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Applied Catalysis A: General 296 (2005) 30–48

APPLIED CATALYSIS A: GENERAL

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Competitive CO and CO_2 methanation over supported noble metal catalysts in high throughput scanning mass spectrometer

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Received 24 April 2005; received in revised form 1 July 2005; accepted 6 July 2005
Available online 12 October 2005

Abstract

High-throughput synthesis and screening methods have been developed for the heterogeneously catalyzed gas phase hydrogenation of CO and CO_2 ('methanation') over zirconia and ceria supported noble and base metal catalysts at 300–400 °C and ambient pressure. The discovery libraries, for primary screening, consisted of 11 × 11 arrays of 111 catalysts on 3 in. quartz wafers, and 16 × 16 arrays of 256 catalysts on 4 in. quartz wafers. Catalysts were prepared by liquid dispensing techniques and screened for catalytic activity in scanning mass spectrometers (SMS). This primary screening tool uses quadrupole mass spectrometry for rapid serial detection. More than 500 potential catalysts could be screened in a single day. A kinetic model based on fast equilibration by the reverse water–gas-shift reaction in parallel with about an order of magnitude slower CO hydrogenation is in good agreement with CO_x conversion data. CO_2 is mainly reverse shifted to CO. Ru, Rh, and Ni were found to promote methanation whereas Pt tends to catalyze the reverse WGS reaction. Methanation activity can be enhanced by some acidic and redox dopants or suppressed by basic dopants. High conversions were achieved in SMS demonstrating the minimal scalability risk for short contact time reactions.

Keywords: Methanation; Water–gas-shift; High throughtput screening; Primary screening; Mass spectrometer; Scanning; Library; Wafer; Kinetic modeling

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1. Introduction

The methanation reaction of CO was developed as a gas-purification process, in particular in ammonia and hydrogen plants where CO is a catalyst poison. Methanation catalysts are also used for the purification of hydrogen in refineries and ethylene plants [1–3]. The production of synthetic natural gas (SNG) from synthesis gas was of considerable interest in the 1970s as a shortfall of natural gas supplies was anticipated [2]. In "ultramethanation" in caprolactam plants, carbon oxide concentrations have to be reduced to few ppm or less [3]. CO_x methanation may have other practical applications as a means of toxic CO removal from process gas streams or gas separation purposes and is also being discussed as an alternative to PROX (preferential oxidation of CO to CO_2) in fuel processors for mobile fuel cell applications. Ni catalysts are commonly used in GC detection for the methanation of both CO and CO_2 at about 350 °C. Moreover, it is desirable to develop technology for recycling of disposed CO_2 with methanation as one of the possibilities. Heat transfer applications to transport chemical energy in the form of hydrogen and carbon oxides produced by methane steam reforming with subsequent release of the energy for consumption via methanation are also important [3].

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doi:10.1016/j.apcata.2005.07.052

The methanation of CO and CO_2 (i.e. hydrogenation to CH_4) as well as the related Fischer–Tropsch reaction have been extensively studied and reviewed [1–3]. Recent publications describe CO and/or CO_2 hydrogenation over Rh/SiO_2 [4], noble metal doped Co-based FT catalysts [5], Fe/SiO_2 and Ni/SiO_2 [6], promoted Fe–Cu catalysts [7], Ni/Al_2O_3 [8], Rh/SiO_2 [9], Ni/ZrO_2 [10], $Ni–Zr/SiO_2$ [11], Pt/ZrO_2 [12], Rh/Y zeolitee [13], molybdenum carbide catalysts [14], Ru, Co and $RuCo/SiO_2$ catalysts [15], Co/SiO_2 [16], Co/Nb_2O_5 and niobia-promoted Co/Al_2O_3 [17], $Rh/SiO_2–CeO_2$ [18], supported Ni catalysts [19], $Pd–Co/SiO_2$ [20], Rh/Y zeolite [21], Ru/ZrO_2 [22], Co/activated carbon [23], molybdenum nitride catalysts [24], Fe/TiO_2 [25], Rh/SiO_2 and $Rh/VO_x/SiO_2$ [26], $Rh–Ce/SiO_2$ [27], Ni/sepiolite [28], Re–Co on SiO_2, Al_2O_3 on NaY [29], promoted Ru/sepiolite [30], Ru/Al_2O_3 [31], Co/Al_2O_3 [32], $PtCo/Al_2O_3$ and PtCo/NaY [33], Rh/TiO_2 [34], $RhVO_4/SiO_2$ [35], and Ru-promoted Co/MCM-41 [36].Most relevant to this work is the application of silica-supported Rh catalysts to CO_2 hydrogenation, for which the main product was CO for low metal loadings and CH_4 for high Rh loadings [9]. The characterization of Rh particles in Y zeolite during CO_2 hydrogenation showed that CH_4 is mainly produced from CO_2/H_2 on RhY while CO is formed on Li-doped RhY under similar conditions [13].

We have screened supported noble and base metal catalysts, doped with acidic and basic promoters, for the CO_x hydrogenation at 300–400 °C and ambient pressure in high-throughput scanning mass spectrometers, with the goal of ranking active metal activities and identifying general trends. We have compared a mixed $CO/CO_2/H_2$ feed with a CO_2-free CO/H_2 model feed to gain more insight into reaction pathways and kinetics.

2. Integrated workflow for high-throughput screening

Generally, high throughput workflows can be divided into primary and secondary screening. Primary screening approaches such as those described here are typically very high throughput qualitative or semi-quantitative screens performed on small samples. They allow the key bottleneck in the R&D process to be removed, resulting in much higher productivity in discovery research than is possible utilizing conventional techniques. Unconventional reactor designs are often employed in primary screens. The objective is to broadly screen a large and diverse set of material types that may perform the desired catalytic reaction. Discoveries, termed ‘‘hits’’, are then taken to the secondary screen and compositional space that is not useful is discarded. The primary screen must be designed to minimize both false positives and especially false negatives. Secondary screening is used for confirmation and optimization of primary hits and, in contrast to the primary screen, the catalyst form, reactor, and process analytics are designed to closely represent those of the real bench-scale material and reaction, with the data quality and precision equivalent to that of a standard laboratory reactor.

High-throughput combinatorial synthesis, screening and data analysis techniques and instrumentation used for the rapid identification of active and selective catalyst lead compounds within large compositional spaces (primary screening) for the methanation of CO_x over supported noble and base metal catalysts are described below. Although no novel catalysts were discovered for CO_x methanation, we have validated our primary screening methodology and hardware via reproduction of the literature, thus demonstrating the applicability of scanning mass spectrometry to the methanation reaction.

3. Synthesis workflow

Wafer formatted catalyst libraries were synthesized in situ using proprietary software. Commercial 3 and 4 in. diameter round quartz wafers were cleaned, silanized, and bead blasted through masks to produce 11 × 11 and 16 × 16 arrays of wells. These wells were then precoated with a zirconia carrier layer (commercial ZrO_2 powder supplied by Norton) using a slurry dispensing technique. The catalyst libraries were designed using commercially available software. Gradients of metal precursor solutions are chosen in order to obtain an array of solution mixtures within a single microtitre (MT) plate. A catalyst library substrate (wafer) is defined with an array of wells to which a portion of the premixed solutions from the microtitre plate is transferred. If precursor solutions are incompatible, gradients of the individual solutions are prepared in different MT plates and transferred sequentially to the wafer. The library design software is integrated with the impregnation mechanics. Automated liquid dispensing robots physically prepare the wafer libraries. Standards (pre-synthesized master batches of Pt/CeO_2 and Pt/ZrO_2 catalysts) were slurried into three first row and three last column wells. The remaining spots in first row/last column were left blank to correct for the background signal during data processing.

Aqueous metal nitrates (alkali, earth alkali, rare earth, Group IIIB, IB, IIB metals, Zr, Cr, Mn, Fe, Co, Ni, Al, Ga, In, Pb, Bi, Ru, Rh, Pd, Pt), nitrites (Na, Pd, Pt), oxalates (Ti, V, Nb, Ta, Mo, Sn, Ge, Pt), ammonium salts (vanadate, tungstate, Sb oxalate), acetates (alkaline earth, some rare earth), hydroxy complexes (hexahydroxy platinates, tetrahydroxy aurates), acids (boric, perrhenic, telluric, selenic, phosphoric) and in some cases chlorides (Hf, Sn, Ir, Pt, Au) were used as the standard metal precursors. Concentrations of stock solutions varied between 0.1 and 1.0 M for transition metals, RE and main group metals, while noble metals ranges were between 0.5 and 5.0 wt.%. A typical post-synthesis treatment involved a drying step at 110 °C, an air calcination step at 300–500 °C for 2 h, followed by a reduction step in a continuous flow of 5% H_2/N_2 at