FISCHER-TROPSCH SYNTHESIS OVER ZEOLITE-SUPPORTED RUTHENIUM CATALYSTS DERIVED FROM $Ru_3(CO)_{12}$

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ABSTRACT

A set of zeolite-supported Ru catalysts was prepared from $Ru_3(CO)_{12}$ using zeolites NaX, NaY, KL and NaMordenite. These catalysts were characterized and studied under Fischer-Tropsch conditions in order to determine their unique properties and the effect of the zeolite support. For comparison, a catalyst using SiO_2 as support was also used. $Ru_3(CO)_{12}$ did not appear to be able to diffuse into NaX. Overall, the best catalyst in terms of high Ru dispersion, low methane selectivity and high olefin selectivity was Ru/NaY. The type of zeolite used as the support had a strong effect on methane selectivity. This method of preparation, compared to the ion-exchange method, is much superior in producing low yields of methane and high yields of olefins.

INTRODUCTION

Supported carbonyl complexes are currently receiving wide attention both for their potential application as an important new class of catalysts and for their utility as models for more traditional types of heterogeneous catalysts [1]. There have been four techniques used to adsorb metal carbonyl complexes on inorganic supports: (i) wet impregnation [2], (ii) extraction [3], (iii) solvated metal atom dispersion (SMAD) [4], and (iv) vapor-impregnation [5-7]. While silica, alumina, and other metal oxides have been widely used as supports for transition metal carbonyl complexes, the use of zeolite supports has been fairly limited. Due to their high surface area, shape-selective character, acidic nature, and well

defined structure, zeolites can play an important role in Fischer-Tropsch catalysis [8-10]. The high surface area allows a high degree of metal dispersion in the zeolite, while the acidity and shape-selectivity can significantly affect the selectivity of the catalyst. In addition, using zeolites as the support may better preserve the original $Ru_3(CO)_{12}$ metal cluster character [5].

Ruthenium has been shown to be one of the most active FT catalysts [11]. Several researchers [12-14] have reported that highly dispersed catalysts prepared from $Ru_3(CO)_{12}$ are much more active and selective for C_2-C_4 olefins and higher hydrocarbons in atmospheric pressure F-T synthesis than those prepared from $RuCl_3$. In contrast, Ferkul et al. [15] found that methane was the primary product for $Ru_3(CO)_{12}$-derived catalysts supported on Al_2O_3, SiO_2 and NaY zeolite. In addition, they reported that catalyst activities decreased in the following order: Ru/Al_2O_3 > Ru/NaY > Ru/SiO_2. The Ru/Al_2O_3 catalyst was also very active for carbon dioxide hydrogenation.

The present studies were undertaken to investigate the effect of zeolite supports on the catalytic properties of ruthenium catalysts prepared from $Ru_3(CO)_{12}$. These catalysts utilized as supports zeolites NaX, NaY, KL and NaMordenite. A silica-supported catalyst was also used for comparison.

EXPERIMENTAL

Catalyst Preparation

Synthetic zeolites (NaX, NaY, KL), SiO_2 and $Ru_3(CO)_{12}$ were obtained from Strem Chemicals Inc., NaMordenite (NaM), a synthetic large port mordenite, was obtained from the Norton Company. The supports were heated under vacuum at 450°C prior to their impregnation by vapor phase $Ru_3(CO)_{12}$. This impregnation process took place in an evacuated, sealed Pyrex cell held at a temperature of 80°C. The detailed procedure is well documented elsewhere [6-7]. The supported complex was then decomposed on heating (0.5°C min^{-1}) to 420°C and holding at this temperature for 2 h under a vacuum of 10^{-5} Pa.

Characterization

The decomposed catalysts were found to be in a completely reduced state, and subsequent reduction in H_2 was unnecessary. Thus, following decomposition under vacuum, H_2 and CO chemisorption measurements were carried out. After the chemisorption of H_2 was measured, the catalyst was heated under vacuum for 2 h at 420°C to completely desorb the hydrogen. The chemisorption measurements were carried out at room temperature in a glass adsorption system capable of achieving a dynamic vacuum of ca. 10^{-5} Pa. Total chemisorbed H_2 or CO was determined by extrapolation of the linear part of the first isotherm to zero pressure. A second isotherm was measured after evacuation of the sample for 2-3 minutes following the first isotherm. The second isotherm provided a measure of the reversibly bound hydrogen or

carbon monoxide (both chemisorbed and physisorbed). The difference between these two isotherms gave the amount of irreversibly chemisorbed hydrogen or carbon monoxide. Metal loadings were determined by atomic absorption.

FT Reaction

The kinetic data at a total pressure of 101 kPa were gathered using a 3/8 in. (1 in = 2.54 cm) stainless steel microreactor containing approximately 0.4 g of catalyst. Gases used were H_2 (99.999%), He (99.997%) and a H_2/CO mixture ($H_2/CO=1$, 99.9%), which were further purified by passage through Drierite and molecular traps to remove water and metal carbonyl contaminants. Prior to passage through the molecular sieve trap, the hydrogen was passed through a Deoxo unit to remove the oxygen as water. All gases were obtained from Air Products. The product gas was transferred from the reactor to the sampling valve of the gas chromatograph via a heated transfer line and was analyzed by a Perkin-Elmer Sigma 115 Gas Chromatograph equipped with TCD and FID. Products were separated using a 6 ft x 1/8 in. (1 ft = 30.48 cm) stainless steel column packed with Porapak Q. A 0.5 cm^3 sample was injected into the column which was held at 50°C for 2 min and then programmed at 15°C min^{-1} to 200°C. This permitted the separation of products up through C_8. The previously decomposed catalysts were reduced overnight in flowing H_2 at 300°C prior to the measurement of the reaction kinetics. Product samples were taken after 30 min of reaction. Based on catalyst life studies, 30 min of reaction was sufficient to establish the product distribution. No problem with product holdup in the zeolite support was observed at 1 atm for reaction times of 30 min or more. All reported results were obtained through a range of ascending and descending reaction temperatures. The bracketing technique [11], which gave the catalyst a 30 min exposure to H_2 after every kinetic measurement, was used to maintain a clean Ru surface and to give reproducible, consistent kinetic results. The CO conversion was kept below 5% to minimize the effects of heat and mass transfer and secondary reactions.

RESULTS AND DISCUSSION

The solvent used [16], support OH groups [17] and water physically adsorbed on the support [18] have been found to affect the properties of supported metals derived from organometallic compounds. In this study, the alkali-zeolites were calcined in vacuum at 420°C and did not contain any free water. Because these supports were in the unexchanged alkali form, they also had very low concentrations of OH groups. In addition, no solvent was used in the vapor impregnation preparation process.

The results of H_2 and CO chemisorption for the various Ru catalysts are given in Table 1. The average metal particle diameters, as estimated by H_2 chemisorption, were larger than the free diameter of the major zeolite cavities for all except

TABLE 1

Catalyst characteristics

Support	Si/Al ratio	Metal Loading (wt%)	H_2 (irr.) (µmole/g)	CO (irr.) (µmole/g)	CO/H (irr.)	$\bar{d}_0$ (Å)	%D
NaX	1.2	0.75	3.7±2.0	46±2.0	ca. 6.8	85	10
	1.2	0.27	5	55	ca. 5.6	22	37
NaY	2.4	1.3	58	274	2.4	9	90
KL	3	1.4	32	220	3.5	18	45
NaM	5	0.74	18	105	3.0	18	48
SiO_2	-	0.43	19	111	2.9	9	90

the NaY-supported catalyst. These results can be interpreted in four possible ways. The first explanation, proposed by Verdonck et al. [19], involves the localized destruction of the lattice to form cracks and holes. Filling of these voids by Ru metal would result in large particle sizes being measured. The second explanation, suggested by Gustafson and Lunsford, [20], is that in the presence of H_2 the mobility of Ru is increased, resulting in the agglomeration of Ru in several adjacent unit cells where the particles may be connected through the windows of the zeolite framework. This behavior would be expected to be more significant for the KL and NaMordenite due to their straight channel frameworks. The third explanation is that the suppression of irreversible hydrogen chemisorption might occur. Takasu et al. [21] have reported that, as metal particle size decreases, the adsorption energy of hydrogen on metal particles also decreases. However, a study by chemisorption and transmission electron microscopy (TEM) of catalysts prepared from $Ru_3(CO)$/NaY showed that for a highly dispersed Ru catalyst (ca. 100%) there was no indication of H_2 chemisorption suppression at ambient temperature, and the use of irreversible H_2 chemisorption at room temperature was appropriate for determining average particle diameters [22]. The CO/H chemisorption ratio can be a significant indicator of H_2 chemisorption suppression [23]. In the absence of such suppression, the CO/H ratio normally takes on values between 2.5 and 4 for highly dispersed Ru [24]. As can be seen in Table 1, the ratios for Ru supported on NaY, KL, NaM and SiO_2 suggest little or no H_2 chemisorption suppression on those catalysts. The large values of CO/H found for Ru/NaX are probably a consequence of errors associated with the measurement of small amounts of H_2 chemisorption rather than H_2 chemisorption suppression. A fourth explanation is that the presence of even a few very large particles on the external surface of the zeolite is able to skew the average metal particle diameter calculated from chemisorption to a size larger than the zeolite pores, even though most of the metal may exist

as very small particles inside the zeolite. It can be concluded, then, that for Ru supported on NaY, KL, NaM and SiO_2, the average particle diameters calculated should be relatively accurate. The large average diameters found for Ru/KL and Ru/NaM probably reflect the fact that some metal is encapsulated in the zeolite pores and some exists as large particles on the external zeolite surfaces. Such a situation has been observed by TEM for even highly dispersed Ru/NaY catalysts [22].

A miscalculation of the average particle size for Ru/NaX, resulting in a gross over estimation of average Ru particle size, can be ruled out. Ru can be totally reduced in catalysts prepared by this method, thus no decrease in H_2 chemisorption can be related to incomplete reduction. In addition, no H_2 chemisorption suppression is exhibited by zeolite-supported Ru prepared from $Ru_3(CO)_{12}$. Furthermore, where H_2 chemisorption suppression exists (zeolite-supported Ru prepared by ion exchange), no suppression is seen when the zeolite support has a low Si/Al ratio (as in the case for NaX) [23]. Activity and selectivity results, compared to previous results for zeolite-supported Ru [14] confirm the conclusion based on the H_2 chemisorption results that Ru/NaX has a relatively low Ru dispersion.

The average particle size, as calculated from H_2 chemisorption, for NaX-supported catalysts was found to increase monotonically with increasing Ru loading. Such an increase in particle size with loading is typical of zeolite-supported Ru where Ru is deposited primarily on the external surface of the support [14]. Since NaX has the same structure and cage dimensions as NaY but approximately twice as much Na, one may assume that most of the Ru was on the external surface of NaX due to the inhibition of diffusion of $Ru_3(CO)_{12}$ into the zeolite by a larger number of cations in the cage openings. The particle size obtained for the SiO_2-supported sample is comparable to the results of Kellner and Bell [25] for Ru/SiO_2 prepared by impregnation with a solution of $Ru_3(CO)_{12}$.

After several cycles of FT synthesis with hydrogen-bracketing, the catalytic properties of these catalysts were stabilized. The activity increased during this stabilization period and was accompanied by a shift to higher hydrocarbons. Such an increase in activity during the initial reaction period is not observed for Ru catalysts in general and seems to be unique for catalysts prepared from $Ru_3(CO)_{12}$.

The catalytic properties of these catalysts at steady state are shown in Tables 2 and 3. The primary hydrocarbon products under reaction conditions were methane, α-olefins and normal paraffins. Trace amounts of acetaldehyde and methanol were detected and increased with increasing Si/Al ratio of the supports. Interestingly, no correlation between the reaction rate and support Si/Al ratio was observed. Significant selectivities for olefins and carbon dioxide (see Table 2 and 3) were, however, an important feature. Previous results in the literature [26,27] have indicated that, in the FT synthesis, the weight ratio of CO_2/CH_4 is less than unity for Ru catalysts, in contrast to the present findings.

TABLE 2
Catalytic properties[a] of Ru catalysts.

Support	Metal loading (wt%)	CO Turnover No. × 10^3 (site^{-1} s^{-1})	Activity		E_{CO} (kcal mol^{-1})	α[b]	$R_{CO(3)}/R_{CO(1)}$[c]	CO_2/CH_4[d]		R_{CO_2}/R_{HC}[e]
			μmole/ g cat. s	μmole/ g Ru s				250°C	280°C	
NaX	0.75	40	0.296	39.5	21	0.42	0.74	1.3	0.5	1.0
NaY	1.3	5	0.580	44.6	23	0.76	1.25	2.1	0.8	0.6
KL	1.4	4	0.252	18.0	23	0.64	1.31	8.2	4.1	1.3
NaM	0.74	8	0.280	37.8	22	0.60	1.14	5.3	3.7	1.2
SiO_2	0.43	2	0.076	17.6	24	0.54	1.30	4.0	1.5	1.2

[a]Reaction conditions: 1 atm, 250°C, H_2/CO = 1, GHSV = 2700 h^{-1}
[b]Chain growth probability
[c]The ratio of the reaction rate in the third cycle to that in the first cycle.
[d]Weight basis.
[e]The ratio of rate of carbon consumption for CO_2 formation to that for hydrocarbon formation.

TABLE 3
Product selectivity (C_1-C_5) of Ru Catalysts (wt%)[a]

Support	Metal loading (wt %)	C_1	C_2	$C_2^=$	C_3	$C_3^=$	C_4	$C_4^=$	C_5+
NaX	0.75	42	7	4	1	16	9	4	17
NaY	1.3	18	5	2	0	39	6	4	26
KL	1.4	38	4	4	1	21	5	5	22
NaM	0.74	42	5	3	1	17	5	5	22
SiO_2	0.43	28	5	5	1	29	7	7	18

[a]Reaction conditions: 1 atm, 250°C, H_2/CO = 1, GHSV = 2700 h^{-1}

Results from this study indicate that r_{CO_2}/r_{HC} ratios (where r_{HC} is the rate of carbon atom incorporation in hydrocarbons) were greater than unity at 250°C, except for the Ru/NaY catalyst, and decreased with increasing reaction temperature. Since one mole of CO converted to any type of non-oxygenate gives one mole of H_2O or CO_2 as a byproduct, the maximum possible r_{CO_2}/r_{HC} that can be obtained via conversion of all the H_2O to CO_2 by the water gas shift reaction is unity. Therefore, any r_{CO_2}/r_{HC} ratio greater than one indicates the occurrence of the Boudouard reaction which provides another route for CO_2 formation. Our results are in good agreement with those reported by Okuhara et al. [13], who found that catalysts prepared from $Ru_3(CO)_{12}$/Al_2O_3 were more active for CO_2 formation than ones prepared from $RuCl_3$/Al_2O_3. In contrast to these results, Ferkul et al. [15] reported that, for the catalysts derived from $Ru_3(CO)_{12}$, the production of methane was predominant. In addition, they found that CO_2 formation was significantly suppressed. The different results may be due to the high temperature of reaction (375°C) and the high conversion (80%) used in the study, which possibly resulted in secondary reactions such as hydrogenolysis [28]. In our study, the CO conversion was kept below 5% to limit effects due to the water gas shift reaction as well as other secondary reactions.

As can be seen in Table 2, on a per gram Ru basis, specific activity decreases in the order NaY > NaX, NaM > KL, SiO_2. The lower turnover number (TON) in the case of NaY-supported Ru is compensated by the higher Ru surface area. The high TON observed on the NaX supported catalyst is likely due to its large average Ru particle size [8,14,35]. No significant effect of the support on TON was found in this study for similarly dispersed catalysts.

The activation energies for CO conversion over these various catalysts center around 23 kcal $mole^{-1}$ and are quite consistent with values reported previously
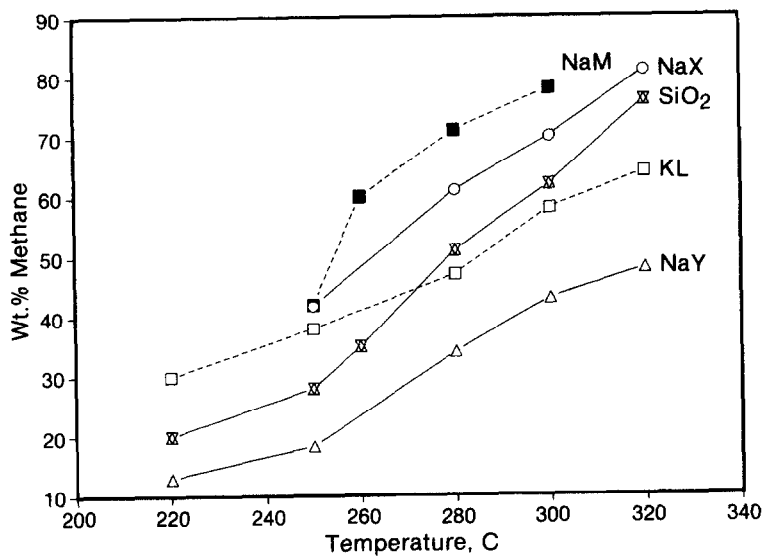
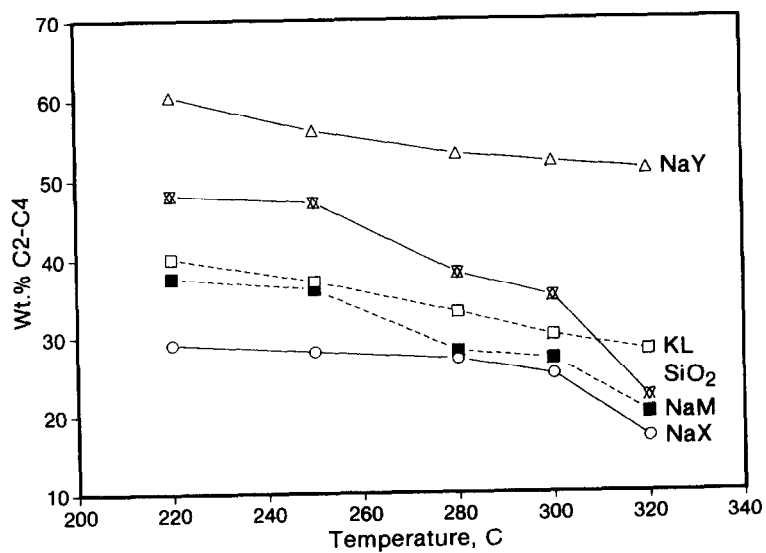FIGURE 1 Temperature dependence of methane formation.

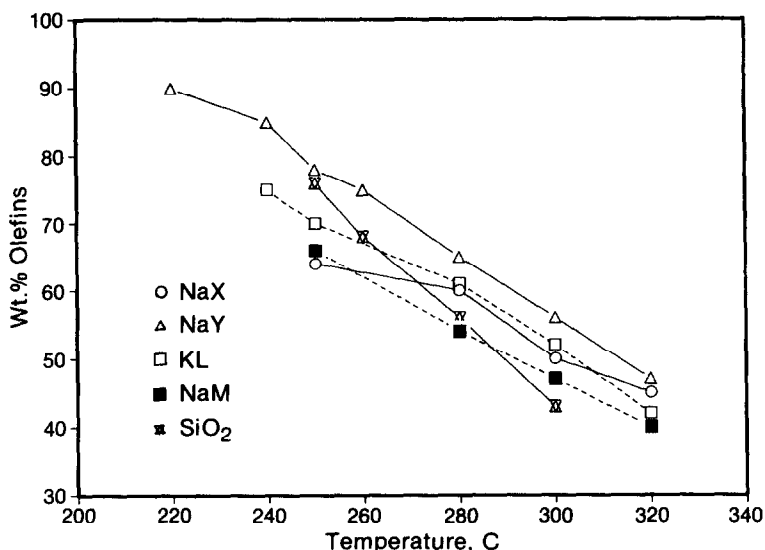FIGURE 2 Temperature dependence of C_2-C_4 formation.

FIGURE 3   Temperature dependence of olefin formation in C_2-C_4 fraction.

[27,30,31]. The hydrocarbon distribution was able to be fitted to the Anderson-
Schulz-Flory equation. It was found that the chain-growth probabilities in this
study, based on the C_3-C_7 distribution, were much higher than those for ion-exchang-
ed Ru/NaY catalysts [14] and Ru/Al$_2$O$_3$ catalysts [25] having similar metal loadings.
The chain growth probability decreased slightly with increasing reaction tempera-
ture in the range 240-300°C.

The effects of reaction temperature on the methane, C_2-C_4 hydrocarbon, and
C_2-C_4 olefin fractions over these catalysts are shown in Figures 1, 2 and 3 res-
pectively. Methane formation increased with increasing temperature of reaction,
as expected. A trend towards increasing methane formation with increasing Si/Al
ratio of the support was also observed, except for the NaX-supported Ru catalyst.
The results for Ru deposited on NaX in this study are in accord with the
previous results where ruthenium was primarily in the form of large particles
on the external surface.

It is interesting to note that C_2-C_4 hydrocarbon formation is only slightly
decreased with increasing temperature in the range 220-300°C. It can be concluded
that the increase in methane formation with temperature comes mainly from a de-
crease in the formation of liquid hydrocarbons (C_5^+) and is almost independent
of C_2-C_4 formation. Over the samples studied, the fraction of olefins in C_2-C_4
was nearly 3 times greater than that for comparable, similarly dispersed NaY-
supported Ru catalysts prepared by ion-exchange [14]. The selectivity for propylene

was as high as 40% of all hydrocarbons (including CH_4) at a reaction temperature of 250°C. It seems appropriate to ascribe the C_2-C_4 olefin formation to a property of Ru resulting from the method of preparation rather than to just a particle size effect, since the ion-exchanged catalysts previously studied [14] had approximately the same particle sizes but exhibited quite different selectivities.

As shown in Figure 3, the formation of olefins decreased with increasing temperature and Si/Al ratio of the zeolite support, except in the case of Ru/NaX. However, the zeolite support appeared to exert only a relative weak effect upon the ability to make olefins. Of greater importance for olefin selectivity appears to be factors influenced by the method of preparation. Thus, Ru/SiO_2 prepared by vapor impregnation exhibited a similar olefin selectivity as zeolite-supported Ru. A previous study of Ru/NaY catalysts has shown the effect that preparation method can have on this selectivity [14]. Of the three preparations methods employed, vapor impregnation produced catalysts having the greatest selectivities for olefins.

The relationship between selectivity and the nature of the catalyst may be attributed to the effect of metal dispersion, metal location in/on the zeolites, metal precursor species, and properties of the zeolite support. The extent to which each of these factors play a role is unknown and must await further investigation. In principle, the acidity of alkali zeolites is essentially nil and therefore independent of the Si/Al ratio [33-34]. The concentration of residual alkali cations, however, may affect the catalytic properties of Ru metal [23]. Finally the TON number is a strong function of average Ru metal particle size in the catalyst.

CONCLUSIONS

The results presented in this study indicate that the activity and selectivity for CO hydrogenation of zeolite-supported ruthenium catalysts prepared from $Ru_3(CO)_{12}$ are strongly influenced by the nature of the support. The properties of these catalysts differ significantly from those of incipient wetness and ion exchanged Ru catalysts. On the basis of specific activity (per g of Ru) and selectivity for olefins and higher hydrocarbons, the most effective support was NaY. This catalyst had a smaller average metal particle size than ion exchanged Ru/NaY catalysts previously studied [14]. In addition, the selectivity for methane was decreased and that for olefins was greatly increased for the carbonyl-based catalyst.

Surprisingly, $Ru_3(CO)_{12}$ did not appear to be able to diffuse into NaX, even though it was able to diffuse easily into NaY. This resulted in significantly poorer dispersions of Ru on NaX. Average particle size was a function of metal loading. It is suggested that the extra Na cations in NaX were able to act as a barrier for $Ru_3(CO)_{12}$ diffusion during preparation. From the dispersions and

selectivities obtained for KL and NaMordenite-supported catalysts, it can be assumed that, while diffusion of $Ru_3(CO)_{12}$ was not rapid, a significant amount of $Ru_3(CO)_{12}$ was able to migrate into these zeolites.

Finally, excluding Ru/NaX because of its poor dispersion of Ru in the zeolite, the catalytic selectivity for methane appeared to be a function of Si/Al ratio. However, due to the difficulty in getting Ru/KL and Ru/NaM as well dispersed as Ru/NaY, it is difficult to say whether this variation in methane selectivity was a true function of Si/Al ratio or was, in fact, a function of a related property such as alkali cation type and concentration as previously found for zeolite-supported Ru prepared by ion exchange [23]. Selectivity for C_2-C_4 olefins was not a strong function of zeolite type.

These results point out that, for zeolite-supported F-T catalysts, a number of parameters (metal particle size, particle location, Si/Al ratio, alkali type and concentration, etc.,) play major roles in determining catalytic properties.

ACKNOWLEDGEMENTS

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