Development of catalyst system for selective combustion of hydrogen

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Abstract

The selective catalytic combustion of hydrogen in ion-exchanged ZSM-5 was investigated at 823 K and one atmosphere in this research. The results of TPR and hydrogen combustion in MeZSM-5 (Me represents the exchanged metal ion) showed that the sequence of reducibility following the order: CuZSM-5>FeZSM-5>NiZSM-5, was the same as that of reaction activity. It is concluded that, the greater the reducibility of these catalysts, the higher the catalytic activity for hydrogen combustion. The method of chemical vapor deposition of silicon alkoxide on CuHZSM-5 was used to modify the catalyst pore opening size, and to prepare a series of novel catalysts (SiCuHZSM-5). From the adsorption measurements, and the combustion of a reactant mixture (containing isobutane, hydrogen and air) over these catalysts, it was demonstrated that some SiCuHZSM-5 possessed reactant shape selectivity due to an effective pore blocking. Therefore, during combustion reactions, hydrogen was selectively oxidized within the ZSM-5 pores containing copper ion catalysts; in contrast, isobutane was not, because of a diffusion limitation into the pores. © 1997 Elsevier Science B.V.

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1. Introduction

In recent years, the usage of unleaded gasoline is definitely becoming a popular trend as a result of global environmental protection. Therefore, the modification of gasoline formulation [1,2], including the reduction of the contents of butanes, benzenes, aromatics, olefins, lead and the increase of oxygenates such as ethers (methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME)), is considered carefully by many

countries. The primary oxygenate used is MTBE, although other oxygenates including ETBE and TAME are also used. According to a report [3], the worldwide MTBE annual capacity amounted to nearly 14 million metric tons (MMmt) in 1992 and is projected to increase to over 24 MMmt in 1997. The oxygenates MTBE and ETBE are produced by the reaction of methanol/ethanol with isobutylene [4]. Therefore, the demand of isobutylene rose dramatically in recent years.

The commercialized process for the production of isobutylene is mainly from *n*-butane; the process is composed of two series of reaction units. At first, *n*-

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butane is isomerized to isobutane in the isomerization units. Then, isobutane is dehydrogenated to isobutylene in the dehydrogenation units. Because the reaction is endothermic, the dehydrogenation unit is generally constituted by several adiabatic reactors arranged in series, between which heat exchangers are used to raise the reaction temperature at each reactor inlet. Nevertheless, the production rate of isobutylene is still limited by the low equilibrium conversion of dehydrogenation. Recently, researchers attempted to design membrane reactors [5,6], which can remove hydrogen from the product stream, in order to enhance the reaction rate of isobutane to isobutylene. However, several problems are encountered in such a membrane reactor: the big capital cost for the construction of new membrane reactors for dehydrogenation reaction, and low hydrogen permeation rate in the membrane [6] which in turn would boost the reactor size and cost. On the other hand, without building new reactors, the production rate of isobutylene can be improved in the present commercialized process if only the hydrogen product in the reactors can be oxidized to water by selective catalytic combustion. There are two advantages for the selective hydrogen combustion: (1) the equilibrium conversion of isobutane can be promoted because of the removal of hydrogen produced in the reactors; (2) the heat of hydrogen combustion can be used for the endothermic dehydrogenation reaction, which can reduce the load of the heat exchangers.

In the past, selective oxidation of hydrogen was investigated by O'Hara et al. [7] in order to enhance the production rate of styrene from ethylbenzene dehydrogenation. Platinum supported on a porous inorganic support, e.g. alumina, was used to catalyze the oxidation of hydrogen product. Nevertheless, the selective catalytic combustion of hydrogen was not satisfactory because about 8% of ethylbenzene was also combusted under the reaction conditions investigated.

In this work, we attempted to develop novel catalysts which can be applied to the selective combustion of hydrogen in the isobutane dehydrogenation process or the other dehydrogenation processes. The oxidation would occur in the pores of ZSM-5 zeolite, which supports metal ions as combustion catalysts. Following the methods developed by Niwa et al. [8–12] and Wang et al. [13], we designed catalysts where com-

bustion reactant shape selectivity will be controlled by reducing the pore mouth of ZSM-5 by chemical vapor deposition of silicon alkoxide. Only molecules as small as oxygen and hydrogen can be allowed into ZSM-5 pores for a combustion reaction; in contrast, molecules as large as isobutane cannot be allowed. Therefore, we will report a development of novel catalysts which can be applied to the dehydrogenation process for the selective catalytic combustion of hydrogen.

2. Experimental

2.1. Catalysts

Commercial NH_4ZSM-5 (AdvChem Laboratories, Inc.) of SiO_2/Al_2O_3 equal to 51 was used for the preparation of NaZSM-5, which was ion exchanged in 1 M of sodium nitrate solution (1 g of NH_4ZSM-5 per 100 ml of solution) at room temperature for 8 h. During the preparation, the pH of the solution was controlled at 9 by adding 0.5 M of sodium hydroxide solution. FeZSM-5, NiZSM-5 and CuZSM-5 (designated MeZSM-5, Me=Fe, Ni or Cu) were prepared by ion exchange of NaZSM-5 in 0.01 M of aqueous solution (1 g of NaZSM-5 per 100 ml of solution) of $Fe(NO_3)_3 \cdot 9H_2O$ (Riedel-DeHaën), $Ni(NO_3)_2 \cdot 6H_2O$ (Janssen Chimica) or $Cu(NO_3)_2 \cdot 3H_2O$ (Riedel-DeHaën) at room temperature for 12 h. Similarly, CuHZSM-5 was prepared by ion exchange of NH_4ZSM-5 in 0.1 M of copper nitrate solution.

2.2. Chemical vapor deposition

CuHZSM-5 catalysts were modified by chemical vapor deposition (CVD) in a continuous flow system which was similar to the apparatus used by Niwa et al. [14,15]. In general, 0.5 g of CuHZSM-5 was placed on a bed fixed with glass-wool in the CVD reactor. After the catalyst had been pretreated in a nitrogen flow at 673 K for 4 h, the reactor temperature was reduced to 593 K. The saturated vapor of tetramethyl orthosilicate (TMOS) maintained in a saturator at 273 K was brought into the reactor and contacted with the catalyst at 593 K for a prescribed time in a stream of nitrogen. The total flow rate of TMOS and nitrogen was 50 ml/min. After the deposition, the deposited catalyst was

calcined in situ by a 50 ml/min air at 673 K for 4 h. Then, the catalyst was recalcined in atmosphere at 823 K for 4 h. The amount of deposited SiO_2 can be controlled by choosing the time for deposition of TMOS.

2.3. XRD, metal loading and BET surface area

The XRD patterns were taken using a MAC Science Diffractometer MXP-3 with Cu K_α radiation in order to examine the structure and the crystallinity of zeolites. The metal loading of each sample, which was dissolved in 5% HF solution, was determined by a GBC 906 atomic absorption unit. The BET surface area was measured by an ASAP 2000 Surface-Area Pore-Volume Analyzer; before the measurement, each sample was pretreated at 623 K for 15 h until the pressure of each sample tube was below 10 μm Hg.

2.4. Temperature-programmed reduction

Reduction and oxidation properties of MeZSM-5 were characterized by temperature-programmed reduction (TPR). The experiments were carried out in a flow system of which the schematic diagram was described previously [16]. The temperature was monitored by a K-type thermocouple in a quartz thermowell located at the center of the catalyst bed. The reduction process was monitored by a TCD detector. A 0.1 g amount of each zeolite sample was contained in a quartz reactor tube. Prior to TPR measurements, each sample was pretreated in a 30 ml/min flow of air at 823 K for 4 h. The samples were then cooled to 313 K and the system was flushed in a 30 ml/min flow of nitrogen. The first TPR measurement was made with a 30 ml/min flow of 10% hydrogen in nitrogen, and the temperature of reactor was raised at a rate of 10 K/min from 313 to 823 K. Reoxidation of the reduced sample after the first TPR measurement was carried out in air at 823 K for 4 h; then the second TPR measurement was taken following the same steps as the first TPR.

2.5. Adsorption of nitrogen and isobutane

The adsorption isotherms of nitrogen and isobutane were measured by an ASAP 2000 Surface-Area Pore-Volume Analyzer. The pretreatment of each sample followed the same steps as those for BET surface area

measurement. The adsorption isotherm temperatures of nitrogen and isobutane were 77 and 273 K, respectively.

2.6. Catalytic combustion of hydrogen in air

The activity measurement for the catalytic combustion of hydrogen was carried out in a continuous flow fixed-bed reactor. The activity values of various catalysts were compared on the basis of the same metal loading (mole base). About 0.2 g of each sample was packed in a quartz tube. Before each reaction test, the sample was pretreated in a 25 ml/min flow of air at 823 K overnight. Activity was measured with a flow mixture composed of 2 ml/min of hydrogen and 98 ml/min of air at the reactor inlet. Reaction conditions were maintained at 823 K and one atmosphere. The reactants and products were analyzed by a gas chromatograph (Chinese Chromatograph 8700T) with nitrogen as a carrier gas. A 1.9 m Molecular Sieve 5A column (1/8 in. o.d., SS, Supelco Inc.) was used for the separation of H_2 and O_2.

2.7. Selective catalytic combustion of hydrogen/isobutane/air

Selective combustion reactions were carried out in the same reactor as catalytic combustion of hydrogen in air. The reactant mixture was composed of 2 ml/min of hydrogen, 2 ml/min of isobutane and 96 ml/min of air. The other reaction conditions were the same as those for the catalytic combustion of hydrogen. Hydrocarbons in the product stream were analyzed by a Shimadzu GC 14A with a SP1700 column. Argon was the carrier gas.

3. Results and discussion

3.1. Metal loading, BET surface area and XRD of MeZSM-5

The metal loading and BET surface areas of each sample are listed in Table 1. It can be observed that, after ion exchanges at room temperature, the loadings of Fe and Cu ions in FeZSM-5 and CuZSM-5 were about 1 wt%, which corresponded to 32.6% and 32.3% full exchange capacity of NaZSM-5. Never-

Table 1
Metal loading and BET surface area of zeolite catalysts

Catalysts	Metal loading			Surface area (m^2/g)
	Na	Transition metal		
	wt%	wt%	% of exchangeable sites[a]	
NaZSM-5	1.27	—	—	431
FeZSM-5	0.08	0.93 (Fe)	32.6 (Fe)	454
NiZSM-5	0.44	0.43 (Ni)	14.3 (Ni)	444
CuZSM-5	0.11	1.05 (Cu)	32.3 (Cu)	441
ICu/silicalite[b]	—	1.01 (Cu)	—	451

[a]: Al loading in ZSM-5 is 1.38 wt%.
[b]: Prepared by the incipient wetness impregnation.

theless, the loading of Ni ion in NiZSM-5 was only
0.43 wt%, even though NaZSM-5 was exchanged
three times in 0.01, 0.01 and 0.1 M nickel nitrate
solutions (pH~5.5), which corresponded to only
14.3% full exchange capacity of NaZSM-5. This
was apparently due to the nickel ions existing as large
tetrameric polyoxo cations in solutions at pH>3.5;
such cations encountered high diffusion resistance
for ion exchange within ZSM-5 pores [17]. The
BET surface areas of MeZSM-5 catalysts were
approximately equal to 450 m^2/g; such areas were
no less than the surface area of NaZSM-5. Moreover,
XRD patterns of MeZSM-5 were similar to that of
ZSM-5. Both suggest that MeZSM-5 maintained good
crystallinity after ion exchange processes.

3.2. TPR of MeZSM-5

The first TPR profiles of MeZSM-5 after oxidation
in air at 823 K for 4 h are shown in Fig. 1; the second
TPR profiles after reoxidation of the reduced samples
(from the first TPR) at 823 K for 4 h were also
measured. It was observed that the first TPR curves
were the same as the second TPR curves for most of
the MeZSM-5 samples, except that NiZSM-5 pos-
sessed a reduction band at 654 K in the first TPR and
this band disappeared in the second TPR. The differ-
ence was owing to some reduced nickel oxide which
could not be reoxidized at 823 K. FeZSM-5 showed a
broad reduction band at a temperature between 500
and 750 K; this band possessed a T_{max} at about 668 K
and was similar to that published by Kaliaguine et al.
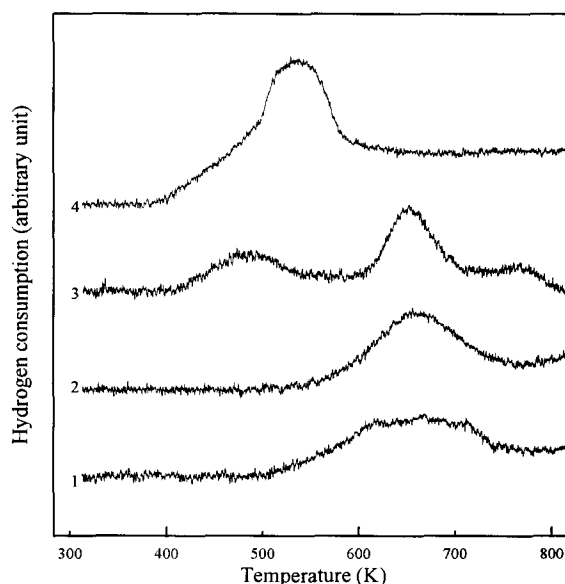[18]. They assigned the band as being from the

Fig. 1. TPR profiles of MeZSM-5 catalysts after calcination in air
at 823 K for 4 h: (1) FeZSM-5; (2) NiZSM-5; (3) CuZSM-5; (4)
ICu/silicalite.

reduction of Fe^{3+} to Fe^{2+}. Our calculation of band
area in Fig. 1 agrees with the conclusion that it was
caused by reducing Fe^{3+} to Fe^{2+}. ICu/silicalite pre-
pared by impregnation method had a reduction band at
536 K with a shoulder at lower temperature, which
was the same as the TPR band of impregnated Cu/
ZSM-5 studied by Lee et al. [19]. The shoulder in ICu/
silicalite was from the reduction of CuO to Cu^+ and
the main band was from that to Cu^0. However, two
major bands at 483 and 651 K were observed in the

TPR profiles of copper-exchanged CuZSM-5. The first band, which appeared at a position similar to that of the shoulder from ICu/silicalite, was apparently due to the reduction of Cu^{2+} to Cu^+. The second band was close to the reported reduction temperature (i.e. 673 K) from Cu^+ to Cu^0 [20]; moreover, we noticed that a shoulder around 760 K was on the second band, which indicates the reduction of Cu^+ at different sites of ZSM-5. On the other hand, two reduction steps of Cu^{2+} to Cu^+ and Cu^+ to Cu^0 in CuZSM-5 can be further demonstrated from the ratio (which was close to 1) of the first TPR band area to the second band area. Two similar reduction steps were also observed in X-type zeolite by Mahoney et al. [21] and in Y-type zeolite by Jacobs et al. [22].

According to the reduction temperatures of MeZSM-5 in this research, the order of reducibility is CuZSM-5>FeZSM-5>NiZSM-5. This sequence is the same as that for X-type zeolites containing transition metal ions of Cu, Fe and Ni [21]. Furthermore, the reducibility of ICu/Silicalite, which is close to CuZSM-5, is also higher than those of FeZSM-5 and NiZSM-5.

3.3. Combustion of hydrogen over MeZSM-5

The catalytic activities of MeZSM-5 for hydrogen combustion (based on the same mole number of metal ions in MeZSM-5) were examined at 823 K and one atmosphere. The results are shown in Fig. 2(a). It can be observed that the activities of MeZSM-5 were in the order: CuZSM-5>FeZSM-5>NiZSM-5. This order is in agreement with the orders in X-type and Y-type zeolites [21,23]. In those papers, they correlated the reaction activity with the content of reactive oxygen presented in Me–O–Me bridges. It was proposed that such Me–O–Me bridges were active centers for hydrogen oxidation on zeolites containing transition metal ions. The reason that CuX and CuY catalysts exhibit higher activity than the other transition metal catalysts is because the Cu–O–Cu bridges possess the partially covalent character of bonding. Me–O–Me bridges existing in zeolites were demonstrated by Iwamoto et al. [24] using TPD of oxygen. They observed that NiY possessed no oxygen desorption, in contrast to the desorption of extra framework oxygen from FeY and CuY zeolites. Therefore, the activity sequence of MeZSM-5 in this work may be due to the reactive
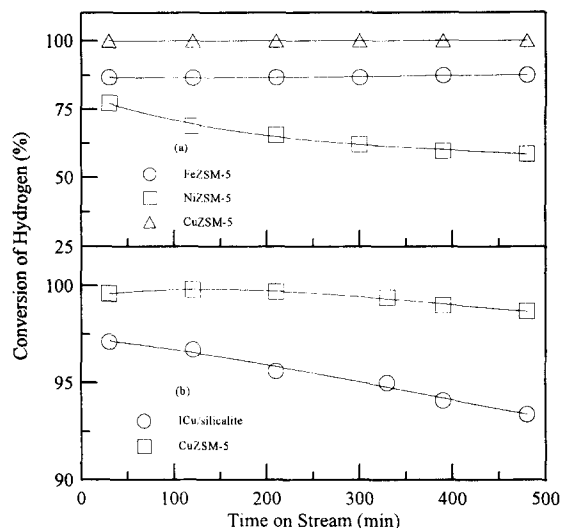

Fig. 2. Hydrogen combustion at 823 K, flow rate of H_2=2 ml/min, flow rate of air=98 ml/min, total pressure=1 atm: (a) over MeZSM-5 catalysts, the amount of transition metal=3.69× 10^{-5} mole per catalyst; (b) over ICu/silicalite and CuZSM-5 catalysts, the amount of copper=7.40×10^{-6} mole per catalyst.

oxygen in ZSM-5 pores. Moreover, the severe deactivation of NiZSM-5 on time stream can be explained from previous TPR results that part of the reduced nickel ions in ZSM-5 could not be reoxidized, so the reduced nickel in ZSM-5 during hydrogen combustion could not act as catalysts for hydrogen oxidation any longer.

The theory of reactive oxygen in MeZSM-5 can also be suggested from the reducibility sequence obtained in our TPR work. We found that the more the reducibility (easier to release oxygen) of the catalyst was, the higher the catalytic activity for hydrogen combustion was. Similar correlations were also observed in the studies of X-type and Y-type zeolites [21,23]. These demonstrate that hydrogen combustion in copper, iron or nickel exchanged zeolites proceeds through a reduction (release oxygen) and oxidation (adsorb oxygen) cycle. Because the reaction activity is well correlated to the reducibility from TPR, the rate limiting step of hydrogen combustion is the reduction of metal ions by hydrogen. In all the activity measurements calculated from this research, CuZSM-5 exhibited a higher hydrogen combustion activity than any other catalyst. Therefore, it was used for the later CVD studies and selective combustion studies. Moreover,

ICu/Silicalite prepared by impregnation also exhibited high activity (however, less than CuZSM-5), as shown in Fig. 2(b).

3.4. Deposition of silica on CuHZSM-5

A series of SiCuHZSM-5 samples loaded with different amounts of SiO_2 on CuHZSM-5 by CVD method were prepared in this research. Cu loadings in CuHZSM-5 and SiCuHZSM-5 measured by atomic absorption were used as a base to calculate the amount of SiO_2 deposited on each sample, because the exchanged Cu ions per weight of HZSM-5 of each sample should not be changed before and after CVD. It was found from the results of AA that Cu loading per weight of sample decreased with the increase of deposition time, owing to the weight increase of SiO_2 deposited; and the weight of sample per Cu increased with the deposition time. Therefore, the amount of SiO_2 deposited per Cu on each SiCuHZSM-5 sample can be calculated from the difference of sample weight per Cu between SiCuHZSM-5 and CuHZSM-5, and can be converted to the amount of deposited SiO_2 per weight of CuHZSM-5 by the product of (deposited SiO_2 per Cu) and (Cu per weight of CuHZSM-5). It can be found in Table 2 that the weight of deposited SiO_2 per gram of CuHZSM-5 increased with the increase of deposition time. The deposition rate of SiO_2 by chemical vapor deposition of TMOS was higher in the CVD period of 2–10 h and was lower in the period of 10–40.5 h.

3.5. Control of the pore-opening size

In order to clarify the reduction of the pore-opening size by SiO_2 deposition, adsorption experiments on CuHZSM-5 and on SiCuHZSM-5 were carried out by using nitrogen and isobutane as adsorbates. Nitrogen and isobutane uptakes at different relative pressure (P/P_0) values are shown in Table 2. The amount of adsorbed nitrogen on CuHZSM-5 increased obviously with the increase of nitrogen pressures when relative pressures were less than 0.35. However, this relationship was not obvious for SiCuHZSM-5 with the increase of SiO_2 deposition, the major uptake of nitrogen on SiCuHZSM-5 samples gradually shifted to lower relative pressures, which indicates the reduction of pore sizes with the increase of SiO_2 deposition. As can be further observed in Table 2, the total amount of adsorbed nitrogen decreased with the increase of SiO_2 deposition at each relative pressure. This indicates that some of the blocked pores, after CVD process, possessed an opening less than the size of nitrogen molecule; this was not expected in this research, because oxygen with slightly smaller size than nitrogen is required to diffuse into the pores for combustion reaction. Nevertheless, the situation was more severe when more SiO_2 was deposited on CuHZSM-5 surface. Similar phenomena can also be observed for the adsorptions of isobutane on CuHZSM-5 and on SiCuHZSM-5, as shown in Table 2; however, the reductions of isobutane adsorption amount on SiCuHZSM-5 were more pronounced than those

Table 2
The amount of SiO_2 deposited on CuHZSM-5 and the amount of volume adsorbed by nitrogen and isobutane adsorption in various catalysts

Catalyst	SiO_2 loading (g/g CuHZSM-5)	N_2 adsorbed (cm^3/g cat)			i-C_4H_{10} adsorbed (cm^3/g cat)		
		P/P_0[a]			P/P_0		
		0.12	0.35	0.55	0.12	0.35	0.55
CuHZSM-5	—	134.1	147.3	153.2	40.5	47.0	51.1
SiCuHZSM-5 (2)[b]	0.060	108.5	119.5	124.1	32.7	37.7	40.7
SiCuHZSM-5 (4)	0.098	100.3	109.6	112.9	30.1	34.9	37.7
SiCuHZSM-5 (10)	0.363	74.3	79.2	80.6	17.4	20.8	23.1
SiCuHZSM-5 (20)	0.534	60.6	64.6	66.4	10.3	12.8	14.8
SiCuHZSM-5 (40.5)	0.585	53.1	55.2	55.4	5.6	7.6	9.2

[a]: P_0=760 mm Hg for nitrogen, P_0=1174 mm Hg for isobutane, P=pressure in mm Hg for adsorption.
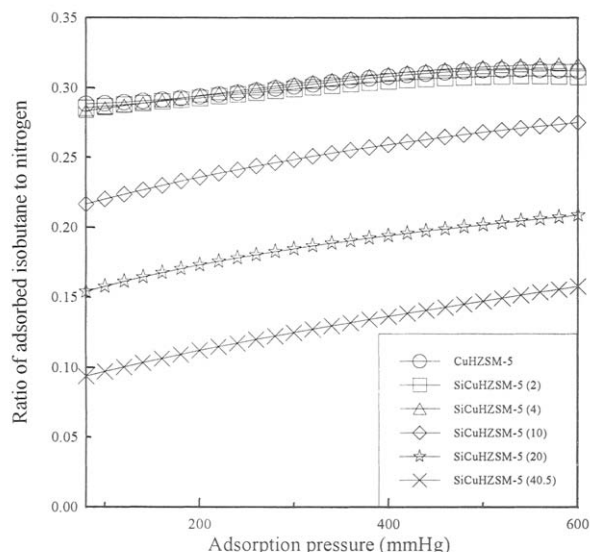[b]: The number in parentheses represents the deposition time in hours.

Fig. 3. The ratios of adsorbed isobutane (273 K) to nitrogen (77 K) on CuHZSM-5 and on SiCuHZSM-5 at different adsorption pressures.

Table 3
Hydrogen and isobutane conversions in mixtures of hydrogen, isobutane and air (flow rates=2, 2 and 96 ml/min) over CuHZSM-5 and SiCuHZSM-5 at 823 K and 1 atm (the amount of copper in each catalyst=7×10^{-6} mole)

Catalyst	Conversion at reaction time=30 min	
	Hydrogen	Isobutane
CuHZSM-5	86.10	94.98
SiCuHZSM-5 (2)[a]	81.22	85.94
SiCuHZSM-5 (4)	84.61	82.06
SiCuHZSM-5 (10)	78.38	48.11
SiCuHZSM-5 (20)	68.50[b]	10.20[b]
SiCuHZSM-5 (40.5)	74.97	1.55

[a]: The number in parentheses represents the deposition time in hours.
[b]: Reaction time=80 min.

of nitrogen adsorption; this is expected in this research, because isobutane is not desired to diffuse into the pores for combustion reaction.

Based on the uptakes of nitrogen and isobutane, the adsorption ratios of isobutane to nitrogen versus adsorption pressures were calculated and are shown in Fig. 3. It can be observed that the adsorption ratio of CuHZSM-5 was nearly the same as those of SiCuHZSM-5 (2) and SiCuHZSM-5 (4) which were from CVD processes for only 2 and 4 h. The deposition of SiO_2 to form SiCuHZSM-5 (2) and SiCuHZSM-5 (4) cannot improve the selectivity of isobutane and nitrogen adsorptions in these two samples, although the reductions of adsorption amounts were observed in Table 2 because of the pore blockings. However, when the depositions of SiO_2 were increased to form SiCuHZSM-5 (10), SiCuHZSM-5 (20) and SiCuHZSM-5 (40.5), Fig. 3 shows that the adsorption ratios were dramatically reduced and gradually shifted to less selectivity toward isobutane. Therefore, at this stage we can conclude that the shape selectivity of CuHZSM-5 for the adsorption of nitrogen and isobutane can be improved by CVD of TMOS for more than 10 h and by the later calcination process, to form SiO_2 and pore blocking on the surface.

3.6. Selective catalytic combustion of hydrogen in isobutane/hydrogen mixture

The conversions of hydrogen and isobutane at 823 K and 1 atm, in mixtures of hydrogen, isobutane and air (ratio=2 : 2 : 96), over CuHZSM-5 and SiCuHZSM-5, are shown in Table 3. No reaction activity occurred in the blank tests under the same reaction conditions. However, it can be found that high conversion of hydrogen can be reached over different catalysts, and there was not much difference between catalysts for hydrogen combustion. This indicates that hydrogen combustion activities were not influenced significantly by the pore size modification of SiCuHZSM-5. Nevertheless, the conversion of isobutane on SiCuHZSM-5 was significantly reduced, as shown in Table 3. The combustion of isobutane decreased with the increase of SiO_2 deposition on CuHZSM-5. For reactions over SiCuHZSM-5 (40.5), the conversion of isobutane was even less than 2%. This indicates that very little isobutane could diffuse into the pores of SiCuHZSM-5 (40.5), with deposition time of 40.5 h, for the combustion reaction; its pores were almost exclusively utilized for the selective combustion of hydrogen.

Fig. 4 shows the time on stream conversion ratios of hydrogen to isobutane. A higher value of the ratio would indicate a higher combustion selectivity of hydrogen. It can be observed that the conversion ratios over SiCuHZSM-5 (2), SiCuHZSM-5 (4) and SiCuHZSM-5 (10) were similar to that of
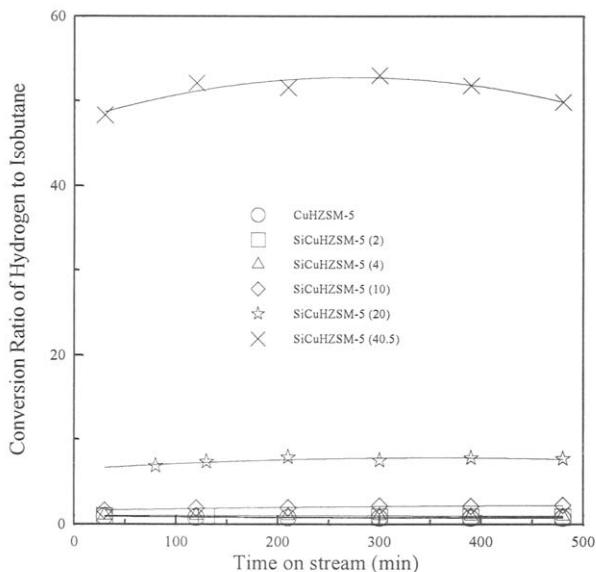
Fig. 4. Ratios of hydrogen to isobutane conversion in mixtures containing hydrogen, isobutane and air over CuHZSM-5 and SiCuHZSM-5 catalysts at 823 K and 1 atm; the amount of copper in each catalyst=7×10^{-6} mole; flow rates of hydorgen, isobutane and air at reactor inlet are 2, 2 and 96 ml/min, respectively.

CuHZSM-5, close to 1. The deposition of TMOS on CuHZSM-5 for 2, 4 or 10 h cannot significantly improve the combustion selectivity of the catalysts. However, when the deposition time was increased to 20 and 40.5 h, the conversion ratios over SiCuHZSM-5 (20) and SiCuHZSM-5 (40.5) were increased dramatically to about 8 and 50. Their combustion selectivities toward hydrogen were obvious. In other words, our research results suggest that better reactant shape selectivity of CuHZSM-5 for hydrogen combustion can be achieved by chemical vapor deposition with TMOS at 593 K for 40.5 h, and the subsequent calcination process at higher temperatures. Only small molecules such as hydrogen and oxygen can diffuse into the pores of the resulting catalyst for reaction; in contrast, a larger molecule (i.e. isobutane) cannot diffuse into its pores for combustion reaction.

4. Conclusions

From TPR results and catalytic activity for hydrogen combustion over ZSM-5 exchanged with iron, nickel or copper ions, it can be concluded that the greater the reducibility of these catalysts is, the higher the catalytic activity for hydrogen combustion is.

A novel catalyst, SiCuHZSM-5, modified by chemical vapor deposition of tetramethyl orthosilicate over HZSM-5 exchanged with copper ions and the later calcination processes can be applied for the selective combustion of hydrogen in a mixture containing isobutane and hydrogen.

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