Editor's choice paper

Non-precious metal catalysts supported on high Zr loaded-SBA-15 for lean NO reduction

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ABSTRACT

Various non-precious metal (M = Co, Ni, Cu, and Ag) catalysts supported on high Zr-loaded SBA-15 were developed for lean NO reduction. Several properties such as mesoporous structure, high specific area, moderate surface acidity, homogenous dispersion of Zr and M species, and strong interaction between support and doped metals were investigated by various techniques. The NO reduction efficiency of the developed catalysts in the propene selective reduction of NO was in the order of Co-2.5-Zr-SBADP > Ni-2.5-Zr-SBADP > Cu-2.5-Zr-SBADP > Ag-2.5-Zr-SBADP in the temperature range of 250–450 °C. Amongst, Co-2.5-Zr-SBADP displayed 42%, 55% and 46% N_2 yield at 300, 350 and 400 °C, respectively, in the dry feed whereas a slight decrease was observed in the wet feed. The catalyst activity improved significantly when a higher ratio of hydrocarbon to NO ($\frac{C}{N} = 8$) with the minimum fuel penalty (1%) was applied. The catalyst activity increased to 68% and 71% of NO conversion to N_2 at 350 and 400 °C, respectively, in the presence of water vapor. The catalyst showed excellent hydrothermal stability and durability during prolonged reaction so that 68% of N_2 yield was achieved in the extreme condition in the presence of 5.3 vol% of water vapor at 400 °C for 96 h.

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1. Introduction

Against the backdrop of increasing demand for fuel efficiency and severe strictures placed on NOx emission standards in recent years, the demand for fuel-efficient (lean-burn) and clean-exhaust engines has been growing. NO_x can be reduced by traditional three-way catalysts effectively in standard gasoline engine exhausts when the ratio of air to fuel is regulated in the stoichiometric range. However, it cannot operate beyond the stoichiometric conditions when higher concentration of oxygen for complete combustion is used [1]. However, it has been found that the hydrocarbon selective catalytic reduction (HC-SCR) catalyst can reduce NO_x to N_2 and O_2 in the lean-burn exhaust conditions. So far, various catalytic systems have been developed for HC-SCR such as zeolite, precious metal and metal oxide based- catalysts. Among them, silver supported on alumina (Ag/Al_2O_3) has been the most promising catalyst for practical applications. However, Ag/Al_2O_3 suffers from negligible activity at low temperature due to insufficient hydrothermal stability [2,3]. Therefore, the development of new catalysts for lean NO_x reduction (LNR) is still called for. Recently, mesoporous materials such as SBA-15 and MCM-41 have been of interest owing to their pore volume, large surface area and hydrothermal stability to be used as catalyst or support in various gas and liquid catalytic reactions. Pt/MCM-41, Pt/Al-MCM-41 and Pt/Ru/MCM-41 have been employed for LNR with propane and propene. Among them, 1% Pt/MCM-41 exhibited ~50% NO conversion at 220 °C in the presence of propene [4,5]. The reaction window has been widened as a result of Ru introduction to the catalyst (1% Pt/5% Ru/MCM-41). However, the crystal structure of MCM-41 declined in prolonged exposure to the hydrothermal conditions [6]. Subsequently, Pt supported on the modified SBA-15 with Al has been used for LNR catalytic systems to overcome the hydrothermal instability of MCM-41. 10 wt% Pt/Al-SBA-15 showed 33.3% and 42.3% NO conversion to N_2 and N_2O, respectively at 250 °C. However, using high amount of precious metals (Ru and Pt) is associated with two major disadvantages; not only does it drastically increase the cost of the catalytic system development but also a significant amount of N_2O gas (greenhouse gas) forms during the reaction [4,5]. Therefore, developing a cost-effective and more environmentally-friendly catalyst with high SCR activity and N_2 selectivity is still very much in demand.

Among various mesoporous materials, Zr-SBA-15 has several important properties such as high surface area, surface acidity, excellent hydrothermal stability and strong interaction with an

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introduced metal, which are essential for the selective catalytic reduction of NO$_x$ [6]. Transition metals (Co, Ni) supported on Zr-SBA-15 have been used for H$_8$C$_3$-SCR by Sabbaghi et al. [7,8]. However, to the best of our knowledge, the presence of propene as the main component (27.5 mass%) of the unburned hydrocarbons in gasoline engine exhausts [9] as well as the effect of a wider variety of transition metals such as Co, Ni, Cu and Ag loaded on Zr-SBA-15 for C$_3$H$_6$-SCR have not been reported yet. Hence, the performance of the transition metal (Cu, Co, Ni, and Ag) catalysts supported on high Zr loaded-SBA-15 in the propene selective catalytic reduction of NO was investigated in this study.

2. Experimental

2.1. Support preparation

The details on the preparation procedure of support can be found elsewhere [7,8]. The following is a brief summary: In the first step, Zr-SBAD is prepared using the direct synthesis method. 3.35 g of amphiphilic triblock copolymer P123 (EO$_{20}$PO$_{70}$EO$_{20}$), as the structure directing agent, is dissolved in 125 ml hydrochloric acid solution at pH=1.3. Then a calculated amount of ZrONO$_3$·xH$_2$O is added to the solution before adding 7 g of tetraethyl orthosilicate for obtaining the desired Si/Al ratio of 10. The mixture is stirred for 24 h at 35 °C. Afterwards, the solution is transferred into a Teflon-lined stainless steel autoclave and ages at 100 °C for 24 h under static conditions. The final product, Zr-SBAD, is filtrated, washed several times with deionized water, dried at 60 °C overnight and calcined at 600 °C for 8 h with a heating rate of 1 °C min^{-1}. In the second step, 1.2 g of Zr-SBAD and 2 ml of zirconium (IV) propoxide [Zr(n-PrO)$_4$] (70 wt% solution in 1-propanol) are added to 8 ml of absolute ethanol. The mixture is stirred overnight under the nitrogen atmosphere at room temperature. The mixture is filtered and washed with absolute ethanol three times to remove excess Zr(n-PrO)$_4$. The solid material, Zr-SBADP, is recovered by filtration and dried overnight at room temperature prior to calcination at 550 °C for 6 h with a heating rate 1 °C min^{-1}. SBA-15 is prepared according to the method described elsewhere [10].

2.2. Catalyst preparation

2.5 wt% of transition metal catalysts supported on Zr-SBADP, M (Co, Cu, Ni, and Ag)-2.5-Zr-SBADP were prepared using the incipient wetness impregnation technique [11]. A required volume of aqueous solution of cobalt, copper and nickel acetate, and silver nitrate was impregnated into the support to obtain 2.5 wt% of M on the Zr-SBADP. The impregnated supports were dried overnight at 70 °C and calcined at 550 °C for 5 h in the tube furnace with a heating rate of 1 °C min^{-1}. For comparison purposes, 2.5 wt% of Co catalysts supported on Zr-SBAD and SBA-15 were prepared with the same cobalt precursor, impregnation and heat treatment procedures.

2.3. Characterization

Various techniques, including powder x-ray diffraction technique (XRD), nitrogen adsorption and desorption, x-ray photoelectron spectroscopy (XPS) and x-ray fluorescence spectroscopy (XRF) were applied for the characterization of catalysts and supports.

The crystallinity of the materials was investigated by means of PANalytical X-ray diffractometer (model Xpert Pro) and powder x-ray diffraction system (model PW1830 (Philips), 2 kW, Cu anode, graphite monochromator). The scanning range (2θ) was adjusted in the range of 0.3–3° and 10–90° for low and high angle spectra, respectively.

The specific surface area of the supports and catalysts was determined via N$_2$ adsorption–desorption by a Coulter SA3100 surface area analyzer at liquid nitrogen temperature. The required amount of samples (0.1 g) was outgassed at 250 °C for 120 min prior to the analysis. Linear region of the Brunauer–Emmett–Teller (BET) equation (relative pressure between 0.05 and 0.22) and relative pressure of 0.98 were considered for the specific surface area and total pore volume measurement, respectively.

The surface chemistry of the materials was analyzed by a Kratos Axis Ultra DLD multi-technique XPS instrument under ultra-high vacuum where the energy source was a monochromatic Al Kα X-ray source (excitation energy, hυ = 1486.6 eV) at a voltage of 10 kV and a current of 15 mA. The low and high resolution spectra were obtained at 70 and 20 eV pass energy, respectively. The collected spectra were corrected by C (1s) at a binding energy of 284.6 eV as reference.

A JEOL JSX-3201Z XRF instrument was used for determining the elemental composition of the prepared supports and catalysts. The x-ray source for the experiments was acquired when the voltage and current of the tube was adjusted at 30 kV and 0–1 mA, respectively.

A pulse chromatographic technique was used for surface acidity measurement. The experiment was performed in gas-phase at 300 °C. The total acidity (sum of Brönsted and Lewis acid sites) and Brönsted acid sites were measured by the adsorption of pyridine (PY) and 2,6-dimethylpyridine (DMPY) as probe molecules (basic compounds), respectively [28]. 0.05 g of sample was loaded in a micro reactor and fed by a very small amount of probe molecules. The adsorption of PY and DMPY compounds continue into the saturation level from where the probe molecules can be detected by a GC. Therefore, the amount of adsorbed PY and DMPY can be measured.

2.4. Catalytic tests

The catalytic activities of M (Co, Ni, Cu, and Ag)-2.5-Zr-SBADP, Co-2.5-Zr-SBAD and Co-2.5-SBA-15 catalysts in the selective catalytic reduction of NO by propene were evaluated continuously at atmospheric pressure in a fixed bed stainless steel reactor at steady-state conditions. Typically, 0.5 g of catalyst was packed in the reactor and fed by a gas mixture consisting of 553 ppm of NO, 553 and 1500 ppm of C$_3$H$_6$ to provide $\frac{C}{N}$ = 3 and 8, respectively, 0.0–5.3 vol% of H$_2$O, and 5.3 vol% of O$_2$ (balanced in He) with the total flow rate of 150 ml min^{-1} (GHSV ≈ 18000 h^{-1}). The reactor was placed in a Carbolite tube furnace to provide the desired temperature for the reaction. The furnace temperature was controlled by an additional thermocouple. The concentration of N$_2$, CO$_2$, N$_2$O in the reaction effluent was analyzed by a GC (Agilent 7890B) equipped with Porapak Q, Hayesep D columns and TCD and FID detectors. The effect of catalyst composition such as the type of transition metals, reaction temperature and reactants concentration on the catalyst performance in C$_3$H$_6$-SCR were studied. The performance of the catalyst in NO and C$_3$H$_6$ conversion was calculated as follows:

$$NO\,conversion\,to\,N_2 = \frac{2 \times [N_2]_{outlet} \times 100}{[NO]_{in}}$$

$$C_3H_6\,conversion\,to\,CO_x = \frac{([C_3H_6]_{inlet} - [C_3H_6]_{outlet}) \times 100}{[C_3H_6]_{inlet}}$$

3. Results

3.1. Characterization of the supports and catalysts

Low and high angle XRD patterns of the supports and catalyst are presented in Fig. 1a and b, respectively. Three distinct peaks related to (100), (110) and (200) planes can be seen through the low angle