impregnation, the catalysts were dried at 105 °C for 24 h, calcined at 800 °C for 1 h and cooled in a desiccator. The nickel catalyst was reduced in situ in a gas stream containing 10% H₂ in nitrogen for 1 h at 900 °C before being tested for catalytic activity. The catalyst materials are described in Table 1.

2.2. Catalyst testing

The experimental setup consisted of a laboratory-scale, fixed-bed tube reactor working at atmospheric pressure, a gas mixing system and gas analysers. The simulated gasification gas feed was mixed with independent mass flow controllers. The liquid reactants were fed through HPLC pumps and vaporised before mixing into the gas stream. The gas lines were heated to avoid condensation of water and toluene. The feed gas flow rate was adjusted to 2 dm³ min⁻¹ (NTP). The space velocity in the experiments was 3500 h⁻¹. Toluene from BDH Laboratory Supplies was used as a tar model compound. The choice of toluene as model compound has been discussed elsewhere [24]. The gases were supplied by Oy AGA Ab. Table 2 gives the composition of the synthetic gasification gas feed and the purity of the components. Disregarding oxygen, the feed composition is typical for fluidised bed gasification of biomass with air as gasifying agent. Oxygen was added to enable the oxidation reactions typical for zirconia catalysts. Nickel and dolomite catalysts do not require the presence of oxygen, but oxygen is useful in supplying the heat needed for the endothermic reforming reactions. The MEZR 0500 and nickel catalysts were also tested in a gas mixture containing 100 ppm of H₂S.

A quartz reactor with a quartz grid and a thermocouple pocket in the centre axis of the catalyst bed was used in the experiments. The reactor was packed with 36 cm³ of catalyst. The catalyst bed was 22 mm in diameter and

Table 1
Catalysts, their BET specific surface areas, particle sizes and compositions

Catalyst	S _{BET} (m ² g ⁻¹)	Particle size (mm)	Composition (wt.%)
Dolomite (Kalkkimaä)	8	2–3.15	21 CaO, 16 MgO, 1 Fe ₂ O ₃ , 2 Al ₂ O ₃ , 7 SiO ₂ , 42 CO ₂ ^a
MEZR 0404	35	3	ZrO ₂
MEZR 0500	65	2–3.15	87 ZrO ₂ , 13 Al ₂ O ₃
Al ₂ O ₃	132	3	Al ₂ O ₃
5ZrO ₂ /Al ₂ O ₃	122	3	5 ZrO ₂ , 95 Al ₂ O ₃
10ZrO ₂ /Al ₂ O ₃	114	3	10 ZrO ₂ , 90 Al ₂ O ₃
20ZrO ₂ /Al ₂ O ₃	94	3	20 ZrO ₂ , 80 Al ₂ O ₃
7NiO/Al ₂ O ₃	119	3	7 NiO, 93 Al ₂ O ₃

^a Before calcination.

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