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Amino-grafted metallosilicate MCM-41 materials as basic catalysts for eco-friendly processes

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ABSTRACT

The compounds 3-aminopropyl-trimethoxysilane (APMS), [3-(2-aminoethylamino)propyl]trimethoxysilane (2APMS) and 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane (3APMS) were loaded by grafting on MCM-41 matrices of various chemical compositions, aluminosilicate (AlMCM-41; Si/Al = 64) and niobosilicate (NbMCM-41; Si/Nb = 64). The materials prepared were characterized using XRD, N₂ adsorption/desorption, thermogravimetric analysis, FTIR spectroscopy and elemental analysis. Thermal stability of APMS was found not to depend on the chemical composition of the support. The higher stability of 2APMS and 3APMS was related to the hydrogen bonding between amine groups and surface hydroxyls. The models of amine grafted in MCM-41 materials were proposed. Basic activity in 2-propanol dehydrogenation and Knoevenagel reactions was found strongly dependent on the nature of the support and changed in the following order: APMS/AlMCM-41 > APMS/NbMCM-41. The acidity of the support is considered for the explanation of the activity sequence.

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1. Introduction

The end of the 20th century has brought increasing interest in the use of silica materials modified with aminopropyl and/or other organic moieties as catalysts [e.g. 1–4] mainly in base-catalysed reactions. An important drawback of these materials is the lack of uniform and well ordered mesoporosity, which is of significance in catalysis. Discovery of the M41S family of mesoporous materials [5] has stimulated research in the area of surfactant-templated, periodic mesoporous hosts. Much progress has been made in the last few years in the development of organo-modified mesoporous molecular sieves [6–10]. Several reviews have been devoted to this important type of materials [e.g. 11–15].

Development of clean processes for production of fine chemicals requires the use of recyclable solid catalysts. Besides acid catalysts, solid base catalysts need to be explored. The design of base catalyst featuring large mesoporous surfaces allows performing base-catalysed reactions in the fields of production of perfumes, pharmaceuticals and agro-chemicals. Post-synthesis grafting of organotrialkoxysilane [6,8,13,16,17] has been effectively used to incorporate active organic functional groups onto the mesoporous silicas surface. Such prepared catalysts show high activity for base-catalysed reactions because of their high surface area and large pore channels. Moreover, their activity is expected to vary by controlling the amine content, its nature and strength (primary, secondary, or tertiary amine).

The primary amino groups bound on mesoporous silicas, the materials MCM-41, SBA-15, have been previously reported efficient catalysts for the Knoevenagel condensation reaction under mild conditions [6,8]. The mechanism of their catalytic activity has also been discussed. The reaction of benzaldehyde and ethylcyanoacetate (ECA) in the presence of primary amine may proceed very fast via the formation of imine in which the benzaldehyde molecule first reacts with the -NH₂ group present on the catalyst surface to form an intermediate imine (C=N double bond) compound. Next, the acidic methylene group of ECA attacks the C=N double bond of imine and forms the condensation product leaving behind the -NH₂ group. However, in the same reaction in the presence of secondary or tertiary amines, the more common aldol type mechanism prevails. Thus, the higher activity of primary amine vs. secondary or tertiary one has been attributed to the faster reaction through imine formation [e.g. 8].

The idea of our work was to get a better insight into the role of chemical composition of metallosilicate mesoporous ordered supports on the catalytic activity of amino-grafted



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materials. In our previous work [18] the focus was on silicate and niobosilicate MCM-41 grafted with one amine (3aminopropyl-trimethoxysilane – APMS). One of the aims of this study was to determine the influence of the nature of the amine (3-aminopropyl-trimethoxysilane – APMS, [3-(2aminoethylamino)propyl]trimethoxysilane – 2APMS and 3-[2-(2aminoethylamino)ethylamino]propyl-trimethoxysilane – 3APMS) linked to MCM-41 mesoporous molecular sieves containing various T atoms (Al and Nb) on the properties and catalytic activity of the catalysts obtained. The thermal stability of the amines grafted on aluminosilicate and niobosilicate MCM-41 supports and their activity in the base-catalysed reactions (tested in Knoevenagel condensation) have been analysed. Moreover, the role of the type of metal (Nb or Al) in MCM-41 support has been considered.

2. Experimental

2.1. Synthesis of the catalysts

Mesoporous molecular sieves of MCM-41 type were synthesized by the classical hydrothermal method [5] and modified in the preparation of AlMCM-41 and NbMCM-41-64 [19].

2.2. Grafting

The ammonium forms of mesoporous molecular sieves, NH₄AlMCM-41 and NH₄NbMCM-41 were obtained via cation exchange with NH_4^+ ions (from NH₄Cl solution). They were transformed to hydrogen forms by calcination at 673 K for 2 h.

The hydrogen forms, HAIMCM-41 and HNbMCM-41, were the supports for grafting of 3-aminopropyl-trimethoxysilane (APMS), [3-(2-aminoethylamino)propyl]trimethoxysilane (2APMS) and 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane (3APMS) (Aldrich). The grafting procedure was carried out according to [20] and was as follows: 2.3 g of the support powders were refluxed in a dry toluene solution (200 mL) containing 10 mL of APMS at 373 K for 18 h. The catalysts were recovered by filtration followed by washing in dry toluene (200 mL), water (100 mL) and acetonitrile (20 mL). The powder was dried in an oven at 373 K and stored for the later use. The catalysts obtained were labelled as APMS/TMCM-41, 2APMS/TMCM-41, 3APMS/TMCM-41.

2.3. Catalysts characterization

The materials prepared were characterized using XRD, N_2 adsorption/desorption, thermogravimetric analysis, FTIR spectroscopy and elemental analysis.

XRD measurements were carried out with a Bruker AXS D8 Advance diffractometer with Cu K α radiation (λ = 0.154 nm), with a step size of 0.02° and 0.05° in the small-angle and high-angle ranges, respectively.

The N_2 adsorption/desorption isotherms were obtained in a Micromeritics ASAP equipment, model 2010. The samples were pre-treated in situ under vacuum at 333 K for 24 h. The surface area was calculated by the BET method. The pore size distributions (PSD) and the mesopore volumes were determined from the adsorption/desorption isotherms using DFT.

The thermogravimetric analyses of the solids were carried out with ATA Instruments thermogravimetric system, model SDT Q600 TG–DSC.

The elemental analyses of the solids were carried out with Elementar Analyser Vario EL III.

Infrared spectra were recorded with the Vector 22 (Bruker) spectrometer (resolution 4 cm^{-1} , number of scans=64). The

pressed wafers of the materials ($\sim 5 \text{ mg cm}^{-1}$) were placed in the vacuum cell and evacuated in the range RT-673 K for 1 h.

2.4. Catalytic tests

2.4.1. 2-Propanol decomposition

The 2-propanol conversion (dehydration and dehydrogenation) was performed, using a microcatalytic pulse reactor inserted between the sample inlet and the column of a CHROM-5 chromatograph. The catalyst bed (0.02 g with a size fraction of 0.5 < 0 < 1 mm) was first activated at 673 K for 2 h under helium flow (40 cm³ min⁻¹). The 2-propanol (Aldrich) conversion was studied at 423, 473, 523, 573 K using 2 μ l pulses of alcohol under helium flow (40 cm³ min⁻¹). The reactant and reaction products: propene, 2-propanone (acetone) and diisopropyl ether were analysed using CHROM-5 gas chromatograph on line with microreactor. The reaction mixture was separated on 2 m column filled with Carbowax 400 (80–100 mesh) at 338 K in helium flow (40 cm³ min⁻¹) and detected by TCD.

2.4.2. Knoevenagel probe reaction

The experimental work was carried out in a Pyrex-glass batch reactor. The equimolar mixtures of the two reactants, benzaldehyde and the active methylenic compound (ethylcyanoacetate, or diethyl malonate) without any solvent were pre-heated to the reaction temperature, 393 K, under continuous stirring. Then, depending on the active methylenic compound employed, ethylcyanoacetate or diethyl malonate, 1, 2 or 10 wt% of solid catalyst was added respectively and the reaction started. Samples were taken periodically, and the evolution of the reaction was followed by gas chromatograph, using an Agilent Technologies 6890N chromatograph.

The influence of external and internal diffusion on the total rate of the reaction was determined by changing the stirring rate in the range 1000–3500 rpm and by the use of different particle sizes (0.074, 0.140, 0.250 mm diameter), respectively.

The catalysts were recycled by washing them in acetone, subsequently dried in an oven at 373 K overnight.

3. Results

3.1. Texture/structure

XRD patterns of niobosilicate MCM-41 shown in Fig. 1A indicate that grafting of APMS on this material leads to the disordering of the hexagonal arrangement of mesopores in the long range (deduced from the drop in intensity of the XRD peaks at 2Θ = 3–5°). It is seen even after normalisation of (100) peak to the same intensity value (Fig. 1B). Interestingly, the disordering is less pronounced in amino-grafted AlMCM-41 (Fig. 1C) which preserves the ordering of mesopores after APMS immobilization. It is important to stress that the amount of nitrogen in the APMS-grafted materials (Table 1) differs depending on the chemical composition of the support (APMS/NbMCM-41 > APMS/AIMCM-41). The grafting of 2APMS and 3APMS on aluminosilicate support giving rise to a

Table 1

Texture parameters of the catalysts and the amount of nitrogen in the amino-grafted MCM-41 materials.

Catalyst	Surface area	Average pore	Mesopore	N loading
	BET (m ² /g)	diameter (nm)	volume (cm ³ /g)	(mmol/g)
AIMCM-41	909	3.9	0.76	0.2
APMS/AIMCM-41	637	3.3	0.37	1.8
3APMS/AIMCM-41	277	2.9	0.19	4.5
NbMCM-41	1049	3.8	0.96	0.1
APMS/NbMCM-41	707	3.2	0.44	2.0
2APMS/NbMCM-41	279	2.9	0.14	2.1



Fig. 1. XRD patterns of MCM-41 catalysts in the small-angle range; (A) and (C) original XRD patterns, (B) after normalisation of (100) peak to the same intensity value.

higher amount of nitrogen only slightly decreases the intensity of XRD reflexes indicating that even these amines do not change significantly the ordering of the material.

The textural parameters calculated from N_2 adsorption/desorption isotherms are shown in Table 1. They indicate a decrease in the surface area of amino-grafted AlMCM-41 (about 30% decrease) and NbMCM-41 (ca. 33% drop). The mesopore volume also decreases in the amino-grafted metallosilicate materials. The decrease in the mesopore volume after grafting of amines when compared with the pristine support suggests the collapse of some mesopores or blockage effect.

3.2. Thermal stability of aminoalkoxysilanes in mesoporous matrices

The thermal stability of all APMS in MCM-41 type supports was estimated on the basis of infrared spectroscopy (FTIR) measurements after evacuation of the material at various temperatures and the thermogravimetric measurements. The stability of amine is deduced from the temperature at which the drop in the band intensity of the N-H vibration in the NH₂ group takes place (the band at 1596 cm⁻¹) [21]. As follows from Table 2, irrespective of the nature of the support, the first intensity drop of the FTIR (NH₂) band, in the APMS-grafted materials, occurs at the same temperature, i.e. 473 K. It should be added that this FTIR band loses ca. 61-63% of the initial intensity after evacuation at 573 K, also irrespective of the nature of the support. Moreover, evacuation at 673 K causes almost total disappearance of the -NH₂ IR band for all the samples described in Table 2. However, it does not mean that amine has undergone total decomposition and has been removed after such treatment, because the chemical analysis of these samples indicates the presence of ca. 20% of the initial amount of nitrogen.

Table 2	
Stability of aminoalkoxysilanes -	FTIR study.

Catalysts	Start of amine decomposition from IR, temp. (K)	Disappearance of amine IR band, temp. (K)
APMS/AIMCM-41	473	673
2APMS/AIMCM-41	573	673
3APMS/AIMCM-41	573	673
APMS/NbMCM-41	473	673

The results in Table 2 also show that 2APMS and 3APMS decompose at higher temperatures than APMS. The temperature of the first intensity drop ($(-NH_2)$ IR band) for both, 2APMS and 3APMS is 573 K.

The thermogravimetric analyses (TGA), exemplary shown in Fig. 2 for AlMCM-41 based materials, confirmed the results of FTIR spectroscopy. The TG curves for silicate and niobosilicate MCM-41 have been compared in our earlier paper [18]. It has been evidenced that the pristine niobosilicate NbMCM-41 exhibits one drop of weight at ca. 373 K caused by desorption of water adsorbed. APMS-grafted sample shows additional weight loss that ends at ca. 900 K, irrespectively of the chemical composition of the matrix. The same is true for APMS/AlMCM-41 (Fig. 2). TG curve of 3APMS/AlMCM-41 has a shape similar to that obtained for APMS immobilized material, but the temperature of total decomposition of the amine is higher. Moreover, the DTG curve reveals three maxima indicating three steps of 3APMS decomposition.

3.3. Surface characterization

FTIR spectra were measured for identification of functional groups in the amino-modified materials evacuated at room temperature (Fig. 3). The band at 1596 cm^{-1} assigned to the NH₂ vibration dominates in the spectra of amino-grafted materials suggesting that methoxy species are involved in APMS grafting on the surface of the supports. Interestingly, the presence of methoxy species is observed in the IR spectra of 2APMS and 3APMS/AIMCM-41 (1455 cm⁻¹) [22,23] indicating that not all methoxy species are involved in the chemical interactions with surface hydroxyls leading to amino-grafting. On the contrary, in grafting of APMS most methoxy species take part in the chemical bonding with the surface. It should be emphasised that in 2APMS- and 3APMSgrafted AlMCM-41, the hydrogen bonded species were observed in hydroxyl region of IR spectra. Hydrogen bonding between amine groups of 3-aminopropyl(trimethoxysilane) and surface hydroxyls had been already suggested by Das and Sayari [8]. Our results confirmed this suggestion.

3.4. 2-Propanol decomposition

The reaction of 2-propanol decomposition has been used as a test for basic–acidic properties of the samples [24,25]. It allows estimation of the nature of acidic and basic centres and the strength



Fig. 2. DTG curves of APMS/AIMCM-41 and 3APMS/AIMCM-41 catalysts.

Table 3The results of 2-propanol decomposition.

Catalysts	2-PrOH conv. (%)	Temp. (K)	Acetone selectivity (%)	Ref.
APMS/MCM-41 APMS/AIMCM-41 2APMS/AIMCM-41 3APMS/AIMCM-41 APMS/NbMCM-41 2APMS/NbMCM-41	0.3 0.3 0.3 0.3 0.3 0.3 0.3	573 423 423 423 423 423 423	8 35 43 51 15 16	[18] This work This work This work [18] This work

of the basic centres from the products formed. Both, Brønsted and Lewis, acid sites activate the reaction towards propene formation, whereas basic centres are active in dehydrogenation to acetone. The formation of diisopropyl ether indicates the presence of Lewis acid–base pairs. The acidic route is much faster than the basic one. However, the selectivity to acetone for the same 2-propanol conversion can give a general insight into basicity (strong Lewis basic sites) of the materials. The results collected in Table 3 include those published earlier for silicate MCM-41 based materials. They indicate the following sequence of basicity of APMS-grafted MCM-41 materials:

APMS/AIMCM-41 > APMS/NbMCM-41 > APMS/MCM-41

This order indicates a significant influence of the nature of the support on the basicity.

Considering the influence of the nature of the amine grafted on the same support (AIMCM-41) one can find the following order of basic activity (deduced from acetone selectivity):

$$3$$
APMS/AIMCM- $41 > 2$ APMS/AIMCM- $41 > A$ PMS/AIMCM- 41

It is important to add that the pristine supports revealed acidic properties changed as follows:

HAIMCM-41 > HNbMCM-41 > HMCM-41

3.5. Knoevenagel reactions

Liquid phase Knoevenagel test reactions for Lewis basicity of various strengths were applied for characterization of the materials prepared [26–30]. The test reactions met the green chemistry requirement, it means were performed without any solvent. The condensation of benzaldehyde and ethylcyanoacetate and diethyl malonate was carried out on the supports and amino-grafted materials. In the first reaction activated by medium basic sites ($pK_a = 9$) the only reaction product was Knoevenagel one, whereas in the reaction with diethyl malonate requiring stronger basic centres ($pK_a = 13.3$) also side-reaction products were formed.



Fig. 3. FTIR spectra of the catalyst after evacuation at RT.



Fig. 4. Condensation of benzaldehyde and ethylcyanoacetate at 393 K using MCM-41, AlMCM-41 and NbMCM-41 catalysts (before and after APMS modification).

In liquid phase-solid catalysed reactions special care should be taken to avoid the reaction to be controlled by diffusion of the reactants. To check this, the reactions were carried out at 393 K, on stirring the solution at 1000–3500 rpm. The conversion remained practically the same, which indicated that, under our experimental conditions, the reaction was not controlled by external diffusion. The reactions were repeated under the same conditions for the catalysts with particle size from three different ranges (0.074, 0.140, 0.250 mm in diameter), at 1500 rpm. The same conversions were obtained in all cases, irrespective of the catalysts particle size. Therefore, we can assume that if a catalyst with a particle size in the range studied is used, the results will not be affected by the so-called internal diffusion. Since both external and internal diffusion did not occur, further studies were performed during the reaction.

The reaction curves for APMS-grafted MCM-41 materials are presented in Figs. 4 and 5. It is clearly evidenced that amino-grafting significantly increases benzaldehyde conversion for both Knoevenagel reactions. The order of activity is as follows:

APMS/AIMCM-41 > APMS/NbMCM-41 » APMS/MCM-41

and is in line with the activity sequence observed for 2-propanol decomposition. For the condensation of benzaldehyde with diethyl

malonate the selectivity to Knoevenagel product changes in the same order (Fig. 5B). It should be pointed out that the acidity of mesoporous support decreases in the same sequence.

The role of the nature of amine grafted on AlMCM-41 (the best selected support) can be estimated from the results presented in Fig. 5A. Taking into account the initial step of the reaction, the activity changes in the following order:

APMS/AIMCM-41 > 2APMS/AIMCM-41 > 3APMS/AIMCM-41

Similar results were presented by Das and Sayari [8] for aminografted silicate mesoporous materials. Interestingly, this sequence of activity is in contrast to that noted for 2-propanol decomposition. The difference in these results can be explained by the difficult access to –NH groups in 2APMS and 3APMS modified samples for bulky molecules used in the Knoevenagel reaction and by the decrease in the basicity strength of NH₂ groups in the same order as proposed earlier [8].

4. Discussion

The novelty of our study in comparison to the already published results [3,6,8,13,16–18] was the use of metallosilicate mesoporous materials of different chemical compositions and consequently, different acidities, as supports for three aminopropylalkoxysilanes (APMS, 2APMS and 3APMS). The differences in these three amines



Fig. 6. Models of grafted aminoalkoxysilanes.



Fig. 5. Condensation of benzaldehyde and diethyl malonate at 393 K using MCM-41, AlMCM-41 and NbMCM-41 catalysts (before and after APMS modification); conversion (A) and selectivity (B).

Hann-Lapworth mechanism with tertiary amines as catalysts:



Fig. 7. Possible reaction routes for the Knoevenagel condensation between benzaldehyde and malonic esters.

are in the number of nitrogen atoms in molecules and the alkyl chain length. The acidity of the support is higher for AlMCM-41 than for NbMCM-41 [19,31]. The results of XRD and nitrogen adsorption study indicated that the textural stability and ordering of TMCM-41 (T = Al or Nb) materials during the aminopropylmethoxysilane treatment only slightly depends on the chemical composition of the material. The main point of our interest was the effect of the type of support on the thermal stability of amines and the activity in base-catalysed reactions.

The FTIR and TGA results (Fig. 2. Table 2) indicate that the stability of amines does not depend on the nature of the support (i.e. chemical composition/acidity of aluminosilicate, niobosilicate) for the amino-grafted samples. These results suggest that the type of bonding of the amines with the surface of all mesoporous materials is similar. The results of FTIR study (Fig. 3) show that the grafting of amines occurs via the interaction between silanol OH groups from the support and alkoxy groups from APMS. For 2APMS and 3APMS only one alkoxy group seems to be involved in this chemical interaction and therefore alkoxy species are well detected in the IR spectra. Analysis of these results taking into regard the presence of hydrogen bonded species in 2APMS- and 3APMS-grafted materials allowed us to propose the model of grafted aminoalkoxysilanes shown in Fig. 6. The type of amine bonding proposed in this figure, explains the higher thermal stability of 2APMS and 3APMS. Moreover, the hydrogen bonding between the surface silanol groups and NH₂ decreases the basicity strength of the amino groups. Therefore, the rate of condensation of benzaldehyde with diethyl malonate (the Knoevenagel reaction which requires strong basicity – $pK_a = 13.3$) is lower for 3APMS and 2APMS than that for APMS (Fig. 5). Moreover, the stabilization of amines, proposed in the model, hinders the accessibility of -NH groups for large molecules such as benzaldehyde and diethyl malonate. The molecules of 2propanol reach the NH groups much easier and therefore, the activity in acetone formation is proportional to the number of amine groups in the material.

The effect of the acidity of the support on the basic catalysed Knoevenagel reaction evidenced in this work has to be considered in detail. There are two reaction routes described in literature for the Knoevenagel condensation between benzaldehyde and malonic esters (Fig. 7) [6,8,32–34]. One reaction pathway proceeds by the activation of benzaldehyde towards imine (C=N) salt formation and a further reaction with the methylene group of the ester. The other possibility is the activation of the ester via abstraction of proton by basic centres of the catalyst and a further reaction with benzaldehyde. Small changes in the reaction medium or the surrounding of the basic centres can easily cause the switching of the Knoevenagel reaction route. It should be noted that the amine group facilitates the hydrolytic degradation of both silica framework and organic chain linkage [35–38]. Thus, it is expected that the protonation of amine group renders the hybrid material more stable.

The results presented in this paper show that the increased acidity of the support makes the Knoevenagel reaction more efficient. As the acidity does not influence the stability of amines in mesoporous materials one has to consider the participation of the support in the Knoevenagel reaction. Considering the possible mechanism presented in Fig. 7, one can find that the formation of imine salt (the reaction route via activation of benzaldehyde) requires the abstraction of OH⁻ group from the intermediate. The acidity of the support makes this process faster and as a consequence, enhances the total rate of the Knoevenagel condensation. The iminium reaction path was proposed by Katz et al. [39] for Henry reaction on silica gel modified with amines where primary amines/silanol groups activated hydroxybenzaldehyde. In the same reaction carried out on amine modified MCM-41 Asefa et al. [33] proposed the cooperative catalytic mechanism in which the formation of iminium intermediates occurs by the activation of benzaldehyde by silanols or secondary amines. In our paper the role of acidity of the support in iminium pathway is stressed.

The role of the acidity of the support can be also considered taking into account the APMS loading. Amine loading is lower for APMS/AIMCM-41 than APMS/NbMCM-41 and therefore in the first case a higher surface area of the support is accessible for the reagents and moreover, APMS molecules are more isolated. It is in line with the recent paper [33] where the authors indicated that there is an optimum number of amine grafted groups for the effective activation of benzaldehyde. Too high concentration of amines can decrease the activation of reagent.

Finally, the catalysts were tested for recyclables during four regeneration cycles with no appreciable change of activity.

5. Conclusions

- 1. FTIR study proved the way of APMS bonding to the support. The results have revealed that aminopropylmethoxysilanes (APMS) are grafted on metallosilicate MCM-41 supports via interactions of methoxy species with surface hydroxyls leaving amine groups accessible for reagents.
- 2. Hydrogen bonding of NH₂ with surface hydroxyls has been found for 2APMS and 3APMS grafted on mesoporous MCM-41 sam-

ples and it is responsible for reduction of the basicity strength of amine groups.

- 3. Thermal stability of amines does not depend on the chemical composition of TMCM-41, whereas the basicity tested in 2-propanol dehydrogenation and the activity in the Knoevenagel reactions are influenced by the nature of the supports (AIMCM-41 support gives rise to the higher activity).
- 4. The support has been shown to be involved in the Knoevenagel reaction. The acidity of the supports (AlMCM-41, NbMCM-41) increases the rate of iminium salt formation (from benzalde-hyde and grafted amine) because acid sites can participate in the abstraction of OH⁻ groups from the intermediate.
- 5. Selectivity to the Knoevenagel products significantly depends on the nature of the support for grafted amine (AIMCM-41 > NbMCM-41).

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