Al$_2$O$_3$/SiO$_2$ Materials With Bimodal Pore Size Distribution As Support For Heterogeneous Catalysts

LITVYAKOVA Natalya[a], BUGROVA Tatiana[b] and MAMONTOV Grigory[c]

Tomsk State University, Lenin av. 36, Tomsk, 634050, Russia

[a]natlitv93@yandex.ru, [b]749_violet.ru@mail.ru, [c]GrigoriyMamontov@mail.ru

Abstract. The Al$_2$O$_3$/SiO$_2$ materials prepared by impregnation of mesoporous silica with water solution of Al(NO$_3$)$_3$·9H$_2$O were suggested to be used as supports for catalyst of high-temperature catalytic reactions. It was shown that the distribution of Al$_2$O$_3$ component inside wide pores of silica (10-50 nm) occurs with the formation of Al$_2$O$_3$ layer in case of low loading and porous layer or particles, if Al$_2$O$_3$ loading increases. Thus, materials with bimodal pore size distribution were obtained. The Cr-containing catalysts were prepared on the basis of these supports and tested in the process of isobutane dehydrogenation at 540 $^{\circ}$C. It was observed that the activity of the obtained Cr/Al$_2$O$_3$/SiO$_2$ materials was comparable with the one for Cr/Al$_2$O$_3$ catalyst. Thus, the suggested Al$_2$O$_3$/SiO$_2$ materials with unique porous structure are promising to be used as supports for catalysts for high-temperature reactions.

Introduction

At present, the industrial catalysts preparation meets high requirements. The catalysts must possess both high activity and selectivity, be resistant to catalyst poisons, withstand short overheatings, and have high stability, including maintaining of high catalytic activity and granule strength for a long time [1, 2]. The reproducibility of the structure and composition of catalysts along with the costs for their production are no less important. Special attention is given to the porous structure of the catalysts because it determines the catalyst activity, stability, granule strength and other features. The properties of the supported catalysts are known to significantly depend on the support properties.

Alumina (especially γ-Al$_2$O$_3$) is a most widely used support. It has a surface area of 80-300 m^2/g and pore size of less than 8 nm. Silica, having a wider range of the specific surface (50-500 m^2/g) and pore sizes (2-50 nm), is not used as widely as alumina. The disadvantages of Al$_2$O$_3$ support consist in the necessary granulation and the presence of micropores, resulting in the formation of carbon deposits over the catalysts surface during the high-temperature catalytic processes. The formation of carbon deposits on the catalyst surface leads to reduction of catalyst activity. The oxidative regeneration treatment of catalysts is used for removal of the carbon deposits. It results in release of large amounts of gaseous products (mainly CO and CO$_2$), which may be the reason for the destruction of catalyst grains. The use of support with large pores is required to prevent the formation of carbon deposits and provide easier way to anneal the carbon deposits from the catalyst surface. It is well-known that making an Al$_2$O$_3$ support with wide pores is a challenging task.

Typical silica supports have a high specific surface area and pore volume. The pore size of silica can be varied in a wide range. However, the use of silica gel instead of Al$_2$O$_3$ is impossible because of different functional properties of the silica surface.

The purpose of the present work was to create Al$_2$O$_3$/SiO$_2$ supports by modifying silica with alumina. Such support is expected to have porous structure similar to the one of silica (wide pores) and surface properties as those of alumina. A series of Al$_2$O$_3$/SiO$_2$ supports with various Al$_2$O$_3$ loading was prepared, and their porous structure was studied using low temperature N$_2$ adsorption. A series of Cr-containing catalysts on the basis of these supports was prepared and tested in the

process of isobutane dehydrogenation as appropriate catalytic reaction to compare the properties of SiO_2 and Al_2O_3 support and reactions proceeding with the formation of carbon deposits [3, 4].

Experimental

The industrial silica was used as primary support. Silica grains possess necessary strength and porous structure (both high specific surface area and pore volume). Silica was exposed to hydrothermal treatment using an aqueous solution of ammonia in order to increase the pore size [5]. A series of Al_2O_3/SiO_2 supports with Al_2O_3 loading from 5 to 40 % wt. was prepared by incipient wetness impregnation using an aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$. Then the samples were dried at 80 °C for 12 hours and calcined at 500 °C for 4 hours.

The porous structure of the samples was measured by low-temperature (-196 ^oC) nitrogen adsorption using "TriStar 3020" analyzer (Micromeritics, USA). Specific surface area (S_{BET}) was determined using a multipoint BET method to straighten the adsorption isotherm in the range of p/p_o of 0.05-0.30. The pore size distribution plot was obtained using BJH-Desorption method. The samples (100-120 mg) were subjected to vacuum treatment at 200 °C for 2 hours before sorption measurements.

The Cr-containing catalysts were prepared by impregnation of supports, pretreated at 750 ^oC, with H_2CrO_4 and KNO_3 solution. The amount of Cr was calculated taking into account the monolayer coating of supports (5 atoms per nm^2 of support) [6]. The K/Cr molar ratio was 1 to 5. The Al_2O_3 support, prepared by decomposition of $Al(NO_3)_3 \cdot 9H_2O$ at 750 ^oC, was taken to prepare the Cr/Al_2O_3 catalyst as a reference catalyst. The catalytic activity of Cr-containing catalysts was measured in a flow fixed-bed quartz reactor (i.d. = 1.2 cm) at atmospheric pressure. Typical tests were carried out with 0.25-0.3 g of catalyst at 540 ^oC, a feed composition of 15 mol % isobutane/N_2 and a total flow-rate of 30 cm^3/min at STP. The analysis of reactants and products was carried out by gas chromatography equipped with HP-PLOT Q column (60 m, 90 ^oC) to separate the components.

Results and discussion

The isotherms of nitrogen adsorption-desorption and pore size distributions for primary silica support and Al_2O_3/SiO_2 supports are presented in Fig. 1. The hysteresis on the isotherms in the range of 0.5-1.0 p/p_o indicates the mesoporous structure of the supports. The hysteresis from 0.85-1.0 p/p_o is observed for SiO_2 sample corresponding to wide pores with sizes of 10-50 nm, which correlate with pore size distribution (Fig. 1b). The introduction of 5 %wt. of Al_2O_3 to the silica surface leads to the decrease of hysteresis intensity in the range of 0.85-1 p/p_o, which indicates an insignificant reduction of pore volume with the sizes of 10-50 nm (Fig. 1b). The following decrease of hysteresis intensity is observed for samples with Al_2O_3 loading of 10, 20 and 30 % wt. Simultaneously, the appearance of additional hysteresis at 0.5-0.85 p/p_o takes place for these samples. This accounts for the bimodal pore size distribution (Fig. 1b). The presence of wide pores of 10-50 nm can be associated with the initial porous structure of silica support. The pores of 3-8 nm are associated with formation of porous Al_2O_3 phase inside the SiO_2 pores. It is worth notifying that pores of 3-8 nm are not observed for sample with 5 % wt. of Al_2O_3. This specifies the monolayer or thin-layer distribution of Al_2O_3 on the SiO_2 surface.

The properties of porous structure of supports are presented in Table 1. Both insignificant decrease of specific surface area and reduction of pore volume in a row from SiO_2 to $30Al_2O_3/SiO_2$ can be associated with the distribution of Al_2O_3 (particles or porous layer) inside the SiO_2 pores. The decrease of pore volume can be associated with the distribution of Al_2O_3 inside pores of silica, although the porosity of Al_2O_3 (pore < 10 nm) does not provide significant impact in total pore volume (Table 1). Even for the $30Al_2O_3/SiO_2$ sample the impact of Al_2O_3 porosity is only 15 %.

The contribution of small pores of Al_2O_3 to the total surface area is significant. Thus, about 50 % of S_{BJH} value for $30Al_2O_3/SiO_2$ sample is associated with pores of less than 10 nm.
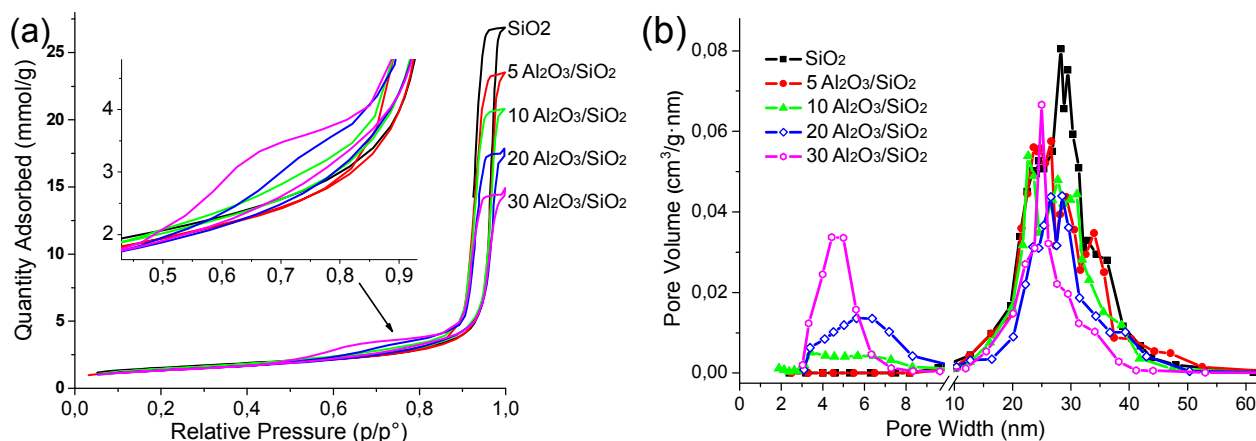

Fig. 1. N_2 adsorption-desorption isotherms (a) and pore size distributions (b) for SiO_2 and Al_2O_3/SiO_2 supports

Thus, the prepared Al_2O_3/SiO_2 supports have bimodal pore size distribution. The formation of Al_2O_3 particles or porous layer takes place inside wide pores of the primary SiO_2 support. The prepared materials possess wide pores of silica and surface properties of alumina.

Table 1. The properties of supports

Sample	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	$S_{BJH-Des.}$ (m^2/g)	pore < 10 nm*		pore > 10 nm*	
				V (cm^3/g)	S (m^2/g)	V (cm^3/g)	S (m^2/g)
SiO_2	119	0.93	134	0.000	0	0.931	134
$5Al_2O_3/SiO_2$	111	0.81	122	0.000	0	0.811	122
$10Al_2O_3/SiO_2$	114	0.72	126	0.027	20.8	0.693	105
$20Al_2O_3/SiO_2$	104	0.62	124	0.061	43.5	0.560	80.1
$30Al_2O_3/SiO_2$	104	0.52	137	0.078	68.3	0.442	68.5

* BJH-Desorption method

To study the effect of textural properties of the prepared supports on the catalytic activity a series of Cr-containing catalysts was prepared. The SiO_2, Al_2O_3 and a series of Al_2O_3/SiO_2 supports with Al_2O_3 loading of 5 (close to 1 monolayer), 20 and 40 % wt. were taken for the preparation of Cr-containing catalysts. Pore size distributions of supports, calcined at 750 ^oC, are presented in Fig. 2a. SiO_2, $5Al_2O_3/SiO_2$ and $20Al_2O_3/SiO_2$ supports have wide pores (10-45 nm) and high pore volumes of 0.62-0.93 cm^3/g (see Table 2). The $40Al_2O_3/SiO_2$ support mainly has pores of 2-10 nm due to high loading of Al_2O_3. The contribution of wide pores (10-40 nm) in total pore volume and surface area is not predominant for this sample. The porous structure of Al_2O_3 support differs from those of SiO_2 and Al_2O_3/SiO_2 supports. Al_2O_3 has the same surface area ($S_{BET} = 110$ m^2/g, Table 2) and low pore volume (0.11 cm^3/g). That associates with the small pore size (less than 5 nm, Fig. 2a). On the basis of comparison of Al_2O_3 and Al_2O_3/SiO_2 supports it may be concluded that primary SiO_2 support provides formation of Al_2O_3 with wider pores (2-10 nm). This is a crucial point for catalysis, since the formation of carbon deposits usually takes place in micropores (less than 2 nm). All prepared Al_2O_3/SiO_2 supports have pores of more than 3 nm (Fig. 1b and Fig. 2a).

The Cr loading was calculated according to the monolayer coverage (5 atom/nm^2) and was 4.40-5.53 % wt. (Table 2). The catalytic activity of the prepared Cr-containing catalysts was tested in the

reaction of isobutane dehydrogenation. The activity denoted as the rate of isobutane conversion (mmol/min) per mass of chromium presented in Table 2 and Fig. 2b. The catalyst on the base of the SiO_2 support has shown the lowest activity. This can be due to the formation of large Cr_2O_3 particles on the SiO_2 surface, which was characterized with the low activity in dehydrogenation of olefins [6, 7]. The isobutene selectivity for this catalyst was only 79.5 %. This means that the formation of non-selective species took place on the catalyst surface. The high yield of C_1-C_3 hydrocarbons as a result of cracking for Cr/SiO_2 catalyst was observed.
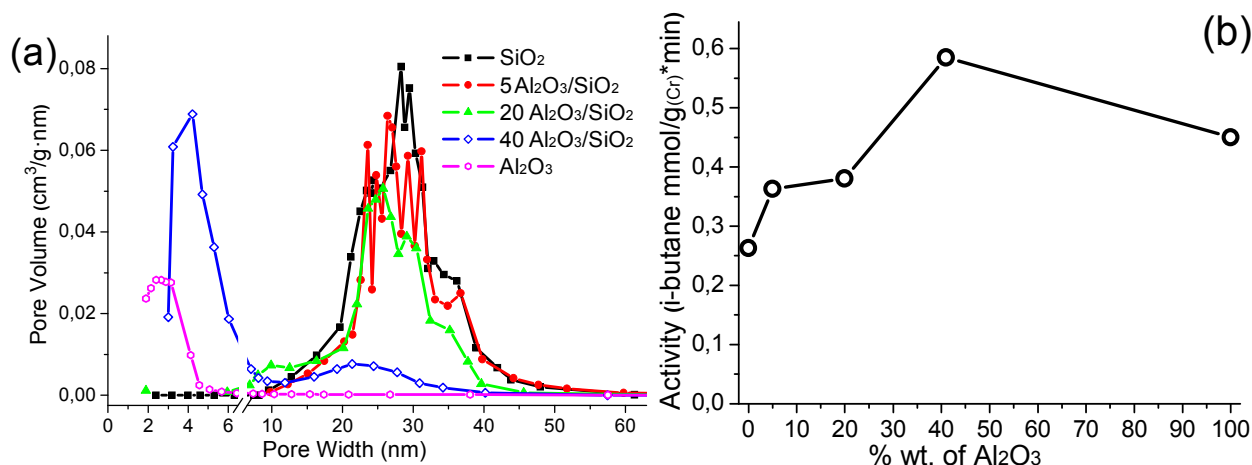

Fig. 2. Pore size distributions of supports calcined at 750 ^{o}C (a) and catalytic activity of Cr-containing catalyst with different Al_2O_3 loading (b)

Cr/Al$_2$O$_3$ catalyst has shown a significantly higher activity in comparison with the one of Cr/SiO$_2$ sample due to the stabilization of Cr(VI) species by Al$_2$O$_3$ surface. The reduction of Cr(VI) species either caused by pretreatment or occurred in the actual course of the catalytic process led to the formation of Cr_2O_3 small clusters which participate as an active species in the dehydrogenation reaction [6]. The activity of Cr/5Al$_2$O$_3$/SiO$_2$ and Cr/20Al$_2$O$_3$/SiO$_2$ samples was higher than the one of Cr/SiO$_2$ catalyst and slightly lower than the one for Cr/Al$_2$O$_3$ catalyst. Therefore the stabilization of Cr-containing compounds was due to the Al$_2$O$_3$ component mainly. Small amount of Cr-containing component can be stabilized by the free surface of SiO$_2$ support what leads to the decrease of both the Cr_2O_3 dispersion and total catalytic activity. It is noteworthy that the selectivity towards the isobutene formation for Cr/5Al$_2$O$_3$/SiO$_2$ and Cr/20Al$_2$O$_3$/SiO$_2$ catalysts was similar to the one for Cr/Al$_2$O$_3$ catalyst (Table 2). These results confirm the stabilization of the main part of Cr-containing species by Al$_2$O$_3$ surface and practically complete the coating of SiO$_2$ surface by Al$_2$O$_3$ layer (even in case of 5Al$_2$O$_3$/SiO$_2$ support).

Table 2. The properties of Cr-containing catalysts

Sample	Characteristics of support		Cr loading (% wt.)	Activity (i-butane mmol per g of Cr in min)	i-butene selectivity (%)
	S_{BET} (m^2/g)	V_{pore} (cm^3/g)			
Cr/SiO$_2$	119	0.93	5.14	0.26	79.5
Cr/5Al$_2$O$_3$/SiO$_2$	106	0.73	4.66	0.36	94.0
Cr/20Al$_2$O$_3$/SiO$_2$	102	0.62	4.40	0.38	94.1
Cr/40Al$_2$O$_3$/SiO$_2$	132	0.36	5.53	0.59	97.2
Cr/Al$_2$O$_3$	110	0.11	4.75	0.45	94.1

The highest activity and selectivity were observed for $Cr/40Al_2O_3/SiO_2$ catalyst. This may be specified by the porous structure of $40Al_2O_3/SiO_2$ support with the highest S_{BET} and the well-defined bimodal pore size distribution (Fig. 2a). Wide pores of 10-40 nm provide an effective transport of reagents and reaction products from the catalyst surface. Pores of 2-10 nm provide enough surfaces for the active component stabilization. These pores are not too small (in comparison with those for Al_2O_3 support) to prevent the transport of reagents or to participate in the formation of carbon deposits.

Summary

Thus, Cr-containing catalysts on the base of Al_2O_3/SiO_2 supports were characterized by comparable or higher activity with respect to Cr/Al_2O_3 sample. The modifying of SiO_2 by Al_2O_3 provides the formation of the specific porous structure with the bimodal pore size distribution and surface properties which were required for stabilizing the Cr-containing component in the active state. Silica modified with alumina can be considered as a promising support for catalysts used in high temperature reactions occurring with the formation of carbon deposits. The variation of porosity of such materials allows creating catalysts with high activity and stability.

Acknowledgements

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