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Microcalorimetric studies of the iridium catalyst for hydrazine decomposition reaction

Lin Li[a,b], Xiaodong Wang[a], Xuqun Zhao[a,b], Mingyuan Zheng[a,b], Ruihua Cheng[a,b], Lixing Zhou[a], Tao Zhang[a,*]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, PR China*
[b] *Graduate School of Chinese Academy of Sciences, Beijing 100039, PR China*

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Abstract

Microcalorimetric studies of H_2, NH_3 and O_2 adsorption, as well as the NH_3 decomposition activities evaluation were used to characterize the iridium catalysts for hydrazine decomposition with different supports (Al_2O_3, SiO_2) and iridium contents (1.8, 10.8 and 22.1%). The higher H_2 chemisorption amounts on Ir/Al_2O_3 catalysts than those on the corresponding Ir/SiO_2 counterparts revealed that the strong interaction of iridium and Al_2O_3 led to higher dispersion of iridium on Ir/Al_2O_3 catalysts than on Ir/SiO_2 catalysts. The larger increase in strong H_2 adsorption sites on highly loaded Ir/Al_2O_3 than the corresponding Ir/SiO_2 ones could be attributed to the interaction not only between iridium atoms but also between iridium and Al_2O_3. The microcalorimetric results for NH_3 adsorption showed that no apparent chemisorption of NH_3 existed on Ir/SiO_2 catalysts while NH_3 chemisorption amounts increased on Ir/Al_2O_3 catalysts with iridium loadings, which arose from the interaction of the catalysts support of Al_2O_3 with chloride anion. Both highly dispersed iridium active sites and chloride anion on Ir/Al_2O_3 catalysts could be beneficial to the intermediate NH_3 decomposition in N_2H_4 decomposition. The similar O_2 plots of differential heat versus normalized coverage on Ir/Al_2O_3 and Ir/SiO_2 catalysts could not be due to the metal–support interaction, but to the formation of strong Ir─O bond.

Keywords: Microcalorimetry; Ir/Al_2O_3 catalyst; Hydrazine; Ammonia; Decomposition

1. Introduction

The catalytic decomposition of hydrazine has been an interesting problem because of its many practical applications: gas generators, fuel cells and the most frequently used in satellite attitude control [1–3]. An important aspect of this process is that hydrazine decomposition usually does not follow the fixed chemical stoichiometry. It could be affected by catalysts, temperature and pressure [4,5]. For example, hydrazine decomposes on Ir based catalyst almost exclusively to form N_2 and NH_3 while N_2, H_2 and NH_3 are the products over Rh, Pt and Pd catalysts between 60 and 160 °C. Another interesting aspect of catalytic decomposition of hydrazine is that greatly different from the general commercial noble metal catalyst, iridium based catalysts exhibiting the highest catalytic activity for hydrazine decomposition always have much higher iridium content. Generally, the most efficient catalyst contains about 36 wt.% metallic iridium dispersed on an alumina support [6].

Up to now, only a few papers have been found to characterize the hydrazine decomposition process on Ir/Al_2O_3 catalysts owing to the complexity of the hydrazine decomposition reaction and the particularity of the high-loading Ir/Al_2O_3 catalysts. TEM, UV and XPS were used to probe the iridium species dispersed on the alumina support [7,8] and TPD combined with measuring the binding energy of adsorbed species was used to study the reaction mechanism

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* Corresponding author. Tel.: +86 411 84379015; fax: +86 411 84691570.
E-mail address: taozhang@dicp.ac.cn (T. Zhang).

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of hydrazine decomposition [9–11]. The reaction process of hydrazine decomposition over Ir/Al_2O_3 catalysts still has not been well understood.

In the present paper, microcalorimetry was employed to study the adsorption characteristics of N_2H_4 as well as its decomposition products and intermediate on Ir based catalysts with different iridium contents (1.8, 10.8 and 22.1%) and supports (Al_2O_3, SiO_2) to elucidate the changes in surface structure and the reaction process of hydrazine decomposition on iridium-based catalyst. Microcalorimetric adsorption of O_2 was also performed to detect the effect of O_2 on hydrazine decomposition reaction since oxygen could exist in the application of this reaction.

2. Experimental

2.1. Microcalorimetry

Microcalorimetric measurements of H_2, N_2 and O_2 at 27 °C and NH_3 at 150 °C were performed using a BT 2.15 heat-flux calorimeter. The calorimeter was connected to a gas handling and a volumetric system employing MKS 698A Baratron Capacitance Manometers for precision pressure measurement ($\pm 1.33 \times 10^{-2}$ Pa). The maximum apparent leak rate of the volumetric system was 10^{-4} Pa/min in a system volume of approximately 80 cm^3. The ultimate dynamic vacuum of the system was ca. 10^{-5} Pa.

The procedures for microcalorimetric adsorption have been described in detail elsewhere [12]. Briefly, the sample was heated to 400 °C in 4 h and held at this temperature for 4 h in a special treatment cell using a dynamic high pure H_2 (99.999%) atmosphere. After being reduced, the sample was evacuated for 2 h at 400 °C, then transferred to a side-armed Pyrex and sealed in a Pyrex capsule. The capsule can minimize the possible contamination in the high vacuum system in the course of thermal equilibrium (6–8 h) with the calorimeter. After thermal equilibrium was reached, the capsule was broken by a vacuum feedthrough and ‘fresh’ catalyst was exposed. The microcalorimetric data were then collected by sequentially introducing small doses (1–10 μmol) of probe molecules onto the sample until it became saturated (5–6 Torr). The differential heat versus adsorbate coverage plots and adsorption isothermals can be obtained simultaneously after a typical microcalorimetric experiment.

2.2. Catalysts preparation

The catalysts were prepared by incipient wetness method. The catalyst supports used in this study were γ-Al_2O_3 and SiO_2 with a BET area of 208 and 400 m^2/g, respectively. The precursor was an aqueous solution of $H_2IrCl_6 \cdot 6H_2O$ (AR). After impregnation, the samples were dried at 110 °C for 12 h and calcined in air at 400 °C for 2 h. Iridium catalysts with different iridium loadings of 1.8, 10.8 and 22.1% were obtained.

2.3. Catalysts characterization

The specific surface areas of Ir/Al_2O_3 catalysts and Al_2O_3 were determined by N_2 adsorption at 77 K using a Micromeritics ASAP 2010 apparatus. Before every experiment, the samples were evacuated at 350 °C for 4 h. The chlorine content of Ir/Al_2O_3 catalysts were determined by X-ray fluorescence spectrum using a Philips MagiX spectrometer.

2.4. Test of catalyst activity

NH_3 decomposition activities were evaluated in a fixed-bed continuous-flow micro-reactor. Typically, about 400 mg (0.5 cm^3) of catalyst particle with 20–40 mesh were used and the feedstock was pure NH_3 maintained at a feeding rate of 20 ml/min (GHSV = 2400 h^{-1}). Prior to reaction, the catalysts were reduced in situ in pure hydrogen at 673 K for 2 h and then purged with pure argon. The products of N_2, H_2, and NH_3, were detected by an on-line gas chromatograph (Agilent 6890A with 13X and Chromossorb 103 columns) equipped with a TCD detector.

3. Results and discussion

3.1. N_2H_4 adsorption

Iridium is very active for hydrazine decomposition and it is very difficult to obtain differential heat of N_2H_4 adsorption on iridium based catalyst at room temperature.

3.2. H_2 adsorption

H_2 is not only the product of hydrazine decomposition, but also one of the most frequently used molecules for probing metal active sites of catalysts. Fig. 1a shows the adsorption isotherms of H_2 on the Ir/Al_2O_3 catalysts with different iridium loadings. The shape of the isotherms is in general similar to that of a classical isotherm of Langmuir chemisorption type. The H_2 monolayer uptake is determined by extrapolating the linear part of the isotherm fitted curve to zero pressure. The capacities of hydrogen adsorption are 46, 175 and 260 μmol/g on 1.8, 11.8 and 22.1% Ir/Al_2O_3 catalysts. Obviously, the amount of hydrogen adsorption on Ir/Al_2O_3 catalysts is in direct proportion to the iridium loadings of catalysts. Thus, assuming that hydrogen adsorbs dissociatively on iridium active sites, this result indicates that Ir/Al_2O_3 catalyst with the higher iridium content possesses the more iridium active sites.

The same microcalorimetric measurements for H_2 adsorption on SiO_2-supported iridium catalysts were also performed as comparison. The corresponding adsorption isotherms are shown in Fig. 1b. It can be seen that the capacities of hydrogen adsorption on 1.8, 11.8 and 22.1% Ir/SiO_2 catalysts are 24, 120 and 165 μmol/g, which are much lower than those on cor-

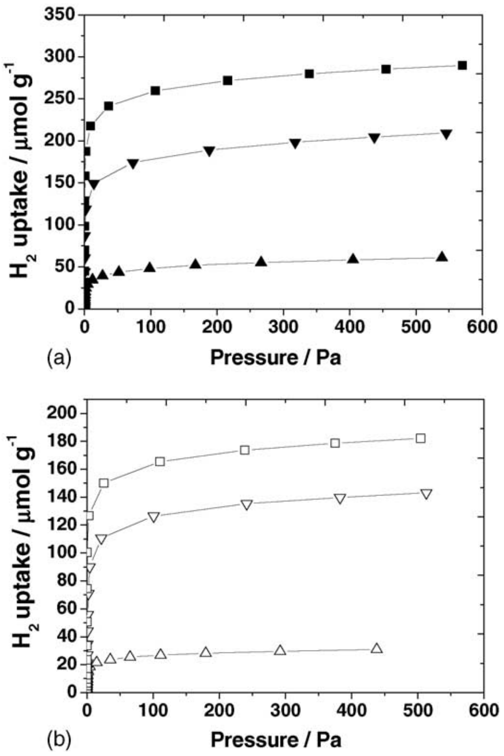

Fig. 1. (a) Isotherms of H_2 adsorption at room temperature on Ir/Al_2O_3 catalysts with different iridium loadings: (▲) 1.8%, (▼) 10.8%, (■) 22.1%. (b) Isotherms of H_2 adsorption at room temperature on Ir/SiO_2 catalysts with different iridium loadings: (△) 1.8%, (▽) 10.8%, (□) 22.1%.

responding Ir/Al_2O_3 counterparts, indicating not only higher dispersion of iridium but also smaller size of iridium crystallite exists on Ir/Al_2O_3 than on Ir/SiO_2. These results imply that there exists a strong interaction between iridium and Al_2O_3 in Ir/Al_2O_3 catalysts, which leads to a better anchoring of iridium on Al_2O_3 than on SiO_2. Thus, Al_2O_3 seems to be a good support for dispersing iridium as iridium loadings increase.

Fig. 2A shows the histograms of the energetic distribution of iridium active sites for H_2 adsorption on Ir/Al_2O_3 catalysts. These histograms were generated by first normalizing the H_2 uptake with the corresponding monolayer uptake on Ir/Al_2O_3 catalysts, then smoothing the differential heat data with a least-squares-fitted polynomial and finally using this polynomial to determine the percentage of active sites on Ir/Al_2O_3 catalysts with a given range of differential heats [13]. It can be seen that although the percentages of iridium active sites contained in the interval of 100–90 kJ/mol are similar among the 1.8, 10.8 and 22.1% Ir/Al_2O_3 catalysts, the ones in the intervals of 90–80 kJ/mol and 80–70 kJ/mol are enhanced greatly with the increase of iridium content at the expense of those in low energetic interval. It suggests that a significant fraction of active sites on the highly loaded Ir/Al_2O_3 catalyst interacts strongly with hydrogen. The same histograms of H_2 adsorption on Ir/SiO_2 catalysts are shown in Fig. 2B. It is interesting to note that although SiO_2 is a neutral support, the percentages of iridium active sites contained in the interval of 90–80 kJ/mol and 80–70 kJ/mol on Ir/SiO_2 catalysts are also increased with increasing iridium loadings, but lower than those on corresponding Ir/Al_2O_3 counterparts. These strongly suggest that not only the interaction between iridium atoms but also the interaction between iridium and Al_2O_3 exists on the high-loading Ir/Al_2O_3 catalysts, which lead to the strong H_2 adsorption sites. Several studies have demonstrated that the hydrogen adatoms produced upon the dissociative adsorption of hydrazine can react with hydrazine to produce ammonia [10,14] through hydrogenolysis reaction of hydrazine ($H_2 + N_2H_4 \rightarrow 2NH_3$). Obviously, the highly loaded Ir/Al_2O_3 catalyst can promote the hydrazine decomposition by hydrogenolysis reaction.

3.3. N_2 adsorption

Generally, iridium is not considered as a metal to adsorb molecular nitrogen. In fact, no differential heat of N_2 adsorption on iridium based catalysts was obtained in our experiment. It is consistent with the N_2-TPD result [10] in the literature.

3.4. NH_3 adsorption and NH_3 decomposition

NH_3 is often used to probe the number and strength of acid sites on catalyst. In hydrazine decomposition reaction, NH_3 is not only the product but also the intermediate. Therefore, the adsorption and decomposition studies of NH_3 on Ir catalysts will help to understand hydrazine decomposition process.

Fig. 3 shows the differential heat versus NH_3 uptake on SiO_2, 10.8% Ir/SiO_2, Al_2O_3 and Ir/Al_2O_3 catalysts. It can be seen that the initial heat and uptake of NH_3 adsorption on both SiO_2 and 10.8% Ir/SiO_2 are very low, suggesting that NH_3 could not adsorb on iridium active sites directly at experiment temperature. But NH_3 adsorption on both Al_2O_3 and Ir/Al_2O_3 produced high initial heat and uptake. It implies that NH_3 adsorption process proceeds mainly on the catalyst support during hydrazine decomposition over Ir/Al_2O_3. It is worthwhile to note that NH_3 uptakes on Ir/Al_2O_3 catalysts increase with iridium contents although the catalysts surface areas decrease (Table 1). Table 1 shows that the chlorine content increases in Ir/Al_2O_3 catalysts with increasing iridium loadings since H_2IrCl_6 was used as precursor in the procedure of the catalysts preparation. So it is reasonable to conclude that the chlorine remained on the catalysts leads to the larger NH_3 uptakes on Ir/Al_2O_3.

Fig. 4 shows NH_3 decomposition activity over Ir/Al_2O_3 and Ir/SiO_2 catalysts. The initial reaction temperature of ammonia thermal decomposition is 600 °C and NH_3 cannot decompose entirely even at 850 °C. Though the initial decomposition temperature of NH_3 over SiO_2 and Al_2O_3 has not been changed as compared to thermal decomposition, slightly higher NH_3 conversion exists over SiO_2 and obviously higher NH_3 conversion exists over Al_2O_3 at the reaction temperature region. This implies that Al_2O_3 exhibits

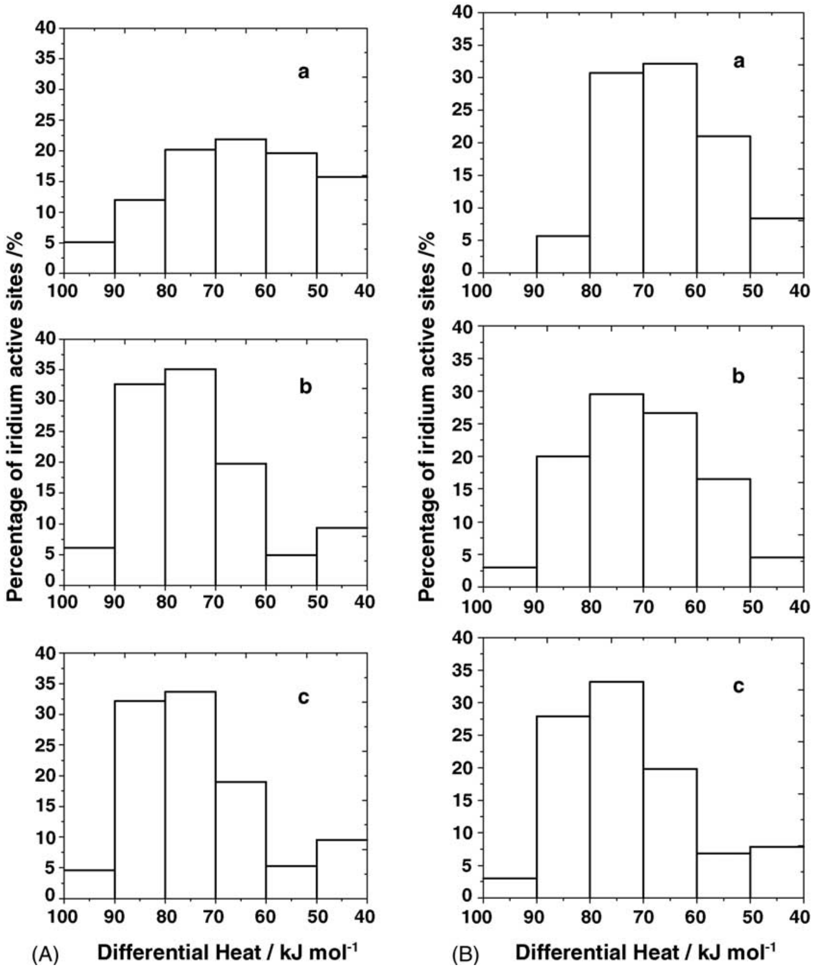

Fig. 2. (A) Histograms of the distribution of site strength for H_2 adsorption on Ir/Al_2O_3 catalysts with different iridium loadings: (a) 1.8%, (b) 10.8%, (c) 22.1%. (B) Histograms of the distribution of site strength for H_2 adsorption on Ir/SiO_2 catalysts with different iridium loadings: (a) 1.8%, (b) 10.8% (c) 22.1%.

certain ammonia decomposition activity. It is worthwhile to note that the initial decomposition temperature of NH_3 is decreased greatly and NH_3 conversions are increased significantly when iridium is introduced into SiO_2 and Al_2O_3.

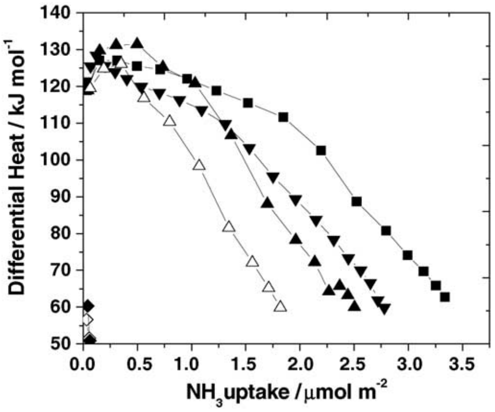

Fig. 3. Differential heat vs. adsorbate uptake for NH_3 adsorption on (◊) SiO_2, (♦) 10.8% Ir/SiO_2, (△) Al_2O_3, and Ir/Al_2O_3 catalysts with different iridium loadings: (▲) 1.8%, (▼) 10.8%, (■) 22.1% at 150 °C.

These results imply that iridium sites are also active center for intermediate NH_3 decomposition in N_2H_4 decomposition reaction. Furthermore, NH_3 conversions on Ir/Al_2O_3 and Ir/SiO_2 catalysts increase with iridium contents, suggesting that higher iridium loadings on iridium catalysts are beneficial to the NH_3 decomposition. Interestingly, NH_3 conversions on Ir/Al_2O_3 catalysts are much higher than those on Ir/SiO_2 counterparts. The microcalorimetric results of H_2 adsorption show that iridium active sites are dispersed better on the support of Ir/Al_2O_3. Furthermore, the microcalorimetric results of NH_3 adsorption indicate that chloride anion in Ir/Al_2O_3 catalysts leads to higher NH_3 uptake. Thus, it

Table 1
BET and chlorine content of Al_2O_3 and Ir/Al_2O_3 catalysts with different iridium loadings

	BET (m^2/g)	Chlorine content
Al_2O_3	208	–
1.8% Ir/Al_2O_3	202	0.896
10.8% Ir/Al_2O_3	190	1.656
22.1% Ir/Al_2O_3	156	1.892

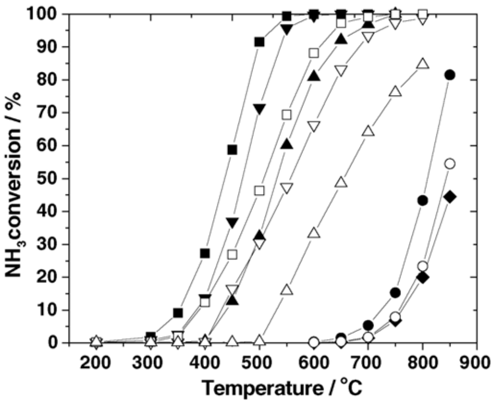

Fig. 4. The decomposition activity of ammonia over Ir/Al_2O_3 catalysts with different iridium contents: (▲) 1.8%, (▼) 10.8%, (■) 22.1%, Ir/SiO_2 catalysts with different iridium contents: (△) 1.8%, (▽) 10.8%, (□) 22.1%, (●) Al_2O_3, (○) SiO_2 and (◆) thermal decomposition.

is obvious that higher NH_3 conversion on Ir/Al_2O_3 catalysts could be attributed to highly dispersed iridium active sites and high chlorine content on Ir/Al_2O_3 catalysts.

3.5. O_2 adsorption

O_2 has been used as probe molecule to study the chemisorption properties of low-loading Ir catalysts [15–18]. In addition, O_2 could exist in the application of hydrazine decomposition. Thus it is desirable to study the adsorption properties of O_2 on highly loaded Ir/Al_2O_3 and Ir/SiO_2 catalysts, as well as the effect of O_2 adsorption towards this reaction. The microcalorimetric results of O_2 adsorption on Ir/Al_2O_3 and Ir/SiO_2 catalysts are shown in Fig. 5a and b. The O_2 saturation uptakes in the calorimetric curves are normalized by dividing the corresponding monolayer uptakes in order to compare the catalysts with different iridium content and dispersion. Different from those of H_2 adsorption on Ir/Al_2O_3 and Ir/SiO_2 catalysts, the normalized differential heat curves of O_2 adsorption on Ir/Al_2O_3 and Ir/SiO_2 catalysts with different iridium loadings are almost the same. All the catalysts show the initial heats of 350 kJ/mol and adsorption heat plateau versus O_2 coverage at 300 kJ/mol up to about 0.8 monolayer. Guil et al. [15,16] also found the similar calorimetric results on low-loading Ir/Al_2O_3 and Ir/SiO_2 catalysts. Obviously, the similar adsorption behavior of O_2 on Ir/Al_2O_3 and Ir/SiO_2 catalysts could not be attributed to the metal-support interaction, but to the formation of strong Ir–O bonds, which restricts the surface mobility of O on iridium; i.e., the oxygen remains on these surface sites where they are first adsorbed. Moreover, the special adsorption behavior of O_2 also implies that O_2 could compete with reactant and intermediate to adsorb on iridium active sites in the course of hydrazine decomposition reaction and further decrease the activity of Ir catalysts in the presence of O_2.

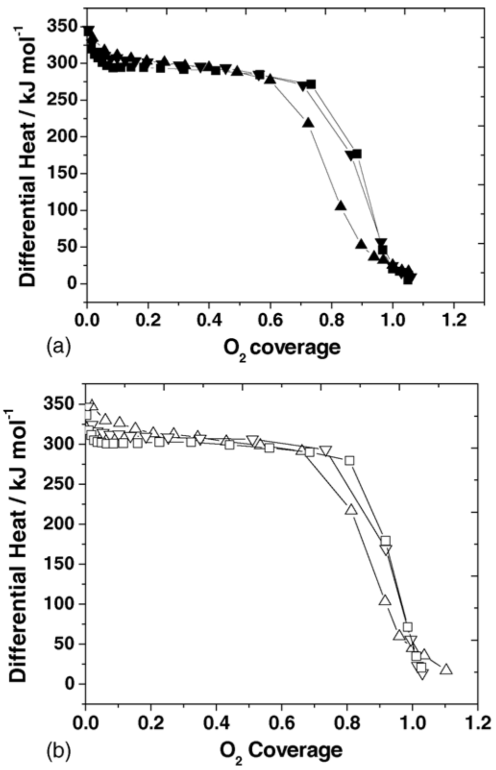

Fig. 5. (a) Differential heat vs. adsorbate coverage for O_2 adsorption on Ir/Al_2O_3 catalysts with different iridium loadings at room temperature: (▲) 1.8%, (▼) 10.8%, (■) 22.1%. (b) Differential heat vs. adsorbate coverage for O_2 adsorption on Ir/SiO_2 catalysts with different iridium loadings at room temperature: (△) 1.8%, (▽) 10.8%, (□) 22.1%.

4. Conclusions

The microcalorimetric results of H_2 adsorption on Ir/Al_2O_3 and Ir/SiO_2 catalysts show that the capacities of H_2 adsorption on Ir/Al_2O_3 catalysts are obviously higher than those on the corresponding Ir/SiO_2 counterparts. It can be attributed to the better dispersion of iridium on Al_2O_3 support, as a result of the strong interaction between iridium and Al_2O_3. Moreover, larger increase in strong H_2 adsorption sites on highly loaded Ir/Al_2O_3 catalysts than on the corresponding high-loading Ir/SiO_2 catalysts could be owing to the interaction not only between iridium atoms, but also between iridium and Al_2O_3 on highly loaded Ir/Al_2O_3.

No apparent chemisorption of NH_3 exists on Ir/SiO_2 catalysts. However, NH_3 chemisorption amounts on Ir/Al_2O_3 catalysts increase with iridium loadings and the largest NH_3 uptake exists the highest loaded Ir/Al_2O_3 catalyst. The increase in NH_3 uptake on Ir/Al_2O_3 catalysts could result from the interaction of Al_2O_3 support with chloride anion. NH_3 conversions are enhanced significantly when iridium is introduced into SiO_2 and Al_2O_3. Furthermore, NH_3 conversions increase with iridium contents. These indicate that iridium is active sites for the intermediate ammonia decomposition in hydrazine decomposition process. Much higher

NH_3 conversions on Ir/Al_2O_3 catalysts than those on Ir/SiO_2 counterparts could be attributed to not only highly dispersed iridium active sites, but also chlorine anion in Ir/Al_2O_3 catalyst.

The plots of differential heat versus O_2 coverage on Ir/Al_2O_3 and Ir/SiO_2 catalysts present almost the same high initial heat and large differential heat plateau, suggesting that the formation of strong Ir–O bonds is responsible for the special O_2 adsorption behavior.

Acknowledgments

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