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Ceria and lanthana as blocking modifiers for the external surface of MFI zeolite

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ABSTRACT

The ceria- and lanthana-modified MFI zeolites were prepared and extensively investigated to verify the function of lanthanide oxides as blocking modifiers. Their catalytic behavior in the methanol-to-olefin (MTO) conversion was explained by the characterization results regarding crystallinity, agglomeration, porosity, surface composition, and the uptakes of *o*-xylene and methanol. The ceria impregnated on the MFI formed nano-sized small particles with two oxidation states of +3 and +4 (Ce_2O_3 and CeO_2) on the surface and was located predominantly on the external surface. So, the ceria impregnation maintained the porosity and activity of the MFI, and induced little change in the conversion and product composition of MTO. However, the lanthana impregnated on the MFI dispersed as a single lanthana (La_2O_3) phase in its micropores, as well as on the external surface. The blocking of the micropores and reduction of acidity by lanthana impregnation lowered the activity of the lanthana-modified MFI in MTO. The ceria located on the external surface of MFI did not have any negative effects on the catalytic performance, while the lanthana dispersed in the micropores lowered the conversion in MTO. The locations and dispersed states of ceria and lanthana were systematically discussed in the relation to their catalytic performance as blocking modifiers.

1. Introduction

Zeolites have been widely used as catalysts in refineries and the petrochemical industry due to their specific framework, large surface area, high acidity, and excellent thermal and mechanical stabilities [1]. Zeolites are very efficient in acid-catalyzed cracking, alkylation, and isomerization processes in terms of high selectivity to desired products [2–4]. Uniform pores of zeolites with similar sizes of reactant molecules increase the feasibility of the material as catalysts with high selectivity. Furthermore, various modification methods enhance the catalytic performance of zeolites. For example, the ion exchange of zeolite cations with various other cations varies their acidity, maximizing their catalytic activity and selectivity. Also the impregnation of phosphorous or potassium hydroxide partially neutralizes strong acid sites, significantly reducing coke deposit, whereas the impregnation of lanthanide oxides suppresses the reaction occurred on the external surface, resulting in better selectivity [5,6].

The particular pore structure of zeolites causes a specific catalytic property called the shape-selectivity, which is defined by a change at the rate or the product composition of catalytic reactions originating from the shape and size of catalyst pores [2,6]. Three kinds of shape-selective catalysis by reactants, products, and transition states enhance the usefulness of zeolites as catalysts [7]. The high selectivity to *p*-xylene in the alkylation of toluene with methanol is a typical example, which minimizes the separation cost of *p*-xylene from xylene mixtures [8]. The combination of a reaction with a separation step due to the specific pore size and shape improves the selectivity to a given desired product, and achieves higher yield than that expected from thermodynamic equilibrium.

In order to enhance the selectivity to a high-selective catalysis over a zeolite, large and highly crystalline zeolites are preferred to suppress the side reactions that occur on the external surface, because the regulation exerted by the shape and size of pores is only effective in zeolite pores [9]. Since thermodynamically equilibrated products are produced on the external surface, the blocking of the external surface increases the selectivity to the desired reactions that occur in the pores [10]. Suggested as feasible methods include the selective poisoning of the acid sites with large basic

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materials which cannot enter the pores, the silination by the reaction between surface acid sites and silane molecules, and the impregnation of lanthanide metal oxides on the external surface [9–11]. The impregnation of ceria deactivates only the acid sites on the external surface, while the impregnation of lanthana considerably reduces strong acid sites because it can intrude into the pores.

Among these methods, the impregnation of ceria on mordenite has been studied to improve the selectivity to linear products in the alkylation of various aromatic materials [12]. Ceria- and lanthana-modified MFI zeolites show enhanced selectivity to *p*-diethylbenzene among diethylbenzene isomers without significant loss of catalytic activity. The ceria and lanthana impregnated on the external surface successively prevent further isomerization of *p*-diethylbenzene. The high improvement of para-selectivity on the lanthana-modified MFI zeolite compared to that modified by ceria is due to the adjustment of pore entrances as well as the deactivation of external acid sites, suggesting a certain difference in the location between ceria and lanthana.

Although the ceria is selectively impregnated on the external surface, the oxides of the lanthanide metals such as lanthanum, samarium, dysprosium, and yttrium do not show such specificity in their impregnation position [13]. The lanthanide oxides except for ceria concomitantly disperse in the pores as well as on the external surface, significantly lowering the acidity and narrowing the pore entrances of zeolite catalysts. The extraordinary preference of ceria in its impregnation on the external surface is explained by the formation of agglomerates comprising small particles rather than a lump that can extend toward pore entrances. However, the reason why the ceria impregnated does not form a continuous solid phase has not been investigated. Furthermore, the isopropylation on ceria-modified mordenites is carried out below 300 °C, so previous studies have not provided any information on the state of ceria at elevated temperatures [9,10,13]. The difference in the state of lanthanide oxides impregnated on MOR zeolites is clear, but its cause has not been systematically investigated.

Methanol-to-olefin (MTO) conversion zeolite catalysts producing lower olefins from methanol requires high shape-selectivity by suppressing the formation of large and long hydrocarbons to achieve a high yield of lower olefins and to extend catalyst life without regeneration [14]. The sinusoidal channels of MFI zeolite do not allow for the formation of longer aliphatic hydrocarbons than C_{12} and polyaromatic hydrocarbon in the MTO conversion, resulting in an extraordinary long catalyst life compared to other zeolites, including SAPO-34 [15,16]. Furthermore, the partial neutralization of strong acid sites of MFI zeolites by phosphorous modification increases the selectivity to propylene, and lengthens their catalyst lifetime [17,18].

We have prepared ceria- and lanthana-impregnated MFI zeolites to investigate their impregnated states and to discuss the effect of the impregnation on their catalytic performance in the MTO conversion. The impregnated amount of ceria and lanthana increased to 40% to achieve the complete masking of the external surface and to observe their catalytic contribution to the MTO conversion. The behavior of ceria and lanthana as blocking modifiers of MFI zeolite was systematically deduced from their agglomeration, surface composition, crystallinity, porosity, uptakes of *o*-xylene and methanol, acidic properties obtained using transmission electron microscopy (TEM), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), nitrogen adsorption, IR spectroscopy of adsorbed pyridine and collidine, and temperature-programmed desorption (TPD) of ammonia. The variations of the activity and selectivity to lower olefins with reaction temperature over MFI zeolites modified by ceria and lanthana in the MTO conversion clearly revealed differences in their dispersed states.

2. Experimental

2.1. Catalyst preparation

A commercial MFI zeolite with Si/Al molar ratio of 25 was purchased from Zeolyst and was used as a starting material. The molar ratio was written in parentheses, like with MFI(25). Cerium nitrate hexahydrate (Yakuri, 98%) and lanthanum nitrate hexahydrate (Wako, 97%) were impregnated on MFI(25) by an incipient wetness method with varying their impregnated amounts within the range of 10–40 wt%. After impregnating the aqueous solutions of lanthanide oxides on MFI(25), the zeolites were dried at 100 °C for 6 h. The lanthanide oxide-impregnated MFI(25) catalysts were obtained by calcination of the dried zeolites at 550 °C for 4 h and denoted by M(*x*)-MFI, with M representing the lanthanide metal and *x* standing for the impregnated amount of ceria or lanthana as wt%. For comparison, Ce(40)/Al_2O_3 and La(40)/Al_2O_3 were prepared by impregnating the precursors of ceria and lanthana on γ-Al_2O_3 (Sasol).

2.2. Characterization

Powder XRD patterns were recorded on a Rigaku Ultima III X-ray diffractometer with Cu Kα radiation. In situ XRD patterns were recorded using a PANalytical X'pert Pro with Cu Kα radiation. The samples were purged with oxygen and hydrogen during heating from 25 to 600 °C. The shape and size of zeolites were observed using a Hitachi S-4700 SEM. N_2 adsorption isotherms were recorded on a Mirae SI nanoPorosity-XG analyzer. Surface areas were calculated from the adsorption isotherms using the Brunauer–Emmett–Teller (BET) equation, and the pore size distribution was obtained using the Barrett–Joyner–Halenda (BJH) method. TPD of ammonia was carried out using a laboratory-made apparatus following a procedure described in the literature [19]. The samples were previously saturated with ammonia (Air Korea, 1000 ppmv/He balance) and purged with helium (Sinil, 99.999%) at 150 °C before being heated to 800 °C at 10 °C min^{-1}. The desorbed ammonia was monitored by a Balzers QMS200 mass spectrometer.

The dispersion of ceria and lanthana was observed by TEM (JEM 2000 FXII, JEOL). Catalysts dispersed in acetone were sonicated and sampled using a carbon grid. The surface compositions of ceria and lanthana on the prepared catalysts were investigated by XPS (VG MultiLab 2000) using a monochromated Mg Kα X-ray source (300 W). The binding energies of surface elements were calibrated using the C1s (285 eV) peak as a reference.

Uptakes of *o*-xylene (Yakuri, 99%) and methanol (Aldrich, 99.8%) on the M(*x*)-MFI catalysts were measured using a gravimetric adsorption system equipped with a quartz spring [19]. The samples were evacuated at 300 °C for 1 h prior to exposure to these adsorbates. The mass gain due to the uptake of *o*-xylene was measured under 7 Torr of *o*-xylene vapor at 90 °C for 90 min, and that of methanol was measured under 37 Torr of methanol vapor at 30 °C for 60 min. IR spectra of pyridine (Aldrich, 99.8%) and collidine (Aldrich, 99%) adsorbed on the zeolite catalysts were recorded on a BIO-RAD 175C FT-IR spectrophotometer equipped with a Graseby Specac in situ cell. A self-supported catalyst wafer (about 10 mg) was activated in a nitrogen (Sinil, 99.9%) of 50 ml min^{-1} at 500 °C for 1 h. 1 μl pyridine or collidine was injected at 50 °C, and maintained for 30 min. Differential IR spectra of adsorbed pyridine were recorded with increasing temperature to 400 °C across the range 4000–700 cm^{-1} with a resolution of 4 cm^{-1}. The spectra of adsorbed collidine were obtained after purging at 50 °C because of its easy desorption.