Catalysis at the interface of nano-oxides and nanozeolites*

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Abstract: The catalysts that can efficiently hydro-reform higher n-paraffin to lower iso-paraffins for environmentally friendly gasoline were studied. The catalysts were examined by the conversion of \( n \)-hexadecane, \( n-C_{16}H_{34} \) to \( i-C_{6}H_{14} \sim i-C_{12}H_{26} \). The tri-modally nanoporous (nanometer-size) catalysts composed of (Ni–Mo)/[\( \gamma \)-Al\(_2\)O\(_3\)], nano-oxide, and nanocrystalline zeolite have some active and selective performances because of the cooperation between (Ni–Mo)/[\( \gamma \)-Al\(_2\)O\(_3\)] and the composite of nano-oxide–nanozeolite. The (Ni–Mo)/[\( \gamma \)-Al\(_2\)O\(_3\)] component holding the skeletal isomerization activity enhances the cracking activity on the composite of nanoporous (np)-Al\(_2\)O\(_3\)-USY (ultra-stable Y-type zeolite) to result in \( i-C_{6}H_{14} \sim i-C_{12}H_{26} \) as the isomerization of \( n \)-hexadecane followed the cracking reaction. The catalyst composed of nanocrystalline BEA (beta-type zeolite) or MFI (ZSM-5-type zeolite) zeolite can be more activated with the nano-SiO\(_2\) than with the nano-Al\(_2\)O\(_3\). The catalyst composed of the dealuminated zeolite, USY (SiO\(_2\)/Al\(_2\)O\(_3\) = 12) cannot be activated with the nano-SiO\(_2\) but with the nano-Al\(_2\)O\(_3\). This activation depends on the SiO\(_2\)/Al\(_2\)O\(_3\) ratio of the USY.

It is considered that the catalytic property of the three components is partially due to the novel active sites formed concertedly at the interface of the nano-oxides and the nanozeolites. The novel sites have a major role for the isomerization and cracking as the moderate and strong acids and are generated when Si–OH in the nanopores of the USY resulted from the dealumination catches Al–OH in the nano-Al\(_2\)O\(_3\) to form Si–O–Al–O–Al–O–Si instead of Si–O–Al–O–Si–O–Si.

Keywords: nanopores; nano-oxides; nanozeolites; nanointerfaces; nanocatalysis.

INTRODUCTION

Since recent catalyst research is usually focused on zeolites with various sub-nanometer space and surface, or unimodally porous materials with tens-nanometer space and surface, one-nano- (nanometer) order space and materials remain outside of well-studied catalysis in industrial applications [1–5]. If technologies based on one-nano-order space and materials such as nanopores, nano-oxides, nanozeolites, and nanointerfaces can be designed and prepared well in an industrial sense, they interest us as keys for opening up novel catalysis fields in industrial applications.

The nanopores combined with two other kinds of nano-orders in the pore-mouth can be used to design the concerted pore structures for catalytic reaction fields. Sub-nanometer-order pores are sensi-
tive to the molecular structure of the reactants and the products in the gas or liquid phase [6–12]. The pores of the order of one to tens of nanometers are common to supporting surface for active metals [13,15]. It is possible that designing and preparing the catalyst with the concerted pore structure leads to not only controlling chemical properties of the catalyst at the order of nanometers but also provides the preferable reaction circumstance and loop at the nano-orders [15,16].

The catalysts designed by those nanotechnologies, which can efficiently hydro-reform higher n-paraffins into lower isoparaffins, were studied. The conversion of higher n-paraffins into lower isoparaffins without aromatization is an important catalytic reaction from an industrial viewpoint. Indeed, higher n-paraffin reforming leads to the formation of the higher-value liquid hydrocarbons (mainly, iso-hexanes, -heptanes, and -octanes), which are valuable fractions for environmentally friendly gasoline.

The conversion of \( n \)-hexadecane, \( n-C_{16}H_{34} \) to \( i-C_{6}H_{14} \sim i-C_{12}H_{26} \), were examined as a typical catalysis at the interfaces of nano-oxides and nanozeolites. This reaction involves hydrocracking and skeletal isomerization as different reaction steps.

**CATALYST: ITS PREPARATION AND TEST**

Three kinds of different nanoporous materials were prepared by our own methods, referring to previous works [13,15]. The sub-nano-order components, H-BEA (beta-type zeolite), H-MFI (ZSM-5-type zeolite), and USY (ultra-stable Y-type zeolite), were prepared at the laboratory. USY as H-type dealuminated Y zeolite was adjusted with thermal treating followed by acidic leaching. Typical SiO\(_2\)/Al\(_2\)O\(_3\) ratios of those zeolites were 25 for H-BEA, 50 for H-MFI, and 12 for USY. A typical crystalline size of those zeolites was 40 nm for H-BEA, 20 nm for H-MFI, and 200 nm with 4-nm pores for USY, measured by X-ray diffraction and porosimetry. The crystalline size of USY as the catalyst component was considered from the porosity to be reduced to tens of nanometers by 4-nm pores. The nano-order components, Na-free pseudo-boehmite and silica aerosol, were selected as the modification or binding materials serving to connect nanopores. They were Al\(_2\)O\(_3\) or SiO\(_2\) precursors holding 4–5-nm pores after calcination since those particle sizes were adjusted to 4–5 nm. The over-nano-order component Ni–Mo supported on \( \gamma \)-Al\(_2\)O\(_3\) with unimodal and fractal 11-nm pores (uniformity: 1.1) was precisely prepared [13,15].

To prepare the catalysts with concerted pore structure, the three inorganic solid powders were mixed with water. The dough of the powder mixture was kneaded mechanically. The kneaded composite was extruded to shape finally to catalyst pellet, followed by drying at 120 °C for 12 h and calcination at 550 °C for 3 h [15].

Models of the composite prepared as a tri-modally nanoporous catalyst are shown in Fig. 1 in two ways: (a) components dispersed in the catalyst pellet, and (b) simplified trio of tri-modally nanoporous composite.

The well-designed nanopore hybrid catalysts for conversion of higher n-paraffin (hexadecane) to lower isoparaffins were examined by the reaction test unit equipped with fixed-bed, flow-type reactor under hydrogen pressure.
A typical result of the concerted effect from the novel active system on the tri-modally nanoporous catalyst composed of zeolite and nanoporous oxides was obtained on (Ni–Mo)/[γAl₂O₃]–np-Al₂O₃-USY. The conversions on the tri-composite catalyst (filled circle) are higher than the theoretically additive value without the concerted effect (unfilled circle) at higher temperature as shown in Fig. 2. Though the carbon numbers of the product on (Ni–Mo)/[γAl₂O₃]–np-Al₂O₃-USY are similar to that on np-Al₂O₃-USY, the conversions are higher and the product selectivity of the iso-hydrocarbon is improved on the concerted catalyst composed of (Ni–Mo)/[γAl₂O₃] catalyst due to isomerization as shown in Fig. 3.

Fig. 1 Model of tri-modally nanoporous catalyst prepared. (a) Components in the catalyst pellet, (b) simplified trio of tri-modally nanoporous composite.

**CONCERTED EFFECT OF NOVEL ACTIVE SYSTEM ON TRI-MODALLY NANOPOROUS CATALYST**

Fig. 2 Concerted effect of novel active system on tri-modally nanoporous catalyst composed of USY and nanoporous oxides. GHSV: 5000/h, pressure: 0.12 MPa, C₁₆H₃₄/H₂: 1/15, catalyst/filled circle: (Ni–Mo)/[γ-Al₂O₃]-np-Al₂O₃-USY, unfilled circle: theoretical w/o concerted effect, triangle: (Ni–Mo)/[γ-Al₂O₃], square: np-Al₂O₃-USY.

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Fig. 3 Product distribution on (a) (Ni–Mo)/[γAl₂O₃] catalyst, (b) np-Al₂O₃-USY catalyst, and (c) (Ni–Mo)/[γAl₂O₃]-np-Al₂O₃-USY catalyst. Shadowed: iso-hydrocarbon, white: n-hydrocarbon.
It is considered that the catalytic properties above resulted from the tri-modal pore structure controlling the following equations:

\[
\begin{align*}
  n-C_{16}H_{34} & \rightarrow i-C_{16}H_{34} \\
  n-C_{16}H_{34} & \rightarrow n-C_{6}H_{14}\sim n-C_{12}H_{26} \\
  n-C_{6}H_{14}\sim n-C_{12}H_{26} & \rightarrow i-C_{6}H_{14}\sim i-C_{12}H_{26} \\
  i-C_{16}H_{34} & \rightarrow i-C_{9}H_{14}\sim i-C_{12}H_{26}
\end{align*}
\]

As shown in Fig. 4a, the skeletal isomerization of \( n \)-hexadecane as eq. 1 mainly proceeds on \((\text{Ni–Mo})/\gamma\text{Al}_2\text{O}_3\) catalyst. As shown in Fig. 4b, the catalyst composed of np-Al\(_2\)O\(_3\) and USY can selectively but less actively produce C\(_6\)–C\(_{12}\) n-paraffins as in eq. 2. The skeletal isomerization of the lighter n-paraffins as in eq. 3 slightly proceeds on the catalyst composed of np-Al\(_2\)O\(_3\) and USY. Therefore, \((\text{Ni–Mo})/\gamma\text{Al}_2\text{O}_3\) component holding the skeletal isomerization activity enhances the cracking activity on np-Al\(_2\)O\(_3\)-USY to result in \( i-C_{6}H_{14}\sim i-C_{12}H_{26} \) as the isomerization of \( n \)-hexadecane followed the cracking reaction as in eq. 4.

This reaction scheme reflects the concerted effect by the tri-modal pore structure as a roundly consecutive reaction chain of eq. 1 on \((\text{Ni–Mo})/\gamma\text{Al}_2\text{O}_3\) and eq. 4 on np-Al\(_2\)O\(_3\)-USY. In the concerted effect, newly generated acid sites maybe have a major role for the isomerization and the cracking. It is also considered that the catalytic property of \((\text{Ni–Mo})/\gamma\text{Al}_2\text{O}_3\)-np-Al\(_2\)O\(_3\)-USY catalyst is due to the novel sites (moderate and strong acids) formed as less active for the isomerization and the cracking of the higher n-paraffins but active for the cracking of the higher iso-paraffins and the isomerization of the lower n-paraffins.

Similar results of the effect enhancing np-Al\(_2\)O\(_3\)-zeolite with \((\text{Ni–Mo})/\gamma\text{Al}_2\text{O}_3\) are also confirmed on H-BEA and H-MFI composite catalyst as shown in Fig. 4. The conversions on the tri-com-
posite catalyst are higher than the theoretically additive value without the concerted effect. There are similar concerted effects in a novel active system on tri-modally nanoporous catalyst composed of zeolite and nanoporous oxides.

As C\textsubscript{6}–C\textsubscript{12} isoparaffins are availed to gasoline fraction with high octane values and highly isomerized C\textsubscript{16}H\textsubscript{34} can be enforced cetane value for diesel, the catalyst composed of zeolite and nanoporous oxides can be used to produce clean gasoline and diesel selectively.

**CONCERTED EFFECT DEPENDS ON SPECIES OF NANO-OXIDES**

The \textit{n}-hexadecane conversions are clearly changed when the component of nano-oxide is replaced from np-Al\textsubscript{2}O\textsubscript{3} to np-SiO\textsubscript{2}. Typical results at various reaction temperatures are shown in Fig. 5. The conversions change in each different way. The conversions on the catalyst composed of USY are depressed into lower levels. On the other hand, the conversions on the catalyst composed of BEA and MFI are obviously improved. Especially on the catalyst composed of MFI and np-SiO\textsubscript{2}, the 90\% conversion is performed at nearly 100 °C lower than the temperature that gives the 90\% conversion on the catalyst composed of MFI and np-Al\textsubscript{2}O\textsubscript{3}.

![Graph showing the effect of nanoporous oxides on tri-modally nanoporous catalysts](https://example.com/graph.png)

**Fig. 5** Concerted effect of novel nanoporous oxides on tri-modally nanoporous catalyst composed of zeolite and nanoporous oxides. Catalyst/circle: (Ni–Mo)/(γ-Al\textsubscript{2}O\textsubscript{3})-np-Al\textsubscript{2}O\textsubscript{3}-USY, triangle: (Ni–Mo)/(γ-Al\textsubscript{2}O\textsubscript{3})-np-Al\textsubscript{2}O\textsubscript{3}-BEA, square: (Ni–Mo)/(γ-Al\textsubscript{2}O\textsubscript{3})-np-Al\textsubscript{2}O\textsubscript{3}-MFI, filled: np-SiO\textsubscript{2} used instead of np-Al\textsubscript{2}O\textsubscript{3}.

These results show that the nano-oxide component in the tri-modally nanoporous catalysts consisting of the various zeolites and the nanoporous oxides plays an important role in the \textit{n}-hexadecane conversion concerted with the nanozeolite.

Since not only the nano-oxide but also the nanozeolite is important for the hydro-isomerization/cracking reaction, the interface between the nano-oxide and the nanozeolite is considered to be further examined.
CONCERTED EFFECT DEPENDS ON SILICA-ALUMINA RATIO OF ZEOLITE AND NANO-OXIDE

The SiO$_2$/Al$_2$O$_3$ ratio of USY can be changed by controlling the degree of the dealumination and composite with np-Al$_2$O$_3$ or np-SiO$_2$ in order to evaluate the interface between the nano-oxide and the nanozeolite. The conversion increases with an increase of the SiO$_2$/Al$_2$O$_3$ ratio in the same way between the np-Al$_2$O$_3$ and the np-SiO$_2$ as a partner as shown in Fig. 6. In both cases of the SiO$_2$/Al$_2$O$_3$ ratio, the conversions on the composite catalyst with the np-Al$_2$O$_3$ are higher than that on the composite catalyst with the np-SiO$_2$. It is considered that the np-Al$_2$O$_3$ combined with Si–OH of the zeolite surface to make new active sites and that the dealumination of USY generates the active sites of Si–OH on the zeolite surface combined with Al–OH of the np-Al$_2$O$_3$.

The size of the np-Al$_2$O$_3$ can be changed by controlling the times of PH-swing and composite with high SiO$_2$ USY in order to estimate the combination between the np-Al$_2$O$_3$ and Si–OH of the zeolite surface to make the new active sites. Though the concerted effect decreases slightly with the size of the np-Al$_2$O$_3$, any np-Al$_2$O$_3$ are still effective to the concerted as shown in Fig. 7. These facts suggest that the Al–OH of the np-Al$_2$O$_3$ precursor surface combined with Si–OH of the nanozeolite surface to make the new active sites by dehydration during calcination.

Fig. 6 Concerted effect depending on the SiO$_2$/Al$_2$O$_3$ ratio of USY and nanoporous oxides. Catalyst: (Ni–Mo)/(γ-Al$_2$O$_3$)-np-Al$_2$O$_3$-USY, SiO$_2$/Al$_2$O$_3$: circle = 6, triangle = 12, filled: np-SiO$_2$ used instead of np-Al$_2$O$_3$. 

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NOVEL ACTIVE SITES FORMED CONCERTEDLY AT THE INTERFACE OF NANO-OXIDE AND NANOZEOLITE

The newly generated acid sites are confirmed by NH₃ TPD and IR measurement [15]. The acid amount of (Ni–Mo)/[γ-Al₂O₃]-np-Al₂O₃-USY catalyst is larger than that of (Ni–Mo)/[γ-Al₂O₃]-USY or that of (Ni–Mo)/[γ-Al₂O₃]-np-SiO₂-USY as shown in Fig. 8. This result means that the existence of the np-Al₂O₃ generates the new acid sites in medium and strong acid strength. The new acid generation is not observed either when the np-SiO₂ is used instead of the np-Al₂O₃ or when the npAl₂O₃ or the USY component is impregnated by metal species before catalyst calcination. Therefore, both Al–OH in the np-Al₂O₃ and Si–OH in the USY have inevitable roles for new acid generation in (Ni–Mo)/[γ-Al₂O₃]-np-Al₂O₃-USY catalyst.

It is considered that these novel active sites (moderate and strong acids) are formed as shown in Fig. 9. Si–OH in the nanopores of USY resulted from dealumination catches Al–OH in np-Al₂O₃ to form Si–O–Al–O–Al–O–Si instead of Si–O–Al–O–Si–O–Si.

Fig. 7 Concerted effect depending on size of np-Al₂O₃. Catalyst/(Ni–Mo)/[γ-Al₂O₃]-np-Al₂O₃-USY, np-Al₂O₃ size: circle = 5 nm, triangle = 9 nm, square = 15 nm, filled circle: theoretical w/o concerted effect.
The catalysts which can efficiently hydro-reform higher n-paraffin to lower isoparaffins were studied. The tri-modally nanoporous catalysts composed of zeolite, np-Al$_2$O$_3$, and Ni–Mo/γ-Al$_2$O$_3$ have some selective performances. The catalyst composed of zeolite, especially USY or BEA, can selectively produce isoparaffins for gasoline. It is considered that these catalytic properties result from the tri-modal pore structure. Therefore, the nanopores combined with the other two kinds of the nano in the mouth can be used to design concerted pore structure for the catalytic reaction field.

It is considered that the catalytic property of (Ni–Mo)/γ-Al$_2$O$_3$–USY catalyst is partially due to the novel active sites (moderate and strong acids) formed. In the concerted effect of the catalyst, the newly generated acid sites have a major role for isomerization/cracking. These novel active sites (moderate and strong acids) are considered to be generated when Si–OH in the nanopores of USY

CONCLUSION

The catalysts which can efficiently hydro-reform higher n-paraffin to lower isoparaffins were studied. The tri-modally nanoporous catalysts composed of zeolite, np-Al$_2$O$_3$, and Ni–Mo/γ-Al$_2$O$_3$ have some selective performances. The catalyst composed of zeolite, especially USY or BEA, can selectively produce isoparaffins for gasoline. It is considered that these catalytic properties result from the tri-modal pore structure. Therefore, the nanopores combined with the other two kinds of the nano in the mouth can be used to design concerted pore structure for the catalytic reaction field.

It is considered that the catalytic property of (Ni–Mo)/γ-Al$_2$O$_3$–USY catalyst is partially due to the novel active sites (moderate and strong acids) formed. In the concerted effect of the catalyst, the newly generated acid sites have a major role for isomerization/cracking. These novel active sites (moderate and strong acids) are considered to be generated when Si–OH in the nanopores of USY

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