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SO_2 promoted alkali metal doped Ag/Al_2O_3 catalysts for CH_4-SCR of NO*x*

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ABSTRACT

A study of the lean NO*x* reduction activity in the presence of SO_2 and water over alkali promoted Ag/Al_2O_3 catalysts has been done using methane as a reductant. The alkali doped materials are synthesized by the co-impregnation method. Their promotional behavior, existence of several silver species and improved adsorption properties have been thoroughly investigated by various techniques: XRD, XANES, TEM, UV–Vis DRS, SO_2 TPD and NO TPD. The evaluated samples exhibited high surface area around 220 $m^2\ g^{-1}$. TEM results demonstrated the presence of highly dispersed nano sized silver particles on surface, where the addition of alkali metals slightly enhanced the crystallization of silver. Moreover, standard XRD profiles of fresh and used samples indicate the high durability and mechanical strength of catalysts. These findings are in line with the time-on-stream studies. The XANES results revealed that the edge spectra of prepared materials are similar to that of the reference Ag_2SO_4. From XANES and UV–Vis DRS, the presence of crystalline Ag^0 and Ag^+ species were identified. Poor activity of Na promoted sample is attributed to absence of suitable amount of ionic silver compounds. However, the synthesized alkali doped materials showed the promotional deNO*x* conversions in the presence of SO_2 and H_2O stream. Among the investigated samples $K–Ag/Al_2O_3$ and $Cs–Ag/Al_2O_3$ exhibited higher NO*x* conversions and thermal stability. The higher SCR of NO*x* was explained by the NO adsorption properties identified from the NO TPD studies.
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1. Introduction

Intensive research has been devoted to the selective catalytic reduction (SCR) by hydrocarbons, mainly on auto-catalyst. The unburnt hydrocarbons or fuels have been proved to be promising candidates as reductants. On the other hand, the potential use of methane as reducing agent in the HC-SCR of nitric oxide is a better alternative in specific cases [1–3]. By which the SCR process can replace the usage of toxic chemicals such as ammonia, urea. Methane is also the main component in natural gas turbine-exhausts and natural gas vehicle exhausts, which required the treatment of an active CH_4-SCR catalyst. In general, the principle barrier to the use of hydrocarbons in oxygen rich environments is the competitive reactions between the reduction of NO*x* and hydrocarbon combustion. In addition, water vapor and sulfur oxides are inevitable in the combustion exhaust of any fossil fuel, which cause the suppression of catalytic activity. Usually, high concentration of water vapor exists in the combustion exhaust of natural gas varying with the air ratio [3]. Sulfur oxides (SO*x*) are typically produced during the combustion of organic sulfur compounds, most of the SO*x* eluted as sulfur dioxide (SO_2). In recent years, the SO*x* concentration in exhaust is reduced to a sub-ppm level, which is resulted from the use of feedstock practically free from sulfur compounds. Never the less, there are still many sources for SO*x*. Therefore, it is still challenging to attain higher activity of CH_4-SCR of NO*x* under H_2O and SO_2 atmosphere.

Currently, various catalysts synthesized by zeolites (ZSM-5, HZSM, FER, and HMOR) [3] and mixed oxide (Al_2O_3, TiO_2, and ZrO_2) with active metals Pt, Rh, Pd, Ir, Co and Cu [3–7] have been reported for the title reaction. However, the performance and durability of these catalysts are still insufficient for practical applications. Most of these catalysts lose activity in the presence of SO_2 and water vapor [8,9]. Among the various catalysts reported for the reaction, metal oxide catalysts would be an alternative. Since Miyadera and Yoshida [10] reported that silver–alumina catalysts exhibited relatively high activity and selectivity for NO reduction to N_2 and moderate resistance to water and sulfur dioxide, many studies have been performed on this catalyst system. Several authors reported that the increase in the carbon number of alkane resulted in an increase in the rate of alkane oxidation to the oxygenated hydrocarbon on the surface as a possible intermediate [11–13]. Therefore, the effects of various hydrocarbons and oxygenated hydrocarbons on the activity of Ag/Al_2O_3 for SCR are studied by many researchers. Relatively few reports are known over CH_4-SCR due to the poor performance of these catalysts even though methane is the chief component of natural gas. Moreover, Ag-based catalyst seems to be advantageous owing to its low cost, high availability, ecological benevolence and stability at high temperatures. Thus, in the

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