

Application of Ti pillared clays in selective catalytic reduction of NO_x by C₃H₆*

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Abstract: Ti pillared clays (TiPILCs) were synthesized from Na⁺ montmorillonite. Cu doped pillared clays were studied as catalysts for selective catalytic reduction (SCR) of NO by propylene. Cu/TiPILC showed high activity at relatively low temperatures. The method of copper loading influences the catalytic activity of the catalysts. The following catalysts were also prepared and studied: Fe/TiPILC, Ce/TiPILC, Zn/TiPILC, Co/TiPILC, Ag/TiPILC and Ni/TiPILC. N₂ adsorption/desorption isotherms and pore size analysis were applied to study the influence of the pillaring process and Cu loading on the clay structure.

Key words: pillared clays; TiPILC; NO_x; selective catalytic reduction; catalyst

CLC number: O 643.36 **Document code:** A **Article ID:** 0258-7971(2006)03-0235-06

Nitrogen oxides emitted by automobiles are one of the main pollution of the atmosphere. Energy crisis results in the development of lean burn (i. e., O₂-rich) gasoline and diesel engines. The selective catalytic reduction (SCR) of NO by hydrocarbon has drawn much attention due to its potential for the effective control of NO emission in oxygen-rich environments.

The majority of studied catalysts for SCR of NO by hydrocarbons in the presence of oxygen were Cu²⁺ ion-exchanged ZSM-5 and other zeolites, noble metals and their ion-exchanged forms. Metal oxides supported on alumina have also been studied, but are less active^[1-3].

Pillared clays (PILCs) are two-dimensional zeolite-like materials. Since pillared clays have a number of attractive features, such as high porosity, high thermal stability and exchangeable cations, they have been widely used as catalysts and adsorbents. More specifically, the PILC based catalysts have been

found excellent and can be used as H₂O/SO₂ resistant catalysts for the SCR reactions by NH₃ and by hydrocarbons^[4,5].

In this work, TiO₂PILC (TiPILC) was synthesized. Cu/TiPILC was studied for SCR of NO with propylene. The SCR activities of pillared clays loaded with a number of other metals were also studied. The structure of PILCs was studied by N₂ adsorption isotherms and pore size distribution analysis.

1 Experimental

1.1 Syntheses of TiPILC The parent clays were purified Na⁺ montmorillonite (NaMt). This NaMt had a cation exchange capacity (CEC) of 80 mmol/100 g. The pillaring solution of partially hydrolyzed Ti⁴⁺ polycations was prepared by adding TiCl₄ into HCl solution at first, then diluted by slowly adding deionized water with vigorous stirring. The solution was aged at room temperature. The pillaring

* Received date: 2005-10-12

Foundation item: This work is supported by Scientific and Technical Project of Guangdong Province(2003C34501).

solution was slowly added into the suspension of clay with vigorous stirring until the amount of pillaring solution reached a certain Ti/clay ratio. Subsequently the mixture was filtrated and washed with deionized water until the liquid phase was free of chloride ions. The sample was dried and calcined.

1.2 Catalyst preparation

1.2.1 Cu^{2+} -exchanged Ti-PILC (Cu-Ti-PILC)

Pillared clays were added to 0.1 mol/L copper nitrate solution. The mixture was stirred for 24 h at 50 °C. The pH of the starting solution was adjusted to 7.0 by adding a proper amount of ammonia solution. The ion-exchange product was filtrated and washed with deionized water. The obtained solid sample was dried and calcined in air.

1.2.2 Cu-doped Ti-PILC (Cu/Ti-PILC), and other metal-doped Ti-PILC (Fe/Ti-PILC, Ce/Ti-PILC, Zn/Ti-PILC, Co/Ti-PILC, Ag/Ti-PILC and Ni/Ti-PILC) Metals were introduced into PILC by incipient wetness impregnation using nitrate solution of different metal at 5% wt. metal loading amount. Then the samples were dried and calcined in air.

1.3 Surface area and pore size distribution studies

A SA3100 surface area analyzer (Beckman Coulter) was used to measure the N_2 adsorption isotherms of the samples. The nitrogen adsorption/desorption experiments were performed at liquid N_2 temperature. The pore size distribution was calculated from the adsorption branch of the N_2 adsorption/desorption isotherms using the BJH formula.

1.4 Catalytic studies

The catalytic tests were carried out in a fixed-bed flow reactor system. The reactor temperature was controlled by a programmable temperature controller. The typical reactant gas composition was as follows: 0.22% of NO , 0.15% of C_2H_4 , 2% of O_2 , and balance of He. The space velocity was $40\,000\text{ mL}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ (ambient conditions). The catalyst size fraction was 50–70 mesh, and 0.5 g catalyst was used in a typical experiment. The concentration of the product stream was continuously monitored by a FGA-4015 exhaust gas analyzer and 102 G GC. The GC had two columns: a

Poropak Q column and a molecular sieve of 5 Å column.

2 Results and discussion

2.1 Comparison of the SCR activities of NaMt, Ti-PILC, and Cu/Ti-PILC

Fig. 1 shows the catalytic behaviors for SCR of NO by propylene in the presence of oxygen for NaMt, Ti-PILC, and Cu/Ti-PILC.

As shown in Fig. 1, both NaMt and Ti-PILC have almost no catalytic activity in this reaction system. The NO conversion is very low on these two samples. But the highest NO conversion on Cu/Ti-PILC is 68.1%. It illustrates that Cu is the main active species and Cu/Ti-PILC is an effective catalyst for the SCR reaction. The catalytic activity of Cu/Ti-PILC is higher than other catalysts reported (e.g. Cu/AF-PILC, Cu-ZSM-5, Cu/ Al_2O_3)^[1,2,6,7]. It also can be seen that the catalytic activity increased as temperature increased, reaching a maximum NO conversion, and then decreased at higher temperatures. For Cu/Ti-PILC, the peak temperature is 250 °C, lower than other Cu-loaded catalysts^[1,2,6,7]. It shows that Cu/Ti-PILC has good catalytic activity at low temperature and within a relatively broad temperature range, in contrast to other catalysts. The peaking of NO conversion at a certain temperature for SCR is the result of two competing reactions: NO reduction by hydrocarbon and oxidation of hydrocarbon by oxygen. The oxidation of hydrocarbon, which reduces the amount of reductant, become dominating at higher temperatures.

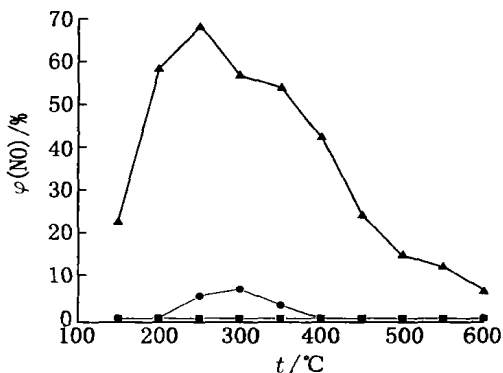
2.2 The BET surface areas, adsorption isotherms and pore size distribution analysis

The BET surface areas (S_{BET}) and the pore volumes of NaMt, Ti-PILC, and Cu/Ti-PILC are summarized in Tab. 1.

As shown in Tab. 1, pillaring of NaMt with titania results in a increase in surface area and pore volume. The S_{BET} increases from 79.94 m^2/g to 198.44 m^2/g , and the pore volume from 0.247 43 mL/g to 0.364 05 mL/g . This means that the large surface areas and pore volumes were the results of successful pillaring. Introduction of copper to the

TiO_2 pillared clays causes some decrease of the surface area and pore volume. It can be explained that the pores of the pillared clays are partly blocked by copper species.

The nitrogen adsorption/desorption isotherms of NaMt, Ti-PILC, and Cu/Ti-PILC are shown in Fig. 2.



--- Na-Mt ···· Ti-PILC -·-·- Cu/Ti-PILC

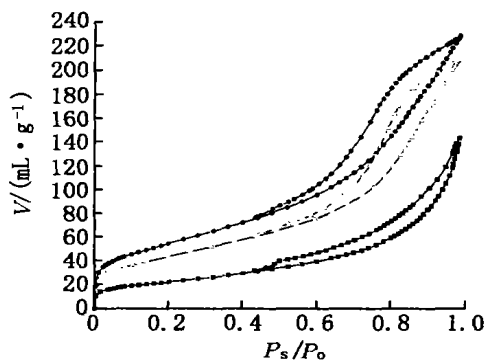
Fig. 1 SCR activities over NaMt, Ti-PILC, and Cu/Ti-PILC

The three adsorption/desorption isotherms are the type II according to IUPAC classification, a typical isotherms of mesoporous materials. The hysteresis loop of NaMt is type H3, according to IUPAC classification. It is consistent with the materials of a layer structure, which is the typical structure of montmorillonite^[8]. The shapes of the isotherm and the hysteresis loop of Ti-PILC are largely different from those of NaMt. The hysteresis loop of Ti-PILC is between type H2 and H3. This illustrates that the structure of the Ti-PILC is not just a layer structure as NaMt. The pillaring of NaMt with titania changes the pore structure of the clays. The adsorption isotherms of Cu/Ti-PILC are similar to that of Ti-PILC, it means that the introduction of copper only decrease the N_2 adsorption surface area, and it does not change the pore structure of the Ti-PILC.

Fig. 3 and Fig. 4 show the BJH pore size distribution of NaMt, Ti-PILC, and Cu/Ti-PILC. The three samples all present a unimodal and narrow peak, it means that the pillared clays has a uniform pore size distribution after the pillaring process. The

Tab. 1 BET surface areas and pore volumes of NaMt, Ti-PILC, and Cu/Ti-PILC

Catalyst	$S_{BET}/(m^2 \cdot g^{-1})$	Pore volumes/ $(mL \cdot g^{-1})$
NaMt	79.94	0.247 43
Ti-PILC	198.44	0.364 05
Cu/Ti-PILC	182.57	0.345 66



--- Na-Mt ···· Ti-PILC -·-·- Cu/Ti-PILC

Fig. 2 N_2 adsorption/desorption isotherms for the NaMt, Ti-PILC, and Cu/Ti-PILC

main pore diameter of NaMt is less than 4 nm. After pillaring by titania, the pore size increases, mainly centered at 4—12 nm, especially at 4—9 nm. It illustrates that the successful pillaring process changes the pore structure and increases the pore size and surface area of the clays. This is favorable for the reactant and product molecules pass in and out the pore, and can increase the available surface area of active species. After introduction of Cu, the pore smaller than 6 nm diameter decreased largely, mainly centered near 9 nm diameter. This means the Cu introduced into the Ti-PILC mainly entered and inhabited in the pore smaller than 6 nm diameter.

2.3 The influence of the method of Cu introduction

The introduction of Cu into Ti-PILC gives rise to its catalytic activity. The method of Cu loading can influence the distribution and state of the Cu active species, thus influence the catalytic activity. Fig. 5 shows the SCR activities of two catalysts prepared by ion exchanged (Cu-Ti-PILC) and incipient wetness impregnation (Cu/Ti-PILC).

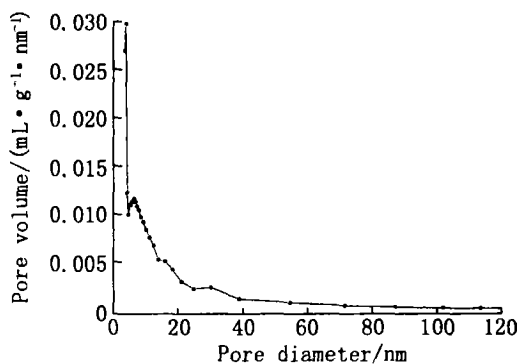


Fig. 3 Pore size distribution of Na Mt

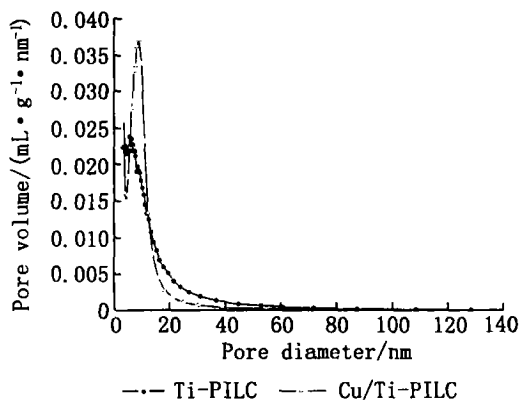


Fig. 4 Pore size distribution of Ti-PILC, Cu/Ti-PILC

It is found that Cu/Ti-PILC gave higher NO conversion than Cu/Ti-PILC, reached 70.6% at 250 °C, compared with 68.1% on Cu/Ti-PILC. But the activity of Cu/Ti-PILC dropped dramatically as temperature increased. The NO conversion on Cu/Ti-PILC dropped to 21.3% at 350 °C, it still maintain 53.9% on Cu/Ti-PILC at the same temperature. This result could be due to the nature of the Cu active sites, and the accessible Cu surface areas.

The BET surface area of Cu/Ti-PILC and Cu/Ti-PILC are listed in Tab. 2. It can be seen from Tab. 2 that the surface area of the Cu/Ti-PILC is higher than that of Cu/Ti-PILC. Surface area can influence the dispersing statue of Cu active species. This maybe one of the reasons why the activities of the two catalysts are different. Further work is need

to elucidate the nature of the Cu active site for this reaction.

Tab. 2 BET surface area of Cu/Ti-PILC and Cu/Ti-PILC

Catalyst	$S_{BET}/(m^2 \cdot g^{-1})$
Cu/Ti-PILC	182.57
Cu/Ti-PILC	117.85

2.4 Ti-PILC doped with other metals In these experiments, a number of other different metal loaded Ti-PILC catalysts were also studied for SCR of NO by C₃H₆. The SCR activities as functions of temperature for Cu/Ti-PILC, Fe/Ti-PILC, Ce/Ti-PILC, Zn/Ti-PILC, Co/Ti-PILC, Ag/Ti-PILC and Ni/Ti-PILC are compared in Fig. 6 as NO conversions.

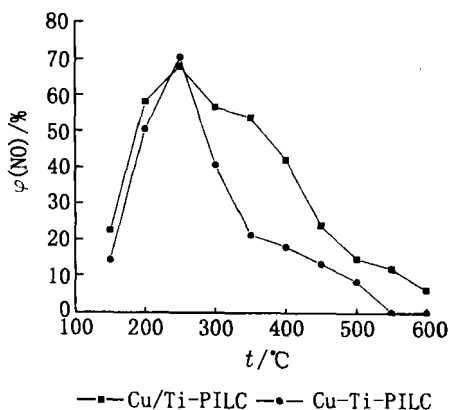


Fig. 5 The influence of the method of Cu introduction on catalyst activities

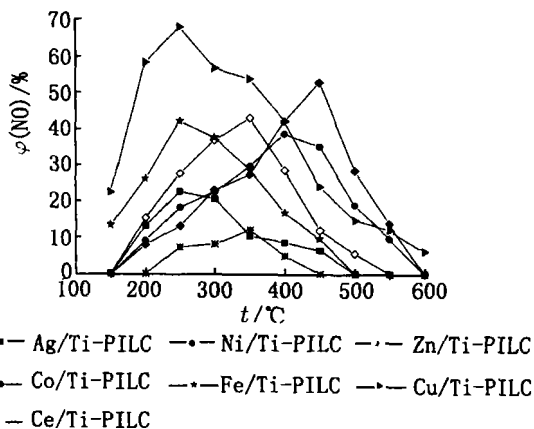


Fig. 6 SCR activities over Ti-PILC loaded with different metals

As shown in Fig. 6, all catalysts mentioned above have SCR activities at different degrees. Comparing with other catalysts, Cu/Ti-PILC and Co/Ti-PILC have relatively high activities. The NO conversion on these two catalysts reaches 68.1% and 52.8% respectively. The peak temperature on Co/Ti-PILC is 450 °C, it shows that Co/Ti-PILC has good catalytic activity at high temperature range. Cu/Ti-PILC, Fe/Ti-PILC have good low-temperature range activities. The peak temperature of these two catalysts is 250 °C. By comparing with other metal loaded Ti-PILC catalysts, Fe/Ti-PILC, Ce/Ti-PILC and Ni/Ti-PILC have medium SCR activities, the NO conversions are 42.3%, 43.1%, 38.7% respectively. The optimal reactive temperature on Ce/Ti-PILC is around 350 °C, while 400 °C on Ni/Ti-PILC. Contrastively, Zn/Ti-PILC and Ag/Ti-PILC have poor activities for SCR reaction.

3 Conclusions

Ti-PILC have been synthesized from NaMt, the SCR activities of Ti-PILC doped with different metals is studied. Cu/Ti-PILC shows good activities for the SCR reaction. The catalyst prepared by incipient wetness impregnation (Cu/Ti-PILC) has better catalytic activity than that prepared by ion-exchanged (Cu-Ti-PILC). By N_2 adsorption isotherms and pore size distribution analysis, the influence of the pillaring process and the introduction of copper on the structure of the clays are studied. The pillaring process changes the pore structure of the clays. It also changes the pore size distribution and increases the surface area. The introduction of copper does not

change the pore structure of the Ti-PILC.

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钛交联粘土在 C_3H_6 选择性催化还原 NO_x 中的应用研究*

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摘要: 从钠基土合成了钛交联粘土(Ti-PILC). 以交联粘土作为载体负载 Cu, 考察了对 C_3H_6 选择性还

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原(SCR)NO 反应的催化活性. Cu/Ti-PILC 显示了很好的低温活性. Cu 的负载方法影响催化剂活性. 还研究了 Ti-PILC 负载其他金属 (Fe/Ti-PILC, Ce/Ti-PILC, Zn/Ti-PILC, Co/Ti-PILC, Ag/Ti-PILC, Ni/Ti-PILC) 催化剂的催化活性. 用 N₂ 吸附脱附等温线和孔径分布考察了交联过程及铜的负载对粘土结构的影响.

关键词: 交联粘土; Ti-PILC; 氮氧化物; 选择性催化还原; 催化剂

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Evolution analysis of *Leptospira interrogans serovar* Lai

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Abstract: It was studied that a analysis of duplicate genes of *Leptospira interrogans serovar* Lai. Through the concept of divergence time S , by means of comparing the rates of nucleotide substitution at replacement and silent sites by performing least-squares analysis, the result shows that early in their history, many gene duplicates experience a phase of relaxed purifying selection, subsequently selection constraint gradually increases and eventually tends to the stability.

Key words: *Leptospira interrogans serovar* Lai; gene duplication; evolution; nonsynonymous substitution; synonymous substitution