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Deactivation of manganese oxide-based honeycomb monolith catalyst under reaction conditions of ammonia decomposition at high temperature

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Abstract

The synthesis of manganese oxide-containing catalysts on honeycomb monolith support and their performance in reaction of ammonia decomposition are described. The catalytic activity of manganese oxide-containing catalysts drops within a temperature range 800–900°C due to a strong interaction of manganese species with the support. Ways of increasing of thermal stability and catalytic activity under elevated temperatures are described. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: High-temperature catalytic ammonia decomposition; Honeycomb monolith; Manganese oxides

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1. Introduction

Coal gasification is an effective process for electric and heat energy production. The composition of hot coal gas produced by coal gasification can vary over a wide range, depending upon the type of gasifier and the type of coal used. The concentration of main compounds varies in the following ranges: H_2 — 29–40 vol.%, CO — 16–65 vol.%, CO_2 — 1–31 vol.%, H_2O — 1–20 vol.%, H_2S and carbonyl — 0.1–1.5 vol.%, and CH_4 — 0–10 vol.% [1]. Small amounts of NH_3 (up to 0.3 vol.%) are also produced during coal gasification [2]. The effective direct utilization of the gases after an integrated gasification combined cycle (IGCC) in a high-temperature turbine is substantially limited, since those gases contain undesirable impurities, first of all, ammonia and hydrogen sulfide. The development of an effective catalytic system for the high-temperature abatement of ammonia via its decomposition to $N_2 + H_2$ and simultaneous H_2S adsorption is the most promising way to solve this problem. Oxides of transition metals are considered as the perspective systems for both processes, manganese oxide being the most promising in view of its high capacity in H_2S adsorption [1] and high activity in ammonia decomposition [3]. Development of the catalysts/sorbents of monolith-type structure makes their industrial application very attractive due to low pressure drop, small dust and attrition sensitivity. In this paper, the

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synthesis and catalytic performance of manganese-based honeycomb monolith catalysts for high-temperature ammonia decomposition is described.

2. Experimental

2.1. Catalysts preparation

Titania-based monolith supports prepared on the base of 64% TiO_2 + 36% Ca- or Na-forms of montmorillonite were used. Ca- or Na-forms of montmorillonite were chosen as a binder to provide absence of defect during drying as well as high surface area and acceptable mechanical strength of the prepared monolith supports. The catalysts were prepared by wet impregnation of monolith supports with aqueous solution of manganese nitrate (2 M) with subsequent drying at 110°C and calcination at 500, 700, 900 and 1000°C. To obtain higher manganese loading, the procedure was repeated. The main characteristics of the monolithic catalysts are given in Table 1.

2.2. Instrumental details

Ammonia decomposition was carried out in a flow reactor in temperature range 400–1000°C and at a space velocity of $1000\,h^{-1}$. The ammonia concentration in feed gas mixture was 1 vol.%, balance helium.

3. Results and discussion

The manganese oxide-containing monolithic catalysts have a rather high activity in ammonia decomposition. At 740°C, the ammonia conversion is more than 80%. A considerable decrease of the activity for the samples with manganese oxide content 5 and 10 wt.% MnO_2 is observed upon their exposure at temperatures above 750–800°C in the reaction mixture. The catalysts containing 15 and 20 wt.% MnO_2 exhibit high conversion at a reaction temperature up to 950°C (Fig. 1).

For catalysts, prepared on monolith containing Na-montmorillonite, an optimal manganese loading of 15 wt.% has been found. The catalytic activity of

Table 1
Properties of monolithic catalysts

Type of support	MnO_2 (wt.%)	T (°C)	S_{BET} (m^2/g)	Phase composition
64% TiO_2 + 36% Na-f[a]	10.3	500	95	TiO_2 (anatase), $D \sim 17\,nm + MnO_2$, $D \sim 60\,nm$
		700	52	$\sim$ 98% anatase + 2% rutile + β-Mn_2O_3 (orthor), $D \sim 40\,nm$
		900	<1	$\sim$ 20% anatase+ $\sim$ 80% rutile + β-Mn_2O_3, $D \sim 50\,nm$
64% TiO_2 + 36% Na-f	15	500	79	TiO_2 (anatase), $D \sim 17\,nm + MnO_2(D_1 \sim 6\,nm + D_2 \sim 20\,nm)$
		700	42	$\sim$ 99% anatase+ $\sim$ 1% rutile + β-Mn_2O_3, $D \sim 40\,nm$
		900	<1	$\sim$ 20% anatase+ $\sim$ 80% rutile + β-Mn_2O_3, $D \sim 50\,nm$
64% TiO_2 + 36% Na-f	20	500	71	TiO_2 (anatase), $D \sim 17\,nm + MnO_2(D_1 \sim 6\,nm + D_2 \sim 20\,nm)$
		700	41	$\sim$ 99% anatase+ $\sim$ 1% rutile + β-Mn_2O_3, $D \sim 40\,nm$
		900	<1	$\sim$ 20% anatase+ $\sim$ 80% rutile + β-Mn_2O_3, $D \sim 50\,nm$
64% TiO_2 + 36% Ca-f	6.8	500	104	TiO_2 (anatase), $D \sim 17\,nm + MnO_2$, $D \sim 6\,nm$
		700	65	$\sim$ 99% anatase+ $\sim$ 1% rutile + β-Mn_2O_3, $D \sim 40\,nm$
		900	<1	$\sim$ 9% anatase+ $\sim$ 91% rutile + β-Mn_2O_3, $D \sim 50\,nm$
64% TiO_2 + 36% Ca-f	15	500	93	TiO_2 (anatase), $D \sim 17\,nm + MnO_2$, $D \sim 5\,nm$
		700	42	Anatase, $D > 30\,nm$ + rutile (trace) + β-Mn_2O_3, , $D \sim 30\,nm$
		900	0.8	Rutile, $D > 50\,nm + MnMn_6(Al)SiO_{12}$[b]
64% TiO_2 + 36% Ca-f	20	500	52	Anatase, $D > 30\,nm + MnO_2$, $D \sim 20\,nm$
		700	8.7	Anatase, $D > 30\,nm$ + rutile (trace) + β-Mn_2O_3, $D \sim 30\,nm$
		900	<1	Rutile, $D > 50\,nm + MnMn_6(Al)SiO_{12}$[b]

[a] Na-f and Ca-f means the pillared clay of montmorillonite-type in Na- or Ca-forms.

[b] Structure, like as $MnMn_6SiO_{12}$ with substitution of part of Mn-cations by Al^{3+} or Si^{4+}.

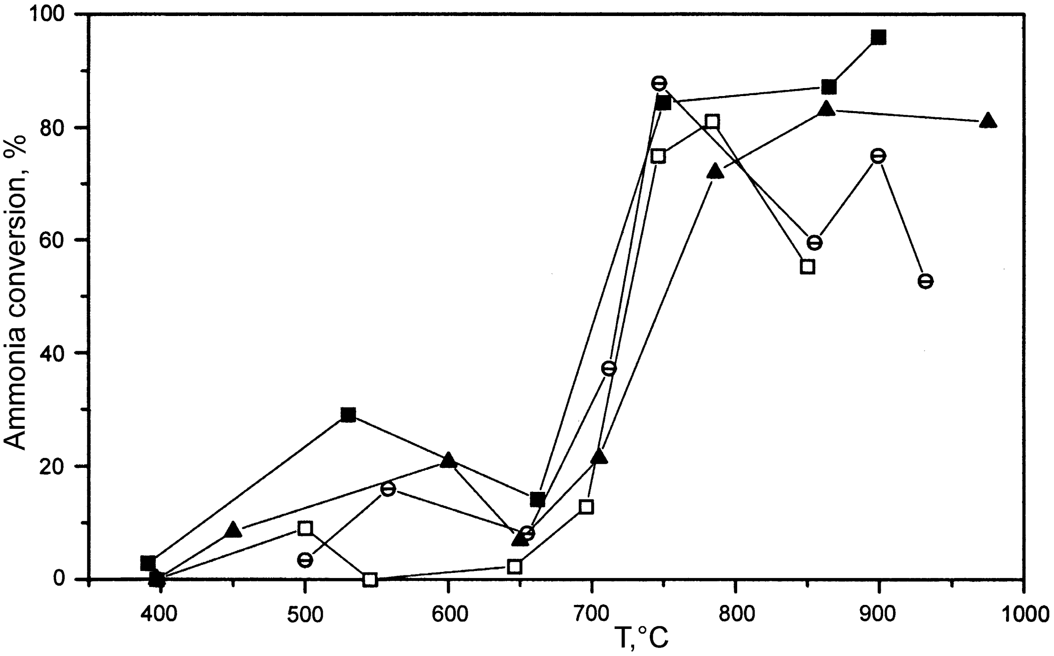

Fig. 1. Initial ammonia conversion vs temperature over $MnO_2/(TiO_2 + Na\text{-}f)$ monolith catalyst with MnO_2 content 5 (⊖), 10 (□), 15 (■), and 20 wt.% (▲). Calcination temperature was 700°C.

the Mn-containing catalysts prepared on the monolith containing Ca-montmorillonite drops only at high temperatures (800–900°C). The catalysts preliminarily calcined at 500 and 700°C lose their activity at reaction temperature of 900°C. The sample preliminary calcined at 900°C demonstrates high conversion only at temperature above 900°C.

Deactivation of the manganese oxide-containing catalysts may be explained by the chemical interaction of Mn oxides and the support materials resulting in the formation of inactive phases of Mn cations with the Ca-montmorillonite (binder) or the titanium oxide.

It should be stressed that the ammonia conversion curves for bulk MnO_2 and Mn_2O_3 are similar in the temperature range 500–700°C. The conversion on these oxides reaches maximum value at 700°C (100%) but decreases to 20% within 2 h operation at this temperature. In accordance with XRD data for both precursors, manganese oxides are reduced into MnO and Mn_3O_4. At reaction temperatures above 700°C, the ammonia conversion curves of bulk MnO_2 and Mn_2O_3 are similar to that of MnO. Hundred percent conversion of NH_3 is achieved at 830°C (Fig. 2).

For the impregnated 15% Mn_2O_3/TiO_2 (anatase) catalysts, the decomposition of NH_3 reaches 100% conversion at 850°C. Operation of this catalyst under reaction mixture at 850°C within 1–2 h results in the transformation of active manganese oxide Mn_2O_3 into $MnTiO_3$. The reduced forms of manganese oxide, such as MnO and $MnTiO_3$, or solid solution on the bases of β-Mn_2O_3 and $MnTiO_3$, which is thermodynamically stable at high temperatures, can be considered as the active components in NH_3 decomposition at temperatures above 700°C.

To elucidate the nature of catalyst deactivation due to the interaction of the catalytically active Mn species with the monolith support, a special series of samples supported on bulk Ca-form of montmorillonite were prepared. After operation at 900°C, catalysts lose their conversion activity to 55%. According to XRD data, the active manganese oxide, β-Mn_2O_3, interacts with the support in forming a solid solution like $MnMn_6SiO_{12}$.

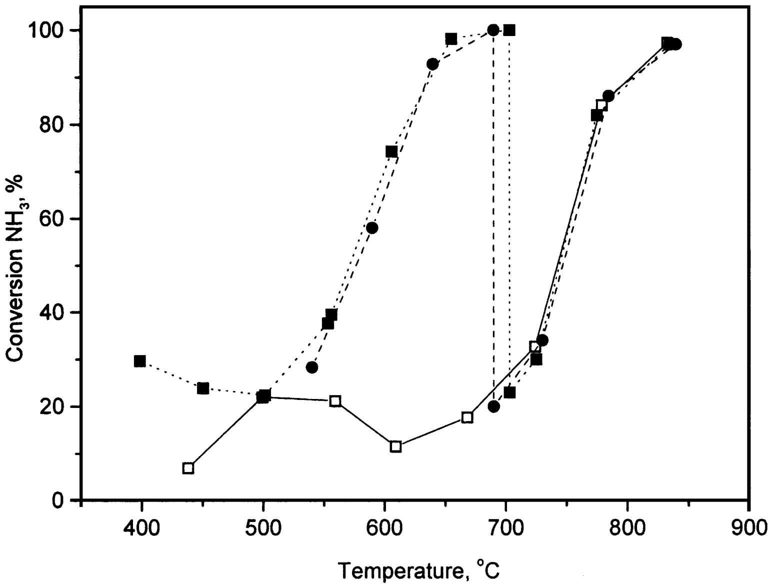

Fig. 2. Initial ammonia conversion vs temperature over bulk MnO_2 (■), Mn_2O_3 (●), and MnO (□).

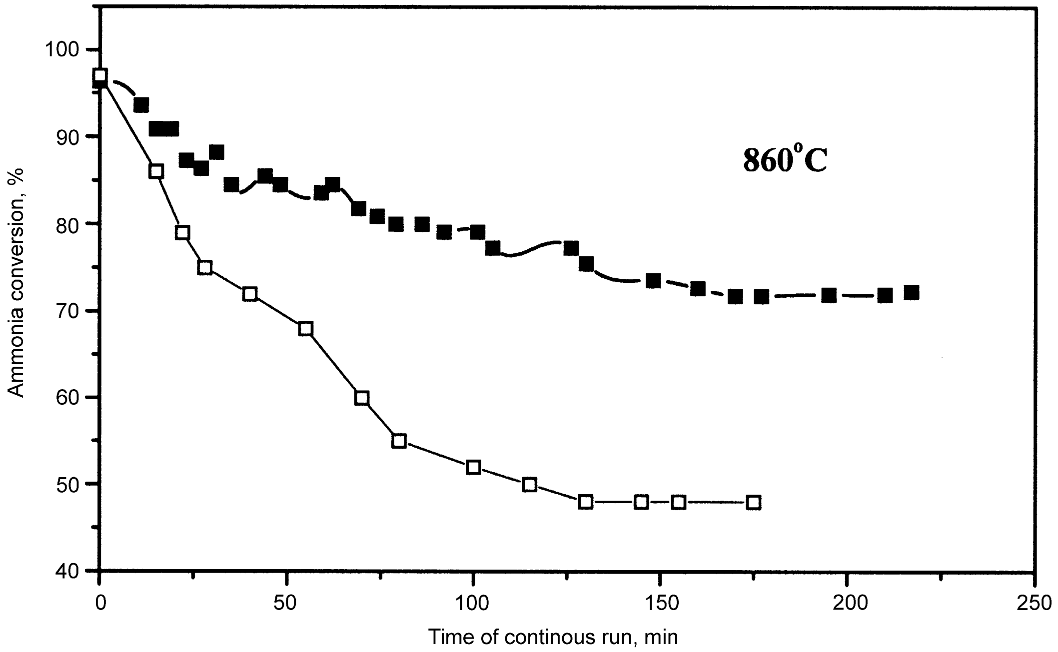

Fig. 3. Stability of (8% Fe_2O_3 + 15% MnO_2)/[64% TiO_2 + 36% Ca-f] (■) and 15% MnO_2/[64% TiO_2 + 36% Ca-f] (□) monolith catalysts upon ammonia decomposition at 860°C.

There are two ways to stabilize the monolithic catalysts: (1) modification of the monolithic support, and (2) introduction of modifying elements into the supported active component.

To stabilize the impregnated manganese-containing catalysts, 4–8 wt.% of iron oxide was introduced into the supported active component. The modified catalyst with 7–8 wt.% of Fe_2O_3 demonstrates high activity and stability under elevated temperatures (Fig. 3).

4. Conclusion

Manganese oxide-based honeycomb monolith catalysts have been synthesized. Their performance in the reaction of high-temperature ammonia decomposition has been studied. Supported manganese oxide catalysts above 700°C show a high initial activity but lose their activity in the temperature range 800–900°C due to a strong interaction with the monolithic support material. The introduction of iron oxide into catalyst matrix improves thermal stability and catalytic performance.

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References

[1] J.P. Wakker, A.W. Gerritsen, J.A. Moulijn, Ind. Eng. Chem. Res. 32 (1993) 139–149.

[2] E.N. Gobina, J.S. Oklany, R. Hughes, Ind. Eng. Chem. Res. 34 (1995) 3777–3783.

[3] Japanese Patent Application JP 08141398 A2 (1996).