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Hydrogen production by ammonia decomposition using Co catalyst supported on Mg mixed oxide systems

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ABSTRACT

Ammonia decomposition for hydrogen production was studied using cobalt catalysts supported on different Mg mixed oxide systems (MgAl, MgCe and MgLa) to elucidate the influence of support composition on the activity of these catalysts. For this purpose three supports of Mg to X ratio (X = Al, Ce or La) equal to two were prepared. These supports were applied to synthesis 5 wt% cobalt samples by impregnation. The catalytic performance was evaluated in the temperature range of 300–550 °C at atmospheric pressure. It was found that 5CMLa-2 (5 wt% Co impregnated on MgLa support with Mg:La = 2:1) has the highest activity among the other catalysts and the decreasing order of NH₃ conversion as follows: 5CMLa-2 > 5CMCe-2 >> 5CMAl-2. Another series of mixed Mg–La oxide supports with different Mg/La molar ratios (Mg/La = 1, 2,3,5,9 and 14) were prepared and impregnated with 5 wt% cobalt. The prepared catalysts were characterized by BET, XRD, TPR, XPS and CO chemisorptions techniques. Investigation of the effect of La content in the mixed oxide support showed that the 5 wt% cobalt with Mg/La ratio 5 catalyst was the most active. This could be attributed to enhance the interaction between Mg and La which leads to suitable basicity for ammonia decomposition reaction. The increase of MgO content creates high surface area, high active metal area and high surface lattice oxygen (i.e. O²⁻). From TPD data the basic sites become stronger in the Mg–La mixed oxide at Mg/La = 5 ratio. 5CMLa-5 (5 wt% Co on MgLa with ratio 5:1) is showing highest activity among all catalysts with other Mg/La ratios. The enrichment in activity of 5CMLa-5 catalyst could be attributed to increase in surface area, metal dispersion, easily reducible Co species and high basicity.

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Introduction

Hydrogen is an important energy carrier, especially for fuel cell applications. However, for most purposes the low volumetric energy density of hydrogen in a compressed gas form makes its storage a difficult problem. This limitation is severe concerning on-board storage, but it is also an obstacle in hydrogen delivery and distribution. Hydrogen's low energy density is perhaps one of the greatest barriers to its implementation in fuel cell vehicles [1]. Ammonia has the largest hydrogen weight fraction of 17.65%. Therefore, it is a potential hydrogen carrier for hydrogen delivery. It can liquefy under mild conditions (ammonia vapour pressure at room temperature is 9.2 bars). It is readily available, exhibits a narrow explosion limit, and decomposes relatively easily without addition of steam or oxygen [2]. For these reasons, ammonia decomposition on metal catalysts has extensively studied as a method for producing very clean hydrogen.

Much research has been devoted mainly to Group VIII metals (Ru, Ni, Ir, Fe, Co, and Rh) or metal carbide/nitrides (MoN_x, VC_x, MoC_x, VN_x, etc.) [3–6]. It has been found that ruthenium is the most active catalyst for ammonia decomposition [6]. However, its high price and limited availability is an obstacle for large-scale applications. Hence developing an affordable and active catalyst for ammonia decomposition is highly desirable. Transition metals such as Fe, Co and Ni are good candidate for this reaction. Unfortunately, the iron system is forming stable nitrides at low temperatures [7]. Although nickel is less expensive than cobalt, Ni catalysts are active at high temperatures [8–10].

Different supported metal catalyst systems have been examined for ammonia decomposition including a variety of supports such as SiO₂, Al₂O₃, TiO₂, ZrO₂, activated carbon, mesoporous and microporous materials, multi walled (MWCNTs), etc. [4,8–10]. Among all tested supports, the MWCNT-supported metal catalyst system has been found to be the most active, and this is attributed to excellent electronic conductivity and a specific pore system [4,11,12]. However, there are some disadvantages in the use of carbon nanotubes as a catalyst carrier in this reaction, e.g. high cost, methanation at temperatures above 550 °C, and weak metal support interaction. Recently, core-shell nanostructures of SiO₂, Al₂O₃, and MgO with different metals like Fe, Co, Ni, and Ru were synthesised and applied as catalysts for ammonia decomposition. While metal nanoparticles of 50–150 nm average size are formed among unique environment, they manifest a certain activity at high temperatures (above 600 °C) [13]. Another study reported that support basicity is a necessity of efficient catalysts for the ammonia decomposition reaction. The stronger the basicity of the support the better the catalyst performance is [4]. The effect of La₂O₃ and CeO₂ as promoters has also been studied. It was found that these promoters enhance catalyst intrinsic activity. However, the metal loading in these catalysts is high and they are active at temperatures over 600 °C [5,14].

The use of mixed oxides as supports may enable catalyst tailoring to attain proper basicity strength. Hydrotalcite-like (HT) compounds are a class of precursors useful for the preparation of catalytically active mixed oxide systems of

wide spectrum of basic properties. The present work is aimed at elucidating the influence of mixed oxide supports prepared from Mg–La, Mg–Ce, and Mg–Al hydrotalcite precursors on the activity of cobalt-based catalysts in ammonia decomposition. Preliminary experiments indicated that the use of Mg–La support was promising for the preparation of very active catalysts. Because of this reason, we decided to study this support in detail by using different Mg/La ratios to prepare catalysts for ammonia decomposition.

Experimental

Catalyst preparation

A series of Mg–X (Al, La, Ce) mixed oxide support materials were prepared by co-precipitation of Mg and X (Al, Ce, La) nitrates under high super saturation conditions using a base mixture of KOH and K₂CO₃ [15]. In a typical synthesis of MgLa support with molar ratio of 2:1, solution A was prepared by dissolving 0.129 mol of Mg(NO₃)₂·6H₂O and 0.0645 mol of La(NO₃)₃·9H₂O in distilled water for a 1 M solution. Solution B was prepared by dissolving 0.453 mol of KOH and 0.1225 mol of K₂CO₃ in distilled water for a 2 M solution. Then solution B was added dropwise to solution A at 60 ml h^{−1} under vigorous stirring at 25 °C and the precipitation continued until pH = 11. Further, the suspension was filtered and the solid residue was washed with distilled water, dried at 120 °C overnight, and calcined at 450 °C for 18 h in air. The prepared material was designated as MLa-2. The same procedure was followed for MgX (Al, Ce) supports with a Mg/X ratio of 2 which were denoted as MAl-2 and MCE-2, respectively.

These supports were impregnated with 5 wt% of cobalt in a rotary evaporator using an aqueous cobalt nitrate solution. After impregnation, the catalysts were dried overnight in an oven at 100 °C and then calcined at 500 °C for 5 h in a nitrogen flow. These catalysts are denoted as 5CMAl-2, 5CMCe-2, and 5CMLa-2.

Following the procedure mentioned above another series of Mg–La mixed oxide catalysts of varying Mg/La mole ratio (1, 2, 3, 5, 9, 14) were prepared and impregnated with 5 wt% Co. The obtained catalysts were designated as 5CMLa-1, 5CMLa-2, 5CMLa-3, 5CMLa-5, 5CMLa-9, and 5CMLa-14, respectively. Aldrich and Fluka chemicals were used to prepare these samples.

Catalyst characterisation

BET surface area of the catalysts was determined by N₂ physisorption at −196 °C using a Quantachrome NovaWin2 apparatus. Prior to experiments the samples were degassed at 300 °C for 4 h under vacuum.

X-ray diffraction (XRD) patterns of the samples were recorded on EQUINOX 1000 Inel (France) using Co K α radiation ($\lambda = 1.789 \text{ \AA}$) in the 10–115° scan range at 40 kV and 30 mA.

Temperature-programmed reduction (H₂-TPR) experiments were performed using a Quantachrome Pulsar automated chemisorption analyser. For this purpose, a 150 mg sample was loaded into reactor and pretreated by a helium flow at 120 °C for 60 min to remove adsorbed water. After

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