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ADVANCED MICRO- AND MESOPOROUS MATERIALS – 13

Proceedings of the Fifth International Symposium
“Advanced Micro- and Mesoporous Materials”
held from September 6th till 9th 2011 in the Golden Sands Resort, Bulgaria.

Edited by K. Hadjiivanov, V. Valtchev, S. Mintova, G. Vayssilov

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Preface

This book from the series “Topics in Chemistry and Material Science” contains selected contributions presented at the Fifth international symposium “Advanced micro- and mesoporous materials” held in Golden Sands Resort (Bulgaria), September 6–9, 2013. More than 130 scientists from 29 countries from Europe, Asia, Africa and America participated in the symposium. Scientists working in different fields, including synthesis, characterization, application and modeling of various types of porous materials shared ideas, opinions and learned more about the latest developments and challenges in the area.

The scientific program of the meeting included 3 plenary, 5 keynote and one topic lectures, 24 oral and 10 short oral presentations, and 81 posters. The plenary and keynote lectures were delivered by K. B. Yoon, C. Serre, R. Catlow, M. Jaber, Y. Román-Leshkov, P. Nachtigall, J. Szanyi, S. K. Henninger, and M. Thommes. The high level of the meeting reflected on the excellent publications included in this book.

The symposium was held in very friendly atmosphere and the discussions often continued outside the conference hall. The splendid weather, beautiful environment and rich social program contributed to the full success of the symposium.

We would like to express our gratitude to the Total, Quantachrome, and Bulgarian Ministry of Education and Science for the financial support ensuring the success of the symposium. We also thank our colleagues R. Nikolova, V. Georgieva, P. Petkov, and E. Ivanova for their help in organizing the meeting and preparation of the proceedings.

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Conversion of Acetic Acid to Ethanol over Novel InNi/faujasite and InNi/SBA-15 Catalysts: Comparison of Micro- and Mesoporous Supports

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Abstract

Conversion of acetic acid (AA) in hydrogen was studied over novel supported bimetallic catalysts of In and Ni. A fixed bed flow-through tube reactor was used at 21 bar total pressure in the temperature range of 240-360°C. Supported-NiO was mixed with In₂O₃ and reduced in H₂ to obtain active catalyst. It was shown that In and Ni forms alloy, having the stoichiometry of Ni₂In. Alloying with In inhibited the hydrogenolysis activity of the supported Ni catalyst. The catalyst steered the AA conversion in the direction of step-by-step reduction to ethanol by high selectivity. Regarding both activity and ethanol selectivity the mesoporous silica SBA-15 material was found to be more advantageous catalyst support than the microporous zeolite faujasite.

1 Introduction

On some biomass degradation pathways carboxylic acids are generated, which acids are considered as platform molecules of the chemical industry [1]. The alcohols obtained by selective reduction of these acids can be used, for instance, as biofuel. The process of acid hydroconversion requires novel, efficient catalyst. Bimetallic catalysts often show enhanced activity, higher selectivity and better stability relative to the single metal catalysts, containing any of the component metals. These properties made bimetallic catalysts useful to convert materials of biomass origin to fuels and chemicals [2]. From the 1960s, as a result of the extensive investigations, bimetallic catalysts became widely utilized in many catalytic applications. The effect of Sn additive, for example, on the catalytic properties of Pt/alumina has been reported in numerous studies [3], whereas the promoting effect of the Sn neighbor indium received much less attention [4-6].

The hydrogenolysis of C-C and C-O bonds is the dominant process of carboxylic acid hydroconversion over some monometallic catalysts, such as noble metals and nickel. Over these catalysts hydrodecarbonylation proceeds and hardly any alcohol formed. The indium additive changes the catalytic mech-

anism [7,8]. The carboxylic acid is converted in consecutive hydrogen addition/dehydration/hydrogen addition steps resulting finally in the selective formation of alcohol.

In the nickel-indium bimetallic catalysts Ni_2In phase was found to be present substantiating that this phase was responsible for the significant improvement of alcohol selectivity and yield relative to the corresponding properties of the monometallic forms [7,9]. Regarding the catalytic activity, the structure and composition of the metal particles are the decisive properties, which are affected to some extent by the structure and composition of the support. Moreover, the catalyst can show activity that cannot be assigned to the supported metal phase but comes from the support [10]. The present work shows the importance of the support properties by comparing a highly ordered mesoporous silica SBA-15 and a microporous zeolite faujasite as supports of nickel-indium catalysts.

2 Experimental

2.1 Materials

Supported Ni and NiIn catalyst precursors were prepared, which precursors were converted to catalyst by H_2 reduction prior to the experiment in situ in the high-temperature X-ray diffraction cell (XRD) or in the high-pressure catalytic reactor (vide infra).

Nickel faujasite catalyst precursors were prepared from NaX (product of the late VEB CKB, Bitterfeld-Wolfen, Germany) and NaY (Grace Corp.) powders by conventional aqueous ion-exchange using nickel(II)acetate solution. The obtained zeolite NiX and NiY have Ni contents of 10 and 6 wt%, respectively.

Silica supported Ni catalyst precursors, containing 9 wt% Ni, were prepared by impregnating silica support with NH_4OH solution (Reanal, Hungary) of $\text{Ni}(\text{acetate})_2$ (Aldrich), dried at 120°C and calcined at 400°C in air stream. Two different silica materials were applied as catalyst supports. Amorphous silica SBA-15 material, containing hexagonally ordered, uniform, parallel mesopores of about 6 nm diameter was synthesized by a sol-gel method using an amphiphilic triblock copolymer Pluronic P123 as organic structure-directing agent [11]. The specific surface area (SSA) of the material, determined by the BET method, was $893\text{ m}^2/\text{g}$. Commercial CAB-O-SIL M-5 (Cabot Corp.) fumed silica, consisting of agglomerated amorphous, colloidal silica particles, was also applied. In contrast to the SBA-15 material it has as a wide size distribution of mesopores and an SSA of $200\text{ m}^2/\text{g}$.

Bimetallic catalyst precursors were prepared by adding indium (III) oxide (Aldrich) to precursors of Ni catalysts in amounts to attain Ni_2In stoichiometric composition of the metallic phase, and the mixture was grinded in an agate mortar.

The same designation was used for the catalyst precursor and the corresponding catalyst, containing the symbol of the metal(s) and the name of the support, such as, NiX, InNiX, InNi/SBA-15, InNi/Cab-O-Sil, etc.

3 Methods

The catalyst precursor was loaded into a high-pressure, fixed bed, flow-through reactor and reduced in a flow of 100 cm³/min pure hydrogen *in situ* in the reactor at 450°C and 21 bar for 1 h to obtain active supported metal catalyst. The hydrogenation of AA (96%, Reanal, Hungary) was studied at 21 bar total pressure and at in the 220–380°C temperature range. The reactor effluent was cooled to room temperature, the liquid and gaseous products were separated. The liquid was analyzed using gas chromatograph (Shimadzu 2010) equipped with a Restek Rt-U-BOND capillary column, and a flame ionization detector. The gas was analyzed by on-line gas chromatograph (HP 5890) equipped with Carboxen 1006 PLOT capillary column and thermal conductivity cell. The product distributions are represented as stacked area graphs where the distance between two neighboring curves represents the yield of a given product in mole percent.

XRD patterns of the catalysts were recorded at elevated temperatures in hydrogen flow using a high-temperature XRD cell a Philips PW 1810 diffractometer. The mean crystallite size of the metal particles was calculated by the Scherrer equation. The morphological analysis of the samples was carried out with a FEI Morgagni 268D type TEM. Adsorption isotherms of nitrogen were determined at -196°C using Quantochrome Autosorb 1C sorptometer.

4 Results and Discussion

The type I N₂ physisorption isotherm of the reduced zeolite NiX sample is shown in Figure 1. The isotherms of NaX, and reduced InNiX zeolites were quite the same as that of the NiX, suggesting that no any structural destruction takes place during catalyst preparation. The zeolite structure of the NiX preparation is more resistant to hydrogen reduction that of zeolite CuX, CuA and CuP [12].

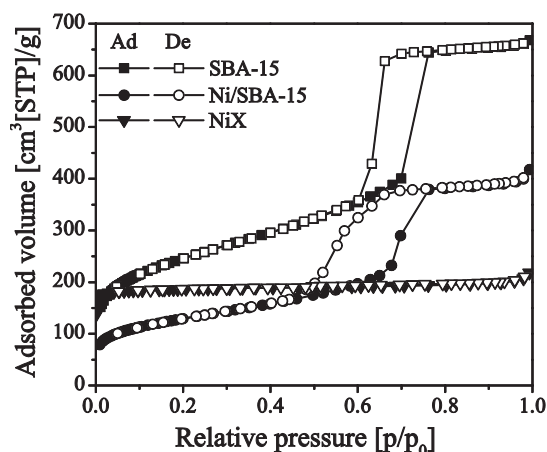


Figure 1. Isotherms of nitrogen adsorption (full symbols) and desorption (open symbols) at -196°C of NiX (▼, ▽), SBA-15 material (■, □) and Ni-loaded SBA-15 material (●, ○) after treatment in H₂ flow at 21 bar and 450°C for 1 h.

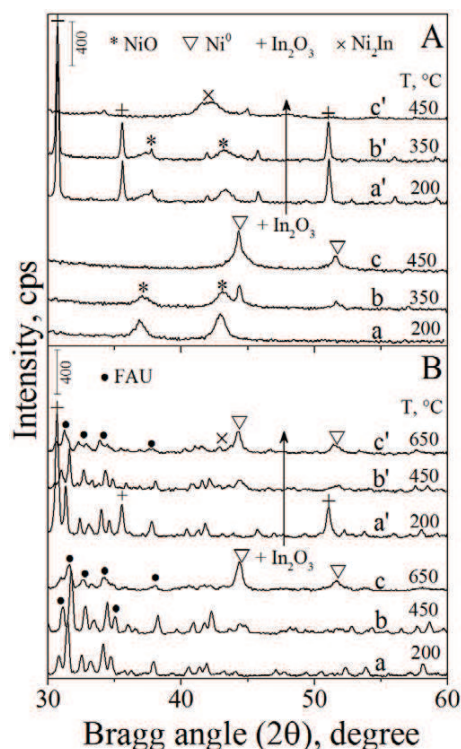


Figure 2. HT-XRD patterns of the (A) SBA-15 and zeolite X (B) material supported catalysts recorded in H_2 flow. The materials were kept at the indicated temperature for 30 min, then a diffractogram was recorded and the temperature was increased to the next higher temperature. Patterns a, b, and c refer to the indium free Ni-containing preparations, whereas patterns a', b', and c' to the mixture of the corresponding Ni-containing preparation and 10 wt% In_2O_3 .

The adsorption isotherms of the SBA-15 samples are also shown in Figure 1. The isotherms of the two reduced Ni-containing SBA-15 samples were found identical, therefore only the isotherm of the Ni/SBA-15 sample is shown. The isotherms of the SBA-15 samples are type IV with H_2 hysteresis loop. The mean diameter of the mesopore is approximately 6 nm. The conventional incipient wetness capillary impregnation technique generated nickel oxide particles in the channels. Upon H_2 reduction at temperature above the melting point of the indium metal mobile indium atoms are formed from the In_2O_3 . These atoms can easily reach the Ni particles, formed in the channel, and generate alloy. Generation of metal particles resulted in catalyst having a smaller SSA ($SSA=468\text{ m}^2/\text{g}$) than the parent SBA-15 material.

Evolution of active metallic phases during reduction by H_2 was followed by HT-XRD measurements (Figure 2). The NiO, formed upon calcination of the Ni-acetate-impregnated SBA-15 material, could be fully reduced to nickel at 450 °C (Figure 2A). The average size of Ni^0 particles in the Ni/SBA-15 catalyst,

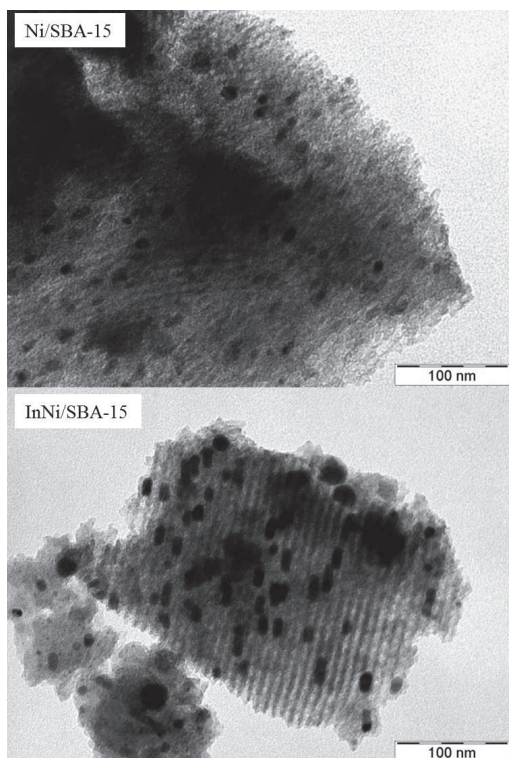


Figure 3. TEM images of the SBA-15 supported mono- and bi-metallic catalyst after treatment in H_2 flow for 30 min at $450^\circ C$.

estimated by the Scherrer equation was 21 nm. That infers that only short metal nanowires could have been formed instead of spheres because of the spatial constraints posed by the channels of 6 nm diameter. The metal particles inside the channels diameter can be seen on the TEM images of Figure 3. The particles of the intermetallic compound Ni_2In detected by XRD (Figure 2B) are also observable on the TEM image of the catalyst. These Ni_2In particles are longer cylinders. The Ni metal and the Ni-In alloy fully blocks short sections of the channels, providing explanation for the lower SSA of the SBA-15 catalysts that of the pure support.

In the diffractogram of NiX strong reflections of crystalline Ni^0 appeared only at reduction temperature $650^\circ C$ (Figure 2B). Unlike to the mesoporous silica support, carrying Ni-oxide particles, the nickel cations are distributed on the cationic sites of the faujasite framework balancing negative framework charge. Only a small fraction of nickel could be reduced at $450^\circ C$ (Figure 2B). The residual Ni^{2+} lattice cations stabilized the structure of the aluminum-rich zeolite X. It was shown in an earlier study that zeolite CuX, containing easy-to-reduce copper ions, suffers complete structural collapse upon reduction under similar conditions [12]. The reduction of the nickel cations becomes complete at tem-

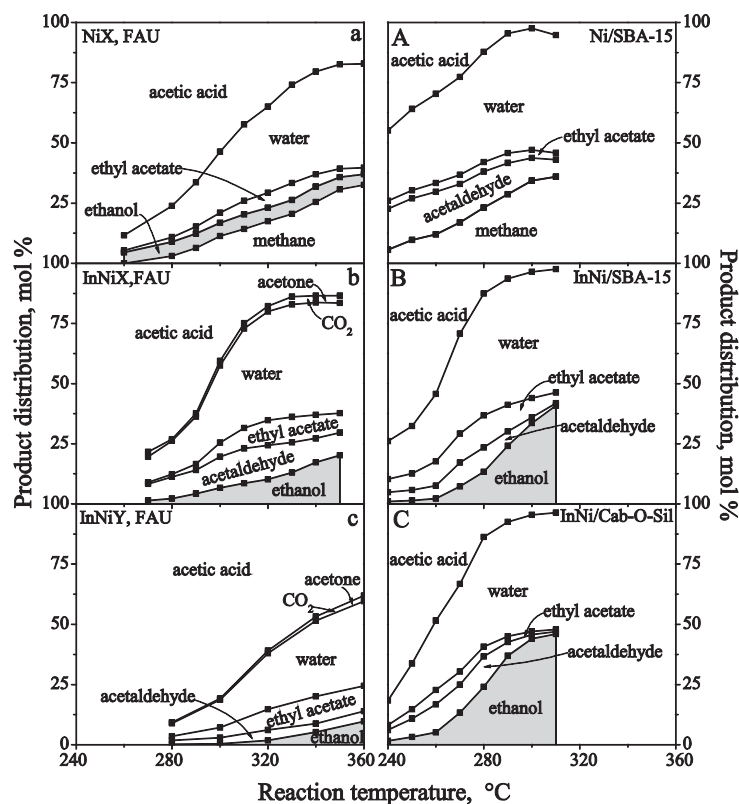


Figure 4. Stacked area graphs of product distribution of AA hydroconversion as a function of reaction temperature at 21 bar and $1 \text{ g}_{\text{AA}} / (\text{g}_{\text{cat}} \cdot \text{h})$ WHSV over (a, A) In-free and (b, B, c, C) In-modified nickel catalysts. Supports are (a, b) zeolite X, (c) zeolite Y, (A,B) SBA-15, and (C) Cab-O-Sil.

perature about 650°C . The H-form of the zeolite X was generated that carried Ni^0 particles. In the virtual absence of steam the crystallinity of the zeolite was preserved to a significant extent. The average size of the Ni^0 particles, estimated by the Scherrer equation, was 19 nm. This infers that the catalytically active particles can be only on the outer surface of the micron-size zeolite crystals. The In_2O_3 mixed with NiX could be completely reduced up to 450°C , nevertheless, neither In nor Ni_2In phases could be detected at any temperature of the XRD measurement. These results suggest that the indium must be present in highly dispersed form in the zeolite cavities and probably a small fraction of the introduced indium modified the active surface of the large nickel crystallites.

Monometallic, nickel containing catalysts are very active in AA hydrogenolysis giving CH_4 and H_2O as products. Carbon dioxide and carbon monoxide might have been formed only as intermediate that was rapidly reduced to methane (Figure 4a, A). The Ni/SBA-15 catalyst was found to be significantly more active than the NiX catalyst in line with the finding that latter catalyst con-

tained lower amount of active metal because the nickel cations were reduced in the zeolite to a low extent only at the pretreatment temperature (Figure 2). Surprisingly, acetaldehyde and no ethanol was formed over Ni/SBA-15 catalyst, whereas ethanol and no acetaldehyde was obtained as product when NiX catalyst was used.

Indium admission to both supported nickel catalysts can completely eliminate the methane formation. The absence of CO as product shows that the In-modified catalysts do not have hydrodecarbonylation activity. Similar effects of In-modification was reported in earlier studies [9,12]. The selectivity change of the SBA-15 supported catalysts is more pronounced than that of the zeolite catalysts. The modification reduced somewhat the activity but not affected the specific surface area of the catalysts. The TEM images show that accessible surface area of the metal in the channels of the SBA-15 material hardly changes with the metal loading. Only the length of the nanowires, i.e., the inaccessible superficieses grow.

The yield of intermediate product acetaldehyde and the ethyl acetate product of esterification are suppressed if more severe reaction conditions are applied. Main product ethanol and reactant acid can form ethyl acetate as a product of Fischer esterification, proceeding on a non-catalytic route. At higher reaction temperatures, the ester yield decreases indicating that the activation energy of ester hydrogenolysis is higher than that of ester formation.

The indium-modified NiX catalyst is somewhat more active than the monometallic NiX. The effect of In modification is similarly drastic on the selectivity, as it was in the case of the SBA-15 supported catalysts. The ethanol yield and the acetaldehyde formation increases. The NiY catalyst, having the same structure but lower Ni-content than the NiX catalyst, shows much lower activity (Figure 4b, c). Surprisingly the activity of the Ni/SBA-15 and NiX catalysts and is commensurable despite of the low content of Ni⁰ in the latter one. Most of the metal atoms are not accessible for the reactants in the zeolite channels as is the case with the SBA-15 support. As a consequence similar amounts of active centers can be accessible in the two very different catalysts resulting in similar catalytic behavior.

The catalyst made using commercial fumed silica support has much lower specific surface area than the catalyst made using SBA-15 support. Nevertheless, the two catalysts show similar activity and selectivity in the AA hydroconversion reaction (Figure 4B, C). More efficient contacts for carboxylic acid hydroconversion are expected to be obtained if particles, much smaller size than the channel diameter, can be bound to the inner walls of the SBA-15 channels. The highly ordered mesopore system of the SBA-15 support may favor diffusion and allow higher rate of transformation.

Over the indium modified NiX and Ni/SBA-15 catalysts the rate of AA hydroconversion increases linearly with the partial pressure of hydrogen at low conversions, whereas it is decreasing as the partial pressure of AA is increased. This is in line with Langmuir-Hinshelwood type kinetics and mechanism.

5 Conclusion

Indium co-catalyst applied with nickel makes an efficient supported catalyst for the hydroconversion of AA with to ethanol. The reaction mechanism, found when supported Ni catalyst was used, changed on the effect of indium addition. The active catalyst was developed by co-reduction of the two metals, being in contact with a support, by H₂. This process and the catalytic efficiency of the obtained bimetallic particles were found to be strongly affected by the structure of the support. The active metal particles can block the channels of the supports limiting the accessibility of the active metal surfaces. Such bimetallic preparations have broad perspectives to be used by the chemical industry for producing fine chemicals.

Acknowledgements

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